

Bismuth.—Oeschner de Coninck and Gérard,¹ by reduction of bismuth chloride to metal, found Bi = 208.50.

Molybdenum.—Müller,² by oxidation of the metal, found Mo = 96.035.

Neodymium.—Baxter, Whitcomb, Stewart, and Chapin,³ by analyses of the chloride, find Nd = 144.27.

Columbium.—Smith and Van Haagen,⁴ from the ratio between sodium columbate (NaCbO_3) and sodium chloride, find Cb = 93.13. The value 93.1 might be adopted in the table.

Argon.—Schultze⁵ has redetermined the density of argon. The corresponding atomic weight is A = 39.945.

Signed, F. W. CLARKE,
T. E. THORPE,
G. URBAIN.

NOTE.—Because of the European war the Committee has had much difficulty in the way of correspondence. The German member, Professor Ostwald, has not been heard from in connection with this report. Possibly the censorship of letters, either in Germany or *en route*, has led to a miscarriage.

F. W. CLARKE, *Chairman*.

[CONTRIBUTION FROM RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY, SCHENECTADY, N. Y.]

THE CONSTITUTION AND FUNDAMENTAL PROPERTIES OF SOLIDS AND LIQUIDS.

PART I. SOLIDS.

BY IRVING LANGMUIR.

Received September 5, 1916.

The importance of the work of W. H. Bragg and W. L. Bragg in its bearing on chemistry has not, as yet, been generally recognized. In hearing two of W. H. Bragg's lectures in this country a few years ago, the writer was impressed with the very great significance of this work in the field of chemistry. The structure of crystals as found by the Braggs leads to new and more definite conceptions as to the nature of chemical forces.

The writer has constantly endeavored to apply this new conception in his work on heterogeneous reactions and particularly in connection with a study of the phenomena of adsorption and surface tension. In this way he has gradually been led to form more or less definite theories of the mechanism of evaporation, condensation, liquefaction, adsorption, and capillary phenomena. According to this theory, both solids and liquids

¹ *Compt. rend.*, 162, 252 (1916).

² THIS JOURNAL, 37, 2046 (1915).

³ *Ibid.*, 38, 302 (1916).

⁴ *Ibid.*, 38, 1783 (1916).

⁵ *Ann. Physik*, [iv] 48, 269 (1915).

consist of atoms held together entirely by *chemical forces*. The conception of the molecule thus almost entirely loses its significance except in the case of gases. In fact, we may well look upon any solid or liquid body as constituting a single large molecule. Any change of phase, such as the melting of a solid, is thus a typical chemical reaction. The mobility of liquids, according to this viewpoint, is due to a kind of tautomerism.

The present paper is merely an outline of this theory. The more detailed description of the experimental work upon which it is largely based, will be reserved for future papers.

STRUCTURE OF CRYSTALS.

The idea that a crystal should constitute an effective diffraction grating for X-rays originated with Laue,¹ who also saw that by means of such a grating not only could the wave length of the X-rays be determined, but also a powerful method for studying the structure of crystals was made available. The detailed theory developed by Laue proved incorrect in certain important respects. W. L. Bragg² called attention to these errors and gave a theory by which the true structure could be determined from the diffraction pattern. Since then the method has been greatly simplified, so that at present it is usually a matter of no great difficulty to find the exact arrangement of the atoms in a crystal. In this way the structures of some 30 or more kinds of crystals have been determined.

The alkali halides NaCl, KCl, KBr, and KI all have a similar structure in which the *atoms* are arranged according to a simple cubic lattice. Thus, in the case of sodium chloride crystals, sodium and chlorine atoms alternate along three sets of lines at right angles to each other. Each sodium atom is surrounded by six equidistant chlorine atoms arranged around it, as the corners of an octahedron are arranged around its center. Similarly, each chlorine atom is surrounded by six equidistant sodium atoms.

Up to this time it had been taken for granted that crystals were built up of molecules. But from this work of the Braggs it is clear that in crystals of this type the identity of the molecules is wholly lost, except in so far as we may look upon the whole crystal as composing a single molecule. From the arrangement of the atoms we must conclude that the forces holding the crystal together (cohesion) are forces which exist directly between sodium and chlorine atoms. Every chemist looks upon such forces as chemical in nature.³

¹ *Sitzb. d. Bayer. Akad. d. Wiss.*, June, 1912.

² *Proc. Camb. Phil. Soc.*, 17, 43 (1912). The subsequent papers of W. H. and W. L. Bragg were published in 1913 and 1914 in the *Proc. Camb. Phil. Soc.*, the *Proc. Roy. Soc.*, and the *Phil. Mag.* All of these papers were translated into German and were published together in one volume of the *Z. anorg. Chem.*, 90 (1914).

³ Of course all chemical forces are probably of electromagnetic origin, but for this reason we do not need to call the forces in crystals by the vague term "physical forces" (and thus distinguish them from chemical force).

But the significance of this structure for the chemist extends further. Sodium is invariably regarded as a monovalent element, yet in the sodium chloride crystals we see a structure which in no wise suggests the monovalent character of the atom. The sodium atom is held by chemical forces to six chlorine atoms. If we retain the conception of valency in such a case, we must clearly admit that the valency of the sodium is divided equally between the six chlorine atoms.

If a sodium chloride crystal evaporates at high temperature, the atoms leave the surface in pairs in the form of sodium chloride molecules. These molecules are formed in the process of evaporation, since they do not exist as such in the crystal. The process of evaporation is thus a chemical process.

In the diamond, each carbon atom is surrounded by four others equidistant from it. These are arranged around the central one in the same way as the four corners of a regular tetrahedron are arranged around its center. In this case the tetravalent character of the carbon atom manifests itself clearly. When a model of a diamond crystal is examined, it is seen that the atoms appear to be arranged in rings of six, corresponding to the benzene ring. The remarkable strength of the carbon chain and especially the stability of the benzene ring, so familiar to chemists, is thus seen to be the cause of the hardness, the high melting point and the low vapor pressure of the diamond.

It is interesting to note that the structure of zinc blend, ZnS , is very similar to that of the diamond, the zinc and sulfur being alternately substituted for adjacent carbon atoms. Thus each zinc atom is surrounded by four symmetrically placed sulfur atoms, while each sulfur atom is surrounded by four zinc atoms. The valency is thus again divided.

With fluorite, CaF_2 , each fluorine atom is surrounded by four symmetrically placed calcium atoms, while each calcium atom has eight fluorine atoms arranged around it like the eight corners of a cube about the center of the cube.

The structure of pyrites, FeS_2 , is much more complicated. Each iron atom has four equidistant sulfur atoms around it, but there are other sulfur atoms at distances only slightly greater. Similarly, each sulfur atom has three equidistant iron atoms forming a triangle around it, but above and below the plane of this triangle there are other iron atoms whose distance is only slightly greater.

Hauerite, MnS_2 , has a similar structure to that of pyrites.

In the case of calcite, $CaCO_3$, the carbon and oxygen atoms lie in planes perpendicular to the crystal axis. Three oxygen atoms are arranged in groups around each carbon atom, forming an equilateral triangle. The calcium atoms lie in planes just above and just below the carbon-oxygen planes. Each calcium atom has six equidistant oxygen atoms around it.

The distance between the calcium and the carbon atoms is considerably more than either the distance between oxygen and carbon, or between oxygen and calcium. Thus the crystal is evidently held together by forces acting between carbon and oxygen and between oxygen and calcium. The group CO_3 appears as a unit, since each carbon atom is associated with three oxygen atoms while these are associated with only the one carbon atom. But each CO_3 group is equidistant from six calcium atoms, so that it is impossible to pick out any one of these as forming a molecule with the CO_3 . If we are to retain the idea of a molecule at all, we must consider that the entire crystal is a single molecule.

In dolomite, CaMgCO_3 , the structure is exactly similar except that calcium and magnesium planes alternate. The structures of rhodochrosite, MnCO_3 , siderite, FeCO_3 , and sodium nitrate, NaNO_3 , are like that of calcite. This last case is of special interest to the chemist, since a monovalent atom replaces a divalent, and a pentavalent (?) atom replaces a tetravalent one without causing a change in the arrangement of the atoms.

The crystals of magnetite afford an illustration of a structure in which different atoms of the same element have different functions. Two-thirds of the iron atoms occur in positions in which each is surrounded by four oxygen atoms (tetrahedral arrangement), while the other third of the iron atoms are each surrounded by six oxygen atoms. The iron atoms have thus a divalent and trivalent character, but each unit of valence is divided between two oxygen atoms. Spinel, MgAl_2O_4 , has an exactly similar structure in which the Mg atoms take the place of the divalent iron atoms, while the Al atoms replace the trivalent iron atoms.

Crystals of metallic copper and metallic silver have been found to have their atoms arranged according to the face-centered cubic lattice. This arrangement is the same as the familiar one obtained when round shot are piled in layers as regularly and compactly as possible. In this structure each atom is equidistant from the twelve adjacent atoms.

The structures of crystals of rhombic sulfur and quartz have been partly worked out. In the sulfur crystals the atoms are found to be arranged in a lattice structure in groups of eight. The particular arrangement of the atoms within these groups is not yet known. To the chemist it is of significance that these groups of eight contain the same number of atoms as are found in molecules of sulfur vapor. Here, then, for the first time, the crystal has a structure in which the identity of the molecules (as found in the gas phase) is apparently not wholly lost.

In a recent article¹ L. Vegard shows that the structures of gold and lead crystals are the same as those of silver and copper. He also describes the structure of the zircon group of minerals represented by zircon, ZrSiO_4 ,

¹ *Phil. Mag.*, 32, 65 (1916).

rutile, TiO_2 , and cassiterite, SnO_2 . The structure of zircon proves to be especially interesting, for it is found "that each of the Zr or Si atoms is associated with two oxygen atoms; thus the groups SiO_2 and ZrO_2 form a kind of 'molecular elements' of the lattice. This is not merely a way of regarding the geometrical arrangement of the atoms; but we have reason to believe that the groups SiO_2 and ZrO_2 form chemically saturated compounds" within the crystal.

Two facts stand out clearly as a result of the consideration of these crystal structures. In the first place, it is evident that crystals are built up of atoms in such a way that each atom is chemically combined to all the adjacent atoms, while these in turn are combined to those beyond.

Secondly, we see that the arrangement of the atoms in general does not follow the usual rules of valency, but that each atom is combined with a much larger number of atoms than corresponds to its normal valence.

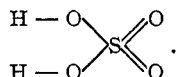
In the past it has been customary to consider that solids and liquids are held together by the "forces of cohesion" and to call these "physical forces" as distinguished from chemical forces. Often these distinctions are known to be rather vague, but in the more recent years, with growing confidence in the atomic theory, we have been accustomed to consider that chemical phenomena are those involving an alteration of the structure of molecules, while physical phenomena are those in which only the molecule as a whole is concerned. This distinction throws the whole difficulty back on to the definition of the molecule. In gases there is usually no uncertainty as to the size of the molecules, but in liquids and solids no really satisfactory methods have been found for determining molecular weights. As long as we cannot definitely determine the molecular weights, it thus remains impossible to distinguish sharply between chemical and physical phenomena. Nevertheless, much discussion has arisen of late years over such questions as whether adsorption and surface tension are chemical or physical phenomena. The overwhelming consensus of opinion seems to be that these are both physical phenomena.

In the following pages the writer hopes to show that there is no present justification for this distinction between chemical and physical forces. Cohesion, adsorption and surface tension are all manifestations of forces similar in their nature to those acting between the atoms of solid bodies. It is therefore advantageous to look upon these forces as direct results of chemical affinity. In this way it becomes possible to correlate these so-called physical phenomena with the known chemical characteristics of the atoms and groups of atoms forming the bodies.

Theories of Chemical Constitution.—The fact that each atom in a crystal is usually combined with a larger number of adjacent atoms than corresponds to its valence, is not in conflict with recent theories of the constitution of chemical substances.

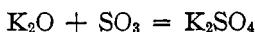
A. Werner¹ has made a very extensive study of complex inorganic compounds, and as a result has established a theory of residual or secondary valence.

In accordance with the ordinary theory of valency which has proved so invaluable in organic chemistry, it has been customary to assign structural formulas of similar type to inorganic compounds. Thus the graphic formula for sulfuric acid is often written

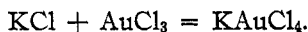


Whereas among organic compounds the structural formulas can be determined with certainty and undoubtedly correspond to the actual arrangement of the atoms in the molecules, no such certainty is ever found in the case of complex inorganic compounds. As a result, such formulas have served no useful purpose in the development of inorganic chemistry. In fact, Werner claims that the common acceptance of such conceptions was responsible for the fact that our knowledge of the constitution of inorganic compounds failed to progress for so many years.

Werner² then shows clearly that such formulas are untenable. In the first place, the formula would lead to a sharp distinction between the combination of oxides and halides, whereas such a distinction does not actually exist. A proper theory should show a close relationship between such reactions as



and



The same kind of relations exist with complex cyanides, nitrites, etc., and these cannot be accounted for by the ordinary theory of valency.

Secondly, the ordinary theory would indicate that oxides such as OsO_4 , RuO_4 , etc., should easily form acids by combination with water. Actually, it is found that the number of molecules of water which can be taken up by an oxide does not bear any definite relation to the number of doubly bound oxygen atoms.

Several other good reasons are given against the ordinary graphic formula for such compounds.

Werner then proceeds to show that the ordinary conception of (primary) valence applies (except in organic compounds) practically only to compounds of the first order; that is, to simple compounds containing not more than two elements, such as H_2O , NaCl , SO_3 , etc.

Compounds of higher order are formed when compounds of the first

¹ *Neuere Auschauungen auf dem Gebiete der Anorganischen Chemie, Braunschweig (1905).*

² *Loc. cit.*, p. 42.

order combine together. Thus Werner draws no sharp distinction between the combination of P_2O_5 and Na_2O to form Na_3PO_4 , and such a process as the taking up of "water crystallization" by a salt such as $BaCl_2$ to form $BaCl_2 \cdot 2H_2O$.

When two elements combine to form a compound of the first order, their primary valences become saturated. But there is still a field of force around the molecule which enables it to combine with other molecules to form compounds having almost any degree of stability. The molecules are then said to be held together by residual or secondary valence.

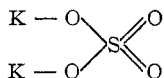
Werner gives the following definitions of primary and residual valency:

(a) "Primary valence serves to unite those simple or complex radicals which can exist as separate ions or whose chemical combining power is equivalent to an ionizable radical."

(b) "Residual valence represents the affinity that binds together radicals which can neither act like nor be equivalent to separate univalent ions."

As illustrations of primary valence, he gives $-Cl$, $-Na$, $-NO_2$, $-CH_3$, and for residual valence: $:OH_2$, $:NH_3$, $:ClK$, and $:CrCl_3$.

R. Abegg¹ advanced a somewhat similar theory of the constitution of inorganic compounds. He looks upon salts of oxygen acids, for example, as consisting of basic and acid oxides held together by secondary valence. He considers Berzelius' idea of the structure of such compounds ($K_2O \cdot SO_3$, for instance) to be much preferable to the structural or graphic formula



and gives many good reasons to support his contention.

Stark² has developed a theory of the mechanism of chemical valency based on the electron theory. This electroatomic theory gives symbolically a very satisfactory picture of the different types of valence. According to Stark, portions of the surfaces of atoms contain an excess of positive electricity. In the neutral atom one or more electrons are held close to the surface of the atom by this positive charge. Compounds are formed when the lines of force from one of these "valence electrons" reach out and end on the positive areas of other atoms. In the case of strongly polar compounds, an electron is almost wholly drawn over to the atom which it holds in combination. Primary valences are due to a pair of valence

¹ *Z. anorg. Chem.*, 39, 330 (1904); 50, 309 (1906), and *Z. physik. Chem.*, 69, 1 (1909).

² *Jahr. d. Radioakt. und Elek.*, 5, 125 (1908); *Prinzipien der Atomdynamik*, Vol. 3; "Die Elektrizität im chemischen Atom," Leipzig, 1915. A short description of Stark's theory of valence was given by Misses Hahn and Holmes in *THIS JOURNAL*, 37, 2611 (1915). This article is essentially an abstract of Paul Ruggli's book, "Die Valenzhypothese von J. Stark vom Chemischen Standpunkt," Stuttgart, 1912.

electrons whose field binds two atoms together. The stray electric field in the space around the resultant molecule is the cause of the residual valence. This theory accounts particularly well for the gradations between primary and secondary valence.

Thus when two atoms combine chemically, they are held together by certain electrons which are common to both atoms. Bohr's model of the hydrogen molecule assumes a similar function of the electrons. According to Bohr's theory, a hydrogen atom consists of a positive nucleus around which (at a distance of 0.55×10^{-8} cm.) an electron revolves with very high speed. The hydrogen molecule, on the other hand, consists of two hydrogen nuclei (at a distance apart of 0.60×10^{-8} cm.) and two electrons which revolve in an orbit in a plane perpendicular to the line joining the nuclei. The radius of the orbit of the electrons is 0.52×10^{-8} cm. In the hydrogen atom the electron forms part of the atom. When two atoms combine the two nuclei share the two electrons equally. If the two atoms separate again, there is an even chance that they will have exchanged electrons. The two electrons held in common by the two nuclei hold the molecule together and are thus equivalent to the bond by which we ordinarily imagine two univalent atoms to be jointed. This model of the univalent bond is remarkably similar to that proposed by Stark.

J. J. Thomson¹ has also developed a theory of the mechanism of chemical affinity. On the whole, his theory is very much like that of Stark. Thomson considers that the electrons near the surface of an atom, together with the positive charge in the core of the atom, constitute one or more electric doublets which exert forces not only on free electrons or ions in their neighborhood, but also on other electric doublets. The force of attraction between such doublets varies much more rapidly with the distance than the inverse square. Thomson uses the dielectric constant of the substance in the gaseous condition as a measure of the moment of the electric doublets. In this way he concludes that there has been an actual transfer of an electron from one atom to another in such compounds as H_2O , NH_3 , SO_2 , HCl , CH_3OH , C_2H_5OH and CH_3Cl , even when these are in the gaseous condition. This "intra-molecular ionization" greatly increases the moment of the doublet by increasing the distance between the charges. In other types of compounds, however, Thomson believes that the atoms are electrically neutral and are held together by one or more doublets on each atom. As compounds of this type he cites H_2 , O_2 , N_2 , Cl_2 , CO , CO_2 , CS_2 , CCl_4 , C_6H_6 , CH_4 , N_2O .

It should be noted that Stark's theory recognizes both these types and indicates how there may be all possible gradations between these extremes.

¹ *Phil. Mag.*, 27, 757 (1914).

Thomson also believes that the more complex compounds are "molecular compounds" in which simple molecules are held together by the stray field around the molecules. In the first paragraph of his paper he says: "These forces will be exerted by the atom not merely on the atoms which are associated with it in the molecule of a chemical compound, but also on the atoms in other molecules, giving rise to forces between the molecules and producing thereby the intrinsic pressure and surface tension of liquids, latent heat of evaporation, cohesion of solids and liquids, the rigidity of solids and so on. These physical phenomena are the effects of forces between different molecules, whereas chemical affinity and chemical phenomena in general are the effects of forces having the same origin, but acting between the atoms of the same molecule."

We shall see that this division of solids and liquids into molecules is very arbitrary and that the same kind of chemical relationships exist between these forces, which Thomson calls physical, as exist among the forces which cause the formation of molecular compounds.

In regard to saturated valence, Thomson considers that two electrons are involved in holding two univalent uncharged atoms together. In this respect his theory is like those of Stark and Bohr. He points out, however (as Stark has also done), that by this theory three univalent atoms may be held together in the form of a ring, one electron being located between each pair of adjacent atoms. He says: "The difference between the theory we are considering and the accepted theory of valency may be expressed by saying that not only is every possible valency compound on the old theory a valency compound on this theory, but every compound which would be a valency one on the old theory if the valency of every element was doubled, would be a valency compound on the new, with the atoms retaining their original valency. This only applies to the compounds when the atoms are uncharged; when the atoms are charged the valency conditions are the same as on the old theory."

This theory would seem to fit in badly with the facts of organic chemistry, for we find no evidence of organic compounds in which carbon acts as if it had a valency of eight or hydrogen a valency of two. But in the formation of crystals this theory suggests an explanation of the divided valence observed in crystals of the spinel group. For instance, it was found in magnetite that the *divalent* iron atoms were surrounded by *four* symmetrically placed oxygen atoms, while the *trivalent* iron atoms were surrounded by *six* oxygens.

An extremely important theory of the "Atom and Molecule" is that recently described by G. N. Lewis.¹ Substances are classified into two general groups: polar and nonpolar. The polar type, represented by H_2O , NH_3 , $NaCl$, etc., is characterized by reactivity, high dielectric constant,

¹ THIS JOURNAL, 38, 762 (1916).

tendency to form molecular complexes, etc. Tautomerism is a "predominant trait of most inorganic substances (polar type), which behave as if a great variety of forms were existing together in extremely mobile equilibrium."

For this reason Lewis¹ believes that the constitution of the more complex inorganic compounds cannot be represented by any single structural formula.

We shall see that these ideas on tautomerism will prove of value in connection with a study of the constitution of liquids.

Crystal Structure from the View Point of Chemical Theory.—The work that has been done so far on crystal structure testifies to the general applicability of such theories of chemical constitution as that of Werner.

Except in the case of diamond crystals, no structural formula can be written consistent with our ordinary ideas of (primary) valence, which adequately represents the constitution of the crystal. We see, however, that the arrangement of the atoms in crystals is just what we should expect if the forces binding the atoms together are similar to those forces which, by Werner's theory must hold together the *molecules* in molecular compounds (compounds of higher orders).

