

iodine, the amount of iodine soluble in pure water. In this way, the amount of iodine is found which is present in the form of the complex salt; and, if the ratio of this quantity to the total amount of potassium iodide is calculated, it can be seen at once to what extent the simple proportionality exists which the law of mass action requires in case only the compound KI_3 is formed. The results (expressed in millimols) of this calculation are arranged in the following table:

$KI+KI_3$.	$KI+I_2$.	KI_3 .	Ratio. $KI_3 : (KI+KI_3)$.
106.3	55.28	53.94	0.5074
53.15	28.03	26.69	0.5021
26.57	14.68	13.34	0.5021
13.29	8.003	6.661	0.5012
6.643	4.667	3.325	0.5005
3.322	3.052	1.710	0.5148
1.661	2.235	0.893	0.5376
0.8304	1.814	0.472	0.5684

It is evident from the last column of this table that between the concentrations 0.1 and 0.006 normal the iodine present in the form of a complex salt is closely proportional to the total quantity of potassium iodide. In the case of the more dilute solutions, however, the relation of these two quantities seems to increase; but this is probably to be attributed to experimental error, for the quantity of iodine present as complex salt is less in these cases even than the solubility in pure water. Aside from these very dilute solutions, the assumption that the iodine exists exclusively as free iodine and as a constituent of the salt KI_3 (or of its anion) is therefore in complete accord with the law of mass action. The conclusion of Jakowkin in regard to the constitution of the complex salt is thus confirmed by the solubility relations.

THE NATURE OF VALENCE.

[SECOND PAPER.]

BY F. P. VENABLE.

Received January 23, 1899

AS the preceding paper upon this subject was in the form of an address before one of the local sections of the society, the hypothesis as to the cause of valence there suggested was given in outline only and could not be enlarged upon as far as

may have been necessary. In the present paper it is proposed to elaborate certain points and to test, as far as possible, the reasonable nature of the hypothesis.

While the whole subject of valence has been much confused, and the use of some of the terms connected with it unfortunate, no part of it has given greater trouble than its variability. This is the very point, however, which affords the best clew to its solution and should therefore be treated at some length.

The most instructive cases of varying valence are those where the variation is shown towards the same element, as in the compounds PCl_3 and PCl_5 , FeCl_2 and FeCl_3 , Hg_2O and HgO , CO and CO_2 , and many other similar compounds. There are two possible views regarding these. Either the valence varies or the valence remains the same and the differences are explained by some such assumption as that of a state of saturation of the atom and of various unsaturated states.

The terms 'saturated' and 'unsaturated' present a number of anomalies as commonly used. In the first place the term saturated is not always used for that condition of the atom in which it is united with the largest number of other atoms. Thus, ferrous oxide (FeO) is called unsaturated, and ferric oxide (Fe_2O_3) saturated, though there is a larger proportion still of oxygen in ferric acid and the ferrates. The same is true of the three series of manganese and chromium compounds.

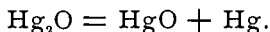
Again the term saturated does not carry with it any definite relation to the stability of the compound. Sometimes the compound called unsaturated, and containing the least number of atoms is the most stable, sometimes that with the largest number. Phosphorus trichloride is more stable than the pentachloride, but the pentoxide is more stable than the trioxide. The most stable of the manganese compounds are the so-called unsaturated manganous salts; in the case of chromium it would appear to be the chromic salts. In the case of carbon the saturated compounds are the most stable. It is manifest that these two terms cannot cover all cases of combination for a number of elements. It would seem wiser and simpler then to speak of the valence directly when discussing the elements, as bivalent carbon or quadrivalent carbon; bivalent or trivalent iron, etc. In the case of carbon compounds the terms have acquired a

somewhat different meaning and are too thoroughly incorporated in the literature for a change to be suggested. Saturated here means a compound which can take on no further atoms by addition, while an unsaturated compound can have such atoms added.

