

- IV. "Electrolytic Conduction in relation to Molecular Composition, Valency and the nature of Chemical Change: being an Attempt to apply a Theory of 'Residual Affinity.'" By HENRY E. ARMSTRONG, Ph.D., F.R.S., Professor of Chemistry, City and Guilds of London Central Institution. Received March 11, 1886.

In my recent address to the Chemical Section of the British Association at Aberdeen, I have specially called attention to the "affinity" of *negative* elements—chlorine, oxygen, sulphur, &c.—for negative elements; and I have sought to show that the formation of so-called *molecular compounds* is largely, if not entirely, an outcome of this peculiarity of negative elements. I have also ventured to suggest "that in electrolysing solutions, the friction arising from the attraction of the ions for each other is perhaps diminished, not by the mere mechanical interposition of the *neutral* molecules of the solvent—in the manner suggested by F. Kohlrausch—but by the actual attraction exercised by these molecules upon the negative ion in virtue of the affinities of the negative radicles." In this passage I but vaguely hinted at a modification of the current theory of electrolysis which had occurred to me; as further consideration of the question, especially of Ostwald's electrochemical studies, has strengthened my views, I am led to think that it may be justifiable to submit them for discussion.

It is usual to divide bodies into three classes according to the mode in which they are acted on by an electromotive force: metals forming one class, electrolytes a second, and dielectrics a third. In making this division, perhaps the fact is not sufficiently borne in mind that some compounds—silver chloride, for example—are *per se* electrolytes, while others—such as hydrogen chloride and water—are *individually* dielectrics, but behave as electrolytes when conjoined. On this account, it appears to me desirable to distinguish between—

- (a) *Metals.*
- (b) *Simple* electrolytes—compounds, like silver chloride, which in the pure state are electrolytes.
- (c) *Pseudo*-dielectrics—compounds like water, hydrogen chloride and sulphuric acid, which behave as dielectrics when *pure*, but as electrolytes when mixed with other members of their own class. Conducting mixtures of members of this class may conveniently be termed *composite electrolytes*.
- (d) Dielectrics.

Simple Electrolytes.

It is undoubtedly a fact that only a limited number of binary compounds are simple electrolytes; and it is especially noteworthy that, with the single doubtful exception of liquefied ammonia, no hydrogen compound—whether binary or of more complex composition—can be classed with the simple electrolytes. Indeed, all the simple electrolytes with which we are acquainted are either compounds such as the *metallic* chlorides, or *metallic* salts—nitrates, sulphates, &c. Including metallic chlorides and their congeners and the corresponding oxides and hydroxides among salts—regarding water as an acid, in fact—and denying the title of salts—hydrogen salts—to the acids, Hittorf's proposition ("Wied. Ann.," 1878, 4, p. 374): "Electrolyte sind Salze" may be safely upheld. But only some of the binary metallic salts are electrolytes: beryllium chloride, for example, belongs to the class of "pseudo-dielectrics" (Nilson and Petterson, "Wied. Ann.," 1878, 4, p. 565; Humpidge, "Phil. Trans.," 1883, p. 604); and in the case of those elements which readily form two classes of salts—so-called *ous* or *proto*-salts and *ic* or *per*-salts, the *ous* compounds alone appear to be electrolytes.

It is highly remarkable that whereas fused silver chloride is easily decomposed on passage of a current of low electromotive force, hydrogen chloride is a "pseudo-dielectric" which forms when coupled with the "pseudo-dielectric" water a readily conducting "composite electrolyte;" while mercuric chloride conducts with great difficulty—possibly not at all when pure—not only in the fused state, but even when coupled with water. No explanation of these facts seems to be afforded by thermochemical data.*

The consideration of these and other similar cases, I think, can

* The following numbers are given by Thomsen as representing the amounts of heat developed in the formation of the specified chlorides in the state of aggregation in which they exist under ordinary conditions (2×35.4 grams of chlorine being in each case used in the production of the chloride):—

| | |
|--|----------------------------|
| Hydrogen chloride..... | 44,000 units (gram ° C.). |
| Silver " | 58,760 " |
| Mercuric " | 63,160 " |
| Stannic " | 63,625 " |
| Stannous " | 80,790 " |
| Lead " | 82,770 " |

Only three of the chlorides in this list are simple electrolytes. As much more heat is developed in the formation of two of these three—stannous and lead chlorides—than in the case of any of the others, it would appear probable *à priori* that these would be the most stable; obviously, therefore, the study of the heats of formation throws no light on differences in electrical behaviour such as are manifest between hydrogen, mercuric and stannic chlorides, on the one hand, and silver, stannous and lead chlorides on the other.

but lead to one conclusion: that electrolysability is conditioned both by the nature of the elements in the compound and its molecular structure. I have put forward the hypothesis in my address—"that among metallic compounds, only those are electrolytes which contain more than a single atom of metal in their molecules." The mere presence of two or more associated atoms of metal in the molecule, however, probably does not constitute a compound an electrolyte; and although the hypothesis may be applicable to the majority of simple electrolytes, it certainly does not appear to include all the facts, and it does not serve to explain why certain salts are electrolytes while others are not.

The remarkable difference in the electrical behaviour of two compounds of the same element, such as stannous chloride, in which the ratio of tin to chlorine atoms is as 1 to 2, and stannic chloride, in which $\text{Sn} : \text{Cl} = 1 : 4$ —the one being a simple electrolyte; the other a pseudo-dielectric, if indeed it be not a dielectric—would appear almost to justify the conclusion that in the case of per-salts such as stannic chloride the metal is, as it were, enveloped in a non-conducting sheath of the negative radicle. But whether this be so or not, if—as appears to be the case—all simple electrolytes are *metallic* compounds, and if only proto-salts are electrolytes, may it not be that electric conduction in simple electrolytes is of the nature of ordinary metallic conduction, differing from it only in the circumstance that the compound is decomposed as a consequence of the passage of the current?

This would lead to the conception of an electrolyte as being a metallic compound of such elements, and so constituted, that electric conduction may take place through its mass in a manner similar to that in which it takes place through a mass of metal: in fact through the agency of its metallic atoms. On this view, it is essential that the metallic atoms in the molecules comprising a mass of an electrolyte should be in proximity—as they probably are in proto-salts, but not in many per-salts. The conductivity of two-metal alloys is in many cases much less than that of either of the contained metals: for example, the conductivity of the alloy SnCu_4 is about $\frac{1}{4}$ th that of tin and about $\frac{1}{80}$ th that of copper. The specific conductivity of metals may, therefore, be much reduced by association with one another; and this being the case, it appears probable that the specific conductivity of a metal would be still more reduced by association with a non-metal, and that if the metal were one of low specific conductivity, it might thus practically become altogether deprived of conducting power: perhaps the "exceptional" behaviour of mercuric and beryllium chlorides is to be explained by considerations such as these.

To discuss such questions at all satisfactorily, however, we require to know much more of the electrical behaviour of *pure* fused salts;

it is surprising how little accurate knowledge we possess on this subject.

Composite Electrolytes.

I assume it to be admitted that neither water nor liquid hydrogen chloride, for example, is an electrolyte, although an aqueous solution of hydrogen chloride conducts freely and is electrolysed by an electromotive force of but little more than a volt.

The theory put forward by Clausius in 1857 in explanation of electrolysis is well stated in Clerk Maxwell's "Elementary Treatise on Electricity" (p. 104), in the following words:—

"According to the theory of molecular motion, every molecule of the fluid is moving in an exceedingly irregular manner, being driven first one way and then another by the impacts of other molecules which are also in a state of agitation. The encounters of the molecules take place with various degrees of violence, and it is probable that even at low temperatures some of the encounters are so violent that one or both of the compound molecules are split up into their constituents. Each of these constituent molecules then knocks about among the rest till it meets with another molecule of the opposite kind, and unites with it to form a new molecule of the compound. In every compound, therefore, a certain proportion of the molecules at any instant are broken up into their constituent atoms. Now, Clausius supposes that it is on the constituent molecules in their intervals of freedom that the electromotive force acts, deflecting them slightly from the paths they would otherwise have followed and causing the positive constituents to travel, on the whole, more in the positive than in the negative direction and the negative constituents more in the negative direction than in the positive. The electromotive force, therefore, does not produce the disruptions and reunions of the molecules, but finding these disruptions and reunions already going on, it influences the motions of the constituents during their intervals of freedom. The higher the temperature, the greater the molecular agitation, and the more numerous are the free constituents: hence the conductivity of electrolytes increases as the temperature rises."