Werner's theory, however, needs to be modified in some respects, to fit in with the new work. According to Werner, compounds of the first order are held together by primary valence, and only when these simple compounds form compounds of higher orders are the residual valences called into play. But when we consider the structure of the halide salts of the alkalis and the structure of such crystals as fluorite, we must conclude that even in the case of these first order compounds the ordinary rules of valence do not always apply.

It thus seems that secondary, or residual valence is active, not only in the higher order compounds, but that a valency of the secondary type may also characterize single atoms when these are combined with others in crystals.

It is evident that solid bodies could not be built up of atoms held together exclusively by primary valences except in the case of atoms having valences of four or more. Thus, when two monovalent atoms combine to form a gas molecule, they are held together by primary valence. If there were no residual valence, these molecules could not condense either as a solid or liquid. Divalent atoms could combine together in long chains, but these chains could not be linked together except by secondary valence. With trivalent atoms branching chains could be formed which could interlock so as to cover a plane surface, but except by secondary valence no atoms could be held outside of this plane. With tetravalent

¹ THIS JOURNAL, 35, 1448 (1913).

atoms, on the other hand, the atoms can be linked together by their primary valences, as in the diamond crystal, so as to fill a volume.

We thus see that primary valences cannot play an important part in crystal structure in the case of atoms with a valency of less than four. Most of the crystals containing tetravalent atoms which have been studied so far, have shown that the primary valences of the tetravalent atoms seem to exert their influence. This is shown not only in the case of the diamond, but in zircon, cassiterite and rutile, in which each atom of Zr, Si, Ti or Sn is clearly associated with two atoms of oxygen.

From these considerations it seems that in general there is a strong tendency for every atom to form compounds by means of its primary valence, but where the conditions are such that combination by primary valence is no longer possible, then secondary valence is called into play and may entirely supersede the primary valence.

Thus, when sodium atoms and chlorine atoms combine at high temperatures to form gaseous NaCl, the primary valence holds the atoms together. But when the pressure is raised or the temperature is lowered, the secondary valence is enabled to completely supersede the primary valence, since the primary valence cannot cause the combination of the molecules necessary to form a solid body.

With divalent and trivalent atoms a sort of divided valence like that suggested by J. J. Thomson, is apparently often manifest and is probably a sort of transition between primary and secondary valence. This is seen particularly in crystals of the spinel group, in which the divalent atoms have assumed a tetravalent character and the trivalent atoms a hexavalent character.

By this division of each of the valence units into two parts, the apparent valency is raised to four or more, so that the solid body can then be held together by this means. According to Stark and J. J. Thomson's theories, we should never expect the subdivision of a primary valence unit into more than two parts. Furthermore, we should not expect that a monovalent element would often exhibit this divided valence in solid bodies, because, even if its apparent valence was doubled by this means, it still would not be able to make use of this valence in forming a crystal.

The compounds whose crystal structures have been studied thus far, are all more or less of the polar type. It is not safe to conclude that the structures of nonpolar compounds will be similar to those already found.

For example, when an organic compound such as methane, is crystallized as a solid and is then converted again into a gas, it is certain, from chemical considerations, that none of the hydrogen atoms have been separated from the carbon atoms to which they were originally attached. The identity of the original molecules must, in a sense, have been preserved even when the methane was in the solid condition.

On the other hand, with crystals of the types studied so far, the substance could not be condensed from the gaseous condition and be re-evaporated again without most of the atoms having exchanged partners. Thus, when a crystal of sodium chloride evaporates, a sodium atom on the surface may escape with any one of the four adjacent chlorine atoms as a molecule of salt vapor. There is only a small chance that the particular chlorine atom with which it escapes will be the same one as that with which the sodium atom was combined before it formed part of the crystal.

From these considerations we are forced to conclude that in crystals of methane each carbon atom is surrounded by four hydrogen atoms held to it by primary valences. The crystal is then held together by residual valences. Since the methane is so thoroughly saturated chemically, these residual forces are very weak and, therefore, methane melts and boils at a very low temperature. But there is absolutely no reason for assuming that these residual forces are any less chemical in nature than those which cause the combination of K_2O and SO_3 to form K_2SO_4 . We certainly cannot limit chemistry to a study of only those substances whose atoms are held together by primary valence.

Determination of the crystal structure of organic compounds should prove of very great value in clearing up the true distinctions between primary and secondary valence. Unfortunately, the very low absorption of X-rays by the hydrogen makes it difficult to determine the positions of the atoms of this element by the present methods. This difficulty can be avoided by choosing such substances as C_2Cl_6 and C_6Cl_6 .

Similar considerations to those used with methane apply to such substances as H_2 , N_2 , O_2 , etc., and nearly all typical organic substances. That the crystal structure, even with these substances, depends on the space arrangement of the atoms, is clear from the work of W. Wahl¹ on the crystal forms of the lower members of the aliphatic hydrocarbon series. He finds methane crystallizes in the isometric system, ethane in the hexagonal, propane apparently rhombic, trimethyl methane probably rhombic. Tetramethyl methane occurs in two modifications, one isometric and one tetragonal. Normal butane also has two forms, hexagonal and rhombic. Normal pentane is rhombic, while normal hexane, heptane and octane are monoclinic or triclinic.

The lower members of this series show a remarkable agreement between the chemical constitution and the crystal form. Thus the symmetry of the methane molecule requires a crystal of the isometric form, probably with an arrangement rather similar to that of the diamond. If we look upon the carbon atom as having its bonds arranged symmetrically after the pattern of the tetrahedron, then the ethane molecule would con-

¹ *Proc. Roy. Soc., (A)* **88**, 354 (1913).

sist of two carbon atoms each with three hydrogen atoms (in planes 120° apart) arranged around them. This leads naturally to the hexagonal form.

The definiteness of this dependence of the crystalline form upon the arrangement of the atoms indicates that even with these nonpolar compounds the forces holding the *molecules* together in the crystals are of the same nature as those holding the *atoms* together in the polar types of crystals.

Since the forces acting between the molecules in these crystals are then quite similar to those acting in the more complex inorganic compounds we would still be justified in regarding a crystal of methane as one large molecule. We thus have molecules within the molecule.

This leads us to consider whether it is not desirable to revise our conception of the molecule. There is an advantage in looking upon every crystal (and in fact every mass of liquid) as a single large molecule, in that this viewpoint brings out strongly the *chemical* nature of the forces holding the crystal together, and thus encourages us to apply to the study of these forces the knowledge already available from other fields of chemistry.

On the other hand there is a real need for a term to denote a group of atoms which can pass from the gas phase to the solid (or liquid) and back again without the exchange of any atoms. If, however, we should limit the word molecule (in liquids and solids) to this narrow definition, we would have to say that there are no molecules at all in the great majority of inorganic substances.

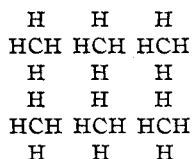
On the whole, it seems best to define a molecule as a *group of atoms held together by atomic forces*. We must then distinguish between various kinds of molecules.

The *gas molecule* may be defined in terms of Avogadro's Law, and is thus only sharply definable in so far as the gas follows the laws of ideal gases. We may define a *fixed molecule* as the largest aggregate of atoms which may pass from the gaseous phase to the solid (or liquid phase) and back again to the gaseous phase without exchange of atoms with other aggregates. With substances which are wholly nonpolar, such as the saturated hydrocarbons, this definition of fixed molecule is probably never ambiguous. But with molecules which are partly polar, as for example acetic acid, this definition may lack sharpness. Thus when CH_3COOH vapor dissolves in water (or condenses as a solid), it is probable that the replaceable hydrogen atom will be exchanged with that of the other CH_3COO groups. According to our definition of fixed molecule we must, therefore, consider that the *fixed molecules* in liquid or solid acetic acid consist of CH_3COOH groups. Cases will frequently arise, as for example in the alcohols, where the rate of exchange of the hydrogen atoms is so

slow as to be almost negligible, so that it will be impossible to limit sharply the extent of the fixed molecule. This difficulty, however, seems an inherent one, for it depends upon the fact that all possible degrees of tautomerism may actually exist in the large molecule forming the whole mass of the solid or liquid.

It will also be convenient to distinguish another type of molecule which we may call the *group molecule*. This may be defined as an aggregate of atoms which are interrelated in such a way (by position or mobility) that the atoms in the group may be distinguished from atoms outside the group. Thus in solid methane each hydrogen atom is associated with a particular carbon atom, while the carbon atom is associated with four hydrogen atoms. All other hydrogen atoms beside these four may be distinguished from these by their being combined with a different carbon atom.

If we represent a methane crystal diagrammatically as follows:



it is evident that we might also look upon the crystal as consisting of group molecules of hydrogen (H_2) held together by carbon atoms. Chemical considerations, however, would lead us to choose CH_4 as the group molecule.

In liquid methane we could distinguish the group molecule either by the fact that four atoms of hydrogen must be geometrically associated with a single carbon atom, or by the fact that four hydrogen atoms always move with a particular carbon atom, whereas all other neighboring hydrogen atoms in the course of time gradually (by diffusion) become separated more and more from the given carbon atom.

A crystal of zircon would thus be a compound consisting of group molecules of ZrO_2 and group molecules of SiO_2 .

In inorganic compounds in the solid or liquid state there are usually no fixed or group molecules. It is probable, however, that an ion of the type CO_3^- in solution constitutes a group molecule, since the structure of the calcite crystal suggests the carbon atom may be more or less permanently associated with three particular oxygen atoms. An ion of the type OH^- , however, can probably not be properly looked upon as a group molecule since the high mobility of the OH^- ion and other factors indicate that this ion is continually exchanging its atoms with the surrounding mass of water.

Besides these types of molecules, there are the large molecules which constitute colloid particles. These may be called *colloid molecules*. They probably usually consist of large aggregates of atoms or group molecules

combined together by means of secondary valence. In the second part of this paper the probable structure of these colloid molecules will be discussed in more detail.

Finally, every continuous solid or liquid mass whether homogeneous or not may be looked upon as consisting of one large molecule. We may speak of molecules of this type as *solid* or *liquid molecules*.

Forces between Atoms in Crystals.—From our knowledge of the structure of crystals and from such properties as specific heat, compressibility, thermal coefficient of expansion, elasticity in different directions, melting point, vapor pressure, and latent heat of evaporation, it should be possible to determine the laws governing the forces around the atoms. Such a study would give us the clearest kind of insight into the nature of chemical affinity.

In view of the marked influence of temperature on the properties of liquids and solids, it is evident that the motions of the atoms in solids are of great importance. A study of specific heats gives us considerable information regarding the kinetic energy of the atoms. According to the Principle of the Equipartition of Energy¹ the average kinetic energy of any particle is $\frac{1}{2}kT$ for each degree of freedom, where k is the Boltzmann gas constant and is equal to 1.372×10^{-16} ergs per degree. In other words, each particle should contribute the amount $\frac{1}{2}k$ to the specific heat for each degree of freedom which it possesses. Thus for a gram molecule of particles (6.06×10^{23}) we find a specific heat of $\frac{1}{2}R$ for each degree of freedom. Here R is the gas constant ($6.06 \times 10^{23} \times 1.372 \times 10^{-16} = 83.1 \times 10^6$ ergs/deg.). Expressed in calories this gives 0.993 calorie per degree per gram atom for each degree of freedom. We thus have the simple rule that the atomic or molecular heat should be numerically equal to 0.993 times the number of degrees of freedom (n) of the atoms or molecules.

Each atom of a monatomic gas has three (translational) degrees of freedom and we should thus expect the atomic heat to be $C_v = 3 \times 0.9935 = 2.98$. Actually for all the monatomic gases we find exactly this value with the single exception of helium, which gives a slightly lower value.

The specific heats of most diatomic gases is approximately $C_v = 5$, from which we may conclude that there are five degrees of freedom (three translational and two rotational). The possible motion of the two atoms along the line joining them, evidently does not represent a degree of freedom. However, the diatomic gases like chlorine, bromine and iodine which are easily dissociated into atoms, have specific heats considerably greater than 5. There is thus evidence that with very strong chemical forces between atoms the number of degrees of freedom is less than with weaker forces.

¹ For a short description of this principle and its present significance, see Dushman, *General Electric Review*, Sept., 1914.

The atoms of copper, silver, gold and lead are arranged according to a simple face-centered lattice with single atoms at each point of the lattice. It is evident that there are no group molecules. Each atom must possess (at high temperatures) three degrees of freedom corresponding to the directions in which it may move.

We know, however, in accordance with Dulong and Petit's law that the atomic heat of these metals is approximately 6.0,¹ and this is usually explained by assuming that the atoms vibrate in such a way that their energy is equally divided between kinetic and potential energy. When a body such as a pendulum describes *harmonic* vibrations, the time average of its kinetic energy is equal to the time average of its potential energy, if we assume that its potential energy is zero when it passes through its equilibrium position. The equipartition principle is concerned directly only with kinetic energy, but if the average potential energy is equal to the average kinetic energy it is evident that it will contribute as much as the latter to the specific heat. Thus if the atoms of the solid body describe harmonic oscillations about their equilibrium positions, the atomic heat should be double that corresponding to the three degrees of freedom, in other words it should be $6 \times 0.9935 = 5.96$.

It is often said that in this case there are three kinetic and three potential degrees of freedom. This statement is open to serious objection, for it implies that the Equipartition Principle is applicable to potential energy. As a matter of fact, if the forces around the atoms are such as to lead to oscillations that are not harmonic in character there will in general be no equality between the time averages of the kinetic

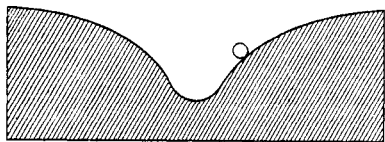


Fig. 1

and potential energies. For example, let us consider a ball rolling on a surface, such as that represented in Fig. 1. If the ball is displaced from its lowest position and released, it will oscillate about this position. If the displacements are small the motion will be approximately

harmonic in character. But with oscillations so large that the ball frequently mounts up on to the comparatively level parts of the surface, it is evident that the oscillations will be far from harmonic. In this case, the motion of the ball on the flatter parts of the surface will be

¹ According to Dulong and Petit's Law, the atomic heats of the elements at *constant pressure* are about 6.3. The specific heat of 6×0.993 calculated by the Equipartition Principle is the atomic heat at constant volume. Lewis, Nernst, Lindemann and others have shown that the atomic heats of metals at *constant volume* gradually approach the above value asymptotically at higher temperatures, but at lower temperatures the atomic heat is considerably less. Elements with atomic weight less than about 20 form an exception to this rule in that their atomic heats are less than 6×0.993 even at room temperature.

so slow that the length of time it remains in these positions will be much larger than it would be if the slope of the surface increased steadily from the center outwards. Thus with such a surface the time average of the potential energy may be much greater than the time average of the kinetic energy.

The same considerations apply to the oscillations of atoms. If the restoring force acting on an atom is proportional to the displacement from the equilibrium position (condition for harmonic motion) then the average kinetic and potential energies will be equal and the atomic heat will be 6×0.993 . But if the restoring force increases more slowly than proportional to the distance (as in the case cited above), then the potential energy will be greater than kinetic energy so that by the Equipartition Principle the atomic heat will be greater than 6×0.993 . On the other hand, if the restoring force increases more rapidly than the displacement, then the atomic heat will be less than 6×0.993 .

The remarkable closeness with which the atomic heats at constant volume approach the value 6×0.993 at the higher temperatures, may be taken as proof that the forces to which the atoms in solids are subjected vary approximately in proportion to the displacement of the atoms from equilibrium positions. There must then be both attractive and repulsive forces acting between the atoms. On the average, these opposing forces must just balance each other. As one atom approaches another the repulsive force must *gradually* increase and the attractive force decrease until the repulsive force greatly predominates. We cannot consider that the repulsive forces in solids are exerted only during collisions between atoms, for under these conditions there would be no potential energy and the atomic heat would be 3×0.993 .

No adequate explanation has been offered of the repulsive forces between atoms. If matter is built up of positive and negative electricity the ordinary electromagnetic theory would indicate that the two opposite charges would neutralize each other. Actually, however, this neutralization only occurs to the extent of destroying the electric field at a comparatively large distance from the electrons. The positive and negative electrons are never able to destroy one another. Some cause, at present unknown, must operate to keep the positive and negative charges from approaching with less than a certain distance. It is evident that the laws governing the forces and motions of electric charges separated by distances comparable with the dimensions of atoms are in some respects radically different from the laws with which we are familiar. G. N. Lewis¹ believes that such considerations lead "irresistably to the conclusion that Coulomb's law of inverse squares must fail at small distances," and that it may be necessary to modify the law "even to the

¹ THIS JOURNAL, 38, 773 (1916).

extent of changing the sign of the force." This difficulty is undoubtedly connected in some way with those which have forced us to the quantum theory. Some more or less successful attempts have been made to apply this quantum theory to the structure of atoms and molecules. Bohr's theory of the hydrogen atom has been remarkably successful in that it enables one to calculate all the lines in the Balmer series of the hydrogen spectrum, but his theory of the hydrogen molecule is apparently not complete, for it leads to a value of 63000 calories for the heat of formation of H_2 from atoms, while direct measurement¹ gives 84000 calories.

A very suggestive theory has been worked out by A. L. Parson² in which he assumes that the electron itself is not merely an electric charge but is also a magnet. Crehore³ has developed a theory in which the magnetic field produced by the rotation of electrons in extremely small orbits (10^{-12} cm.) is assumed to play an essential part in the structure of molecules. By means of the magnetic fields, it is possible to account for both attractive and repulsive forces. Both of these theories assume that the positive electricity of the atom is distributed uniformly throughout a sphere of definite size, inside of which the electrons are located (Thomson's theory). Rutherford's work on the scattering of alpha particles, Moseley's work on X-ray spectra, and considerations based on the disintegration of the radioactive elements, all seem to compel us, however, to adopt Rutherford's theory of the atom in which the positive electricity is concentrated in the center of the atom and the electrons revolve in one or more orbits of diameters of the order of magnitude of 10^{-8} cm. The strength of this evidence in favor of Rutherford's theory is such that it seems to the writer impossible to accept either Parson's or Crehore's theory in their present forms.

These questions will probably be satisfactorily answered only when we understand the mechanism underlying the quantum theory and know the true relationship between positive and negative electricity. We must have an explanation of the remarkable fact that the charge on an electron is *exactly* equivalent (although opposite in sign) to the unit of positive electricity (for example the nucleus of the hydrogen atom).

At present, therefore, in an analysis of the forces between atoms, we must recognize both attractive and repulsive forces, although we cannot satisfactorily explain the mechanism of the repulsive forces. Thus by admitting the existence of forces which prevent electrons from approaching too closely to positive charges we may accept Stark's and J. J. Thomson's theories of the general character of the forces between atoms.

¹ Langmuir, THIS JOURNAL, 37, 417 (1915).

² "A Magnetron Theory of the Structure of the Atom," *Smithsonian Publication* 2371, Washington, 1915.

³ *Phil. Mag.*, 29, 310 (1915).

There are many other properties of solids which indicate that repulsive as well as attractive forces exist between atoms, and that the repulsive forces act over distances comparable with the dimensions of atoms and not merely during collisions between atoms.

The compressibility and coefficient of thermal expansion are two such properties. In the case of ideal gases, these quantities vary with the pressure and temperature in a way that indicates that the volume would be zero if the atoms or molecules were brought into contact.

From the smallness of the coefficient of expansion of solids we must conclude that even at the absolute zero of temperature, the volume of crystals would not be so very much less than at room temperature. Furthermore, there are no indications that the compressibility would become zero even at the absolute zero. These facts are further evidence that the atoms of solids tend to be held in definite equilibrium positions by forces which vary approximately proportionally to the displacements of the atoms from these positions.

Nernst, Einstein and Lindemann have shown that the natural frequency of vibration of the atoms of elements may be calculated by three independent methods based, respectively, on measurements of the specific heat at low temperatures, the compressibility and the melting point. The fairly good agreement between these methods lends further support to the belief that the atoms vibrate about equilibrium positions.

The intensity of the higher orders in the X-ray spectrum of crystals, increases as the temperature of the crystal is lowered. This effect, known as the Debye effect, constitutes striking proof of the heat vibrations of the atoms and should lead to quantitative measurements of these vibrations.

The magnitude of the heat conductivity of solids, especially metals, throws some interesting light on the character of atomic vibrations. Let us imagine all the atoms in the surface layer of a solid to have their temperature suddenly raised by a given amount. This layer will then rapidly cool and will approach the temperature of the underlying layers. The rapidity with which this temperature equalization takes place will measure the rate at which a motion of one atom affects the adjacent ones. A simple approximate calculation¹ gives for the time necessary for the temperature increment of the surface layer to fall to 37% of its initial value.

$$t_r = \frac{3k}{h\sigma} \quad (1)$$

Here k is the Boltzmann gas constant 1.372×10^{-16} , h is the heat conductivity of the solid and σ is the distance between adjacent atoms. The quantity t_r is exactly analogous to Maxwell's "time of relaxation" in a gas which is the time needed for any abnormal distribution of kinetic energy among gas molecules to subside to $1/e^{\text{th}}$ of its original value.

¹ See Langmuir, *Phys. Rev.*, **8**, 149 (1916).