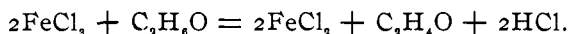
Certain cases of change of valence, as in cuprous and cupric compounds, mercurous and mercuric, ferrous and ferric, etc., have been looked upon as presenting some peculiar relationships. Such cases are spoken of by some as if they occurred among positive elements only. It is not clear how any distinction can be drawn between these and the classes phosphorous and phosphoric, sulphurous and sulphuric, nitrous and nitric, chlorous and chloric, etc. A possible distinction might be made that the more negative the element the greater the number of changes of valence; the more positive the element the less variation in valence is observed. This would be an approximation only.

So great is the difference caused by this variation in the valence that some have even thought it best to arrange what have been called the lower and higher stages under different groups. Thus Mendeléeff placed cuprous copper in Group I, and cupric copper in Group VIII; aurous gold in Group I and auric gold in Group VIII. Such an arrangement would, however, greatly confuse the periodic system. Mercury, thallium, chromium, manganese, phosphorus, arsenic, sulphur, selenium, and others would have to be similarly provided for. It is better to retain them in the positions to which their atomic weights would assign them and to study them more thoroughly, so that we may understand why certain elements, as copper, gold, and mercury show this peculiarity while others closely akin to them, as silver, zinc, and cadmium, do not. In studying the nature of valence from the standpoint of its variability, the means by which these variations can be brought about must have an important bearing upon the subject. There are a number of these agencies.

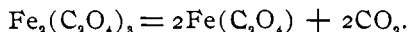
Light.—It is a matter of common observation that light can bring about physical, and the most varied chemical, transformations. In some cases it is apparent that the transformation is one from a higher to a lower valence or *vice versa*. Thus, certain mercurous compounds can be changed to mercuric.



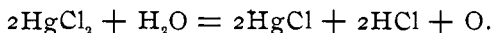
An alcoholic solution of ferric chloride is changed by light to ferrous chloride.



Ferric oxalate under the influence of light gives off carbon dioxide and becomes ferrous oxalate.



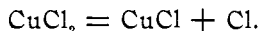
An alcoholic solution of cupric chloride becomes cuprous chloride. Mercuric chloride in aqueous solution is slowly changed to mercurous when exposed to the light.



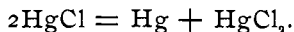
Gold chloride (AuCl_3), in contact with organic substances, when exposed to light, is changed first to aurous chloride (AuCl) and then to metallic gold.

It is quite well known that a ray of light falling upon a piece of selenium changes its conducting power for electricity. This is not a change of valence but has, it would seem, its bearing upon the problem as a possible change in vibration. The chemical action of light is generally attributed to the vibrations set up among the molecules. Rays having the shortest wave-lengths and the greatest frequency are most active in this respect though all the rays of the visible spectrum have been shown to exert some action. So far as this variation in valence is caused by light then the hypothesis of a change in vibration necessitating a change in equilibrium may well serve as an explanation.

Heat.—Again these variations are often easily brought about by changes of temperature. Thus cupric chloride becomes cuprous chloride.



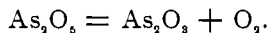
Mercurous chloride is temporarily changed into mercuric, the mercurous re-forming upon cooling.



Phosphorus pentachloride becomes the trichloride.



Arsenic pentoxide becomes trioxide.



An interesting series of changes are those in the sulphur chlorides. Thus sulphur tetrachloride (SCl_4) becomes sulphur

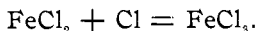
dichloride (SCl_2), if warmed above -22° , and this becomes sulphur monochloride (S_2Cl_2), if heated above 64° . This last can be boiled without change.

These instances might be multiplied but it is not necessary. The most plausible explanation offered as to the effect of heat is a change in the velocity of vibration, and it may well serve to explain the variations caused in valence.

Electricity.—Changes of valence due to electricity are probably not unusual but few observations concerning them have been recorded. One of the most noteworthy is the production of carbon monoxide from carbon dioxide by the passage of the electric spark.