This theory has been widely accepted by physicists; but it appears to me that, on careful consideration of the evidence, and especially of recent exact observations on conditions of chemical change, it must be admitted, as I have elsewhere contended (B. A. Address), that proof is altogether wanting of the existence of a condition such as is postulated by Clausius. Moreover, it has been shown by Hittorf that cuprous and silver sulphides, and by F. Kohlrausch that silver iodide, all undergo electrolysis in the *solid* state; the partisans of the dissociation hypothesis would, I presume, scarcely contend that it is

easily applicable to such cases as these. It also does not appear to afford any explanation of the *abrupt* change in conductivity which occurs in solid silver iodide and sulphide as the temperature is raised (see p. 280); nor of the peculiar variation in conductivity on diluting sulphuric acid with water (see p. 282).

Again, I venture to think that the conductivity of a *mixture* of compounds which themselves have little or no conducting power is accounted for in but an unsatisfactory and insufficient manner by the hypothesis put forward by F. Kohlrausch ("Pogg. Ann.," 1876, 159, p. 233); there appears to be *far too great a difference* in the behaviour of the pure compounds, water and liquid hydrogen chloride, for example, and of a mixture—no decomposition apparently of either *compound* being effected by any electromotive force short of that which produces disruptive discharge, although the *mixture* of the two will not withstand an electromotive force of little more than a volt. Influenced by these considerations, I am led to conclude that there is no satisfactory evidence that the constituents of the electrolyte are either free prior to the action of the electromotive force, or are primarily set free by the effect produced by the electromotive force upon either member *separately* of the *composite* electrolyte; but that an additional influence comes into play, viz., that of the one member of the composite electrolyte upon the other while both are under the influence of the electromotive force. This influence, I imagine, is exerted by the negative radicle of the one member of the composite electrolyte upon the negative radicle of the other member. Assuming, for example, that in a solution of hydrogen chloride in water the oxygen atom of the water molecule is straining at the chlorine atom of the hydrogen chloride molecule, if when subjected to the influence of an electromotive force the molecules are caused to flow past each other—the phenomena of electric endosmose may be held to afford evidence that in composite electrolytes the molecules are thus set in motion—it is conceivable that this influence, superadded to that of the electromotive force upon the electrolyte, may bring about the disruption of the molecule and conduction: in short, that a state may be induced such as Clausius considers is the state prior to the action of the electromotive force.

A large amount of most valuable information on the connexion of dilution and electrical conduction in aqueous solutions has been recently published by Arrhenius, Bouty, F. Kohlrausch and Ostwald. In his most recent paper, Ostwald ("Journal für praktische Chemie," 1885, 32, p. 300) has given the results of his determinations of the *molecular conductivity* m^* in the case of no less than about 120 different

* $m = kv$, k being the specific conductivity as ordinarily defined, and v the volume of the solution, *i.e.*, the number of litres containing the formula weight in grams of the acid. His results are expressed in arbitrary units.

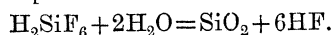
acids: it appears to me that many—indeed all—of his observations afford most distinct evidence in favour of the view I have expressed above. The general result of his investigation is that the molecular conductivity increases with dilution: in other words, that the dissolved substance exercises a greater specific effect, finally attaining a maximum; it then diminishes, but he believes this to be due to impurities in the water, especially to neutralisation of the acid by traces of ammonium carbonate. The maximum, he appears to think, would be the same for all acids if the dilution could only be pushed far enough: in the case of monobasic acids it is about 90 (arbitrary units); it is twice this in the case of dibasic, thrice in the case of tribasic, and so on.

I will quote first his results in the case of solutions of hydrogen chloride, bromide, iodide, fluoride and silicon fluoride.

Table I.

| <i>v.</i> | HCl. | HBr. | HI. | HF. | H ₂ SiF ₆ . |
|-----------|------|------|------|-------|-----------------------------------|
| 2 | 77·9 | 80·4 | 80·4 | .. | 47·81 |
| 4 | 80·9 | 83·4 | 83·2 | 6·54 | 57·29 |
| 8 | 83·6 | 85·1 | 84·9 | 7·59 | 62·20 |
| 16 | 85·4 | 86·6 | 86·4 | 10·00 | 67·08 |
| 32 | 87·0 | 87·9 | 87·6 | 13·14 | 71·52 |
| 64 | 88·1 | 88·9 | 88·7 | 17·38 | 75·61 |
| 128 | 88·7 | 89·4 | 89·4 | 23·11 | 79·22 |
| 256 | 89·2 | 89·6 | 89·7 | 30·30 | 83·39 |
| 512 | 89·6 | 89·7 | 89·7 | 39·11 | 91·62 |
| 1024 | 89·5 | 89·5 | 89·3 | 49·49 | 109·5 |
| 2048 | 89·5 | 88·9 | 89·0 | 59·56 | 144·0 |
| 4096 | 88·6 | 87·6 | 87·8 | 69·42 | 187·1 |
| 8192 | .. | .. | .. | .. | 226·6 |
| 16384 | .. | .. | .. | .. | 258·6 |
| 32768 | .. | .. | .. | .. | 282·6 |

It will be observed that hydrogen chloride, bromide and iodide practically behave alike; the numbers for the chloride are, however, slightly lower than those for the bromide and iodide, and the maximum is not reached quite so soon in the case of the chloride. Hydrogen fluoride is altogether different: its molecular conductivity is exceedingly low to begin with, and is considerably below the maximum even when $v=4096$. But I would call special attention to the numbers for hydrogen silicon fluoride, which is commonly regarded as a dibasic acid: at first, as Ostwald says, it behaves as a monobasic acid of moderate strength—iodic acid, for example; but the maximum for monobasic acids being exceeded, the molecular conductivity increases more and more rapidly, ultimately exceeding the treble value, 270. It must be supposed that it undergoes decomposition in accordance with the equation—



The noteworthy point is *the large excess of water* required to initiate this change: when $v=16$ the solution contains less than 1 per cent. H_2SiF_6 , and at this point, according to Ostwald, decomposition probably begins, but that it is far from complete even when a very much larger excess is present is evident from the fact that the maximum when $v = 32,768$ is 282 and not above 400.

Now it is well known that hydrogen chloride, bromide and iodide are, practically speaking, perfect gases under ordinary circumstances: in other words, masses of these gases would mainly consist of molecules such as are represented by the formulæ HCl , HBr and HI . It has been proved, however, by Mallet that hydrogen fluoride at temperatures near to its boiling point mainly consists of molecules of the formula H_2F_2 . In the aqueous solution the molecules would be brought more closely together, and therefore it is probable that, even in the case of hydrogen chloride, bromide and iodide, a certain proportion of more complex molecules would result; the relatively high boiling point of hydrogen fluoride (19.4°) renders it probable that in the liquid state this compound would at least partially consist of molecules more complex even than is represented by the formula H_2F_2 . On the hypothesis put forward in this paper, the influence exercised by the one member of the composite electrolyte upon the other member during electrolysis is at all events mainly exercised by their respective negative radicles, and the extent of the influence thus mutually exerted by these radicles would depend on the extent to which they are still possessed of "residual affinity." If the hydrogen chloride, bromide and iodide are present chiefly as simple molecules, they should exert, *ab initio*, almost the full effect which they are capable of exerting; and the chief effect of dilution being to decompose the more complex molecules, conductivity should increase to but a slight extent if the extent to which simplification can take place be but small. On the other hand, if owing to the formation of molecular aggregates the residual affinity be more or less exhausted, the initial conductivity will be low, and it will increase on dilution only in proportion as these aggregates become broken up.