For copper we thus find $t_r = 4.6 \times 10^{-16}$ seconds. This has been calculated on the assumption that each atom can receive heat from one direction only. When we consider that a single atom in the interior may receive energy from six different directions, it seems probable that the real time of relaxation of a single copper atom is about 10^{-16} seconds. Now the atomic frequency calculated from the compressibility by Einstein's method is 5.6×10^{12} , or the time necessary for an atom to complete a single oscillation, the reciprocal of this or 1.8×10^{-13} seconds. Thus the time required for an atom nearly to reach equilibrium with its neighbors is only 1/1800th of the time of a single oscillation.¹

Even for nonmetallic substances, such as sodium chloride, the time of relaxation is always very small compared to the natural period of the atoms. This indicates that motions of a single atom must always be very highly damped. In other words, the atoms behave towards each other as though they were almost completely inelastic. However, if all the atoms are stimulated simultaneously by a periodic disturbance having a frequency corresponding to the natural frequency of the atoms, then the oscillations will be practically undamped, for there are then no adjacent atoms to which the oscillating ones can give up their energy.

We shall see that this apparent inelasticity of the atoms of solids is of great importance in the theory of evaporation, adsorption and surface tension.

The principle of the Equipartition of Energy has been found to apply at higher temperatures to the specific heats of monatomic gases, most diatomic gases and most elementary solids. But at low temperatures the specific heats always fall below that calculated by this principle. According to Einstein's theory this is due to the inability of oscillators to take up energy in quantities less than $h\nu$, where h is Planck's quantum 6.58×10^{-27} erg deg. Whether this is the correct explanation or not, it is a fact that degrees of freedom tend to disappear at lower temperatures. Eucken has shown that at temperatures as low as 58° absolute, hydrogen molecules have only three degrees of freedom, whereas they have five at ordinary temperatures. Similarly the specific heat of helium at the lowest temperatures falls even below 2.98. Evidently, therefore, it is possible that a single atom may have less than three degrees of freedom, although it is hard for us to conceive of such a possibility.

¹ A. H. Compton, *Phys. Rev.*, 7, 341 (1916) in a "Physical Study of the Thermal Conductivity of Solids" reached the conclusion "that the average distance through which the energy of an atomic collision in a crystal is transmitted is approximately inversely proportional to the temperature and is many times the distance between atoms." In many ways this is equivalent to our conclusion that the time of relaxation is small compared to the natural period of oscillation. From what has been said above, Compton's statement is open to serious objection, since we cannot look upon the repulsive forces in solids as being due to collisions.

The smaller the atomic weight of an element and the greater the strength of the union between the atoms, the higher is the temperature at which the atomic heat begins to be normal (5.96). Thus there seems to be a relation between the natural frequency of the atoms and the deviations from the equipartition principle.

However, Trautz¹ attempts to explain the decrease in the specific heat of hydrogen at low temperatures by assuming that for each temperature a certain fraction of the hydrogen molecules are transferred into another modification of hydrogen which has the properties of a monoatomic gas. A. H. Compton² makes a somewhat similar assumption regarding solids, namely, that at low temperatures the atoms are agglomerated into larger aggregates in which the individual atoms lose one or more of their degree of freedom.

The specific heat of solids at ordinary temperatures is a distinctly additive property (Kopp's rule), a fact which is in itself an indication that solids are not built up of molecules. With compounds of the heavier elements, each atom contributes an equal amount (about 6.3 calories per gram atom at constant pressure) to the specific heat. In the case of the lighter elements, such as those forming organic compounds, the additive relations still hold fairly well, but the atomic heats of these elements must be taken to be less than 6.4. According to Kopp's rule,³ the following atomic heats should be taken: C = 1.8, H = 2.3, B = 2.7, Be = 3.7, Si = 3.8, O = 4.0, P = 5.4, S = 5.4 and all elements of higher atomic weights about 6.4.

Accurate determinations of the specific heats of organic compounds in the solid, liquid and gaseous condition and at various temperatures will undoubtedly be of great service in establishing the character of the vibrations of the atoms and the nature of the forces controlling them. The available data at present are very meagre and unreliable.

Chemical Compounds Existing Only in the Solid State.—From what has been said regarding the relation between primary and secondary valences in solid bodies, it would follow that in general the composition of a solid body should give us little or no information about the primary valences. Conversely, we should expect more compounds to exist in the solid state than we would be led to predict from the ordinary rules of valence.

When we consider that every atom (and every molecule for that matter) is surrounded by a field of electro-magnetic force, it appears probable that solids can be built up with almost any arrangement of atoms, provided the temperature is sufficiently low. If these arrangements of

¹ *Verh. deut. physik. Ges.*, 15, 969 (1913).

² *Phys. Rev.*, 6, 377 (1915).

³ Nernst, *Theoretische Chemie*, 1903, p. 180.

atoms are regular so as to constitute a space lattice, the resulting solid will have a definite and invariable chemical composition which can be represented by a chemical formula, and would, therefore, be recognized as a chemical compound. The arrangement of the atoms in such compounds would bear no more relationship to the primary valence of the atoms than does the arrangement of the carbon, oxygen and calcium atoms in a crystal of calcite. The formula representing a compound of this type would thus be totally unrelated to the valence of the atoms.

The reason that the composition of solid compounds is so often consistent with the ordinary valence rules, is probably that the compounds are formed from solutions or from gaseous phases. In liquids or gases there is naturally more opportunity for the primary valences to manifest themselves.

As a matter of fact there are vast members of chemical compounds which exist in the solid state only and among these compounds the absence of valence relations is very striking.

Tammann and his students have proven the existence of a hundred or more definite metallic compounds by their studies of alloys. Out of 100 such compounds only 26 have formulas which agree with the ordinary valence.¹ A few typical compounds are AgMg_3 , AgMg , AuZn , Au_3Zn_5 , Cu_3Al , CuAl , CuAl_2 , Mg_4Al_3 , AlSb , Zn_7Fe , Zn_3Fe , Al_5Fe_2 , NaZn_{12} , NaCd_5 , NaHg_4 , NiCd_5 , AuSb_2 , etc. Tammann shows that definite compounds are never formed between metals which are closely related in the periodic system, such as Cu-Ag or Fe-Ni , although solid solutions or mixed crystals frequently form in these cases.

If we consider these metallic compounds from the viewpoint we have developed above, it is evident that the atoms are held together by secondary valence, as are for instance those in a copper crystal or a rock-salt crystal. The reason that they have a definite chemical composition is that the atoms are arranged in some form of regular lattice. For example, if, in a face centered cubic lattice such as that of a copper crystal, we should replace the corner atoms by atoms of an element A, and replace the atoms in the faces of the cubes by atoms B, then we should have a compound of the composition AB_3 . Each atom A would be surrounded by twelve atoms B all equidistant. Each atom B, however, would have 4 atoms of A and 8 of B equidistant from it. Such a structure would reveal nothing as to the valency of the atoms. It is quite probable that the compound AgMg_3 has a structure of this kind.

If the atoms of the copper crystal we have considered should be replaced by atoms of two elements A and B in an irregular manner, then the resulting crystal would not have a definite chemical composition and would, therefore, not be recognized as a chemical compound, but would be con-

¹ Tammann, *Z. anorg. Chem.*, **49**, 113 (1906) and **55**, 289 (1907).

sidered a solid solution or mixed crystal. Yet there is no reason to assume that the forces holding the crystal together in one case are any different from those in the other.

If the two elements have combined together to form a chemical compound in one case, why not assume that the elements are equally combined in the mixed crystal? In the crystal of a pure metal we should also consider the atoms chemically combined with one another.

In mixed crystals or solid solutions, the atoms are evidently arranged in a haphazard manner according to the laws of probability, many different arrangements of atoms occurring side by side in the crystal. If the atoms of the two elements differ sufficiently in size or in their fields of force, then certain of these arrangements will be more stable than others. Thus, although at low temperatures almost any conceivable arrangement of atoms might be stable, it may be impossible to form mixed crystals by cooling a molten mass, because the atoms during the process of solidification have ample opportunity to arrange themselves in the most stable arrangements.

Thus the limitation in the number of compounds actually found is probably due to the restrictions imposed by our present methods of preparing these alloys by solidification from a melt, and is not an indication that such chemical compounds (or solid solutions) are not capable of existence in the solid condition.

Mineralogy also affords us an abundance of compounds which exist in the solid condition only and whose composition is not in accordance with the ordinary valence rules. The complex silicates are apparently built up of compounds of the first order (SiO_2 , K_2O , Al_2O_3 , H_2O , etc.) in much the same way that the metallic compounds are built up of the atoms of the metals. If we consider such typical compounds as $(\text{K}_2\text{O})(\text{Al}_2\text{O}_3)(\text{SiO}_2)_6$; $(\text{MgO})_3(\text{SiO}_2)_4(\text{H}_2\text{O})$; $(\text{MgO})(\text{SiO}_2)_2(\text{H}_2\text{O})_2$, etc., it appears that the number of each of the groups (K_2O), (Al_2O_3), etc., which enter into the formula bears no relation to the valence of the elements. It is probable that in many cases each of the groups K_2O , Al_2O_3 really constitute group molecules and that these are held together in the crystal by secondary valence, just as the atoms of the metallic compounds are.

Solid solutions or mixed crystals are of even more frequent occurrence among minerals than among alloys, and similar considerations must apply in regard to their constitution.

In the field of inorganic chemistry, especially in that of complex salts so well covered by Werner and his students, the relative number of compounds that can exist in the gaseous condition is extremely small.

Practically all complex compounds decompose or dissociate when heated. Even sulfuric acid gives a vapor whose density indicates that it is completely dissociated into H_2O and SO_3 . In fact the great majority of com-

plex compounds do not even show a molecular weight in solution which corresponds to their composition in the solid state. For example, when alum $(K_2O)_3(Al_2O_3)(SO_3)_4(H_2O)_{24}$ is dissolved in water it shows a "molecular weight" very much less than that corresponding to its formula. Crystals containing water of crystallization cannot be made to evaporate and still retain the combined water.

The number of complex compounds that can be formed must be unlimited. If methods can be found for forming them at sufficiently low temperature, probably almost any conceivable arrangements of group molecules could be built up having definite chemical compositions. Or solid solutions consisting of almost any combination of atoms and molecules could theoretically be formed. We are only sharply restricted in the formation of compounds in the case of compounds of the first order. But there is no sharp limit to the compounds that may be formed by secondary valences.

So far we have considered only crystalline solid bodies. It is evident that atoms or group molecules could be arranged irregularly in space (not according to a regular space lattice). A solid body built up in this way would have the properties of an amorphous body or glass. There can be little reasonable doubt, but that the structure of glass is of this nature. Such a structure is naturally much more easily built up of group molecules than of atoms for the greater symmetry of the atom enables it to assume definite and regular positions with respect to its neighbors more readily than group molecules could do.

The nature of the forces acting between the atoms or group molecules in amorphous bodies cannot be essentially different from that in crystals. We should expect the union between adjacent atoms or molecules to be dependent upon exactly the same kind of chemical properties as those which determine the combination of the atoms or molecules to form complex compounds (secondary valence).

From the fact that glasses, when heated, change to the liquid state by a continuous process, we are led to conclude that the structure of a liquid does not differ from that of a glass in any essential respect except that in the liquid there is a certain mobility (entirely analogous to tautomerism). Therefore, even in a liquid we look upon every atom (or group molecule) as combined chemically (or adsorbed) to all the adjacent ones. The molecular weight is, therefore, a term that has very little significance in the case of a liquid. This theory of the structure of liquids will be developed in more detail in the second part of this paper.

STRUCTURE OF THE SURFACES OF SOLIDS.

Unfortunately the study of crystals by the X-ray spectrum has not yet given us any direct knowledge of the structure of the surfaces of solids. From the point of view of the chemist, the structure of the surface must be

of the utmost importance, for chemical reactions in which solids take part are practically always surface reactions.

Our knowledge of the surfaces of solids must, therefore, be derived from indirect sources.

Since the forces that hold the atoms of solids together are of the same kind as those that hold the atoms of complex chemical compounds, we have excellent reasons for believing that the forces decrease extremely rapidly as the distance between atoms increases. We may also draw this conclusion from the compressibility of solids.

The energy which must be expended in separating the atoms of a solid metal from each other is given by the latent heat of evaporation λ (per gram atom). We can also calculate the energy necessary to change the distance between atoms from the compressibility. By comparing this energy with the latent heat, we may estimate the distance through which atomic forces are effective.

Let K represent the coefficient of compressibility of an element having an atomic volume A/ρ . We have good reasons for believing that the atoms of a solid are subject to forces that vary in proportion to the displacement of the atoms from their equilibrium positions.¹

If we compress a unit volume of a solid so as to decrease its volume by the amount ΔV the work expended will be $(\Delta V)^2/2K$. If the body is subjected to tension in all directions (negative pressure) so as to *increase* its volume by the amount ΔV , the work expended will also be $(\Delta V)^2/2K$. This relation will hold accurately only for such small negative pressures that K remains constant. It is evident that as the atoms are being separated from each other, the attractive forces will at first increase in proportion to the displacement, then gradually more slowly, until finally the attractive force reaches a maximum. Beyond this distance the force rapidly decreases (probably according to about the inverse 4th or 5th power) to negligible values. It will be very instructive, however, to calculate on the assumption that K is constant, how far we need to pull the atoms apart before the work expended will equal the known latent heat of evaporation.

We readily obtain

$$(\Delta V_0)^2 = \frac{2\lambda K}{A/\rho}.$$

¹ The specific heats and other properties of the heavier elements compel us to this view when the displacements are small. Richards has shown that the compressibility of the elements decreases gradually as the pressure is raised to very high values. This proves that the repulsive forces between atoms increase more rapidly than the displacement. It is well known that liquids can be subjected to negative pressures and have substantially the same coefficient of compressibility for negative as for positive pressures. Undoubtedly the coefficient K should increase considerably for very intense negative pressures. Nevertheless the assumption of a constant value of K could hardly affect to order of magnitude of the *calculated* range of atomic forces.

In this equation ΔV_0 represents the increase in volume which could cause an expenditure of energy equal to λ per gram atom. The volume is thus increased from 1 to $1 + \Delta V_0$. The relative increase in the distance between the atoms is given by $\sqrt[3]{1 + \Delta V_0}$. In Table I the data for several elements are given. According to Richards, tungsten is the least compressible and caesium the most compressible metal.

TABLE I.

Metal.	K. C. G. S. units.	λ ergs.	A/ ρ .	$\sqrt[3]{1 + \Delta V_0}$.	σ cm.	$\Delta\sigma$ cm.
W	0.28×10^{-12}	9.2×10^{12}	9.6	1.20	2.8×10^{-8}	0.57×10^{-8}
Pt	0.38×10^{-12}	5.4×10^{12}	9.1	1.19	2.78×10^{-8}	0.53×10^{-8}
Mo	0.46×10^{-12}	7.4×10^{12}	11.1	1.21	2.96×10^{-8}	0.62×10^{-8}
Hg	3.95×10^{-12}	0.58×10^{12}	14.8	1.16	3.26×10^{-8}	0.52×10^{-8}
Cs	61.0×10^{-12}	1.0×10^{12}	71.0	1.12	5.50×10^{-8}	0.66×10^{-8}

Thus, if the attractive forces between the atoms varied in proportion to the displacement, the expenditure of energy necessary to increase the distance between the atoms by 12% in case of caesium (or 21% in case of molybdenum) would be as great as that actually required to separate them to an infinite distance.

Actually, the attractive force can vary proportionally to the displacement only for displacements much less than 10% of the distance between atoms. However, the distance calculated by the above rough method is probably very close to that at which the *maximum attractive force* occurs. The work done in separating the atoms beyond this distance probably compensates for the decrease in attractive force before the maximum is reached.

From these considerations it seems safe to say that: *The attractive force between atoms reaches a maximum when the atoms are separated by distances 10-30% greater than the distance at which they are in stable equilibrium.*¹ Since the force varies with a high power of the distance, we may also conclude: *The attractive force becomes practically negligible when the distance between the centers of the atoms becomes twice as great as the distance at which the atoms are in equilibrium.*²

It is interesting to note in Table I that the values of $\sqrt[3]{1 + \Delta V_0}$ are largest for the elements of smallest atomic volume. This suggests that the increase in actual distance at which the attractive force becomes a maximum may be approximately the same for all the elements. In the sixth column are given the distances between the centers of the atoms calculated from the atomic volume on the assumption that the atoms are arranged

¹ Grüneisen (*Ann. Physik*, 39, 298 (1912)) by a mathematical development of a theory of monoatomic solids concludes that the average *amplitude of vibration* of the atoms in a solid at its melting point is 8.5% of the distance between the atoms.

² Probably the best evidence of the very limited range of atomic forces is that afforded by surface tension phenomena. This will be discussed in the second part of the paper.

according to a face-centered cubic lattice. The next column gives $\Delta\sigma$, the increase in this distance corresponding to the increase in volume represented by $1 + \Delta V_0$. It is seen that the values of $\Delta\sigma$ are substantially constant so that we may conclude that: *The attractive forces between atoms increase to a maximum when the distance between the atoms is about 0.6×10^{-8} cm. greater than the distance at which the attractive force is zero.*

We are now in a position to draw certain conclusions regarding the structure of the surfaces of crystals.

Let us consider a crystal such as calcite in which cleavage surfaces may be obtained. To break a crystal into two parts requires the expenditure of a certain amount of energy. Let γ be the *work or free energy* which must be expended in producing each square centimeter of cleavage surface. Thus if we have a crystal of one square centimeter in cross-section (parallel to a cleavage face), γ will be one-half of the work required to separate the crystal into two parts. In general γ will decrease as the temperature rises. If we consider the mechanism of the formation of a cleavage surface, it is evident that as the atoms are pulled away from each other a certain amount of work will be done by the thermal agitations of the atoms. The atoms moving towards the receding surface are repelled by a gradually decreasing force so that they return from the receding surface with a velocity lower (on the average) than that with which they started out. Thus there must be a certain cooling effect accompanying the formation of a cleavage surface and this heat energy must result in a corresponding decrease in the free energy required to produce the surface. This reasoning is entirely analogous to that in the case of the mechanism of the adiabatic expansion of a gas.

Simple thermodynamical reasoning (see first chapter of Nernst's *Theoretical Chemistry*) shows that in the production of a cleavage surface the amount of energy contributed by the thermal agitation is equal to $-T d\gamma/dT$. If we add to this the free energy expended, we obtain, for the total energy involved in the formation of a unit surface, the expression

$$\gamma_0 = \gamma - T \frac{d\gamma}{dT}. \quad (2)$$

This quantity γ_0 represents the total potential energy of the surface. Since we look upon atomic forces as electromagnetic in nature, the quantity γ_0 is a quantitative measure of the increase in the energy of the electromagnetic field surrounding the atoms, produced by the formation of the surface.

Just as we traced a relationship between the compressibility, the heat of vaporization and the range of atomic forces, we may derive a similar relationship between the elastic properties, surface energy and range of atomic forces. Unfortunately, however, few data on the surface energy of solids are available.

There is every reason for believing that the range of atomic forces is of the same order of magnitude in all the states of matter. In forming a cleavage surface, therefore, it is probable¹ that the atoms pull part when the distance between adjacent atoms has been increased by about 0.6×10^{-8} cm.

When electrically charged or magnetized bodies are brought into proximity, they tend to move in such a way that the total energy of the electric or magnetic field becomes a minimum. For example, if we imagine a number of small horseshoe magnets to be placed in a box and shaken, we should expect on opening the box to find that the magnets had become attached to each other in pairs in such a way that in each pair the north pole of one is in contact with the south pole of the other. This arrangement would be a very stable one and would require a maximum amount of energy to break it up.

In a similar manner the atoms in the surface of a crystal must tend to arrange themselves so that the total energy in the field surrounding them will be a minimum.² In general, this will involve a shifting of the positions of the atoms with respect to one another. However, from the fact that energy is always required to separate a solid body into two parts we must conclude that the field energy associated with the surface atoms is always greater than that associated with a like number of atoms in the interior of the solid, notwithstanding the shifting of the positions of the atoms in the surface layer.

The smallness of the range of the atomic forces, compels us to conclude

¹ Further evidence in support of this statement will be given in the second part of this paper.

² In the second part of this paper it will be shown that this principle is of great importance in connection with surface tension phenomena. The group molecules in liquids arrange themselves in the surface layer in such a way that the part of the molecule which has the weakest field around it actually forms the surface, while the more active parts of the molecule are drawn below the surface, and are then without effect on the surface tension except in so far as they crowd the surface atoms apart.

The above principle also seems to be related to the cleavage or crystal habits of solids. In a crystal built up of atoms arranged according to a face centered cubic lattice the number of atoms per sq. cm. of crystal face is $5.56 \times 10^{15} \times V^{-2/3}$ for the 1:0:0 faces; $4.02 \times 10^{15} \times V^{-2/3}$ for the 1:1:0 faces and $6.57 \times 10^{15} V^{-2/3}$ for the 1:1:1 faces. Here V is the atomic volume. Thus the atoms are arranged more compactly in the octahedron faces than in any others.

For such faces the value of γ_0 should be a minimum. When platinum is slowly sublimed at high temperatures as, for instance, in the winding of an electric furnace, it crystallizes in the form of beautiful octahedra. The writer has observed similar crystals of tungsten.

On the other hand, in the simple cubic lattice the most compact arrangement of the surface atoms occurs in the 1:0:0 faces. Crystals of the alkali halides have cubic cleavage and usually crystallize as cubes and the atoms in these crystals are spaced according to a simple cubic lattice.

that in general the distances through which the surface atoms are shifted from their original positions in the solid, are small compared to the average distance between atoms. We must also conclude that the abnormal surface arrangement is usually limited to the surface layer only.