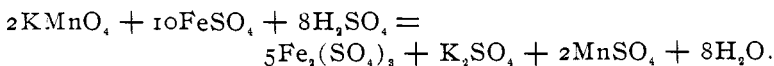


Chemical Action.—The most usual method of bringing about a change of valence is by chemical action. When the change is from a higher proportion of the negative element to a lower it is commonly called *reduction*, and the reverse change is spoken of as *oxidation*. These terms are apparently relics of an older theory, and are confusing, especially to a student beginning the study of chemistry. They should be limited to cases of the actual removal or addition of oxygen. Thus, to speak of the change of ferrous to ferric chloride by the action of chlorine as an oxidation is careless and incorrect.



It is pushing the type theory rather far to speak of the salts of one valence as being derived from the oxide of that valence and yet this is frequently done.

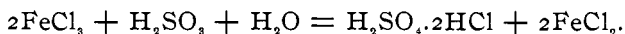
When we take ferric chloride and let sulphurous acid act upon it, it is called a reduction of the ferric chloride to ferrous chloride, although certainly no oxygen is removed from the ferric chloride nor is oxygen added when the ferrous chloride is changed again to ferric chloride by the action of nitric acid, and still this is called an oxidation. The use of terms for these reactions is evidently in need of revision. What shall we call the following reaction, cited by Drechsel as an "oxidizing action?"



Some hydrogen is oxidized with the formation of water but that

is not what is meant. The manganese is changed from its highest valency to its lowest and the iron from its lowest to a higher. The permanganate is of course deoxidized.

It seems that chemical action may induce change when to an existing molecule a third substance is offered capable of combining with one or more of its constituent atoms, thus releasing the former equilibrium. Thus when sulphurous acid takes the oxygen of water setting hydrogen free the hydrogen then takes one of the chlorine atoms held by the iron.



But the presence of all three of these molecules is needed for the reaction to take place. So too, potassium permanganate is stable in the presence of sulphuric acid, unless the ferrous sulphate or some such molecules are present. When molecules of these three substances come together there is immediate rearrangement of molecules with change of equilibrium. Whether we are dealing here with a play of affinity which causes the tumbling down of certain molecules and building up of others, or whether it is a question of vibratory equilibrium between these molecules, cannot yet be told. The only certain thing seems to be that a molecule containing bivalent iron and another containing septivalent manganese cannot exist in the presence of one another but must change, when possible, to trivalent iron and bivalent manganese.

As meagre as our present knowledge is, it does not seem to be a very hopeful task to enter the maze of changes of valence through chemical reactions with a view to clearing up the ideas as to the nature of valence.

Explanations Offered.—Victor Meyer and Riecke have supposed that a solution of the problem could be arrived at best by studying the phenomena of frictional electricity, contact electricity, pyro-electricity, and electrolytic conductivity. Most of those who have suggested hypotheses have based them upon a study of the carbon atom and its compounds and in particular its space relations. I have gathered together such of these hypotheses as have come to my notice and for fear of doing the authors an injustice shall present their views as far as possible in the original language.

The first in point of time is the hypothesis of van't Hoff.¹ I have not had access to the original but will give van't Hoff's views as presented by Rössing and by Ostwald. Rössing² quotes:

“Die einfachste Betrachtung lehrt, dass jede Abänderung von der Kugelgestalt zu grösseren Äusserungen der Anziehung nach bestimmten Richtungen führen muss, da sich das Atom an diesen Stellen so zu sagen besser annähern lässt. Jede derartige Form bedingt also eine gewisse Zahl Hauptanziehungsfähigkeiten, Valenzen.

“Wo nun obendrein noch die Art des gebundenen Atoms die Bindungskraft bedingt, wird auch die Zahl der hervortretenden Valenzen davon abhängig sein, somit beim Vergleich der Verbindungen eines bestimmten Elementes mit verschiedenen anderen öfters eine Änderung der Valenz auftreten.

“Wenn sich ein Atom um eine bestimmte Lage gleichmässig in allen Richtungen hin und her bewegt, ist eine Änderung der äusseren Form, somit auch von Affinität und Valenz, notwendige Folge.