It appears to me that the behaviour of the four hydrides under discussion is absolutely in accordance with these requirements of the hypothesis. Even the difference between hydrogen chloride and hydrogen bromide and iodide is not without its bearing. The determinations of the density of chlorine at various temperatures by Ludwig, and of the density of bromine by Jahn ("Monatshefte für Chemie," 1882, p. 176), have shown that it is necessary to raise the temperature considerably higher above the boiling point in order to reduce the density to the theoretical value in the case of chlorine than in the case of bromine: in other words, there is a greater tendency in chlorine to form aggregates more complex than those of the formula

Cl_2 than there is in bromine to form aggregates more complex than those of the formula Br_2 . It is, therefore, not unlikely that the chlorine in HCl has more "residual affinity" than the bromine in HBr ,* and if so the aqueous solution of the former would have a lower initial conductivity than one of equivalent strength of hydrogen bromide, and the maximum would be obtained only on greater dilution; which is precisely the case.

The evidence afforded by the oxy-acids derived from the halogens appears to me to be equally striking. The following are Ostwald's numbers, including those for nitric acid.

Table II.

| v. | Nitric acid. | Chloric acid. | Per-chloric acid. | Bromic acid. | Iodic acid. | Periodic acid. |
|------|--------------|---------------|-------------------|--------------|-------------|----------------|
| 2 | 77·9 | 77·9 | 79·1 | .. | 42·57 | |
| 4 | 80·4 | 80·2 | 82·2 | .. | 50·56 | 23·71 |
| 8 | 82·8 | 82·3 | 84·6 | .. | 59·00 | 30·59 |
| 16 | 84·9 | 84·0 | 86·2 | .. | 66·3 | 39·49 |
| 32 | 86·3 | 85·3 | 88·1 | 79·4 | 72·3 | 49·23 |
| 64 | 87·4 | 86·4 | 89·2 | 81·7 | 76·9 | 59·48 |
| 128 | 88·2 | 87·9 | 89·7 | 84·1 | 80·2 | 69·06 |
| 256 | 88·4 | 88·7 | 89·9 | 86·1 | 81·8 | 76·70 |
| 512 | 88·8 | 88·7 | 89·8 | 87·4 | 83·0 | 82·59 |
| 1024 | 88·9 | 88·6 | 89·8 | 88·4 | 83·1 | 85·38 |
| 2048 | 88·2 | 87·3 | 89·3 | 89·0 | 82·9 | 87·95 |
| 4096 | 86·6 | 85·7 | 87·8 | 88·8 | 81·8 | 86·62 |

It will be observed that nitric, chloric and perchloric acids differ but little; that bromic acid has a considerably lower initial conductivity, and does not attain the maximum so soon; that iodic acid differs still more; and that the behaviour of periodic acid is

* On other grounds also there is reason to believe that hydrogen chloride differs more from hydrogen bromide or iodide than either of these differs from the other: thus less heat is developed on dissolving hydrogen chloride in water than on dissolution of equivalent quantities of the bromide or iodide, the numbers given by Thomsen being—

HCl , $400\text{H}_2\text{O} = 17,300$ units.

HBr , $400\text{H}_2\text{O} = 19,200$,,

HI , $400\text{H}_2\text{O} = 19,200$,,

The solution of hydrogen chloride which distils unchanged at 112° at the ordinary pressure has approximately the composition represented by the formula $\text{HCl} \cdot 8\text{H}_2\text{O}$; whereas the corresponding solutions of hydrogen bromide and iodide boil at 125° and 127° , and their composition is approximately represented by the formulæ $\text{HBr} \cdot 5\text{H}_2\text{O}$ and $\text{HI} \cdot 5\cdot 5\text{H}_2\text{O}$. A solution of hydrogen fluoride approximately of the composition $\text{HF} \cdot 2\text{H}_2\text{O}$ distils unchanged at 120° .

altogether peculiar—being that of a polybasic acid, it may be added. Ostwald regards it as most surprising—“*in hohem Grade befremdlich*”—that periodic acid should be much weaker than iodic acid, and that the latter should be considerably inferior to iodhydric acid. To my mind, their behaviour is absolutely what might be expected of these acids. Although the molecules in liquid nitric, chloric and perchloric acids are probably not of the simple composition represented by the formulæ HNO_3 , HClO_3 , and HClO_4 respectively, the chemical behaviour of these acids does not indicate any great difference between them; owing, however, to the accumulation of oxygen atoms, perchloric acid may be expected to exercise a somewhat greater influence than chloric acid, as it actually does. Chemists are agreed that bromine has less affinity for oxygen than chlorine; hence it may be inferred that the oxygen in bromic acid would have greater residual affinity than the oxygen in chloric acid, and that, therefore, bromic acid would form complex aggregates more readily than chloric acid, and consequently have less influence in electrolysis than chloric acid. This is true in a much greater degree of iodic, and still more of periodic acid:* it is well known that the former not only yields salts of the type $\text{M}'\text{IO}_3$, but also acid salts such as KHI_2O_6 ; and that periodic acid forms a series of very complex salts.

The acids of phosphorus form another interesting series:—

Table III.

| v. | H_3PO_2 . | H_3PO_3 . | H_3PO_4 . |
|------|---------------------------|---------------------------|---------------------------|
| 2 | 30·89 | 28·63 | 14·22 |
| 4 | 37·91 | 34·29 | 17·00 |
| 8 | 45·81 | 41·14 | 21·26 |
| 16 | 54·13 | 49·09 | 27·09 |
| 32 | 62·10 | 56·96 | 34·41 |
| 64 | 69·06 | 64·52 | 43·05 |
| 128 | 74·05 | 70·21 | 53·11 |
| 256 | 77·84 | 74·54 | 61·8 |
| 512 | 79·92 | 77·57 | 69·9 |
| 1024 | 81·00 | 79·11 | 75·4 |
| 2048 | 81·39 | 79·75 | 79·0 |
| 4096 | 80·48 | 79·07 | 79·8 |

These numbers afford to my mind the clearest possible evidence that we are dealing with complex molecules. It is especially note-

* The existence of a stable oxide of the formula I_2O_5 , as well as thermochemical data, have been interpreted as evidence that iodine has a greater affinity for oxygen than even chlorine. I am inclined to take the contrary view, however, and to regard the stability of the oxide I_2O_5 as due less to the high affinity of iodine for oxygen than to its low affinity for itself and the high affinity of oxygen for oxygen.

worthy that the maximum never exceeds that of the monobasic acids* even in the case of phosphoric acid, which is universally regarded as a tribasic acid, and that the *monobasic* hypophosphorus acid is the strongest and the *tribasic* phosphoric acid is the weakest. In very dilute solution phosphoric acid has less influence than even acetic acid, according to Kohlrausch.

It may be well also to quote Ostwald's numbers for sulphurous, selenious, sulphuric and selenic acids.

Table IV.

| <i>v.</i> | Sulphurous acid. | Selenious acid. | Sulphuric acid. | Selenic acid. |
|-----------|------------------|-----------------|-----------------|---------------|
| 2 | .. | 7·63 | 92·7 | 97·3 |
| 4 | 19·19 | 9·73 | 96·4 | 103·2 |
| 8 | 25·43 | 12·70 | 100·6 | 109·9 |
| 16 | 32·79 | 16·60 | 107·4 | 117·7 |
| 32 | 41·60 | 21·73 | 116·3 | 127·0 |
| 64 | 50·1 | 28·24 | 127·3 | 138·3 |
| 128 | 58·9 | 36·15 | 139·2 | 148·7 |
| 256 | 66·5 | 45·11 | 150·6 | 157·9 |
| 512 | 72·5 | 54·27 | 160·9 | 164·4 |
| 1024 | 77·1 | 62·79 | 169·1 | 169·7 |
| 2048 | 80·4 | 69·40 | 174·4 | 173·4 |
| 4096 | 83·6 | 73·58 | 177·1 | 174·4 |
| 8192 | .. | .. | 176·9 | 173·4 |

It will be observed that sulphuric and selenic acids are nearly alike in behaviour, the latter being somewhat more active in concentrated solutions; it is noteworthy that of all the polybasic acids studied by Ostwald, these are the only two containing a *single* negative radicle ($\text{SO}_4, \text{SeO}_4$) which exhibit a conductivity in excess of that which characterises the monobasic acids.†

The numbers obtained for sulphurous and selenious acids are deserving of study. Sulphur dioxide is far from being a perfect gas under ordinary conditions; in the liquid state it is probably rich in

* Ostwald appears to be of the opinion that if the dilution could be carried far enough, a maximum conductivity = $n \cdot 90$ would eventually be attained in the case of every n -basic acid. It appears to me that neither do his numbers warrant this—and those here under discussion are an especially good illustration—nor is it likely to be the case on my hypothesis.