The surface of a solid (or liquid), therefore, does not contain, as is usually assumed, a transition layer, consisting of several layers of atoms or "molecules," in which the density varies by continuous gradations from that of the solid to that of the surrounding gas or vapor. Instead we find that the change from solid to empty space is most abrupt. In a sense, the rearrangement of the atoms in the surface layer causes this layer to assume the character of a transition layer, but the density of the packing of the atoms in this layer is undoubtedly greater than in the body of the solid, so that there can be no gradual change in density from that of the solid to that of the space. Additional evidence in favor of this view will be given in the remainder of this paper.

The surface of a crystal must then consist of an arrangement of atoms as definite as that existing in the interior of the crystal, although slightly different from the latter. The surface must thus be looked upon as a sort of checker board containing a definite number of atoms, of definite kinds arranged in a *plane* lattice formation. The space between and immediately above (away from the interior) these atoms is surrounded by a field of electromagnetic force more intense than that between the atoms inside the crystal.

There are good reasons for believing that the intensity of this surface field of force is substantially independent of the temperature. The energy in the surface field is measured by γ_0 . (Equation 2.) Now the work done, during the formation of a fresh surface by the thermal agitation of the molecules (namely, $-T d\gamma/dT$), should be approximately proportional to the temperature. Therefore, $d\gamma/dT$, should be independent of the temperature. Thus we may place

$$\gamma = a - bT \quad (3)$$

where a and b are constants. Combining this with (2) we find $\gamma_0 = a$. In other words, γ_0 , the total energy of the electromagnetic surface field should be independent of the temperature.

In the case of liquids, the free energy necessary for the formation of unit surface is called the surface tension. By analogy we would be justified in calling γ the surface tension of the solid. However, on the whole, it seems preferable with both solids and liquids to refer to the quantity γ as the *free surface energy* and γ_0 as the *total surface energy*.

Sublimation of Solids.—Sublimation involves two processes; evaporation and condensation. Condensation being in some ways the simpler of the two will be considered first.

Condensation of Vapors.—When a crystal is in contact with its own saturated vapor the vapor must be continually condensing on the solid while the solid is evaporating at an equal rate. The rate at which the molecules of the vapor come into contact with the surface of the solid is given by the equation

$$m = \sqrt{\frac{M}{2\pi RT}} p, \quad (4)$$

where M is the molecular weight of the vapor, R is the gas constant, p is the pressure of the vapor and m is the rate at which the gas molecules strike against the surface, expressed in grams of vapor per sq. cm. per second.¹

When a molecule of vapor strikes against the solid surface one of two things may happen. The molecule may be *reflected* from the surface, in other words, may rebound elastically, or it may *condense* on the surface, that is, it may be held by attractive forces in such a way that it forms at least temporarily a part of the solid body. It is of importance to know approximately what fraction of the molecules striking the surface are reflected.

In the kinetic theory of gases it has almost universally been assumed that molecules are perfectly elastic. This assumption has become so much a habit of thought that nearly everyone who has applied the kinetic theory to liquids and solids has taken it for granted that the collision between gases and surfaces of solids or liquids are also elastic.²

We have seen, however, from a consideration of the heat conductivity of solids that the time of relaxation of the atoms is usually small compared to the time necessary for the atom to complete a single oscillation. This means that before an atom can be displaced a perceptible distance the energy causing the displacement has been dissipated among all the adjacent atoms. From this fact it appears that the collisions of molecules against solid bodies must in general be almost wholly inelastic.

In a recent paper in the *Physical Review*³ the writer has discussed this question very fully, and gives abundant evidence both experimental and theoretical, for the inelasticity of the collisions between gas molecules and solid surfaces. There are apparently some cases in which a moderate

¹ This equation is a simple modification of the equation giving the rate of effusion of gases through small openings (Meyer's Kinetic Theory of Gases, German edition, 1899, p. 82). Its derivation was given by the writer in an article in the *Phys. Rev.*, **2**, 331 (1913). The importance of this equation in the kinetics of heterogeneous reactions can hardly be over-emphasized. See for example Langmuir, *THIS JOURNAL*, **37**, 1144 (1915).

² N. T. Bacon (*J. Phys. Chem.*, **17**, 762 (1913)) suggests that molecules are not elastic, and in this way explains qualitatively the phenomena of adsorption and catalytic action.

³ *Phys. Rev.*, **8**, 149 (1916).

amount of real reflection does occur, but these cases must be looked upon as the exception rather than the rule.

According to this viewpoint the mechanism of the condensation of a vapor on a solid is as follows:

In the vapor surrounding the solid, the average distance which the molecules travel between collisions (the mean free path) is of the order of magnitude of 10^{-5} cm. if the pressure is atmospheric, while it is correspondingly greater if the pressure is less. When a vapor molecule approaching the surface comes within a distance of about 2×10^{-8} cm. of the surface layer of atoms it begins to be acted upon by the electromagnetic field close to the surface. The vapor molecule thus experiences a force attracting it towards the surface. As it moves closer to the surface the attractive force rapidly increases and soon reaches a maximum intensity. The attractive force then rapidly decreases, and falls to zero when the molecule has traveled a distance only about 0.6×10^{-8} cm. beyond the point at which the force was a maximum. The point at which the force falls to zero may be regarded as an equilibrium position. When the molecule reaches this position its kinetic energy will be very high for a relatively large amount of work has been done upon it by the attractive forces. It will, therefore, not remain in the equilibrium position, but will move still closer to the atoms of the solid, and will thus enter a region in which it is subjected to very strong and rapidly increasing repulsive forces. If the molecule had lost no energy to adjacent atoms it would probably travel a distance $0.2-0.3 \times 10^{-8}$ cm. against these repulsive forces before being brought to rest. It would then pass again through the equilibrium position and finally out through the region of attractive forces, and might thus again escape from the surface forces, in other words, be reflected.

But the improbability of such a reflection is evident when we consider the ease with which energy is dissipated to adjacent atoms. This energy loss occurs in two ways. In the first place, when the molecule is approaching the surface, the attractive force is exerted by *several atoms* on the surface. These atoms are thus all accelerated towards the incident molecule. A little later when the molecule is in the region of repulsive forces, these forces will be exerted principally by a *single atom* of the solid. The energy used in accelerating the surface atoms can, therefore, only partially be delivered back to the incident molecule. This dissipation in energy, even if only relatively small, will usually make it impossible for the molecule to pass out through the region of attractive forces.

The second kind of loss of energy, which is probably the more important, is that which causes the remarkably small time of relaxation in solid bodies. We have seen that in the interior of crystals the time taken for adjacent atoms to reach thermal equilibrium with each other is of the order of 10^{-16} seconds. The duration of a collision between a molecule and a surface

(that is, the time between successive passages through the region of maximum attractive force) must be of the order of 10^{-13} seconds. Thus in general, the energy delivered to the incident molecule by the attractive forces, is practically wholly dissipated to the adjacent atoms by the time the molecule first reaches the equilibrium position. It, therefore, has not sufficient kinetic energy to enable it to penetrate far into the region of repulsive forces, and certainly not sufficient to allow it to work against the attractive forces and thus escape from the surface.

The condensation of a vapor on a solid surface thus takes place independently of the temperature of the surface.¹

This is especially evident when we consider that the intensity of the field of force close to the surface, as measured by the total surface energy γ_0 , is itself independent of the temperature. The rate of evaporation on the other hand varies extremely rapidly with the temperature.

If practically every molecule of vapor which strikes against the surface of the solid condenses, it is not at first evident how the molecules, especially if they are complex, are able to arrange themselves to form a crystalline mass. In analyzing the mechanism of condensation we must distinguish two extreme sets of conditions that may occur. These may be termed *irreversible* and *reversible* sublimation.

By *irreversible* sublimation I mean the type which occurs for instance when a tungsten filament is heated to a high temperature in a well evacuated bulb. Under these conditions there can be no equilibrium, for the bulb is at a temperature thousands of degrees lower than that at which the vapor can be produced. The vapor is thus enormously superheated with respect to the surface on which it condenses. Such conditions as this can only be realized in practice when the vapor is at very low pressure, for, otherwise, the amount of vapor condensed per unit area per second would be so great that the heat liberated by the condensation could not be removed rapidly enough to maintain a low temperature on the condensing surface.

By the term *reversible* sublimation we may designate that which takes place for example, when iodine or naphthalene is sublimed slowly at ordinary temperatures.

In this case we are dealing with small differences of temperature, and we shall see that under these conditions condensation and evaporation are going on simultaneously at nearly equal rates over every portion of the surface where condensation occurs.

The mechanisms of reversible and of irreversible sublimation are in some ways quite different, and from the experimental side the phenomena show marked distinctions.

¹ It must of course be remembered that what we ordinarily observe during the condensation of a vapor is the difference between the rate of condensation and the rate of evaporation.

In the irreversible sublimation the vapor molecules remain where they first strike the surface, since they can neither be reflected nor re-evaporated. The deposit formed by the condensed vapor is, therefore, homogeneous (when gaseous impurities are absent) and is of uniform thickness. If the temperature of the surface on which condensation occurs is sufficiently low, the deposit will be wholly noncrystalline, since the atoms or molecules become rigidly fixed in position when they strike the surface and thus have no opportunity to arrange themselves as in a crystal. With the condensing surface at higher temperatures, however, a sintering or crystallizing process may go on within the deposit even when the temperature is below that at which perceptible vaporization occurs.

By means of this irreversible sublimation it is possible to obtain any volatile body in a noncrystalline form.

In the case of reversible sublimation the deposit formed from the condensed vapor is ordinarily very crystalline, frequently consisting of groups of separate crystals. In the formation of these crystals every molecule of vapor which strikes the surface condenses just as in the case of irreversible condensation, but most of these molecules re-evaporate again. The tendency of different molecules to re-evaporate will depend entirely on how firmly they are held by the atoms of the crystal. Thus the molecules which strike the surface in such a way as to form a continuation of the space lattice already present, will evaporate much less frequently than molecules which are not in positions where they can fit in with the crystal structure. The continual evaporation and condensation going on over the whole surface of the crystal allows the atoms to arrange themselves in the most stable positions. The smaller the differences in temperature and the more nearly equal the rates of condensation and evaporation, the more perfect will be the development of the crystals.

Evaporation of Solids.—We have seen that the condensation of vapors on a solid body takes place at a rate which is practically independent of the temperature. The rate of evaporation, however, increases rapidly with temperature.

Since evaporation and condensation are in general thermodynamically reversible phenomena, *the mechanism of evaporation must be the exact reverse of that of condensation*, even down to the smallest detail.

In the condensation of a monatomic vapor such as that of a metal, each atom as it approaches the surface comes into a region in which it is attracted. It is thus accelerated, but it gives up its newly acquired energy to adjacent atoms nearly as fast as it receives it. It soon reaches a region of repulsive forces, and is then brought to a stop. It then continues to move about an equilibrium position with an irregular motion due to thermal agitation.

Conversely in the evaporation of an atom of a metal the atom must

acquire energy from adjacent ones and thus be accelerated outward. As it moves it must receive successive increments of energy from its neighbors until finally it passes out of the region of attractive forces. From the smallness of the time of relaxation we are thus compelled to believe that an atom only escapes when it thus receives a very large number of successive impulses from the adjacent atoms.

The very small probability of such a sequence of favorable impulses is the reason that so few atoms evaporate at lower temperatures.

We may picture to ourselves the mechanism of evaporation by imagining a large number of heavy balls suspended (according to a two-dimensional lattice) from a ceiling by steel springs. Each ball is to be coupled to each of its neighbors by springs under tension. If some of the balls are set in motion the energy will be rapidly propagated to the others so they will all be in a state of agitation. To properly imitate the structure of a solid the coupling between the balls should be so stiff that the total energy of one ball can be transmitted to its neighbors in a very small fraction of the time required for a single oscillation.

When all the balls have been in motion long enough for a steady state to have been reached the velocities will be distributed among them according to the probability laws, in other words, according to Maxwell's distribution law.

If the springs are of brittle wire so that they snap when elongated more than a certain amount, then from time to time balls which have acquired an unusually large downward displacement will break their springs and escape. This will be quite analogous to evaporation.

The rate of evaporation of a solid is thus determined by the number of surface atoms per second which reach a certain critical condition. By means of Maxwell's distribution law it can thus be readily shown¹ that the rate of evaporation should increase with the temperature according to an equation of the form

$$m = A\sqrt{T} e^{-\lambda/RT} \quad (5)$$

where λ is the internal latent heat of evaporation per gram atom, and A is a constant whose value will depend primarily on the degree of coupling between adjacent atoms.

In the study of the disintegration of radioactive substances it has been

¹ Richardson (*Phil. Trans.*, 201, 516 (1903)) calculated in this way the rate of evaporation of electrons from heated metals (thermionic emission). The derivation of Equation 5 is also given by the writer (*THIS JOURNAL*, 35, 122 (1913)) in connection with a study of the reaction between oxygen and tungsten at high temperatures. It was also pointed out that this equation is substantially equivalent to Arrhenius' equation for the temperature coefficient of reaction velocity.

The significance of Maxwell's distribution law in relation to the kinetics of chemical reactions has been very fully treated in a recent paper by R. Marcellin (*Annales de Physique*, 3, 185 (1915)).

customary to speak of the life or period of the atom. In a similar way we may calculate the "life" of an atom on the surface of an evaporating solid.

The number of atoms evaporating per second per sq. cm. of surface will be Nm/M where N is the Avogadro constant and M is the atomic weight of the substance. If N_0 is the total number of atoms per sq. cm. of surface then t , the average life of an atom on the surface will be

$$t = \frac{N_0 M}{Nm}. \quad (6)$$

The "half period," that is, the time which must elapse before half of any selected lot of atoms will have evaporated, is equal to

$$t_{1/2} = 0.693 \frac{N_0 M}{Nm}. \quad (7)$$

We have just seen that the constant A in Equation 5 is dependent on the coupling between the atoms. The time of relaxation of the atoms is also a measure of this coupling. It should thus be possible to estimate the time of relaxation from the rate of evaporation, and it will be of interest to see how the result calculated in this way compares with that found from the heat conductivity.

We see from Equation 5 that the rate of evaporation, m , depends on the latent heat of evaporation. If we substitute $\lambda = 0$ in Equation 5 we obtain a hypothetical value of m_0 (let this be m), that represents the rate of evaporation which would occur if attractive forces did not prevent the escape of atoms from the surface. Thus we obtain from (5)

$$\frac{m}{m_0} = e^{-\lambda/RT}. \quad (8)$$

By Equation 6 the average life of an atom on the surface of a solid evaporating at the rate m_0 , is

$$t_0 = \frac{N_0 M}{Nm_0}. \quad (9)$$

Eliminate m_0 between (8) and (9).

$$t_0 = \frac{N_0 M}{Nm} e^{-\lambda/RT}. \quad (10)$$

Or from (5)

$$t_0 = \frac{N_0 M}{NA\sqrt{T}}. \quad (11)$$

The quantity t_0 thus represents the average length of time an atom would remain on the surface if there were no attractive forces to hold it. Now the "time of relaxation" has been defined as the time required for an atom to give up all but $1/e^{\text{th}}$ of its excess energy to adjacent atoms. It is evident that the time required for an atom at rest to be set in motion

will also be measured by the time of relaxation. Thus t_0 should be of the same order of magnitude as the time of relaxation, and probably only differs from it by some constant factor not very far from unity.

The rates of evaporation of tungsten¹ platinum and molybdenum² in a very high vacuum, have been measured by Mr. G. M. J. Mackay and the writer. The values of t_0 , calculated from these data by Equation 10 are given in Table II.

TABLE II.

	W.	Mo.	Pt.
N_0	1.46×10^{15}	1.32×10^{15}	1.51×10^{15}
t_0 at 300°K	3.4×10^{-19}	3.5×10^{-20}	1.1×10^{-18}
t_0 at 2000°K	5.2×10^{-18}	1.0×10^{-18}	3.0×10^{-15}
t_r by Equation 1.....	1.3×10^{-15}	2.3×10^{-15}

For comparison, the "times of relaxation" t_r , calculated by Equation 1, are given in the last line. It will be remembered that Equation 1 gives too high a value for t_r because it was assumed in its derivation that an atom could take up energy only from atoms in one given direction. It is seen that the order of magnitude of t_0 is not very different from that of t_r . We must not expect any very good agreement between t_0 and t_r , because of the very great effect of slight errors in λ on the value of t_0 calculated by Equation 10. Thus if λ is taken one per cent. too large the value of t_0 will be 20 times too small. On the whole, therefore, we may conclude that the values of t_0 calculated as above, furnish confirmatory evidence that the time of relaxation of the atoms in solids is hundreds if not thousands of times smaller than the "natural period" of atomic vibrations.

So far we have considered the evaporation of solids which give monatomic vapors. When a crystal such as sodium chloride evaporates the atoms must group themselves together in pairs *before* they escape from the surface forces.

The latent heat of evaporation does not correspond to the energy required to separate the atoms from each other, but only to the energy needed to separate one group of atoms from other similar groups. This makes it appear that evaporation in these cases is the result of a tautomeric change taking place among the surface atoms. Thus in the case of solid sodium chloride the sodium atoms are ordinarily held to the adjacent chlorine atoms by secondary valence. If, however, a tautomeric change occurs by which a pair of adjacent chlorine and sodium atoms becomes attached to each other by *primary* valences, then this pair will be held to the surface by much weaker forces than those holding other atoms not so combined. The pairs held by primary valences may thus be enabled to evaporate from the surface. We should not assume, however, that

¹ *Phys. Rev.*, 2, 329 (1913).

² *Ibid.*, 4, 377 (1914).

every pair of atoms so combined, or even the majority of them, will evaporate, for if we do, it would follow that only a very small fraction of molecules of salt vapor striking a surface would condense. It is more likely that the tautomeric changes take place with high frequency, but that the time during which a pair of atoms exists consecutively in the tautomeric form is comparable with the time of relaxation, that is, of the order of 10^{-17} seconds. Now the time required for an atom or a group of atoms to move out of the region of attractive forces (a distance of about 10^{-8} cm.) must be *at least* 10^{-14} seconds, since molecular velocities are always less than 10^6 cm. per second. We are thus led to believe that a sodium chloride molecule only evaporates when the tautomeric change occurs at a moment when the atoms are already displaced from their equilibrium positions to an unusual degree.

The evaporation of compound substances of the polar type thus involves rather complicated chemical changes in which the atoms rearrange themselves according to their primary valences. This conception of the mechanism of evaporation receives support from the fact that so few complex polar compounds or molecular compounds can be volatilized without dissociation. Thus nearly all inorganic salts except those which are compounds of the first order (halide salts for instance) are decomposed or dissociate on heating. Crystals containing water of crystallization can never be distilled with their water of crystallization. Even compounds like sulfuric acid give vapors which are dissociated.

Nonpolar compounds, such as most organic substances, usually contain fixed molecules which, even in the solid condition, are held together by primary valences, the secondary valences merely serving to hold the fixed molecules together. In this case evaporation involves only a breaking of the secondary valence forces so that it becomes quite similar to the evaporation of metals or other substances giving monatomic vapors.

Relation between Condensation and Evaporation.—When a solid is in equilibrium with its own vapor, condensation and evaporation are occurring simultaneously at equal rates. We have seen that we are justified, in the majority of cases, in considering that all the molecules of vapor which strike against the surface condense (are not reflected). Now the rate at which the molecules strike the surface is given by Equation 4

$$m = \sqrt{\frac{M}{2\pi RT}} p. \quad (4)$$

Since all of the molecules condense, and since the rate of evaporation must be equal to the rate of condensation, we may use this same equation to calculate the rate of evaporation, m , in terms of the pressure p , of the saturated vapor. If the condensation and evaporation go on independently of one another, then Equation 4 should give a means of calculating the rate at which a solid evaporates into a perfect vacuum. Or

conversely if we determine the rate of evaporation of a solid in a high vacuum we can calculate the vapor pressure by the above equation.¹

This theoretical relation between the rate of evaporation and vapor pressure was first obtained by Hertz.² Hertz himself and others who have used the equation have not considered that the reflectivity is negligible and hence looked upon the calculated value of m as being greater than the true rate of evaporation.

R. Marcellin³ has recently attempted to measure the maximum rate of evaporation of naphthalene, nitrobenzene and iodine, in a vacuum, and compares his results with those calculated by Equation 4. He concludes that at 40° only about one molecule out of 20 striking the surface condenses, while at 70° about one out of five condenses. That is, the reflectivity decreases rapidly at higher temperatures. It should be noted on the other hand that R. W. Wood⁴ finds no reflection of mercury atoms from a surface at very low temperatures but concludes that the atoms are all reflected at higher temperatures.

Marcellin measured the rates of evaporation of substances in capillary tubes. By plotting the rate of evaporation against the length of the tube through which the vapor had to pass, he *extrapolated* back to zero length of tube, and expected in this way to find the rate of evaporation in a perfect vacuum. When we consider that this extrapolation was carried out over a length of tube at least eight times the diameter of the tube, we realize how very few of the molecules evaporating from the surface could have escaped, from the end of the tube. The great majority of them must have struck the walls of the tube and thus have been afforded an opportunity of returning back onto the surface. Measurements of this sort, to have any value, must be made so that molecules evaporating from the surface may move off in straight lines without meeting any obstruction until they strike the cooled surface on which they permanently condense.