“Zieht man jetzt in Betracht, dass die Schwingungsgrösse der Atombewegungen von der Temperatur bedingt wird, so führt obige Anschauung zu dem thatsächlich gestützten Schlusse dass Temperaturzunahme die Anzahl der Valenzen verkleinert, die Affinitätserscheinungen abschwächt, also die gegenseitige Atomwirkung allmählich zur einfachen Gravitationsäusserung zurückführt. Thatsache ist, dass es eine obere Temperaturgrenze gibt, wobei von chemischer Wirkung nicht mehr die Rede ist; Thatsache ist auch, dass im entgegengesetzten Falle die chemischen Erscheinungen sich ungeheuer komplizieren, zweifelsohne dadurch, dass bis dahin übersehene Valenzen zur Geltung kommen.

“Die aufgestellten Betrachtungen ergeben als unmittelbare Folge, dass eine Atomvereinigung, ein Molekül, sich anderen gegenüber in der nämlichen Art und Weise, nur weniger scharf, äussert, wie das Atom selbst; auch das Molekül hat Affinität und Valenz, die zwar durch die eigenthümliche Zusammenstellung der Theile bedingt, nicht aber letzteren an und für sich eigen sind. So ergibt sich eine Grundlage für die Betrachtung der sogenannten Molekularverbindungen.”

¹ Ansichten über die organische Chemie, I. 3.

² Rössing: Theoretische Chemie, 180.

Ostwald¹ comments upon this hypothesis as follows :

“ Es bleibt indessen noch eine Möglichkeit, die thatsächliche Verschiedenheit der Valenzwirkungen zu erklären. Wenn wir die Valenz als Frage einer Eigenschaft der Atome auffassen, deren Wirkung durch die Verschiedenheit der Zustände des Atoms insbesondere der Bewegungszustände, modifiziert werden kann, so ist es denkbar, dass obwohl die Ursache der Valenz unveränderlich ist, die Wirkungen dieser Ursache, eben die Valenz selbst, von Fall zu Fall verschieden erscheint.

“ Eine Hypothese der erwähnten Art ist in der That von van't Hoff aufgestellt worden. Indem er annahm dass die chemische Anziehung zwischen den Atomen eine Folge der Gravitation sei, zeigte er, dass wenn ein Atom eine von der Kugelgestalt abweichende Form besitzt, die Intensität der Anziehung auf seiner Oberfläche eine bestimmte Anzahl Maxima besitzen müsse welche von der Form abhängt. Die Maxima können von verschiedenem Werte sein. Ist die Wärmebewegung des Atoms eine lebhafte, so werden nur die grösste Maxima ihre Atome festhalten können, und die Valenz zeigt sich, entsprechende der Erfahrung, bei höherer Temperatur kleiner als bei niederer.”

Lossen's² idea as to valence, deduced from the consideration of the theories of van't Hoff and Wislicenus as to the space relations of the atom seem to be condensed into the single sentence:

“ Diese Auffassung führt, nach meiner Meinung, nothwendig zu der Annahme, dass das mehrwerthige Atom sich überhaupt nicht als materieller Punkt betrachten lässt, dass vielmehr Theile desselben zu unterscheiden sind, von welchen die Wirkung auf andere Atome ausgeht.”

Wislicenus³ expresses his ideas as to valence as follows :

“ Ich halte es nicht für unmöglich, dass das Kohlenstoffatom ein Gebilde sei, welches in seiner Gestalt einem regulären Tetraëder mehr oder weniger vielleicht recht sehr ähnelt : nicht für unmöglich ferner, dass die Ursachen jener Wirkungen, welche in den ‘Affinitäts-einheiten’ zur thatsächlichen Erscheinung kommen, sich in den Ecken dieses tetraëdrischen Gebildes concentriren, möglicherweise ähnlich und aus analogen Gründen, wie dies die elektrischen Wirkungen eines elektrisch geladenen

¹ Lehrbuch der allg. Chemie, I ed. I, 830.

² Ber. d. chem. Ges., 20, 3309.

³ Ibid., 21, 581.

Metalltetraeders thun würden. Die eigentlichen Träger dieser Energie würden schliesslich die Uratome sein, ganz wie die chemische Energie der zusammengesetzten Radicale unzweifelhaft eine Resultirende der den Elementaratomen innewohnenden Energie ist."