† Ostwald infers from the great increase in molecular conductivity that the manner in which the acid is electrolysed varies with the strength of the solution; he supposes that in more concentrated solutions sulphuric acid is resolved into H and HSO_4 , and that both atoms of hydrogen are split off only as the solution becomes more diluted. This appears to me to be altogether improbable.

aggregates of SO_2 molecules, and these may be to a large extent conserved in concentrated aqueous solutions. But the main explanation of the variation in conductivity on dilution must be looked for, I think, in the peculiar relation which sulphur dioxide manifests to water; it is more than probable that the initial interaction involves the formation of a *hydrate*, $(\text{SO}_2)_x(\text{OH}_2)_y$, and that from this on dilution is formed sulphurous acid, $\text{SO}(\text{OH})_2$, and perhaps also "sulphonic acid," $\text{H}\cdot\text{SO}_3\text{H}$. Taking into account the properties of selenious oxide, Ostwald's results appear to me in this case again to lead to but the one conclusion, that conductivity increases in consequence of the specific influence of the fundamental molecule of the compound making itself more and more felt as by dilution it becomes more and more disentangled from its fellows.

The behaviour of solutions of neutral metallic salts on dilution is very similar to that of acids; abundant proof of this is afforded especially by F. Kohlrausch's refined measurements, of which an account has recently been published ("Wied. Ann.," 1886, 26, p. 162). I venture to think that a similar explanation to that above given for oxides will apply to salts; and also that the low molecular conductivities of salts as compared with corresponding acids may be regarded as confirmatory of my hypothesis. I think we must admit that the metals generally have less affinity than hydrogen for negative radicles; if this be granted, we have at once an explanation of the fact that metallic salts are mostly fixed solids, few of which are more than moderately soluble in water while many are very difficultly soluble or insoluble, whereas the corresponding acids are mostly volatile and readily soluble in water, if not miscible with it in all proportions. The affinity of the negative radicles being less exhausted by union with metals than with hydrogen, the fundamental molecules of salts are more prone to unite together to form complex aggregates.

Arrhenius, who has studied the electrical behaviour of solutions of a number of salts,* attributes the change observed in molecular conductivity on dilution—as I have done—to molecular changes; but his deductions are all based on the acceptance of the Williamson-Clausius hypothesis of dissociation.

My hypothesis would also account for the increase in conductivity

* "Bihang till Kongl. Svenska Vetenskaps-Akademien Handlingar." Attonde Bandet. Häfte 2. Stockholm, 1884. Arrhenius, S.: "Recherches sur la Conductibilité Galvanique des Électrolytes. I. La Conductibilité Galvanique des Solutions Aqueuses extrêmement diluées, déterminée au moyen des Depolarisateurs." 63 pp. II. "Théorie Chimique des Électrolytes." 89 pp. Although aware of his work from Ostwald's reference to it, I was unable to study his memoir until after this paper had been elaborated. Ostwald's quotations, moreover, did not enable me to realise the importance which Arrhenius attaches to the occurrence of molecular simplification and changes in composition on dilution.

in composite electrolytes with rise of temperature. It is true that as temperature rises the influence which individual molecules exert upon each other would be lessened; but on the other hand, the complex aggregates would become more and more completely resolved into their fundamental molecules, the velocity of molecular motion would increase, and the tendency of the constituent atoms to remain united would be lessened. From this point of view the determination of the coefficient of change of conductivity with temperature in the case of substances whose molecular conductivity increases considerably on dilution in comparison with allied compounds which exhibit only a slight variation in molecular conductivity on dilution affords an interesting subject for investigation. F. Kohlrausch has already pointed out ("Pogg. Ann.," 1875, 154, p. 236) that in the case of all neutral salts, "der Einfluss der Temperatur auf das Leitungsvermögen mit wachsender Verdünnung sich Anfangswerthen nähert, die zwischen engen Gränzen liegen," and the experiments of F. Kohlrausch and Nippoldt on solutions of sulphuric acid (*ibid.*, 1869, 138, p. 286) show that the resistance diminishes to a much greater extent for equal increments of temperature in concentrated than in dilute solutions. Thus:—

Table V.

| Percentage of sulphuric acid. | Resistance (Mercury=1.) | Percentage increment of conductivity for 1° C. |
|-------------------------------|-------------------------|--|
| 0·2 | 465,100 | 0·47 |
| 8·3 | 34,530 | 0·653 |
| 14·2 | 18,946 | 0·646 |
| 20·2 | 14,990 | 0·799 |
| 28·0 | 13,133 | 1·317 |
| 35·2 | 13,132 | 1·259 |
| 41·5 | 14,286 | 1·410 |
| 46·0 | 15,762 | 1·674 |
| 50·4 | 17,726 | 1·582 |
| 55·2 | 20,796 | 1·417 |
| 60·3 | 25,574 | 1·794 |

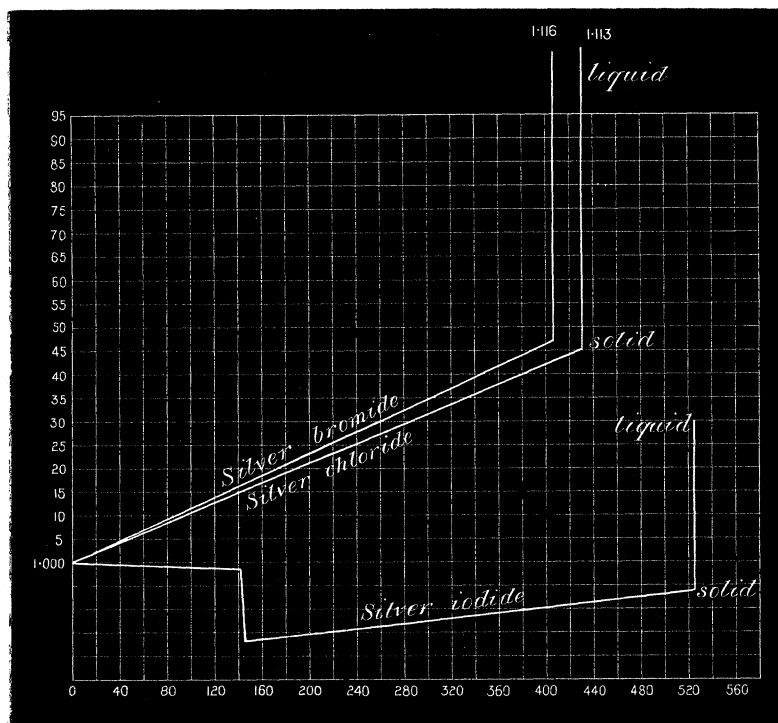
As concentrated solutions would be richer in complex aggregates than dilute solutions, these results are in entire accordance with my hypothesis: it does not appear to me that they can be satisfactorily interpreted in terms of the dissociation hypothesis.

In cases where the influence of the one member of the composite electrolyte upon the other is but slight, it may happen that the effect of temperature in diminishing this influence will outweigh that due to

molecular simplification, and that, in consequence, conductivity will diminish with rise of temperature; a mixture of alcohol and ether would appear to furnish an example of this kind; according to Pfeiffer's recent observations ("Wied. Ann.," 1886, 26, p. 226), such a mixture behaves as a metallic conductor of very high resistance.

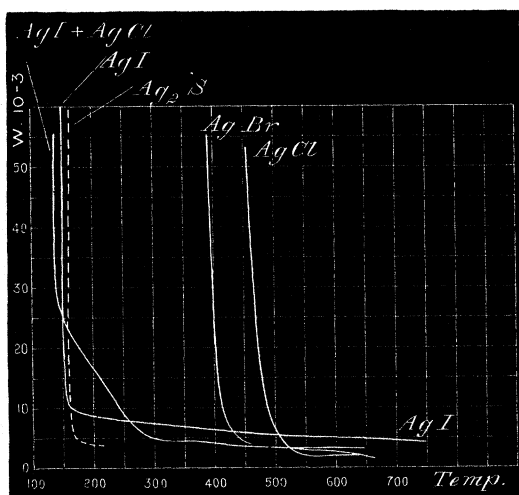
The increase in conductivity of graphite and gas-retort carbon on heating, and the effect of light on the conductivity of (? impure) selenium and some other substances (Shelford Bidwell, "Phys. Soc. Proc.," 7, p. 129, 256), appear to me to be also explicable on the assumption that in all these cases we are dealing with composite electrolytes.