If Marcellin had plotted the reciprocal of the speed of evaporation (which should be a linear function of the length of the tube) instead of the speed itself, it would have been apparent, first that the observed rates were much lower than the true maximum rates, and second, that even with the small capillaries he used he did not succeed in keeping the temperature of the evaporating surface up to that of the bath surrounding the tube. Therefore, it appears that Marcellin's experiments are entirely

¹ The writer, together with Mr. G. M. J. Mackay, has used this method for measuring the vapor pressures of the metals tungsten, platinum, molybdenum, iron, nickel, copper and silver, and the results have been, or will be, published in the *Physical Review*. The reasons which justify the assumption that the reflectivity is negligible, are given in detail in a recent article (*Phys. Rev.*, 8, 149 (1916)).

² *Ann. Physik*, 17, 177 (1882).

³ *Annales de Physique*, 3, 185 (1915).

⁴ *Phil. Mag.*, 30, 300 (1915).

consistent with the view that the true rate of evaporation is accurately given by Equation 4.

The writer has also shown¹ that Wood's experiments may equally well be explained by assuming, instead of a reflection of mercury atoms, at the higher temperatures, a condensation followed by evaporation.

For the case of a clean surface of liquid mercury evaporating into a good vacuum Knudsen has recently² proved that Equation 4 gives the actual rate of evaporation.

Wood makes the statement that atoms of mercury which are "diffusely reflected" (or according to our theory, condensed and re-evaporated) from a surface, do not seem to be distributed quite according to Lambert's cosine law, but there seem to be too few atoms leaving the surface in directions nearly parallel to the surface. Now if evaporation and condensation can go on simultaneously, although independently, it must follow, according to Maxwell, that the number of atoms leaving the surface in different directions must be proportional to the projected area in that direction (Lambert's cosine law).

Observations on the evaporation of metals in high vacuum have convinced the writer that Lambert's cosine law does hold accurately for evaporation, and the Wood's conclusion is incorrect.

Wood drew his conclusions from the *apparent* sudden decrease in the thickness of a film of metal deposited on glass, in the region close to the plane of the surface from which "reflection" took place. In the writer's experience, this sudden decrease which he has often observed, and which certainly seems very real, is only apparent. It is due to the fact that, although the *thickness* of the film varies *linearly* with the distance from the plane of the surface, the *light absorption* varies *exponentially*.

Kaye and Ewen³ have reported that at pressures of a few mm. of gas, the sublimation from heated metals (Fe, W, Cu, Ag or Ir) appear to consist of two parts, one of which, diffuses like a gas, but the other, often the larger part, is projected in straight lines in a direction perpendicular to the surface at which it originates. In the experience of the writer such effects are due to convection currents (which often produce very freakish effects at pressures of a few mm.) or to electric discharges through the gas. They are usually enormously stimulated by the presence of traces of moisture. In a thoroughly dry gas or in a good vacuum, and in the absence of electric discharges, the evaporation of heated metals takes place without any evidences of such "projection" of particles in definite directions. Of course in a really good vacuum the atoms leaving the heated surface, travel in perfectly straight lines until

¹ *Phys. Rev., loc. cit.*

² *Ann. Phys.*, 47, 697 (1915).

³ *Proc. Roy. Soc., (A)* 80, 58 (1914).

they strike an obstacle, and in this way "shadows" of interposed objects may be obtained. But this projection of particles takes place according to Lambert's cosine law and is in full accord with the ordinary conceptions of the kinetic theory.

We have assumed so far that evaporation and condensation can go on simultaneously without influencing each other. For example, in calculating by Equation 4 the rate of evaporation in a vacuum from the pressure of the saturated vapor, we had to assume that the true rate of evaporation in presence of saturated vapor is the same as that in vacuum, in other words, that the condensation of the vapor has no effect on the rate of evaporation.

There are, however, reasons which might lead us to expect a difference in the rate of evaporation in presence of and in the absence of vapor.

In the first place, when a vapor atom or molecule condenses on a surface an amount of energy corresponding to the latent heat of evaporation must be liberated, and must result in a local rise of temperature. It would seem that this might cause the evaporation of an adjacent atom which would otherwise not evaporate. Thus the condensation of vapor might stimulate the evaporation. This would be equivalent in many ways to a reflection of vapor molecules from the surface.

The following considerations make it very improbable that condensation has any such effect on evaporation. The "average life" of an atom on a surface may be readily calculated from Equations 4 and 6. The life will be inversely proportional to the vapor pressure, and will be proportional to \sqrt{MT} . If we choose $M = 25$, $T = 400$ and $p =$ one megabar (atmospheric pressure) and assume that $N_0 = 10^{15}$ atoms per sq. cm. we thus calculate that the life of an atom on the surface would be 3.8×10^{-9} seconds. In the evaporation of substances in vacuum the equilibrium pressure would always be extremely small compared to one megabar, so that the life of the atoms on the surface would be much more than 10^{-8} seconds. Now the time taken by an atom to receive or give up its energy to adjacent atoms is of the order of 10^{-17} seconds, or about 10^{+9} times less than the life of the atom on the surface. These figures show that the critical conditions necessary to cause the evaporation of an atom are of relatively rare occurrence. The chance is negligibly small, therefore, that an atom condensing on the surface will be able to give up its energy to an adjacent atom at a moment when the latter is nearly in its critical condition.

These considerations make it appear probable that the energy liberated by the condensation of vapor is totally without influence on the mechanism of evaporation.

There is, however, another kind of effect by which condensation may, and probably does, influence the rate of evaporation. Let us consider

for example solid naphthalene in contact with its saturated vapor. When a molecule of naphthalene vapor strikes against the surface of the crystalline substance it undoubtedly condenses in the position in which it strikes. The chances are small that this position will be one in which the molecule forms a continuation of the space lattice of the crystal. If the temperature is sufficiently high the molecule may, by a sort of sintering process, readjust its position in conformity with the underlying group of molecules. But at lower temperatures this readjustment will often be impossible.

Such irregularly placed molecules will tend to evaporate from the surface more rapidly than those in the regular lattice positions.

We have already seen that this greater rate of evaporation manifests itself in the tendency for larger and more perfect crystals to be formed, as the sublimation of a substance is made more nearly reversible.

Since the rate of evaporation of the irregularly placed molecules must be finite, it follows that the surface must be more or less completely covered by such molecules. In other words, the surface of a crystalline solid in equilibrium with its saturated vapor may be covered by a layer of irregularly placed molecules, in other words, there may be an amorphous surface film.

The extent to which the surface is covered by such a film will depend upon the ease with which the molecules rearrange themselves, and also upon the relative rates of evaporation of the regularly and irregularly placed molecules.

It is of interest to consider the evaporation and condensation of a crystal of naphthalene under various conditions:

1. *Irreversible Condensation.*—If a stream of naphthalene vapor is admitted at low pressure into a well exhausted bulb immersed in liquid air, we should expect that all the molecules would condense in the positions in which they first strike the cooled bulb. The condensed material should then be wholly amorphous, both on its surface and in its interior.

2. *Irreversible Evaporation.*—If a naphthalene crystal is suspended in an exhausted bulb and the latter is immersed into liquid air, the naphthalene crystal will evaporate irreversibly, since no molecules of naphthalene will return from the surface of the bulb. In this case there will be no amorphous surface layer on the crystal.

3. *Reversible Evaporation or Condensation.*—If a naphthalene crystal is placed in one arm of an inverted and exhausted U-tube and the other arm is maintained at a very slightly lower temperature, the naphthalene will slowly sublime from one arm to the other, and form crystals in the cooler arm. These crystals as well as the one in the warmer arm will have amorphous surface layers.

If we calculate the rate of evaporation from the pressure of the saturated vapor by Equation 4 we obtain a value which corresponds to the rate

of evaporation from the amorphous surface layer, and not from the true crystalline surface. Therefore, the rate of evaporation of a crystal in a good vacuum (Case 2, Irreversible Evaporation) should be lower than that calculated from the vapor pressure, notwithstanding the fact that no reflection of molecules from the surface takes place.

It is probable that in the great majority of cases, especially with substances such as metals which give monatomic vapors, that this effect is entirely negligible, because of the great ease with which the atoms can arrange themselves on the surface.¹

Even with substances having molecules as complicated as that of naphthalene it seems improbable that the difference between the rates of evaporation of crystalline and amorphous surfaces would be great enough to very seriously affect the validity of Equation 4, when applied to the calculation of the rate of evaporation in a vacuum. Accurate experimental determinations of the rates of evaporation of complex organic compounds in high vacuum should prove of great interest.

There are cases, however, where we may expect very radical differences between the true rates of evaporation *in vacuo* and the rate calculated from the vapor pressure by Equation 4.

Red phosphorus should furnish an example of this sort. The transformation of yellow into red phosphorus takes place very much more slowly than the rate at which molecules of phosphorus vapor strike against a surface of red phosphorus. Therefore, the molecules of phosphorus vapor which impinge against the surface and condense, must evaporate again without having been in the condition of red phosphorus.

The surface of the red phosphorus is, therefore, covered, at least in part, by a layer of fixed molecules which constitute an adsorbed film of yellow phosphorus. The rate of evaporation calculated by Equation 4 corresponds to the evaporation from this adsorbed film of yellow phosphorus plus that from the uncovered portion of the surface of red phosphorus. On the other hand if the red phosphorus is placed in a good vacuum the adsorbed film of yellow phosphorus will distill off and the observed rate of evaporation will correspond to the rate of conversion of

¹ According to the principle already enunciated, by which every element in the mechanism of a reversible process must itself be reversible, it follows that any rearrangement of molecules on the surface, which takes place during the condensation of a vapor, must take place to the same extent, but in the reverse direction, in the evaporation of the substance. Thus if molecules rearrange themselves into regular positions, an equal number of molecules must be continually leaving regular positions to assume irregular positions. This leads to the conclusion that even with substances which give monatomic vapors, the surface must in part be amorphous. However, an amorphous structure due to this cause will be present to the same extent when the evaporation is irreversible as it is in the case of reversible evaporation. Therefore no error is made in calculating the rate of evaporation in a vacuum from the vapor pressure, according to Equation 4.

red into yellow phosphorus. This rate will be very much less than that calculated from the equilibrium pressure.

It is thus probable in the case of red phosphorus that the equilibrium pressure is not a true vapor pressure in the ordinary sense, but is rather to be regarded as a dissociation pressure.

The rate of evaporation of ammonium chloride in a vacuum, both in the presence of and in the absence of traces of moisture, should throw a very interesting light upon the mechanism of the evaporation or dissociation¹ of this substance.

The Dissociation of Solids and the Kinetic Interpretation of the Phase Rule.

Sometime ago it was pointed out to the writer by Mr. R. E. Wilson that a difficulty arises in the application of the kinetic theory to the dissociation of a substance such as calcium carbonate.

We may assume that in the equilibrium between calcium carbonate, calcium oxide and carbon dioxide two opposing reactions are taking place at equal rates. Off-hand, the most natural assumption in regard to these reactions would seem to be that the rate at which carbon dioxide is converted into carbonate is proportional to the pressure p of carbon dioxide and to the fraction θ_1 of the surface which is covered by CaO. On the other hand the rate of dissociation of the carbonate would be proportional to the fraction θ_2 of the surface covered by CaCO₃.

If we equate these two rates we obtain for equilibrium

$$p\theta_1 = K\theta_2 \quad (12)$$

where K is the equilibrium constant. This equation indicates that the pressure of the CO₂ should depend on the ratio between θ_2 and θ_1 ; in other words it should depend on the relative proportions of the CaO and CaCO₃. This is contrary to fact. Evidently, therefore, we have made wrong assumptions regarding the mechanism of the reaction.

If we examine Equation 12 in the light of the Phase Rule we see that it would fit the facts well if there were a single solid phase of variable composition instead of two phases of constant composition. It would apply for instance to the dissociation of ferric oxide recently studied by Sosman and Hostetter² who found a "continuous series of solid solutions from Fe₂O₃ over to a point very near Fe₃O₄ if not over the entire range to Fe₃O₄."

Furthermore, when we analyze the assumptions made in the derivation of Equation 12 we readily see that they imply a solid solution phase. Thus if the rate of dissociation of CaCO₃ were proportional to the fraction of the surface covered by CaCO₃ it is evident that the surface would soon

¹ See papers by Abegg and Johnson, *Z. physik. Chem.*, **61**, 455 and 457 (1908); Scheffer, *Proc. Akad. Wetenschappen Amsterdam*, **18**, 446 (1915).

² THIS JOURNAL, **38**, 807 (1916).

consist of CaO and CaCO_3 molecules distributed haphazard over the surface. This is exactly the kind of surface we should expect a solid solution to have.

The assumptions made above evidently are not consistent with the existence of separate phases of constant composition.

The Phase Rule, however, indicates that in the dissociation of calcium carbonate two solid phases, CaO and CaCO_3 , are present together. In order that CaCO_3 may dissociate and form a phase of CaO (instead of a solid solution) it is *necessary that the reaction shall occur only at the boundary between two phases.*

Now the CaO phase is generally so porous that CO_2 readily diffuses through it. We are then forced to conclude that the CO_2 in passing through the CaO does not react until it reaches the boundary of the CaCO_3 phase. In a sense, therefore, calcium carbonate must be looked upon as a catalyst for the reaction between calcium oxide and carbon dioxide.

From the kinetic point of view this must mean that carbon dioxide molecules are only absorbed to form calcium carbonate when by so doing they form a continuation of a calcium carbonate crystal already present.

It will be remembered that in the calcite crystal each carbon atom is surrounded by three systematically placed oxygen atoms. By examining a model of such a crystal it is readily seen that in the cleavage surfaces two of the oxygen atoms are probably close to the surface, while the third lies well under the surface. In the readjustment of the positions of the surface atoms which must occur when a cleavage surface is found, the atoms must tend to assume positions in which the forces between the atoms are balanced against one another. Such an arrangement may have a considerable degree of stability.

If we imagine one of the carbon atoms, with the pair of oxygen atoms adjacent to it, to be removed from the surface, the symmetry of the arrangement of the surface atoms will be destroyed. This disturbance of the surface will certainly have an effect on the balance of forces holding the adjacent atoms. These atoms, therefore, will shift their positions. The neighboring carbon atoms (with their oxygen atoms) will then be held to the surface by a force which is *different* from that obtaining before the first CO_2 was removed.

Now if this force has been *strengthened*, then the adjacent molecules of CO_2 will be less likely to leave than others further from the disturbed region. Therefore, if the crystal is sufficiently heated, CO_2 would leave from all portions of the surface and a *solid solution* of CaO in CaCO_3 would be found. On the other hand if the removal of one CO_2 molecule sufficiently *weakens* the force by which the adjacent ones are held, then the CO_2 molecules will leave the surface only from positions adjacent to those from which they have already left. Under these conditions a

separate phase of CaO would grow, starting from the point (nucleus) where the first CO₂ molecule left the surface.

We may therefore conclude, in the case of the dissociation of calcium carbonate that the removal of a CO₂ molecule causes a weakening of the forces by which adjacent molecules are held, whereas in the case of the dissociation of ferric oxide the removal of an oxygen atom does not weaken the forces holding the adjacent oxygen atoms.

When a molecule of CO₂ strikes a surface of the CaO phase it presumably condenses and may be held to the surface by forces no different in kind from those holding the calcite crystal together. However, if the removal of one CO₂ molecule from a surface weakens the forces by which adjacent ones are held, it is probable that the forces acting on a single CO₂ molecule in the midst of a surface of CaO would be extremely weak. Therefore, the CO₂ molecule would remain on such a surface such a short time, that the total number present in the CaO phase would not be of importance.

If, on the other hand, the forces holding the CO₂ molecule in the CaO phase were at all comparable with those acting at the boundary of the CaCO₃ phase, then we should have a variable phase, consisting of a solid solution of CO₂ in CaO, together with a constant phase of CaCO₃.

It is readily seen that the mechanism we have assumed, is capable of accounting for the different kinds of heterogeneous equilibria covered by the Phase Rule.

When there are two solid phases of constant composition and a gas, as in the dissociation of calcium carbonate, it follows directly from this mechanism that the pressure of the gas is dependent only on the temperature and not on the relative proportions of the phases.

Thus the rate at which CaCO₃ dissociates is proportional to the number of *CaCO₃ groups adjacent to empty spaces*, while the rate at which CaCO₃ is formed is proportional to the pressure of CO₂ and to the number of *empty spaces adjacent to CaCO₃ groups*. Therefore, the pressure must be constant at a given temperature.¹

This theory of the mechanism of heterogeneous equilibria appears to be particularly useful in accounting for various conditions not usually predicted by the Phase Rule.

Faraday² noted a case that fully justifies the assumption that in some

¹ Since developing the above theory of the mechanism of such heterogeneous equilibria I have found that this subject has been treated by A. Thiel (*Sitzber. d. Ges. zur. Beforderung d. gesamt. Naturwiss. in Marburg* (1913); *C. A.*, 8, 2284 (1914)). Thiel accepts as an axiom the relation given by Equation 12 and hence concludes that θ_1/θ_2 is necessarily constant at a given temperature. This result is at complete variance with the theory given above, and, in the writer's opinion, is wholly unsupported by experimental evidence. In a subsequent paper the writer expects to discuss Thiel's theory in more detail.

² "Experimental Researches," page 109, Everyman's Library Edition.

equilibria the reaction can occur only when the surface has been disturbed. To quote from Faraday: "As a curious illustration of the influences of mechanical forces over chemical affinity, I will quote the refusal of certain substances to effloresce when their surfaces are perfect, which yield immediately upon the surface being broken. If crystals of carbonate of soda, or phosphate of soda, or sulfate of soda having no part of their surfaces broken, be preserved from external violence, they will not effloresce. I have thus retained crystals of carbonate of soda perfectly transparent and unchanged from September, 1827 to January, 1833; and crystals of sulfate of soda from May, 1832 to the present time, November, 1833. If any part of the surface were scratched or broken, then efflorescence began at that part, and covered the whole. The crystals were merely placed in evaporating basins and covered with paper."

It is well known that there is often great difficulty in removing the last traces of water of crystallization from a substance even when the hydrate gives a definite vapor pressure. According to the theory given above, the velocity of the dissociation is proportional to the area of the boundary between the phases. This boundary will usually have its maximum extent when both phases are present in more or less equivalent amounts. But the great difficulty in removing the last traces is undoubtedly due to the formation of solid solutions (adsorption!). Let us consider a crystalline substance AB which dissociates into a solid phase A and a gas B. The dissociation of AB and the recombination of A with B takes place most easily at the boundary between the phases AB and A. However, in general, we should expect that A and B also combine throughout the phase A, but that this compound is more unstable, and therefore dissociates at a higher rate. The rate at which A and B combine in this way in a unit volume of the phase A, will be proportional to the pressure p , while the rate at which it dissociates will be proportional to the concentration of B in A. By equating the two rates we see that the concentration of B in A should be proportional to the pressure of B.

There will, therefore, be the same kind of difficulty in removing the last trace of B from A as there is in producing a perfect vacuum.

The tendency of different substances to form these solid solutions will depend upon the extent to which the removal of one molecule of B from the phase AB affects the forces holding the adjacent molecules of B in AB.

It is a common experience that substances that are too thoroughly dehydrated are poor absorbers of moisture. A familiar example is overburnt lime or plaster of Paris. In some cases this phenomena may be due to a decrease in the porosity of the substance by sintering, but there is much evidence that this is not always the explanation.

According to the theory given above, the rate at which a partially dehydrated substance (which has a definite vapor pressure of moisture)

will absorb moisture, should be proportional to the extent of the boundary between the hydrated and dehydrated phases. According to this simple theory a thoroughly dehydrated substance should be incapable of absorbing any moisture. However, in general, there is no reason why vapor should not be slowly absorbed to from a solid solution even with a dehydrated substance. Gradually nuclei would develop in this solid solution and the hydrated phase would appear. The rate of absorption of moisture would then rapidly increase as the surface area of the hydrated phase grows.

Adsorption of Gases by Solids.

Unless the molecules of a gas which may strike a solid surface *all* rebound elastically there will necessarily be a higher concentration of molecules of the gas in the surface layer of the solid than in the body of the gas. If any molecules impinging on the surface are condensed, a certain time interval must elapse before they can evaporate. This time lag will bring about the accumulation of molecules in the surface layer, and may thus be looked upon as the cause of adsorption.

In the condensation of a vapor we have seen that the collisions are wholly inelastic, so that every molecule striking the surface condenses.

The reasons that have led us to this conclusion apply with nearly equal weight to gas molecules of almost any kind striking any surface.¹

Let μ represent the number of gram molecules of gas striking each sq. cm. of surface per second. The quantity μ can be readily calculated from the pressure by means of the following equation, derived from Equation 4:²

$$\mu = 43.75 \times 10^{-6} \frac{p}{\sqrt{MT}} \quad (13)$$

The rate at which gas condenses on the surface will then be $\alpha\mu$, where α is a quantity usually very close to unity (never exceeding unity).

If the surface is that of a crystal, there will be a definite number of spaces, N_0 , on each sq. cm. of surface capable of holding adsorbed gas molecules. A greater number of gas molecules can only be adsorbed by the formation of additional layers of molecules. The forces acting between two layers of gas molecules will usually be very much less than those

¹ There is good experimental evidence that this rule is not of universal application. When hydrogen molecules strike surfaces at room temperature apparently something like 80% are diffusely reflected. This probably represents nearly the extreme case. However, even if 80% of the molecules are reflected, the adsorption of the gas on a surface is only 5 times less than it would be if none were reflected. Therefore every gas must be adsorbed to some extent on every surface. The evidence in regard to the reflection and condensation of gas molecules on surfaces is given in detail in a recent article (*Phys. Rev.*, 8, 149 (1916)).