Victor Meyer and Riecke¹ advance the following hypothesis :

"Auf Grund der mitgetheilten chemischen und physikalischen Erfahrungen haben wir uns nun folgende Vorstellung von der Constitution des Kohlenstoffatoms gebildet. Wir nehmen an, dass dasselbe umgeben ist von einer Aetherhülle, welche bei isolirten Atome, wie dieses selbst, kugelförmige Gestalt besitzt ; das Atom selbst betrachten wir als den Träger der specifischen Affinitäten, die Oberfläche der Hülle als den Sitz der Valenzen. Jede Valenz denken wir uns bedingt durch das Vorhandensein zweier entgegengesetzter elektrischer Pole, welche in den Endpunkten einer im Vergleich zum Durchmesser der Aetherhülle kleinen geraden Linie befestigt sind. Wir bezeichnen ein solches System zweier elektrischer Pole als einen Doppelpol oder Dipol. Den vier Valenzen des Kohlenstoffatoms würden also vier solcher Dipole entsprechen. Die Mittelpunkte derselben denken wir uns gebunden an die Oberfläche der Aetherhülle, in dieser aber frei verschiebbar ; die Dipole selbst seien freidrehbar um ihre Mittelpunkte."

It is scarcely necessary to give the further assumptions. The hypothesis of Knorr² may be also given in brief :

"Ich denke mir die Valenzen bedingt durch die Gliederung der Atome in besondere räumlich gesonderte Massen, die ich 'Valenzkörper' nennen will. Jeder Valenzkörper soll die Fähigkeit besitzen, andere Valenzkörper anzuziehen und durch diese Anziehung festzuhalten. . . . Die Werthigkeit ist bestimmt durch die relative Anzahl der in einem Atom vorhandenen Valenzkörper. Die Bindungen kommen zu Stande durch Berührung von Valenzkörpern. Im Kohlenstoffatom müssen die Valenzkörper gleichwerthig und gleichmässig im Raume gruppiert sein."

Flawitzky³ takes as a basis for his hypothesis the suggestion of N. Beketoff that the cause of the chemical interaction of the

¹ *Ber. d. chem. Ges.*, 21, 951.

² *Ann. Chem. (Liebig)*, 279, 202.

³ *Ztschr. anorg. Chem.*, 12, 182.

elements lay in the interference or coincidence of the motions of the atoms. The chief assumption is that the atoms of each element described closed curves which lie in planes, which are parallel to one another and have a constant absolute position in space. The atoms of different elements move in planes which make definite constant angles with one another. "Nehmen wir in der That an, dass die lebendige Kraft der Atome verschiedener Elemente gleich gross ist, so kann die Bewegung eines Atomes eines Elementes nur dann durch die Bewegung eines Atomes eines anderen Elementes vollständig aufgehoben werden, wenn die beiden Bahnebenen unter einander parallel sind. Widrigenfalls können je nach der Grösse des Winkels zwischen den Bahnebenen Fälle vorkommen, wo ein Atom eines Elementes dazu zwei, drei und mehr Atome eines anderen verlangen wird. Es können nämlich in solchen Fällen nur diejenigen Komponenten zur Wirkung kommen welche der Bewegungsebene des anderen Atoms parallel sind. Somit lässt sich die Wertigkeit der Elemente auf die Verschiedenheit der Winkel zwischen den Bahnebenen verschiedenartiger Atome zurückführen. Die Grössen dieser Winkel müssen augenscheinlich dem Gesetze ganzer rationaler Beziehungen folgen, wodurch die Fähigkeit der Atome, sich in ganzen Zahlen zu verbinden, bestimmt ist."

It is quite possible that other hypotheses as to valence have been formulated but have escaped my notice. These will suffice to give the more recent trend of thought upon the subject. I may state that none of these were known to me when the first paper was sent on for publication as I had not deemed it necessary to look beyond the usual text-books in examining into the literature upon the subject. This statement is not made for personal reasons as that is a matter of small moment, but that there may attach to my hypothesis whatever of value there is in the independent reaching of a conclusion.