If any further proof be needed of an intimate connexion between molecular composition and electrolytic conduction, it is most conclusively afforded, I think, by the observations of W. Kohlrausch on chloride, bromide and iodide of silver ("Wied. Ann.," 1882, 17, p. 642), which are exhibited in the accompanying curves. In the fused



state, these compounds are better conductors than the most highly-conducting mixture of sulphuric acid and water, which of all liquids

is the best conductor at ordinary temperatures. On reference to the curves, it will be seen that the resistance of both silver chloride and bromide suddenly increases when the change from the fused to the solid state sets in; but that no such change takes place in the case of the iodide. Silver iodide fuses at 527° according to Rodwell, but at about 540° according to Kohlrausch; its electrical resistance increases only gradually after it has become solid, and remains almost a linear function of the temperature during an interval of 400° , until suddenly at near 150° it increases enormously, this change taking place at the moment when according to Rodwell ("Phil. Trans.," 1882, p. 1133) it passes from the transparent, plastic, amorphous solid to the opaque, brittle, crystalline state, the volume increasing considerably as shown by the annexed curve. Kohlrausch has proved most conclusively that



the solid iodide may undergo electrolysis. It would seem that almost immediately after solidification in the case of silver chloride and bromide practically the whole mass consists of complex aggregates so constituted as to be exceedingly bad conductors, but that such aggregates are formed much less readily by silver iodide.

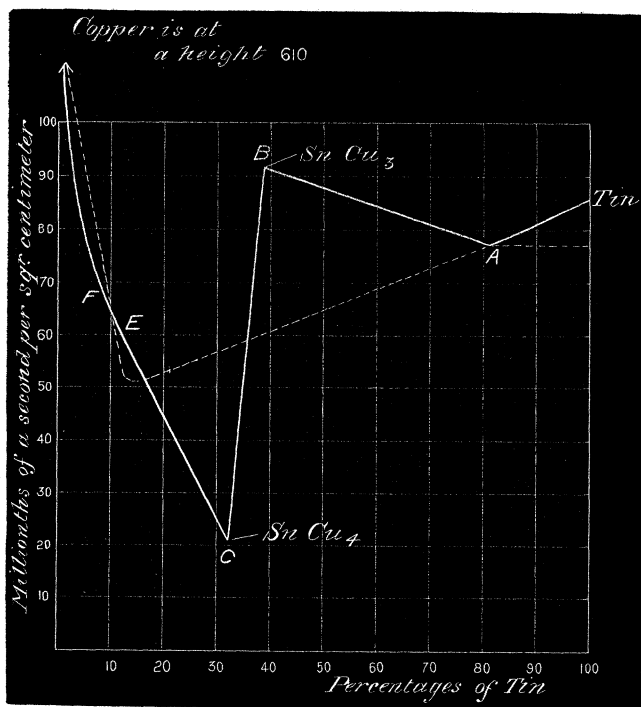
Metallic Conduction.

I do not propose in any way to discuss metallic conduction, but merely to call attention to some of the analogies between it and electrolytic conduction.

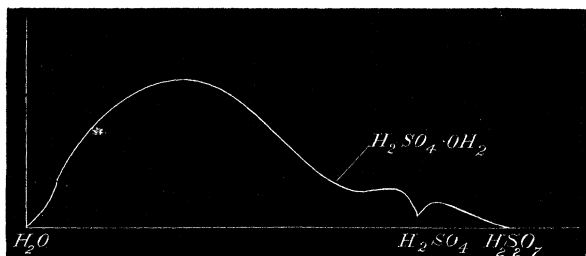
It is conceivable, and it would appear probable from the fairly regular manner in which the electrical resistance of most pure metals

decreases as the temperature falls, the coefficients of change being practically very nearly the same in all cases, that the increase in resistance as temperature rises is mainly due to the increase in molecular inter-distances. As a rule, resistance increases on the passage of a metal from the solid to the liquid state, but there are noteworthy exceptions from which it would appear probable that even in pure metals conductivity to some extent depends on molecular composition: thus the conductivity of bismuth increases at the moment of fusion from 0.43 to 0.73 of that of mercury at 21°, and that of antimony from 0.59 to 0.84 (L. de la Rive, "Compt. rend.," 1863, 57, p. 691); it is well known that bismuth contracts considerably on fusion, and this is probably also the case with antimony. Again, according to Bouty and Cailletet (*ibid.*, 1885, 100, p. 1188), the resistance of mercury decreases at the point of solidification in the ratio 4.08:1; this is a remarkable increase in conductivity, and it is difficult to believe that it is wholly due to mere contraction of volume.

That the behaviour of alloys is worthy of far more attention than it has hitherto received appears most clearly from the few data at disposal. As being the most instructive instance, I append the curve



given by Professor Lodge as representing the specific conductivities of the copper-tin alloys ("Phys. Soc. Proc.," 1879-80, 3, p. 158). He examined five alloys, containing respectively 80·8, 38·2, 31·7, 12·6, and 9·7 per cent. by weight of tin, which were prepared by Professor Chandler Roberts; the dotted curve represents the results obtained by Matthiessen, who did not examine any alloy between those containing 16·4 and 85·1 volume per cent. of copper. The comparison of Professor Lodge's curve with that given by F. Kohlrausch for mixtures of sulphuric acid and water—which I also append—appears to



me to be in the highest degree suggestive. In the case of the latter, it will be observed that, starting from SO_3 on the one side and H_2O on the other, minima occur at points on the curve corresponding to compounds of the formula H_2SO_4 and $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$; it is, however, well known that such compounds are unobtainable at ordinary temperatures, and it is highly probable that if the *pure* compounds could be examined, the minima would touch the base line, as in the case of water.* The point of maximum conductivity does not correspond to any known hydrate, but as I have elsewhere remarked it is almost coincident with that of maximum heat evolution on mixing sulphuric acid and water, and it is therefore doubtless the point at which the maximum chemical change occurs. On reference to the alloy curve, it is seen that the addition of quite a small amount of tin to copper produces a very marked effect just as does the addition of a small amount of water to sulphuric acid, the effect being, however, to diminish conductivity in the one case but to increase it in the other; after the addition of only a moderate amount of tin, a

* The acids richer than H_2SO_4 in SO_3 have been examined by W. Kohlrausch ("Wied. Ann.," 1882, xvii, p. 69). It is especially noteworthy, as I said when reading this paper, that the hydrate $\text{H}_2\text{S}_2\text{O}_7$ is a much worse conductor than either of the hydrates H_2SO_4 or $\text{H}_2\text{SO}_4 \cdot \text{OH}_2$, and that the former of these conducts less readily than the latter, and in this connexion to remember that the compound $\text{H}_2\text{S}_2\text{O}_7$ is the most definite and easily obtained in a crystalline shape, and that the hydrate $\text{H}_2\text{SO}_4 \cdot \text{OH}_2$ is the least definite of the three: the evidence that conductivity depends on absence of homogeneity is overwhelming in this case.—[May 26, 1886.]

pronounced minimum is reached, corresponding to the pronounced maximum attained on addition of a moderate amount of water to sulphuric acid, and at a point moreover corresponding to a definite compound, SnCu_4 ; a further slight addition of tin develops another minimum less pronounced than the first, but also corresponding to a definite compound, SnCu_3 ; the curve then falls slightly and exhibits a third minimum, its course being analogous to that of the sulphuric acid and water curve near to sulphuric acid. If one or the other curve be inverted, the general similarity in form is especially striking. It is obviously important that alloys intermediate between those studied should be examined; a comparison of Lodge's with Matthiessen's curve shows how much may be missed; this remark applies to alloys generally. Whatever may be the explanation,* it appears to me to be clear that in alloys as in composite electrolytes the constituent members of the system influence each other, and thus mutually contribute to the final result. The marked diminution in the conductivity of copper produced by very small quantities of oxygen, of phosphorus or of the metalloid arsenic is well known. It would appear probable that this is in some way due to the occurrence of an electrolytic change, which at least in part is opposed in direction to that taking place in the pure metal during conduction.†

Valency—Chemical Change.