² The nomenclature used here is the same as that employed in a recent paper on the dissociation of hydrogen (*THIS JOURNAL*, 38, 1148 (1916)).

between the crystal surface and the first layer of molecules. The rate of evaporation in the second layer will, therefore, generally be so much more rapid than in the first, that the number of molecules in the second layer will be negligible.¹ When a gas molecule strikes a portion of the surface already covered, it thus evaporates so quickly that in effect it is equivalent to a reflection. Therefore, the rate of condensation of the gas on the crystal surface is $\alpha\theta\mu$ where θ represents the fraction of the surface which is bare. Similarly the rate of evaporation of the molecules from the surface is equal to $\nu_1\theta_1$ where ν_1 is the rate at which the gas would evaporate if the surface were completely covered and θ_1 is the fraction actually covered by the adsorbed molecules. When a gas is in equilibrium with a solid surface these two rates must be equal so we have

$$\alpha\theta\mu = \nu_1\theta_1. \quad (14)$$

Furthermore

$$\theta + \theta_1 = 1. \quad (15)$$

Whence

$$\theta_1 = \frac{\alpha\mu}{\nu_1 + \alpha\mu}. \quad (16)$$

The quantity θ_1 is a measure of the amount of gas adsorbed. It should be noted that for low gas pressures the amount of adsorbed gas is proportional to the pressure, but as the pressure increases θ_1 increases more slowly and finally the surface becomes saturated ($\theta_1 = 1$). These relations are in good qualitative agreement with known facts.²

Equation 16 indicates that at low temperatures (small value of ν_1) the amount of adsorption should be large and nearly independent of the pressure, while at higher temperatures (large value of ν_1) the amount of adsorption should be small, and should be proportional to the pressure even at high pressures. These deductions also are in qualitative accord with experimental facts.

From Equation 16 we see that the tendency of a gas to be adsorbed on a surface is determined by ν_1 , the rate of evaporation from the surface. This quantity in turn depends on the magnitude of the forces acting between the atoms of the crystal and those of the adsorbed substance.

¹ The detailed development of this theory of adsorption, taking into account the evaporation from each of the layers and other complicating factors, will be published as Part II of the paper in the *Phys. Rev.* References to previous literature on the subject will be given at that time. The present paper deals principally with the chemical aspects of the theory.

² Equation 16 gives the amount of adsorption on a plane crystal surface. No reliable quantitative experimental data seem to be available for the adsorption of gases on such surfaces. The writer is, therefore, undertaking measurements of this kind at present and will report the results at a later date. The theoretical reasons for believing that Equation 16 is not quantitatively applicable to adsorption by porous bodies such as charcoal will be discussed further on in this paper.

These forces will be of the same nature as those which hold solid bodies together. We may, therefore, profitably look upon them as chemical forces and apply our knowledge of the chemical properties in studying the phenomena of adsorption.

With a gas such as nitrogen, in which the atoms are mutually very thoroughly saturated, we know that there is only a weak field of force around the molecules. When a nitrogen molecule strikes a surface the forces holding it are only those due to weak secondary valence. It is to be expected, however, in general, that the forces by which molecules or atoms may be held on a surface, should show, for different substances, as great a range of intensity as is observed in the case of the forces acting inside of solid bodies.

Solid nitrogen is held together by comparatively weak forces, while the forces in solid carbon or tungsten are among the most powerful known. In the case of adsorbed films the magnitude of the forces should vary all the way from the weak forces observed with adsorbed nitrogen (or better helium) up to forces which are as intense as those holding together the atoms of the most stable chemical compounds. Just as we find either secondary or primary valences active between atoms in solids, so should we expect both kinds of valence to take part in the formation of adsorbed films. When we thus speak of adsorption as a chemical phenomena it should be remembered that we must also regard evaporation and condensation in general as chemical phenomena. The point to be emphasized is, that there is no real distinction between these so-called physical phenomena, and true chemical phenomena except that in general the "physical" phenomena depend on secondary valence rather than primary. Since, however, chemical phenomena involve secondary valence as well as primary, it seems best to classify all such phenomena as chemical. By so doing we do not in any way fail to recognize the close relationship between evaporation, condensation and the adsorption of the relatively inert gases.

This chemical theory of adsorption has received striking confirmation by many experiments in this laboratory.

Experimental Evidence that Adsorption is a Chemical Phenomena.—It has been found¹ that atomic hydrogen, produced by heating a metallic wire in dry hydrogen at very low pressures, has a remarkable tendency to be adsorbed on surfaces. According to the usual "physical" theory of adsorption by which the adsorbed film is assumed to be a layer of highly compressed gas we should expect that a gas of such low density as atomic hydrogen would be only slightly adsorbed. Furthermore, we should expect that an adsorption film in high vacuum would very rapidly reach equilibrium with its surroundings.

¹ Langmuir, *THIS JOURNAL*, 34, 1310 (1912).

The experiments showed, however, that even in the highest vacuum quantities of hydrogen as large as 0.01 to 0.03 cubic mm. (at atmospheric pressure) per sq. cm. could be adsorbed on cold glass, and that this adsorbed film was remarkably stable, being able to remain unchanged on the surface for several days. To account for these adsorption phenomena it was suggested in 1912¹ that "perhaps the unsaturated chemical affinity of the atomic hydrogen gives it unusual tendencies to be adsorbed on surfaces." It was observed that the amount of atomic hydrogen which could accumulate on a given surface was strictly limited and it was shown that this was not due to a balance between the rate at which atomic hydrogen spontaneously escaped from the surface, and the rate at which it was deposited. On the contrary, it was shown that the amount was limited because, after a certain amount of atomic hydrogen was present on the surface, fresh atoms of hydrogen striking the surface combined with those already present, and thus removed them.

It is interesting to compare the amount of atomic hydrogen adsorbed on the glass with the amount necessary to form a layer one atom deep. If we take the diameter of the hydrogen atom to be the same as that of the molecule, namely about 2.5×10^{-8} cm., we may conclude that the number of hydrogen atoms per sq. cm. needed to form a layer one atom deep is about 1.6×10^{15} . This corresponds to 0.032 cubic mm. of molecular hydrogen at 20° and one megabar pressure. The maximum amounts of atomic hydrogen which were found adsorbed on glass surfaces were of this same order of magnitude (0.01 to 0.03 cubic mm. per sq. cm.).

In a subsequent paper² it was shown that atomic hydrogen could diffuse several feet through glass tubes at room temperature, but could not pass even through a short tube cooled in liquid air. This may be taken as evidence that practically all hydrogen atoms striking a cold glass surface condense. With the glass cooled by liquid air these atoms do not evaporate at a perceptible rate, but from glass at room temperature they evaporate sufficiently rapidly to permit the passage of the atomic hydrogen through a long tube.

The experiments with atomic hydrogen thus furnish evidence that

1. The adsorption is determined by chemical affinity.
2. The adsorbed layer does not exceed one atom in thickness.
3. Hydrogen atoms striking glass surfaces are not reflected.

Similar evidence has been obtained from experiments with tungsten filaments in oxygen at low pressures. It was shown³ that 15% of all oxygen molecules striking a tungsten filament at 2770° K. react with it to form WO_3 . More recent experiments (as yet unpublished) have shown that this

¹ *Loc. cit.*, p. 1313.

² Freeman, *THIS JOURNAL*, 35, 927 (1913).

³ Langmuir, *Ibid.*, 35, 105 (1913).

coefficient continues to increase at higher temperatures, so that at 3300° K. about 50% of all the oxygen molecules which strike the filament react with it to form WO_3 . Since there are three atoms of oxygen in WO_3 , and only two in the oxygen molecule, it is evident that *at least* one-half of the tungsten surface even at 3300° K. must be covered with oxygen in some form. When we consider that the pressure of oxygen in these experiments was usually not over 5 bars we realize the extraordinary stability of the film, and are thus led to believe that the oxygen atoms are held by chemical forces to the tungsten atoms which form the lattice structure of the tungsten crystals.

It is very evident that the adsorbed film does not consist of tungsten oxide WO_3 , since this substance distills very rapidly from the filament even at temperatures as low as 1200° K. The film has no perceptible effect on the optical properties of the tungsten surface, since low pressures of oxygen do not cause any perceptible change in the characteristics (volts, amperes, candle-power) of the tungsten filament.

The existence of this oxygen layer on a tungsten filament in oxygen at low pressure, shows itself in many other ways. Thus a pressure of 0.001 bar of oxygen lowers the electron emission from a tungsten filament at 1800° to a very small fraction of its normal value. Even more striking evidence has been recently found in connection with experiments (as yet unpublished) with tungsten filaments in mixtures of various gases at low pressures. It is found that a tungsten filament at 1500° K. in a mixture of oxygen and hydrogen reacts with the oxygen exactly as if no hydrogen were present. While this oxidation of the tungsten is going on, none of the hydrogen reacts with the oxygen, and the hydrogen does not reduce any of the tungsten oxide¹ formed, nor is any atomic hydrogen produced. However, after all of the oxygen has been used up (partial pressure reduced to less than 0.01 bar) the hydrogen *suddenly* begins to disappear by being dissociated into atoms which then react with the WO_3 previously deposited on the bulb.

Simultaneous measurements of the electron emission show that this emission increases suddenly at the same moment at which the hydrogen begins to disappear.

This experiment proves:

1. That in presence of even 0.01 bar of oxygen the surface of the tungsten at 1500° K. is practically completely covered with oxygen.
2. That this layer of oxygen will not react with hydrogen even at 1500° K.
3. That such a layer of oxygen prevents the formation of atomic hydrogen.

¹ This is especially remarkable since WO_3 is readily reduced by hydrogen at atmospheric pressure at temperatures as low as 500° .

4. That the decrease in electron emission produced by oxygen is due to the same cause as that which prevents the dissociation of hydrogen.

It is very evident from this work that the oxygen layer has totally different properties from those we should expect, either with a layer of oxide, or a film of highly compressed gas. The facts are in good accord, however, with the theory that the oxygen atoms are chemically combined with the tungsten atoms. From this viewpoint the two primary valences of the oxygen are turned downwards, and are saturated by the tungsten, so that a hydrogen molecule striking the surface cannot react with the oxygen, and cannot come in contact with the tungsten. The hexavalent tungsten atoms, on the other hand, are not saturated by the oxygen, so that they are held firmly to the underlying layer of tungsten atoms. Only when the tungsten atoms on the surface become saturated by taking up two other oxygen atoms do they cease to be held to the other tungsten atoms, and thus evaporate off as WO_3 .¹

The stability of the oxygen layer is due to the strength of the chemical union between oxygen and tungsten atoms, which results in a very slow rate of evaporation of the oxygen atoms from the surface.

The action of oxygen in preventing the dissociation of hydrogen by a heated tungsten filament is clearly that of a *catalytic poison*. It has been shown previously² that the dissociation of hydrogen takes place only among hydrogen molecules adsorbed on the surface of the tungsten. The only way in which oxygen can prevent such action in a high vacuum is by the actual presence of oxygen atoms on the surface. Since the dissociation at 1500°K . is entirely prevented by the oxygen, and since the range of atomic and molecular forces does not exceed the dimensions of the atoms, it must follow that much more than half the surface must be covered by oxygen atoms or molecules. For if the surface were only half covered, then, according to probability laws, uncovered areas several times as large as the diameters of atoms would not be of rare occurrence, and on these areas dissociation could occur.

Now if this adsorbed oxygen were present on the surface as a layer of compressed gas³ it would be inconceivable that it should not react at all

¹ The fact that the tungsten atoms leave the surface only after they have been completely saturated chemically seems to be an example of a general tendency. Thus when tungsten is heated in chlorine at very low pressures the hexachloride WCl_6 only is formed, although several stable lower chlorides of tungsten exist. When Pt is heated at high temperatures in oxygen at moderate pressures the oxide PtO_2 distills from the surface, while an osmium filament in oxygen at low pressures gives OsO_4 . Molybdenum in oxygen gives only MoO_3 .

² THIS JOURNAL, 38, 1145 (1916).

³ The commonly accepted theories of adsorption are based upon the assumption that there is a transition layer (van der Waals) in which the density varies gradually from that of the solid or liquid phase to that of the surrounding gas. Eucken (*Verh. deut. physik. Ges.*, 16, 345 (1914)), for example, considers that this transition layer is a

with hydrogen at a temperature of 1500° K. Even if we should regard the adsorbed layer as consisting of adsorbed tungsten oxide we would be no nearer an explanation, for tungsten oxide is readily reduced to metallic tungsten by hydrogen at temperatures of 500° . We should have to say, with Bancroft, that the oxide is stabilized by adsorption. But, of course, this is a mere description and not an explanation of the phenomena.

It is very clear that the oxygen by being adsorbed has undergone a complete change in chemical properties and it is certainly not logical to consider that this has been brought about by a mere compression of the gas into a surface layer.

If, however, we assume that the oxygen atoms are chemically combined to the mass of the tungsten filament and form a *continuous* surface layer, all of the observed facts are readily accounted for. The oxygen atoms are saturated chemically by the tungsten (primary valence) and the field of force holding the oxygen atoms lies wholly below the surface where hydrogen molecules cannot reach it. When the pressure of oxygen falls so low that the supply of this gas at the surface is not sufficient to make up for the loss by evaporation, then gaps are formed in the continuous covering and the hydrogen is then able to make a *flank attack* on the oxygen. In this way the oxygen covering is *suddenly* removed when the pressure of oxygen falls below a certain critical value, and the dissociation of hydrogen, therefore, begins at once.¹

The resemblance between the action of oxygen on a tungsten filament and the phenomena of electrochemical passivity is very striking, so much so, in fact, that the mechanism of passivity is probably similar to that of the effects described above.²

According to this theory the effect of oxygen in poisoning the catalytic activity of tungsten is due to the formation of an exceptionally stable film of oxygen which is combined with and completely covers the surface of the tungsten.

The effects of the poisoning of tungsten by oxygen are also to be seen in many other reactions in gases at low pressures (10–100 bars), of which the following may be briefly mentioned.

sort of miniature atmosphere. Bakker (*Z. physik. Chem.*, **89**, 1 (1915)) has a similar theory to account for surface-tension phenomena.

¹ The strongest evidence of the correctness of this theory is obtained from experiments at higher filament temperatures than 1700° K. The hydrogen and oxygen then begin to react with each other on the surface of the filament. The further development of this theory is reserved for a future paper, in which the detailed experimental results will be published.

² An outline of this theory of passivity together with a brief description of the experiments with mixtures of oxygen and hydrogen in contact with a hot tungsten filament was given by the writer in a discussion of Bennett and Burnham's paper on Passivity, at the Washington meeting of the American Electrochemical Society, April 28, 1916. This discussion has been published in Vol. 29 of the Transactions.

When a tungsten filament is heated in a mixture of carbon monoxide and oxygen, tungsten is oxidized just as if no carbon monoxide were present. None of the CO reacts with the oxygen even when the filament is heated as high as 2800° K., whereas hydrogen begins to react with oxygen in contact with a tungsten filament when the temperature exceeds about 1700° K. Evidently CO will not combine with oxygen adsorbed on a heated tungsten filament even if it has a chance to make a "flank attack."

Mixtures of methane and oxygen at low pressures do not react with one another in contact with tungsten at 1500° or even 1800° K. but the tungsten is oxidized to form WO_3 as in the previous cases. In absence of oxygen, methane is gradually decomposed, setting free hydrogen, while the carbon is taken up by the tungsten filament, forming a solid solution. Even this action is prevented by the presence of traces of oxygen. On the other hand, if the filament is first heated in methane, so that it has taken up carbon, and then oxygen is admitted, the oxygen reacts with the carbon in the filament forming CO, and until all the carbon from the surface layers has been removed, the oxygen does not react with the tungsten. This proves that when carbon is taken up by tungsten some of the carbon remains as an adsorbed layer of carbon atoms.

Dry ammonia at low pressures is decomposed fairly rapidly by a tungsten filament at 1000° K. but with a platinum filament the same rate of decomposition only occurs at a temperature of nearly 1400° K. In the presence of small amounts of oxygen, however, the tungsten filament fails to decompose ammonia even at 1200° K. At 1300° K. the tungsten oxidizes just as if the ammonia were absent, the oxide WO_3 distilling to the bulb. Some of the ammonia seems to react with the oxygen, but with an excess of ammonia this reaction goes on slowly until the oxygen is consumed, and the remainder of the ammonia is then rapidly dissociated. The oxygen thus poisons the tungsten even in the case of the simple dissociation of ammonia by heat. In contact with platinum, however, ammonia and oxygen react together at a temperature well below 1000° K. Particularly interesting effects are observed when a tungsten or platinum filament is heated in mixtures of cyanogen and oxygen. In this case, with a filament at 1500° K. the oxidation of the tungsten is largely prevented until the cyanogen has been slowly oxidized to carbon monoxide and nitrogen. If there is an excess of oxygen this then reacts with the tungsten when the supply of cyanogen is used up. Any excess of cyanogen is decomposed by the filament giving nitrogen, the carbon being taken up by the filament. Thus cyanogen may be looked upon as having a stronger poisoning effect on tungsten than oxygen has.

It is well known that cyanogen poisons the catalytic activity of platinum. Experiments at low pressures furnish a remarkable demonstration of this fact.

A platinum filament at a temperature of 600° K. causes carbon monoxide and oxygen to combine rapidly, the carbon monoxide, however, itself, acting as a catalytic poison.¹ At higher temperatures (900° K.) the poisoning effect of the carbon monoxide disappears and the velocity of the reaction becomes enormously high, being then limited only by the rate at which the two gases can come into contact with the platinum surface, according to Equation 4.

But if a trace of cyanogen is added to the mixture of oxygen and carbon monoxide (at a pressure of 10 bars) the catalytic action of the platinum disappears completely even at 900° K. By raising the temperature to about 1000° the cyanogen reacts with the oxygen to form nitrogen and carbon monoxide. As soon as the cyanogen is all oxidized the catalytic activity of the platinum is restored and the oxygen and carbon monoxide then react rapidly to form carbon dioxide.

The catalytic effect of platinum on the reaction between oxygen and hydrogen is also poisoned by traces of cyanogen. If the temperature of the platinum is then raised, the cyanogen and hydrogen react together to form hydrocyanic acid.

The fact that these low pressures of cyanogen (or oxygen) can exert such a powerful poisoning effect is proof that adsorbed films of great stability are formed, in other words, films in which the rate of evaporation of the adsorbed molecules is remarkably low. The effect of these poisons is thus merely to cover up the active surface.

The property of cyanogen in poisoning metallic catalyzers is thus closely related to the chemical facts that cyanogen forms very stable compounds with metals, and shows an unusual tendency to form complex salts. The cyanogen radical is one in which both the primary and the secondary valences are strongly developed.

Water vapor has the same effect in poisoning the catalytic activity of tungsten that oxygen has. A partial pressure of 0.4 bar of water vapor (vapor pressure of water at -78°) is sufficient to prevent the dissociation of hydrogen by a tungsten filament at 1500° K.

It is a remarkable fact that carbon dioxide, although it oxidizes a tungsten filament to form WO_3 , does not have any effect upon the rate of dissociation of hydrogen. We must, therefore, conclude in this case that only a very small fraction of the tungsten surface is covered by adsorbed oxygen. This conclusion is also supported by the fact that the rate of oxidation of tungsten by carbon dioxide is extremely slow compared to the rate of oxidation by oxygen. We shall see that further evidence of the same kind is furnished by measurements of the electron emission. However, since the oxygen from at least two molecules of carbon dioxide

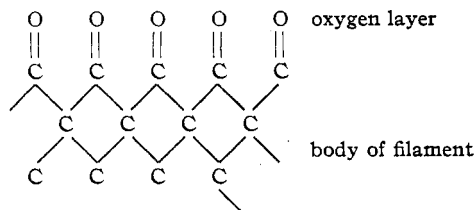
¹ Langmuir, *THIS JOURNAL*, 37, 1163 (1915).

is needed to produce a molecule of WO_3 , it is certain that the reaction depends upon the presence of adsorbed oxygen partially covering the surface. The velocity of the reaction between carbon dioxide and tungsten seems to be approximately proportional to the square root of the pressure of CO_2 and inversely proportional to the pressure of carbon monoxide.

When molybdenum filaments are heated in oxygen at low pressures the filaments become tarnished unless the temperature is maintained above 1500° K. Above this temperature the surface of the filament remains apparently clean, and the oxide formed, MoO_3 , distills to the bulb. With tungsten, notwithstanding the fact that WO_3 is much less volatile than MoO_3 , it is only necessary to keep the temperature above about 1250° in order to have a clean surface.

Although oxygen is clearly adsorbed on molybdenum, it appears that the stability of the film is much less than that of the corresponding film on tungsten. This is shown not only by the electron emission (see below), but by the comparatively small effect of oxygen in poisoning the catalytic activity of molybdenum. Thus when molybdenum is heated to a temperature between 1500 and 1800° K. in a mixture of oxygen and hydrogen, it is found that the hydrogen disappears slowly until the oxygen is all used up, by reacting with the molybdenum. After that the rate of disappearance of the hydrogen is much greater. The fact that a part of the hydrogen disappears before the oxygen is consumed indicates that the poisoning effect of the oxygen is not complete.

Experiments with carbon filaments in oxygen, and in carbon monoxide or dioxide¹ have shown that oxygen acts as a catalytic poison, on the reaction between oxygen and carbon, and on that between carbon dioxide and carbon. It was also proved that this poisoning effect is due to a remarkably stable film of adsorbed oxygen, so stable in fact that the filament must be heated in a good vacuum for nearly half an hour at 2300° K. in order to distill it off. In this case there is very clear evidence that this film consists of oxygen atoms chemically combined by primary valences to the carbon atoms forming the body of the filament, according to the formula



A very peculiar case of adsorption occurs when a tungsten filament

¹ THIS JOURNAL, 37, 1154 (1915).