It is not pertinent to this paper to discuss at any length the citations just given. But a few words are needed to bring out certain differences and distinctions. In most of them we have the assumption of some peculiar form of energy—an "Anziehungskraft." Flawitzky alone makes no explicit assumption of the kind. Besides this assumed force, which is the point of contention after all, we have various other assumptions of a remark-

able character; *e. g.*, as to the forms of atoms, envelopes, primal atoms, and *Valenzkörper*. Flawitzky's hypothesis is based upon the angles made between the planes in which the atoms move.

Now in the place of all this I wish to substitute that which seems to me to be the simpler hypothesis of vibratory equilibrium.¹ There is only one attractive force to be considered and this is called chemical affinity and causes the union of the atoms, binding them together. These atoms may unite atom with atom, or one atom with two or three or more atoms of the other element or other elements. While we speak of union there is no actual contact to be assumed. The individual atoms have their own motion and at the same time the aggregation of atoms, or molecule, has a motion proper to it. The conditions of equilibrium in such a system determine the number of atoms which can enter it: as one to one, one to two, etc. There is no distinct force of valence determining this. The form of the atoms can scarcely be taken into consideration because the distance between the atoms is too great, compared with the mass of the atom, for the form to exert much influence, unless it influences the character of the motion. The atomic weight also has little influence in determining the number of atoms needed to satisfy the conditions of equilibrium except that there seems to be a general rule that with increase in the atomic weight in any one group more stable equilibrium is brought about with the smaller number of atoms and in a choice between several the lesser valence is preferred. (Compare nitrogen and bismuth; sulphur and tellurium.)

There would then appear to be seven, possibly eight, different kinds of motion among the atoms. Different velocities of vibration are not meant, but different phases of motion. For instance, all may have elliptical orbits with different focal distances; or circular, with different radii, etc. In any group of elements the motion of the atoms would have one common characteristic but there would be differences in velocity. In the first and seventh group, showing, for the most part, a tendency towards the same equilibrium, or having the same valence, the motion must be closely analogous. So too for the second and sixth groups, the third and fifth. There may then be a necessity for four distinct

¹ Dr. Jas. Lewis Howe suggests the name "kinetic equilibrium."

phases only, unless we suppose a fifth for the eighth group. If the motion of an atom can be changed from one character to another its valence is changed and in such general properties as are dependent upon motion and not upon atomic weight it is equivalent to changing its group. Electricity, light, heat, and chemical action can cause this change of motion. In so far the properties of the element are subject to change and within our control. But the other factor, atomic weight, with the properties of the element determined by it, is not subject to change nor within our control, so far as our knowledge goes.

While it is freely granted that there is so much of the speculative in what has been said as to make us touch the whole subject with extreme caution, and while it is further admitted that it is quite beyond the reach of present experimental research, yet it is believed that the use of the imagination is legitimate and tends toward the advancement of the science so long as the true value is set upon it and fancy is not allowed to obscure fact nor to be mistaken for it. The hypothesis proposed is simple and if true will be very helpful. It will be a great step forward if it can be shown that the doctrine of valence is a doctrine of vibratory equilibrium.

EMETINE OCTOIODIDE AND THE EXTRACTION AND ESTIMATION OF ALKALOIDS GENERALLY.¹

BY H. M. GORDIN AND A. B. PRESCOTT.

Received November 27, 1898.

IN a previous paper² we have shown that most alkaloids form definite compounds when treated with excess of iodopotassium iodide and that it is possible to estimate the strength of aqueous solutions of alkaloidal salts by means of standardized solutions of iodine and of sodium thiosulphate. In applying this method to the assay of medicinal drugs it is immaterial what method of extraction of the alkaloids from the drug is employed, provided the final alkaloidal solution be sufficiently deprived of non-alkaloidal matter. The simplest and quickest method of obtaining the alkaloidal solution sufficiently free from foreign

¹ In the work of Research Committee D, Section 2, Committee of Revision and Publication of the Pharmacopoeia of the United States. Read by title before the New York meeting of the American Chemical Society, December 28, 1898.

² This Journal, 20, 706, Sept., 1898.