Notwithstanding the fierce controversy which has been waged between the advocates of the doctrine of fixed valency and the advocates of the doctrine of varying valency, our views on the subject are still in an unfortunate degree unsatisfactory and indefinite. Even those—and they probably form a large majority—who regard valency as a variable, dependent both upon the nature of the associated radicles and the conditions—especially as to temperature—under which these are placed, often hesitate to attribute a valency sufficiently high to account for every case of combination; in fact both parties agree in distinguishing “atomic” from “molecular” compounds, and differ only as to where the line shall be drawn.

* It is very remarkable that not only do the heat conductivity and the induction balance curves for the tin-copper alloys correspond (Chandler Roberts, “Phys. Soc. Proc.,” 3, p. 156), but that the curves given by Thurston as representing the strength of these alloys (“Materials of Engineering,” Part III, p. 412) also exhibit a marked similarity to the electrical conductivity curves.

† The change produced in gold by a very small quantity of lead is most astonishing: its conductivity is reduced almost to that of lead and it becomes as brittle as glass. It is difficult to understand this change unless it be that opportunity is given for the gold itself to assume a different molecular state, owing to continuity becoming disturbed. The effect produced appears to be strictly comparable with that observed on lowering the temperature of silver iodide from above about 150° , and in the passage of liquid water at 0° into ice.

It is difficult to over-estimate the importance of the theory of valency: its application has led to an enormous extension of our knowledge of carbon compounds especially, and it has furnished us with a simple and consistent system of classifying the mighty host of these bodies; but on the other hand, it may be questioned whether it has not led us away from the search into the nature of chemical change, and even if the introduction of the terms saturated and unsaturated has not had a directly pernicious effect. The almost universal disregard of molecular composition as an important factor in chemical change in the case of solids and liquids, and the popular tendency to overlook the fact that our formulæ of such bodies are purely empirical expressions, has undoubtedly exercised a prejudicial influence.

No known compounds *are saturated*—if any were, such would be incapable, I imagine, of directly taking part in any interaction, and in their case decomposition would necessarily be a precedent change. The paraffins are apparently of all bodies the most inert and the most nearly saturated, and next to them comes hydrogen—the unsaturated character of which is displayed in interactions such as occur at atmospheric temperatures between it and platinum and palladium, and when it displaces silver from silver nitrate or certain of the platinum metals from their salts. One of the most striking instances perhaps of popular error in this respect is water, which is always regarded as a saturated compound, although its entire behaviour and especially its physical properties characterise the molecule H_2O , I think, as that of an eminently unsaturated compound: I fail to see how otherwise we are to explain the high surface tension and high specific heat of liquid water, its high heat of vaporisation, and its imperfectly gaseous behaviour up to temperatures considerably above its boiling point, let alone its great solvent power and its tendency to form hydrates with a multitude of compounds—*especially oxygenated* compounds, be it added.

The theory was brought most prominently under the notice of chemists by Helmholtz in the last Faraday lecture that electricity, like matter, is as it were atomic, and that each unit of affinity or valency in our compounds is associated with an equivalent of electricity—positive or negative; that the atoms cling to their electric charges and that these charges cling to each other. Thus barely stated, this theory does not appear to take into account the fact that the *fundamental* molecules even of so-called atomic compounds *are never saturated*, but more or less readily unite with other molecules to form molecular compounds—molecular aggregates; and unless the application of the theory to explain the existence of such compounds can be made clear, chemists must, I think, decline to accept it.*

* It is noteworthy that Clerk Maxwell ("Electricity and Magnetism," 1873, vol. i, p. 313), when speaking of the theory of molecular charges, says, "This theory of

There is, however, a most significant passage in Helmholtz' paper, in which it is pointed out that (in a Daniell's cell) the phenomena are the same as if equivalents of positive and negative electricity were attracted by different atoms, and perhaps also by the different values of affinity belonging to the same atom, with different force: are we to seek for an explanation in this direction? The impression which the facts make upon the mind of the chemist certainly is, 1, that no two different atoms have equivalent affinities; and, 2, that affinity is a variable depending on the nature of the associated elements: but owing to the recognised complexity of nearly all cases of chemical change, it is difficult to draw any very definite conclusion on this point.

If, however, the nature and properties of so-called molecular compounds generally be considered, and if an attempt be made to form any conception of their constitution, one striking fact is noticeable, viz., that the *metals* in them apparently retain the properties which they exhibited in the parent atomic compounds. Every one knows the marked difference in properties of ferrous as contrasted with ferric salts: they differ not only in chemical behaviour, but also in their physical properties, and are readily distinguishable by their colour. The properties of the ferrous molecular compounds, however, are those of the simple ferrous compounds: ferrous potassium chloride, for example, $\text{Fe}_2\text{Cl}_4 \cdot \text{Cl}_2\text{K}_2$, is a green salt much like ferrous sulphate. Facts such as these have led me to suggest that in such cases the formation of the molecular compound is due to the attraction of the negative element of the one "atomic" compound by the negative element of the other, the metal having no influence except that the amount of affinity of which the negative element is possessed depends on the nature of the metal with which it is associated. It would in fact appear that hydrogen and the metals generally may be regarded as the analogues of the $\text{C}_n\text{H}_{2n+1}$ and $\text{C}_n\text{H}_{2n-1}$ hydrocarbon radicles, and that their compounds with negative elements may be likened to unsaturated hydrocarbons of the form $\text{C}_n\text{H}_{2n+1} \cdot \text{CH} \cdot \text{CH}_2$. We know that whenever such a compound enters into combination, the $\text{C}_n\text{H}_{2n+1}$ radicle takes no part in the change, combination of whatever kind being effected by means of the unsaturated radicle $\text{CH} \cdot \text{CH}_2$ with which it is associated. I do not

molecular charges—he uses the expression molecular in the sense that the chemist uses the term atomic—may serve as a method by which we may remember a good many facts about electrolysis. It is extremely improbable that when we come to understand the true nature of electrolysis we shall retain in any form the theory of molecular charges, for then we shall have obtained a secure basis on which to form a true theory of electric currents, and so become independent of these provisional theories." And later (p. 315): "While electrolysis fully establishes the close relationship between electrical phenomena and those of chemical combination, the fact that every chemical compound is not an electrolyte shows that chemical combination is a process of a higher order of complexity than any purely electrical phenomenon."

mean to contend that the metals are fully neutralised in their compounds, but merely that as a rule they behave as though they were saturated just as do the C_nH_{2n-1} radicles derived from the benzenes. There can be little doubt that an absolute distinction must be drawn between hydrogen and the metals on the one hand, and the non-metals on the other. Regarding the facts in the light of our knowledge of carbon compounds, it is difficult to resist the conclusion that the differences observed are due to differences in structure of the stuffs of which the elements as we know them are composed, the which differences condition perhaps a different distribution of the electric charge or its equivalent, in the case of each element.

In the earlier part of this paper I have ascribed the influence which the one set of molecules of the composite electrolyte exercise upon the other during electrolysis to the existence of "residual affinity." I believe this view also to apply to the explanation of the occurrence of chemical change. To quote the words of Arrhenius, "*L'activité électrolytique se confond avec l'activité chimique.*" Several pregnant examples of this have already been given by Ostwald ("J. pr. Chem.," 1884, 30, p. 93).