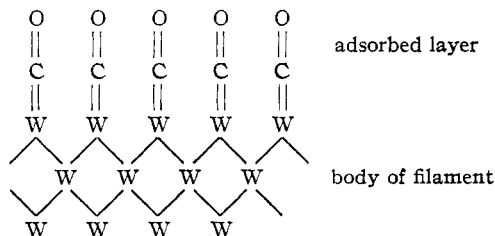
is heated to about 2700° K. in a low pressure of carbon monoxide contained in a bulb cooled by liquid air.¹

With the bulb at this temperature the tungsten filament is attacked by the CO and a very stable adsorbed film is formed on the filament. This distills off at a constant rate (independent of the pressure of CO) taking the tungsten with it as a compound of the composition WCO. The most remarkable fact is that when the temperature of the bulb is raised to 20° or above, the CO no longer attacks the tungsten of the filament, but combines only with the tungsten which evaporates from the filament, still forming the compound WCO.

Before attempting to look for the probable mechanism of this action let us consider one more case of adsorption: that of nitrogen by *molybdenum vapor*. When a molybdenum filament is heated to 2200° K. in nitrogen contained in a bulb cooled in liquid air, nearly every molybdenum atom evaporating from the filament combines with the *first* nitrogen molecule which it strikes to form a compound MoN_2 (stable at 360° in a vacuum). When the bulb is at room temperature the molybdenum atoms still combine with the first nitrogen molecule they strike, but most of the molecules thus formed are so unstable that they decompose when they strike the bulb, giving nitrogen and a spongy molybdenum deposit.

Thus when the nitrogen is at low temperature the compound appears to be MoN_2 in which the atoms are held by primary valence, while the compound formed with the nitrogen at higher temperatures is $\text{Mo} : \text{N}_2$, in which the nitrogen and molybdenum are held by secondary valence. This seems then to be a kind of adsorption of one gas by another.

A somewhat similar explanation seems necessary for the reaction between tungsten and carbon monoxide. Thus when carbon monoxide molecules of low velocity and low internal energy (low temperature) strike the surface of the filament they combine with it by primary valences to form a stable structure, probably as follows:



The strength of the union between the oxygen and carbon, and between the tungsten and carbon, is so great, that the whole group WCO distills off as a single molecule. The fact that the tungsten is partially saturated

¹ A brief preliminary account of these experiments was published in *THIS JOURNAL*, 37, 1160 (1915). A more detailed paper will be presented later.

by the carbon should make this group somewhat more volatile than the tungsten itself. As a matter of fact the rate of evaporation of the WCO from the surface is only about five times greater than that of tungsten.

When the temperature of the bulb is higher, so that the CO molecules possess more internal energy (and a higher velocity) the CO is incapable of combining with the solid tungsten in the above manner. We must still assume that nearly every CO molecule which strikes the filament condenses on it, but that the union in this case is by secondary valence, so that the molecule almost immediately distills off again.

A more thorough study of this reaction may throw some light on the paradox that the residual valence of CO is small, although this substance contains a divalent carbon atom.

The Effect of Gases on the Electron Emission from Heated Metals as Evidence of the Presence of Stable Adsorbed Films.

The effect of adsorbed films of the thickness of a single molecule on the electron emission from heated tungsten filaments was described by the writer in 1913.¹ A little later² the following theory of the effect was proposed. "The decrease in the electron emission from a hot cathode caused by certain gases is due to the formation of a film on the surface of the cathode. Whether this film consists of adsorbed gas, or of a chemical compound of the gas with the cathode material, is not definitely established, but most of the evidence is in favor of the latter view. The amount by which the electron emission is affected depends on the *extent* to which the surface is covered. The film should be looked upon as consisting of a single layer of molecules, or at most, of a very few layers. The extent to which the surface of the cathode is covered by the film depends upon: (1) The rate of formation of the film. (2). The rate of destruction of the film," etc.

The more recent work on chemical reactions at low pressures, and further experiments on electron emission, have furnished abundant evidence of the correctness of the above viewpoint, and have fully verified the conclusion that the film is held to the surface by chemical forces.

In every case with tungsten, chemically inert gases have been found to be without effect on the electron emission, whereas nearly all gases that react with the tungsten lower the emission.

The decrease of the electron current produced by a gas is thus caused by the formation of an adsorbed film of great stability, which covers the surface. The evidence is very strong that the electron emission at a given temperature depends only on the nature of the layer of atoms forming the actual surface of the filament. Here again we have proof of the ab-

¹ Langmuir, *Phys. Rev.*, 2, 450 (1913).

² *Physik. Z.*, 15, 520 (1914).

sence of a transition layer in which the density varies gradually from that of the filament to that of the surrounding space.

The lowering of the electron emission of heated filaments by adsorbed films thus bears a close relationship to the effect of these films in poisoning the catalytic activity of the filament. Both effects are caused by a film of great stability which covers the surface. The following experimental evidence shows, in fact, that there is a remarkable parallelism between the electron emission and the catalytic activity of a filament.

As has already been pointed out, oxygen enormously lowers the electron emission from tungsten. This effect of oxygen is in accord with its action as a catalytic poison for tungsten. Thus in mixtures of oxygen and hydrogen the electron emission undergoes a sudden increase at the moment at which the hydrogen begins to dissociate (after the consumption of all the oxygen).

It might be thought that the electron emission itself would have an effect on the chemical reactions occurring on the surface of a heated filament. But experiment has never shown any such direct effect. Thus the rate at which oxygen, hydrogen, carbon dioxide, and other gases disappear in contact with heated tungsten are found to be entirely independent of the thermionic currents. The presence of a negatively charged electrode close to the heated filament causes all electrons emitted to be driven back into the filament, but this does not affect the rate of disappearance of the gases. In some cases, however, electric discharges do cause the clean-up of gases, but this effect is due to the bombardment of the filament by positive ions, and not to the electron emission.

Nitrogen does not normally attack a tungsten filament at any temperature, although it combines (to form WN_2) with tungsten vapor as fast as this evaporates from the filament.¹ Similarly nitrogen has no effect on the electron emission from tungsten if low voltages are used in making the measurements of the thermionic current. But if voltages high enough to cause ionization of the nitrogen are employed, then the tungsten is attacked by the rapidly moving positive nitrogen ions, and simultaneously the electron emission is greatly decreased, indicating that a film of adsorbed nitrogen is formed. If the filament is now allowed to cool to room temperature and the remaining nitrogen is pumped out, and the filament is then heated again to the same temperature as before, it is found that the electron emission is at first the same as it was in the presence of the nitrogen, showing that the electron emission is determined not by the gas around the filament, but by the film adsorbed on it. Gradually the adsorbed film distills off, and the electron emission returns to its normal value.

By the study of such lag effects, the rate of evaporation and the rate of

¹ THIS JOURNAL, 35, 931 (1913).

formation of the adsorbed films can be measured with accuracy, and it has thus been proved that the fraction of the surface covered often depends upon a dynamic equilibrium.

The fact that the rate of evaporation of these films even at temperatures of 1800° K. is slow enough to measure proves that they are remarkably stable.

Extremely interesting phenomena are observed after a tungsten filament has been heated in CH_4 or C_2N_2 , or other gas which gives up carbon to the filament. The most minute trace of carbon,¹ in the surface of the filament cuts down the electron emission to about one-third of that of an uncontaminated filament. But a filament which has taken up carbon is no longer sensitive to the effect of bombardment by positive nitrogen ions. In other words nitrogen has no effect on the electron emission from such a filament even if high anode voltages are used. Still more remarkable is the fact that oxygen instead of lowering the electron emission of a carbon-containing filament gradually raises it. The carbon is then gradually oxidized and the electron emission returns to the value corresponding to pure tungsten. Then when the carbon has all been removed, the oxygen begins to attack the tungsten and the electron emission suddenly decreases to one per cent. or less of its former value. After the excess oxygen has been consumed it is found that the electron emission is again sensitive to the effect of bombardment by positive nitrogen ions, the thermionic current decreasing as the voltage is raised.

This experiment is an excellent demonstration of the closeness of the relationship between the electron emission and the chemical activity of the filament.

Another illustration is afforded by the fact that water-vapor, which reacts rapidly with tungsten, and poisons the tungsten surface, has as great an effect on the electron emission as oxygen, while carbon dioxide, which reacts slowly with tungsten, and is not a catalytic poison, has practically no effect on the electron emission.

So far we have considered the effects of gases on the electron emission from tungsten. Striking effects of another kind are obtained when the filament contains minute amounts of thorium.² If such a filament is heated in a very high vacuum to 2900° K. for a short time and the electron emission at 1800° K. is then measured, it is found that the emission is the same as that of pure tungsten. By now heating the filament a few minutes at a temperature between 2000° and 2500° K. (preferably 2300° K.),

¹ Probably just enough to form a layer one atom deep over the surface of the filament is sufficient.

² An account of these phenomena was given before the American Phys. Soc., Oct. 31, 1914 (*Phys. Rev.*, 4, 544 (1914)). A paragraph describing the effect was given in a paper before the American Electrochemical Soc. (see *Trans. Am. Electrochem. Soc.*, 29, 353 (1916)).

the electron emission at 1800° K. is found to have increased enormously (more than 10000 fold). By heating again to 2900° the emission returns to its normal value.

This effect is due to the formation of an adsorbed layer of thorium atoms on the surface of the filament. At 2900° K. the thorium, being more volatile than tungsten, distills off the surface and leaves pure tungsten. At 2300° K. however, the rate of distillation is not very marked, but the rate of diffusion of the thorium through the tungsten is sufficient to allow the accumulation of thorium atoms on the surface. At 1800° the rate of diffusion is negligible, so that if the thorium is distilled off a fresh supply does not diffuse to the surface.

The tendency of thorium to form an adsorbed film on tungsten is in accord with other properties of thorium. Gibb's has shown that any substance which lowers the surface energy tends to be adsorbed on the surface. The Eötvös-Ramsay-Shields relation indicates that the surface energy of a substance at temperatures low compared to its critical temperature, should be approximately proportional to $T_c A^{-2/3}$ where T_c is the critical temperature and A is the atomic volume. Now the critical temperature of thorium must be lower than that of tungsten, since the vapor-pressure of thorium is considerably greater than that of tungsten. The atomic volume of thorium is about 21, while that of tungsten is 9.6. Thus both T_c and A differ, for these metals, in such a way as to make the surface energy of thorium less than that of tungsten. Therefore, according to Gibb's rule thorium should tend to be adsorbed on the surface of tungsten.

By a study of the rate of growth of the adsorbed film at 2100° K. and the rate of evaporation at 2700° K. it has been possible to prove that the film grows until it is one atom deep but does not grow beyond this.¹ The real evidence in favor of these conclusions, however, can only be given in connection with a full discussion of the detailed experimental results. It is intended to publish these before long.

When oxygen is brought into contact with a tungsten filament (at 1900° K.) coated with a layer of thorium atoms, the electron emission is suddenly decreased to a value far below that corresponding to pure tungsten. With tungsten the effect of oxygen in decreasing the emission disappears as soon as all the oxygen has been consumed. But with a thorium-coated filament the effect of oxygen is more permanent, so that the emission remains low even after all oxygen has been removed. Only by heating the filament to 2900° and following this by a treatment at 2300° can the

¹ That the layer is never more than one atom deep is readily proved by the fact that the activity of the film always begins to decrease *at once* at 2700° no matter how long it may have been previously heated at 2300° K.

activity be restored. This behavior is in accord with the known facts that thorium has an unusually strong affinity for oxygen.

In the case of this oxidized thorium-coated filament the adsorbed film evidently consists of a layer of thorium atoms covered by a layer of oxygen atoms. It should not be looked upon as a layer of adsorbed thorium oxide.

Interesting effects are observed if a small amount of methane is brought into contact with an oxidized thorium-coated tungsten filament at about 1900° K. The electron emission suddenly increases to that of pure thorium, and then as suddenly decreases to a value below that of pure tungsten. The methane reacts with the oxygen on the surface of the filament, forming carbon monoxide, which evaporates off, leaving the layer of thorium atoms. The excess of methane is then decomposed, and a layer of carbon atoms is formed on the surface of the filament, and covers the thorium atoms. The electron emission then becomes that of a carbon surface which is a little less than that of tungsten, notwithstanding the presence of thorium atoms just under the surface layer.

Kruger and Taeg¹ have recently studied the effect of catalytic poisons on the photoelectric activity of platinum, using ultraviolet light. They find that minute traces of H_2S , HCN or CO very greatly decrease the photoelectric electron emission. The mechanism of this action is undoubtedly identical with that of the effect on the thermionic electron emission. Debye² and Richardson³ have shown that there is a very close relationship between the photoelectric and thermionic electron emission.⁴

Adsorption Phenomena at Higher Gas Pressures.—The effect of poisons on the activity of catalyzers is essentially the same with gases at atmospheric pressure as at lower pressures. There is every reason for believing that the theory of adsorption outlined in the preceding pages is applicable to the adsorption of gas at atmospheric pressures. In the second part of this paper we shall see that a similar theory also applies to adsorption in surface layers of liquids.

As the pressure of a gas increases the amount adsorbed on a plane surface should gradually increase until the surface becomes completely covered by a layer one molecule (or atom) deep. The surface thus becomes *saturated*. This is in full accord with experimental facts.

In the case of the adsorption of vapors at such high pressures that they approach the state of saturated vapors, there will be a tendency for the adsorbed film to become several molecules deep.

¹ *Z. Electrochem.*, **21**, 562 (1915).

² *Ann. Phys.*, **33**, 441 (1910).

³ *Phil. Mag.*, **23**, 266, 615 (1912); **24**, 570 (1912).

⁴ For a review of the recent work on this subject and its relation to contact potentials see a paper by Langmuir, *Trans. Am. Electrochem. Soc.*, **29**, 341 (1916).

According to this theory it is very improbable that films more than one or two molecules deep would ever be held on a surface by adsorption, except with nearly saturated vapors. We must assume that after a layer two or three molecules deep is formed, the rate of evaporation of additional molecules would be nearly identical with that from the liquefied or solidified gas. If the vapor pressure were well below saturation, the rate at which such additional molecules would condense in the surface would be much less than the rate at which they would evaporate. The adsorbed film would thus grow thinner.

There is considerable experimental evidence that the amount of moisture taken up by glass surfaces is greatly in excess of the amount needed to form a layer one molecule deep.

When a 40-watt incandescent lamp bulb is heated to 500° for several hours (after having been exhausted and dried out at room temperature) it gives off about 0.45 cc. of water vapor, 0.030 cc. of carbon dioxide, and 0.005 cc. of nitrogen.¹ The internal surface of this bulb was about 200 sq. cm. The number of molecules of gas given off per sq. cm. was thus 56×10^{15} molecules of H_2O ; 37×10^{15} molecules of CO_2 and 0.6×10^{15} molecules of N_2 . If we calculate the number of molecules of each of the gases necessary to cover a sq. cm. one molecule deep (taking the molecules to be cubical in shape) we find 1.0×10^{15} for H_2O ; 0.77×10^{15} for CO_2 and 0.67×10^{15} for N_2 . Thus the quantities of gas obtained from this bulb correspond to: a layer of water 55 molecules deep, a layer of carbon dioxide 4.8 molecules deep and a layer of nitrogen 0.9 molecule deep.

The adsorption(?) of water vapor by pulverized synthetic quartz and anorthite has been studied by J. R. Katz.² The amount of water taken up reaches a fairly definite limit when the vapor pressure of the water is about 0.7 of the saturated vapor. The quantities of water adsorbed per sq. cm. of surface under these conditions were 1.3×10^{-6} grams for quartz and 6.2×10^{-6} grams for anorthite. These correspond to layers of water 43 and 205 molecules deep, respectively. Freundlich³ reviews the literature on the thickness of adsorbed films, and comes to the conclusion that these films in general range from 10^{-7} to 10^{-6} cm. in thickness. Since the diameters of atoms and molecules usually lie between 2×10^{-8} and 5×10^{-8} cm., the adsorbed films, according to Freundlich, should be many molecules thick. The evidence on which this conclusion is based is very meagre, and for the most part is quite indirect. The best data referred to are probably those of Ihmori.⁴ According to Freund-

¹ Langmuir, *Trans. Am. Inst. Elec. Eng.*, **32**, 1921 (1913).

² *Proc. Amsterdam Acad.*, **15**, 445 (1912).

³ "Kapillarchemie," Leipzig (1909), p. 265.

⁴ *Wied. Ann.*, **31**, 1006 (1887).

lich, Ihmori "found with polished metals (brass, steel, etc.) thicknesses for the surface layer of water ranging between 3 and 10×10^{-7} cm.; and with quartz, an average thickness of 22×10^{-7} cm."

However, by referring to Ihmori's original article, it appears that this investigator found that the amount of "adsorbed" moisture increased greatly (about 10 fold) if the metal had previously been allowed to stand in the air for a few weeks. With carefully cleaned (polished or ignited) platinum he could not detect any adsorption whatever, that is, the adsorbed film in this case must have been less than 2×10^{-8} cm. thick. Ihmori says "the small amount of water adsorbed by the metals designated as 'polished' is, perhaps, due to the presence of a thin film of oxide."

In Ihmori's experiments the pressure of the water vapor was about 92% of that at saturation.

From the cases considered above it appears that certain surfaces adsorb moisture in quantities very large compared to that necessary to form a layer one molecule thick. There is no evidence, however, that in any of the cases studied the phenomena is a true adsorption.

The term adsorption should be restricted to gas taken up *on a surface* without any penetration of the gas molecules between the atoms or molecules of the solid surface. The theory of adsorption developed in this paper indicates that the amount thus truly adsorbed should never exceed a layer one or two molecules in thickness.

But there is no reason whatever why molecules of gas or vapor should not penetrate in between atoms of the surface and thus be absorbed. Dried jellies can absorb large quantities of moisture, and dehydrated salts usually absorb moisture even when no definite hydrates are formed (solid solutions).

The absorption of moisture by a surface of glass is to be looked upon as a process of solution of the water into the glass. Dried sodium silicate absorbs moisture in this way in very large quantities, and it is not at all surprising that this property should not be wholly lost, when lime and other oxides are fused with the alkali silicate. The whole behavior of glass surfaces in giving up their moisture confirms this theory that the moisture penetrates to a very considerable depth into the surface. The remarkable slowness with which the moisture is given up on heating, and the length of time needed for the reabsorption of the moisture indicate that we are not dealing with a true adsorption phenomena.

In the case of Katz's experiments with anorthite and quartz, there is probably also a penetration of the moisture into the crystal substance. It is, however, quite possible that what he measured was the moisture actually condensed as liquid in the fine capillary spaces between the grains of the extremely fine powder experimented with.

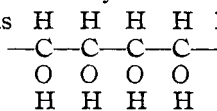
We may safely assume that water vapor would not penetrate at all into

a metal, so that a *clean* metal surface should never take up more moisture than enough to form a layer one molecule deep. This is in accord with Ihmori's results, since he could not detect absorption of moisture by platinum. The other metals used by Ihmori all oxidize in contact with air. The oxide layer formed is usually thick enough to see. When we consider that a film of metallic *tungsten* ten atoms thick only absorbs about 20% of the light striking it, it is evident that a film of *oxide* thick enough to see must be of very great thickness compared to that of a molecule. Furthermore, such a film must be quite porous, since the oxygen required for its growth must have diffused through it. It is, therefore, not remarkable that relatively large quantities of moisture are absorbed by such films.

Adsorption by Porous Bodies.—Nearly all quantitative measurements of the adsorption of gases by solids have been made with porous bodies such as charcoal. In these cases it is impossible to know definitely the area on which adsorption takes place.

It is often assumed that the surface of even a polished metal is porous to such an extent that its "true surface" is much greater than its apparent surface. As far as the writer knows, there is no experimental evidence to support any such assumption and theoretical considerations would make it seem extremely improbable. The strong surface forces (quite analogous to that in liquids) would tend to make the atoms in the surfaces of solids arrange themselves in such a way as to make the total surface a minimum. Therefore, in the absence of definite causes which produce a porous structure (such as those considered below), we should assume that the atoms of the surfaces are packed closely together and are arranged with considerable regularity. Thus a surface of glass should not be considered as porous, although it is capable of absorbing considerable quantities of moisture. The absorption is here a solution process, in other words, a chemical change by which the water molecules become combined (secondary valence) with the atoms of groups of atoms forming the glass. There is no more reason for assuming a porous structure than there is in the case of a liquid.

Truly porous bodies, such as charcoal, probably consist of atoms combined together in branching chains of great complexity. The fibers of cellulose from which charcoal is usually formed probably consist of practically endless groups of atoms



held together by primary valences in the direction of their length and by secondary valence in the transverse directions. When the hydrogen and oxygen atoms are driven out by heat, the carbon atoms for the most part remain in their chains, but a certain number of cross linkages occur between these chains. The

porosity of the charcoal thus undoubtedly extends down to atomic dimensions. The unsaturated state of the remaining carbon atoms explains the practical impossibility of removing the last traces of oxygen and hydrogen from any form of amorphous carbon.