The investigation of the nature of chemical change has assumed an altogether different aspect since the publication of Mr. H. B. Dixon's inquiry into the conditions of chemical change in gases ("Phil Trans.," 1884, p. 617; see also "Chem. Soc. Trans.," 1886, p. 94). Mr. Dixon has clearly proved that it is impossible to explode a mixture of carbonic oxide and oxygen, and that the change $2CO + O_2 = 2CO_2$ is effected when sparks are passed across the tube containing the gaseous mixture *only in the path of the discharge*. If traces of water be present *explosion* takes place, the velocity of propagation of the explosive wave increasing with the amount of water up to a certain maximum. These results completely dispose of the popular explanation of such changes, viz., that the molecules in the path of the discharge undergo *dissociation*, that the dissimilar atoms thus liberated then combine together, and that as the heat developed in their union causes the dissociation of yet other molecules, change gradually extends throughout the mass.* Mr. Dixon's experiments have not only shown that the propagation of change is dependent on the presence of a third body, but that this third body must bear a certain relation to those with which it is associated; CO_2 , CS_2 , C_2N_2 , CCl_4 , SO_2 , and N_2O were found by him to have no action, and only water—or bodies which formed water under the conditions of the experiment—were found capable of determining the explosion. There is an obvious difference

* I am not to be understood to imply that dissociation does not take place in the path of the discharge; on the contrary, for all the facts appear to me to indicate that conduction and electrolysis are inseparable phenomena in gases as in liquids." (Comp. Schuster, "Proc. Roy. Soc.," 1884, p. 317.)

in constitution between water and the bodies found incapable of determining explosion: the former being a compound of a positive with a negative element, the latter being all compounds of two negative elements; and if it be permissible to generalise from this single instance, it may hence be stated, that in order that interaction shall take place in cases such as that under consideration, it is not only necessary that the elements of the "catalyst" shall be *divisible** between the interacting substances—the elements of CO_2 are obviously as divisible between CO and O_2 as are those of H_2O —but that the catalyst shall consist of a positive and a negative and not of two negative radicles. On this view, it is possible to understand that water itself may act as the catalyst in determining the formation of water at high temperatures from hydrogen and oxygen.†

In the case discussed (the oxidation of carbon monoxide), interaction takes place at a very high temperature, and therefore—since high temperature may be regarded as the equivalent of high electromotive force—under conditions under which the catalyst water is probably a simple electrolyte. The behaviour of sulphur dioxide in presence of oxygen and water is instructive as being a case of an analogous interaction occurring at a low temperature. From a most carefully conducted series of experiments by Mr. Dixon ("Journ. of Gas Lighting," 1881, 37, p. 704), it appears that not only does sulphur dioxide not undergo change in contact with dry oxygen, but that it even resists oxidation if water vapour be present and at a temperature of 100° ; as is well known, however, oxidation takes place—but only *slowly*—when an aqueous solution of sulphur dioxide is in contact with oxygen. In this case, in the gaseous mixture the water apparently is not under such conditions that it can act as a simple electrolyte, or even form a composite electrolyte, and action only takes place when the conditions become such that a composite electrolyte can be formed; Ostwald's observations may be held to prove, I imagine, that a very imperfect composite electrolyte results on dissolving sulphur dioxide in water, and in accordance with this is the fact that the aqueous solution is but *slowly* oxidised.‡

* Mr. Dixon's experiments appear to prove that during the interaction of carbonic oxide and oxygen in presence of water an actual division of the elements of the water molecules takes place between the carbonic oxide and oxygen molecules, and hence that the water does not exercise a mere contact action.

† When this question first came under discussion at the Chemical Society, I said that I looked forward to the time when probably it would be found that a mixture of pure hydrogen and oxygen was inexplorable, like one of pure carbonic oxide and oxygen. I was then still under the influence of current opinion and regarded water as a saturated compound, and had not yet realised the important function of "residual affinity" in such changes.

‡ The behaviour here described of sulphur dioxide appears to me to furnish another argument adverse to the dissociation hypothesis, as oxidation takes place under the conditions least favourable to the occurrence of dissociation.

If a clear distinction can be drawn—as I suppose it can—between simple and composite electrolytes, the presence of a member of the latter class will probably be found to be essential to the occurrence of many interactions taking place at moderate temperatures; thus the oxidation of iron, which is generally supposed to take place only in moist air, is doubtless dependent, not merely on the presence of *water*, but of *impure* water—of water rendered conducting by association with foreign matters; similarly it may be expected that zinc will be found to have no action on water even when associated with a less positive metal, and it would doubtless have no action on sulphuric acid, if such a compound were obtainable in a pure state; but a mixture of sulphuric acid and water readily dissolves it, as the two together form a composite electrolyte of comparatively low resistance.

It can scarcely be doubted that when our elements or compounds are resolved into their ultimate atoms, these atoms are capable of *directly* uniting, and that no catalyst is then required. But if this be the case, and if, as I suppose, the atoms rarely *saturate* each other, the *direct* union of compounds should also be possible in cases in which there is considerable residual affinity; such union would not involve a separation from each other of the constituent elements of one or both of the interacting bodies such as takes place in the changes previously considered. Union of two molecules having taken place; the elements of the interacting bodies having thus been brought into intimate association: it is very probable that in many cases intramolecular change will then supervene, resulting sometimes in mere atomic redistribution, at other times in the resolution of the complex molecule into simpler molecules. I am inclined to think that the majority of so-called double decompositions are thus brought about.

The union of sulphuric anhydride with water to form sulphuric acid, and of sulphuric acid with water to form hydrates, are doubtless cases of this kind. The formation of the hydrate $\text{SO}_3 \cdot \text{OH}_2$ must be supposed to be immediately followed by the occurrence of atomic redistribution if we accept the current view that sulphuric acid is a hydroxide of the formula $\text{SO}_2(\text{OH})_2$; whether after the formation of the hydrate $\text{H}_2\text{SO}_4 \cdot \text{OH}_2$ has taken place atomic redistribution in like manner supervenes is a moot point; the large amount of heat developed by the interaction of water and sulphuric acid is, however, specially noteworthy.

Sodium hydroxide is universally regarded as the analogue of water: is its action on sulphuric acid analogous to that of water? I certainly am inclined to hold that it is, and that in the first instance an aggregate, $\text{NaHO} \cdot \text{SO}_4\text{H}_2$, results, owing to the attraction of the oxygen of the hydroxide by the oxygenated radicle of the acid: atomic redistribution thereupon takes place, and either the molecule is resolved into

two others, water and sodium hydrogen sulphate, or a new compound is formed, which is easily resolvable into these latter. Moreover, I am inclined to attribute this change and the consequent displacement of the hydrogen in the acid by the sodium, not to the fact that sodium has a greater affinity than hydrogen has for SO_4 , but to the tendency of hydrogen to displace the sodium in sodium hydroxide and to form water. I do not contend that in such a case as that quoted direct interaction will take place between the substances as we know them in the solid state; these may consist of comparatively inert complex aggregates which require to be resolved into simpler molecules either by dissolution or by application of heat. In other words, the presence of water may be necessary, not because it is essential to have an electrolyte present, but because the occurrence of both molecular interaction and electrolytic conduction depends on identical molecular and intermolecular conditions. The chemical interaction takes place entirely independently of the water molecules, and these latter serve only to separate and keep apart the fundamental molecules of which the interacting bodies are composed.

No final decision for or against the view here put forward can well be arrived at except by the study of the behaviour of gaseous bodies such as ammonia and hydrogen chloride, for example; if proof can be given that these compounds are capable of directly uniting without the intervention of any third body, a most important step will have been made.

Other cases deserving of study are the conversion of nitric oxide into nitric peroxide, oxidation by means of ozone, and the action of metals such as sodium on water. As the formation of nitric peroxide involves the prior separation of oxygen-atoms from oxygen-atoms, and not merely the combination of two molecules, it is not improbable that interaction between nitric oxide and oxygen molecules will only take place in the presence of a catalyst. But it is to be borne in mind that both nitric oxide and ozone are bodies which are capable of interacting with molecules of their own kind, and that considerable heat is thereby developed; and it is conceivable that such bodies being possessed of high residual affinity may directly enter into combination with others which have but little residual affinity. As regards the action of sodium on water, the difference in behaviour with dilute sulphuric acid between moderately pure zinc and very nearly pure zinc is so marked that the vigorous action between sodium and water cannot be held to prove much, as no special care is ever taken to prepare sodium pure; the question whether the affinity of the oxygen in water for sodium is sufficient to cause their direct association and consequent interaction is an interesting one for experimental inquiry, although it would be very difficult to make the experiment properly.

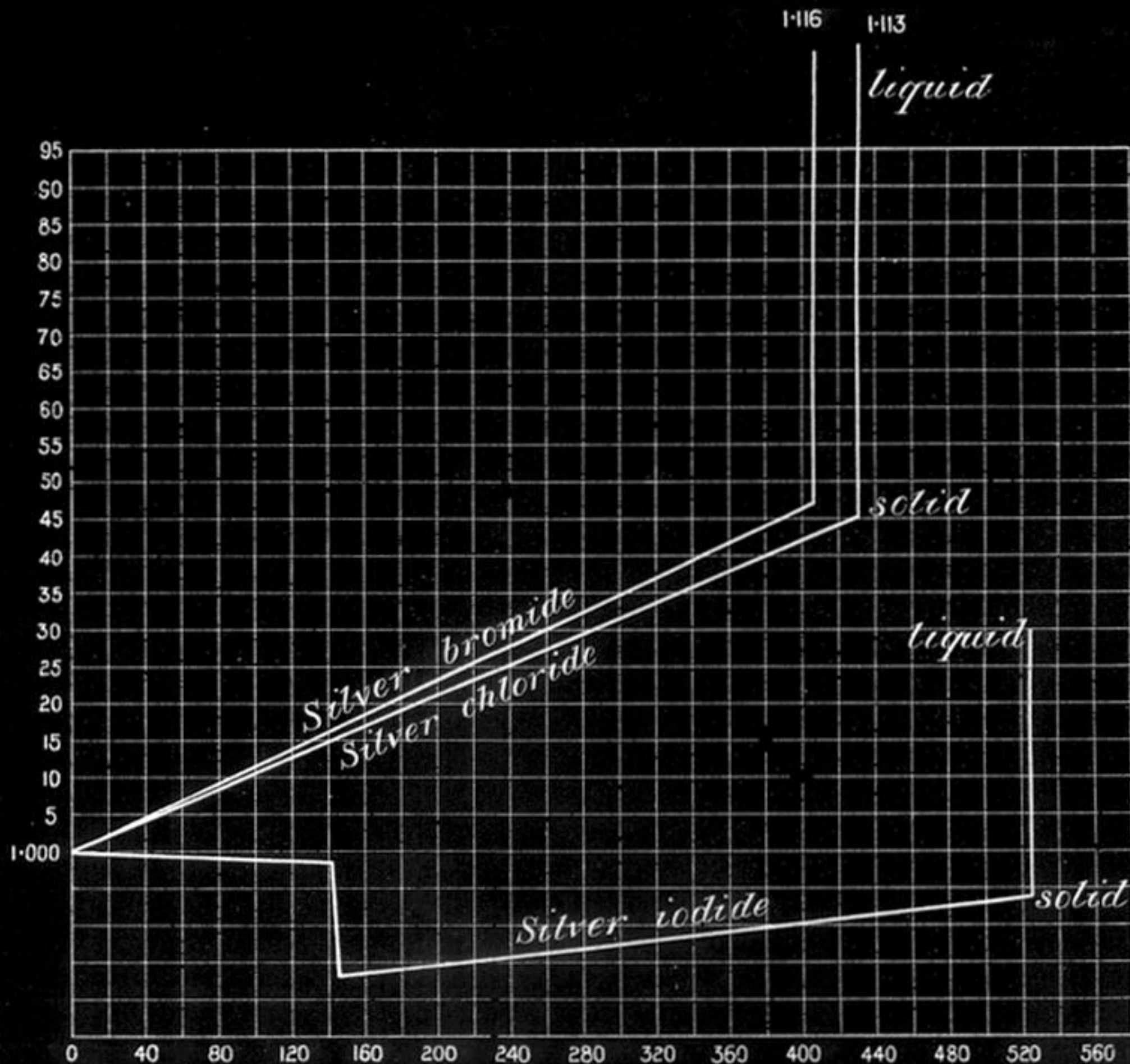
One other application of the theory dwelt on in this paper remains

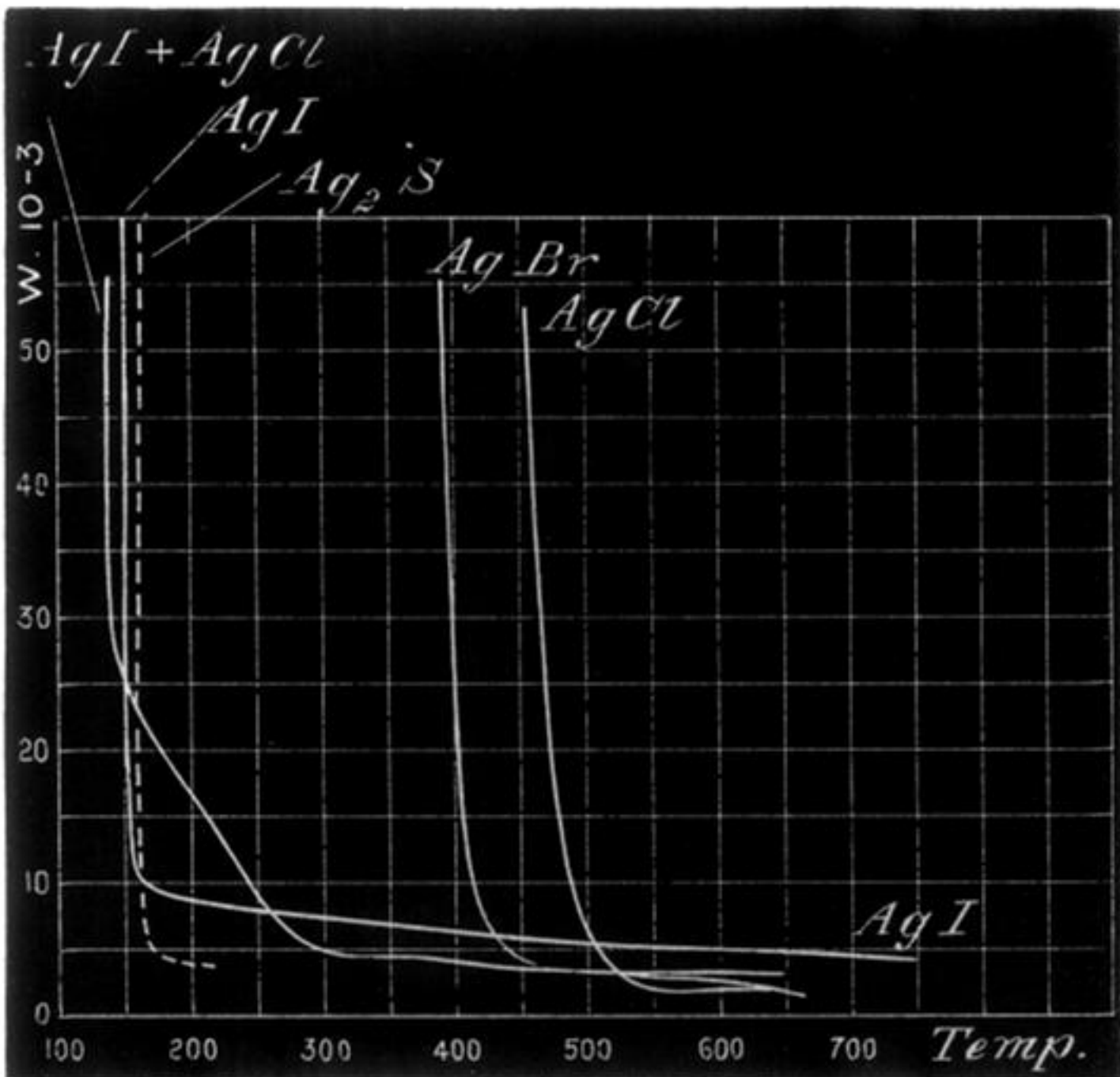
to be mentioned. It is now well established that on exploding gaseous mixtures within a closed chamber, the maximum theoretical temperature is never reached; and this has hitherto always been explained as due to the occurrence of dissociation whereby the change is retarded. If in a mixture, say, of carbonic oxide, oxygen and water gases, the three kinds of molecules act together in the manner I have supposed, it is probable that the extent to which they mutually influence each other would vary with the temperature, and that it would tend to diminish above a certain temperature; if such were the case, change would be retarded in the manner in which it appears to be in explosions within closed chambers. Dissociation undoubtedly does take place in many cases, but there is now a considerable amount of evidence on record to show that the bounding surfaces exercise a most important influence; this is usually not sufficiently taken into account.

Presents, February 4, 1886.

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*Copper is at
a height 610*