It is evident that with a structure of this kind, it is meaningless to talk about the surface on which adsorption can take place. With plane surfaces, we have seen that adsorption is usually limited to the formation of a layer one molecule deep, so that we can estimate the maximum adsorption from the extent of the surface. With charcoal, on the other hand, there is no definite surface which can be covered by a layer one molecule deep. Between the atoms of carbon, there must be spaces of all possible sizes and shapes, some just too small to hold a gas molecule, others big enough to hold one but not hold two, etc. There are some spaces in which a molecule would be closely surrounded by carbon atoms on nearly all sides, whereas in other places a molecule would be able to hold on to only a single carbon atom. Under these conditions there will be some spaces from which evaporation of adsorbed molecules would occur very slowly and others from which it would take place much more rapidly. There would be, however, a fairly sharp limit to the number of molecules which could come into intimate contact with carbon atoms. This limit would correspond to the saturated state observable in adsorption even by porous bodies. But it is evident that Equations 14, 15 and 16 which apply to adsorption by plane surfaces, could not apply to adsorption by charcoal. The real reason for this failure is that we can no longer assume (as in the derivation of Equation 14) that the rate at which the adsorbed gas evaporates from the surface is proportional to the amount present on the surface.

Strong support for the above views on the structure of porous bodies and the nature of adsorption by them is furnished by experiments in which molybdenum filaments were vaporized in nitrogen at low pressures. These experiments will be described in a future publication.¹

General Conclusions Regarding Kinetics of Heterogeneous Reactions.

The theory developed in this paper and the experimental work on electron emission and chemical reactions at low pressures leads to the following conclusion: *In a heterogeneous chemical reaction, the activity of a surface depends in general upon the nature of, the arrangement of, and spacing of the atoms forming the surface layer. The atoms forming the second layer below the surface are of importance only insofar as they determine the arrangement of the surface atoms.*

In the second part of this paper, it will be shown that the surface tension in liquids depends upon these same factors, in other words, it de-

¹ A brief preliminary description of these results was given in *THIS JOURNAL*, 37, 1159 (1915).

pendes primarily upon the *surface layer of atoms* and only secondarily upon the group molecules of which these atoms form parts.

According to this view, the velocity of reactions in general is not limited by the rate of diffusion through an adsorbed film, but by the rate at which the molecules strike (according to Equation 4) against that portion of the surface which is active. Of course, there are many chemical processes which are actually limited by physical factors, such as the rate of diffusion through layers of gas or moderately thick films covering the solids substances. The rusting of iron, the oxidation of aluminum, the solubility of very soluble salts, etc., are examples of this type. But there is no present justification for believing that such physical factors determine the velocity of the typical catalytic reactions.

This theory of heterogeneous reactions can be readily developed along quantitative lines. Some of the principles upon which this development is based have been outlined in a recent paper on the dissociation of hydrogen.¹ A brief, but more general treatment will, however, not be out of place here.

The velocity of a reaction usually depends on the fraction of the surface which is covered by adsorbed atoms or molecules. This in turn depends on the rate of condensation and on the rate of evaporation of the adsorbed substance. In the sections of this paper dealing with condensation and evaporation, we considered only the case where the vapor condensing and the surface on which condensation occurred, consisted of the same substance. In the case where different substances are involved, some additional factors must be taken into account.

Condensation.—The surface on which condensation occurs contains a definite number N_0 of elementary spaces, per unit area. Let θ be the fraction of these spaces which are unoccupied and θ_1 be the fraction occupied by adsorbed atoms or molecules.

If each molecule condensing requires only one elementary space, the rate of condensation will be equal to $\alpha\theta\mu$.² But it may happen that each molecule requires two such spaces before condensation can occur. The chance that one space will be vacant is θ , but the chance that two given spaces will be simultaneously vacant is θ^2 . Therefore, the rate of condensation is equal to $\alpha\theta^2\mu$. In general, the rate of condensation will be $\alpha\theta^n\mu$ where n is an integer.

Evaporation.—In evaporation it may occur that two atoms must lie in adjacent positions in order that they may leave the surface together as a molecule. In such cases the rate of evaporation will be $\nu_1\theta_1^2$ instead of $\nu_1\theta_1$.

Chemical reactions may take place either between adjacent atoms

¹ THIS JOURNAL, 38, 1145 (1916).

² Compare with the derivation of Equation 14.

on the surface or may occur when gas molecules strike molecules or atoms on the surface. In the former case the velocity of the reaction, in general, will be proportional to $\theta^n \theta_1^m \theta_2^p$ where θ_1 and θ_2 are the fractions of the surface covered by the reacting substances and n , m and p are integers. The reason for the occurrence of the factor θ^n in this expression is that the number of elementary spaces occupied by the products of the reaction may be greater than that occupied by the reacting substances. The reaction will thus only occur when vacant spaces are available.

We see that the reaction on surfaces will be governed by a "law of surface action" analogous to the "law of mass action." The velocity in both cases is proportional to a continued product of factors having integral exponents. A radical difference between the two laws exists in the presence of the factor θ^n in the case of reactions on surfaces.¹

Let us consider a few simple special cases of heterogeneous reactions.

To simplify the problem, we will assume that the velocity of the reaction is slow compared to the rate at which the gas condenses and evaporates from the surface. In other words, we will limit ourselves to a consideration of those cases where the velocity of the reaction is not fast enough to materially affect the equilibrium between the adsorbed film and the surrounding gas.

There are two types of cases to consider. First, those in which the adsorbed film covers only a very small fraction of the surface ($\theta = 1$). Secondly, those in which the surface is nearly completely covered by the adsorbed film.

First Case. Surface only covered to a small extent.

Let us consider a single gas which undergoes a chemical change (for example a dissociation) in contact with a solid body. The rate of condensation on the surface will be $\alpha_1 \mu_1$ and the rate of evaporation of the unchanged gas will be $\nu_1 \theta_1^n$ where n represents the number of elementary spaces occupied by each molecule of the substance while on the surface. Then, since the adsorbed film is in equilibrium with the surrounding gas, we have²

$$\alpha_1 \mu_1 = \nu_1 \theta_1^n. \quad (17)$$

¹ Since $\theta + \theta_1 + \theta_2 + \dots = 1$ this law bears a close relationship to Reichenstein's "Constant Sum Hypothesis," which has been used to explain various kinds of passivity phenomena.

² This equation becomes identical with Equation 14 only when $n = 1$ and $\theta = 1$. It is thus seen that the theory of adsorption which led to Equation 16 does not apply to the case where a molecule occupies more than one elementary space. Equation 17 shows that when $n = 2$, the amount of gas adsorbed is proportional to the square root of the pressure, even at very low pressures.

The equations that follow (19), (21), etc., may be derived in several different ways (see THIS JOURNAL, 38, 1149 (1916)) by making different kinds of assumptions. By experiment it will be possible to determine which set of assumptions correspond with the facts.

Now the product of the chemical reaction is formed from the adsorbed film by the combination of the substance from m adjacent spaces. In case of a dissociation m will be equal to unity. If ω represents the velocity of the chemical change, we have

$$\omega = \nu_2 \theta_1^m. \quad (18)$$

Combining these two equations gives

$$\omega = \nu_2 \left(\frac{\alpha_1 \mu_1}{\nu_1} \right)^{m/n} \quad (19)$$

The velocity of the reaction thus varies with the m/n^{th} power of the pressure (μ) of the gas. In the case of the dissociation of hydrogen molecules by a heated wire, we have $m = 1$ and $n = 2$, so that the velocity at which the gas is dissociated is proportional to the *square root* of the pressure of molecular hydrogen. The recombination of hydrogen atoms in contact with a heated wire, however, takes place in proportion to the *square* of the pressure of the atomic hydrogen. It has been shown previously that these conclusions are in accord with experiments.

Bodenstein and Ohlmer¹ mention that the velocity of the reaction between carbon monoxide and oxygen in presence of heated crystalline quartz is proportional to the pressure of the carbon monoxide and to the *square root* of the pressure of oxygen.

Now if we assume that each carbon monoxide molecule occupies one elementary space while each oxygen molecule occupies two (*i. e.*, is present on the surface in the form of atoms), we obtain

$$\begin{aligned} \alpha_1 \mu_1 &= \nu_1 \theta_1 \\ \alpha_2 \mu_2 &= \nu_2 \theta_2^2 \\ \omega &= \nu_3 \theta_1 \theta_2 \end{aligned} \quad (20)$$

where the subscript 1 refers to CO, 2 refers to O₂ and 3 refers to CO₂.

These equations give

$$\omega = k \mu_1 \sqrt{\mu_2} \quad (21)$$

where k is a constant involving α_1 , α_2 , ν_1 , etc. Thus the relation found by Bodenstein and Ohlmer follows directly from the assumption that the oxygen adsorbed on the surface is present as separate atoms.

It has been found by Bodenstein and Kranendieck (p. 99 Nernst Festschrift) that the rate of decomposition of ammonia by heated quartz glass is proportional to the square root of the pressure. It will be shown in a subsequent paper that this fact is readily explainable by assumptions analogous to the above.

Freundlich and Bjercke² have recently found that the rate of oxidation of phenyl-thiourea by oxygen in contact with blood charcoal is proportional to the square root of the concentration of oxygen.

¹ *Z. physik. Chem.*, **53**, 175 (1905).

² *Ibid.*, **91**, 1 (1916).

It should be noted that the velocity of gas reactions is frequently proportional to the square root of the pressure, whereas according to the law of mass action, we should expect velocities proportional to some integral power of the pressure. The above theory of heterogeneous reactions offers a simple explanation of these fractional exponents. According to the Bodenstein-Fink theory of heterogeneous reactions, such square-root relations are to be explained by diffusion through films whose thickness varies in proportion to the square-root of the pressure. There is definite experimental evidence in the case of the dissociation of hydrogen (which gives a square root relation) that the adsorbed film covers only a very small fraction of the surface with a layer one atom deep. Hence the Bodenstein-Fink theory cannot possibly explain this case. It is very probable that such square root relations are never caused by diffusion through adsorbed films.

Second Case. Surface nearly completely covered.

Let us consider a reaction in which two gases are in contact with a solid body. One of the gases, which we shall designate by the subscript 1, is present in such quantity and evaporates so slowly from the surface that the surface remains nearly completely covered by an adsorbed film of this substance. A second gas, 2, undergoes a chemical change when its molecules come in contact with the uncovered surface. This reaction may be of several kinds. For instance, the gas molecules condensing in vacant spaces may dissociate, may react with the underlying solid, or may react with the adsorbed gas in adjacent spaces. The rate at which the first gas will condense is $\alpha_1 \theta^n \mu_1$, where n is the number of elementary spaces occupied by each molecule which condenses. The rate of evaporation will be constant ν_1 , since the surface is nearly covered. Therefore, for equilibrium

$$\alpha_1 \theta^n \mu_1 = \nu_1. \quad (22)$$

The rate at which the second gas will enter into reaction will usually be proportional to $\theta \mu$. It is quite possible, however, in some cases that θ may have any integral or even fractional exponent. We thus obtain for the rate of reaction

$$\omega = \nu_2 \theta \mu_2. \quad (23)$$

Combining these equations we find

$$\omega = \nu_2 \mu_2 \left(\frac{\nu_1}{\alpha_1 \mu_1} \right)^{1/n} \quad (24)$$

The velocity of the reaction is thus proportional to the pressure of gas 2, and *inversely proportional to the n^{th} root of the pressure of gas 1.*

Now this is a relation which has been found to hold for a very great number of heterogeneous reactions in which the velocity is influenced by catalytic poisons. A few of these will be briefly mentioned.

Fink¹ found in the case of the reaction (in contact with platinum)



that the velocity is proportional to the pressure of SO_2 and inversely proportional to the square root of the pressure of SO_3 . This relation follows directly from Equation 24 if we place $n = 2$. We may thus conclude that the platinum surface was practically completely covered by a layer of adsorbed SO_3 in which each molecule of SO_3 required two elementary spaces for its condensation. Fink actually measured the amount of adsorbed SO_3 and found it to be of the order of magnitude of a single layer of molecules. According to the Fink-Bodenstein theory, the amount of adsorbed SO_3 in these experiments should have been proportional to the square root of the SO_3 pressure, whereas according to the above theory the amount adsorbed should have been practically independent of the pressure (saturation). It is, however, obvious that a film one molecule thick (as found by Fink) cannot have a *thickness* which varies in proportion to the square root of the pressures over a wide range.

Bodenstein and Ohlmer found that the reaction between oxygen and carbon monoxide in contact with quartz glass takes place at a rate proportional to the pressure of oxygen and inversely proportional to the pressure of carbon monoxide. Evidently here $n = 1$ so that each molecule of carbon monoxide occupies only one elementary space.

The writer has found² that the same relation holds when these gases react with each other at very low pressures in contact with platinum. It was also found³ that in the catalysis of oxygen-hydrogen mixtures by a platinum wire, the velocity is proportional to the pressure of oxygen and inversely proportional to that of the hydrogen.

An interesting application of this theory arises in connection with enzyme action. The velocity of many of these reactions varies in accordance with Schutz's rule.⁴ Consider a reaction in which a substance A is converted into B by the action of an enzyme. Let x be the amount of B formed in the time t , assuming that the substance B is absent when $t = 0$. Let E be the amount of enzyme present. Then according to Schutz's rule

$$x = k\sqrt{Et}. \quad (25)$$

Thus the amount of B formed is independent of the concentration of A, but is proportional to \sqrt{Et} .

By squaring and differentiating (25) we obtain, if E remains constant

¹ Dissertation, Leipzig, 1907; see also Bodenstein and Fink, *Z. physik. Chem.*, **60**, 1 (1907).

² THIS JOURNAL, **37**, 1162 (1915).

³ More recent experiments show that this is not the usual manner in which hydrogen and oxygen react in contact with platinum even at low pressures. The factors which cause the above type of reaction have not yet been determined with certainty.

⁴ See Euler, *Allgemeine Chemie der Enzyme*, pp. 125, 106 and 113.

$$\frac{dx}{dt} = \frac{1}{2} k^2 \frac{E}{x}. \quad (26)$$

Thus another way of stating Schutz's rule is to say that the velocity of the reaction is proportional to the amount of enzyme, is inversely proportional to the amount of B formed, and is independent of the amount of A.

It is generally recognized that enzymes are colloids on the surfaces of which reactions occur. We may thus interpret Schutz's rule as in indication that the product B of the reaction is adsorbed on the surface of the colloidal particles forming a layer one molecule deep nearly completely covering the surface. By comparing Equations 26 and 24 we see that $n = 1$ from which we conclude that each adsorbed molecule occupies only one elementary space. The reaction thus takes place only on that fraction of the surface which is not covered by molecules of B.

By Equation 24 we should expect the velocity of the reaction to be proportional to the concentration of A, but according to Schutz's rule the velocity is independent of this concentration. This seems somewhat difficult to explain. It is, perhaps, possible that molecules of A are adsorbed over practically all the surface not occupied by B, and that molecules of B are able to *displace* molecules of A thus adsorbed. Let θ_a and θ_b be the fractions of the surface covered by A and B, respectively. Then according to the above hypothesis, we would have

$$\alpha_b \theta_a \mu_b = \nu_b \theta_b. \quad (27)$$

$$\omega = \nu_a \theta_a. \quad (28)$$

Since θ_b is nearly equal to unity, we thus have

$$\omega = \left(\frac{\nu_a \nu_b}{\alpha_b} \right) \frac{1}{\mu_b}, \quad (29)$$

which is of exactly the same form as (26) and is thus equivalent to Schutz's rule.

SUMMARY.

1. The work of the Braggs on crystal structure is reviewed from the viewpoint of the chemist and the relation of this work to theories of chemical constitution such as those of Werner, Stark, J. J. Thomson, and Lewis, is discussed in detail.

2. It is concluded that the substances whose structures have thus far been studied by the X-ray spectrograph are not representative of compounds in general. Only polar compounds have been studied.

3. Solid polar compounds are, in general, built up of atoms bound together by secondary or residual valence. The whole crystal must be regarded as a single molecule.

4. Solid nonpolar compounds consist in general of "Group Molecules" in which the atoms are usually held together by primary valence. These

group molecules in turn are bound together by secondary valence to form a large "Crystal Molecule," which includes the whole solid mass.

5. There is no present justification for dividing interatomic (or intermolecular) forces into *physical* and *chemical* forces. It is much more profitable to consider all such forces as strictly chemical in nature. Evaporation, condensation, solution, crystallization, adsorption, surface tension, etc., should all be regarded as typical chemical phenomena. The object of this paper is largely to show that *chemical knowledge already available* is directly applicable to the study of these phenomena.

6. From a consideration of such properties as specific heat, compressibility, coefficient of expansion, etc., it is concluded that collisions do not take place between the atoms of solids, but that these move about equilibrium positions under the influence of both attractive and repulsive forces.

7. The "time of relaxation" of the atoms of solids is calculated approximately from the heat conductivity and is found to be of the order of 10^{-14} to 10^{-7} seconds. An independent method by which the "time of relaxation" can be calculated from the rate of evaporation of a substance in vacuum, gives substantially similar results. Thus the time necessary for an atom of a solid to reach thermal equilibrium with its neighbors is very small compared to the time necessary to make a single oscillation about an equilibrium position. The "oscillations" are thus extremely strongly damped.

8. Since solid substances in general are held together by secondary rather than primary valence, there are few limitations to the number of compounds that can exist in the solid state. Most of these compounds do not show a composition which could be predicted from the ordinary rules of valence. Metallic compounds, minerals, solid solutions and glasses are discussed from this point of view.

9. By considerations based largely on the compressibility, it is concluded that the attractive forces between atoms usually reach a maximum intensity when the distance between adjacent atoms in solids is increased by about 0.6×10^{-8} cm. (10-30% of the normal distance between atoms).

10. Since energy must be expended in breaking apart a solid, the surfaces of solids must contain more potential energy than do the corresponding number of atoms in the interior. Since this potential energy is probably electromagnetic energy in the field between atoms, the interatomic forces are more intense on the surface than in the interior. This intense surface field of force (unsaturated chemical affinity) is one of the causes of the phenomena of condensation and adsorption.

11. Because of the small time of relaxation and because an atom approaching the surface is attracted by many, but later is repelled by few

atoms, it follows that the surfaces of solids are almost wholly inelastic in regard to collisions of molecules impinging on the surface. There is also a great deal of experimental evidence of this inelasticity. As a result, nearly every molecule or atom striking a solid surface condenses no matter what the temperature may be. While condensed it is held to the surface by forces quite similar to those holding solids together (either primary or secondary valence). At high temperatures evaporation may take place almost immediately after condensation, but at lower temperatures, the condensed atom or molecule may remain indefinitely.

12. The phenomena of condensation and evaporation (sublimation) of solids is discussed at some length. In general, the rate of evaporation (m) of a substance in a high vacuum is related to the pressure (p) of the saturated vapor by the equation

$$m = \sqrt{\frac{M}{2\pi RT}} p.$$

Red phosphorus and some other substances probably form exceptions to this rule.

13. The mechanism of the dissociation of a solid, such as CaCO_3 is discussed. It is shown that when, according to the phase rule, separate phases of constant composition are present, the reaction must take place exclusively at the boundaries of these phases. This kinetic interpretation of the phase rule indicates clearly the distinction between reactions in which solid solutions are formed and those in which separate phases appear. This theory offers a ready explanation for the fact that hydrated crystals frequently fail to effloresce unless scratched and for the fact that thoroughly dehydrated substances often absorb moisture with great difficulty.

14. Adsorption is a direct consequence of the time lag between the condensation and the subsequent evaporation of molecules. The adsorbed substance may be held to the surface either by secondary or primary valence. In either case it is profitable to regard the phenomena as chemical in nature. A large number of experimental results are given which prove conclusively that adsorption is very frequently the result of the strongest kind of chemical union (primary valence) between the atoms of the adsorbed substance and the atoms of the solid.

15. It is shown that the action of a typical catalytic poison depends on the formation of a very stable film one atom deep over the surface of the catalyzer. The chemical activity of any solid surface depends upon the nature of, the arrangement of, and the spacing of the atoms forming the surface layer. There is a very close relation between the chemical activity of a surface and the electron emission from it (either thermionic or photoelectric emission).

16. A brief quantitative development of this theory of heterogeneous reactions is given. A "law of surface action" analogous to but different

from, the "law of mass action" is proposed. This theory is in accord with and affords an explanation of Reichinstein's "Constant Sum Hypothesis." An outline is given of the application of this theory to heterogeneous gas reactions and to enzyme action.

The second part of this paper will deal with the Structure of Liquids with particular reference to surface tension phenomena. It will be shown that the surface tension of organic liquids is a characteristic *chemical* phenomena. It depends particularly upon the *shapes* of the group molecules and upon the relative intensities of the chemical activity of *different portions* of the molecules. A method will be described (together with experimental data) by which the *cross sections*, *lengths* and other dimensions of group molecules of liquids may be determined.

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THE THERMODYNAMIC PROPERTIES OF SILVER AND LEAD IODIDES.

By HUGH STOTT TAYLOR.

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The thermodynamic properties of silver and lead iodides have been the subject of considerable recent experimental investigation. The object of the work has been to obtain accurate data on the free energies and heats of formation with a view to testing the newer thermodynamic conceptions relative to these two magnitudes.

The relation between free energy and heat of formation is representable, according to the two laws of thermodynamics, by the fundamental equation,

$$A - U = T dA/dT.$$

With the aid of this equation, given the maximum work or free energy, A , at any temperature, T , together with its temperature coefficient dA/dT , it is possible to evaluate the heat effect of the reaction U . The values obtained by such a procedure should show concordance with the direct calorimetric observations. Alternatively, if it be desired to proceed from the thermal data to an evaluation of the free energy, classical thermodynamics, without the aid of new assumptions, is inadequate. This will readily be grasped if the form of the above equation be somewhat modified. Since

$$A - U = T dA/dT,$$

it follows that

$$A dT - T dA = U dT.$$

Dividing each side by T^2 there results,