THE CHEMISTRY TANGLE UNRAVELLED

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BEING CHEMISTRY SYSTEMATISED ON A NEW PLAN
BASED ON THE WORKS OF ABEGG, KOSSEL, & LANGMUIR

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PREFACE.

THE territory of chemistry is so vast that only isolated patches, here and there, can be explored by any one person by direct experimenting. For a wider acquaintance with the subject, he must depend upon second-hand knowledge. This applies with special force to the young student, who is required to supplement his limited laboratory knowledge of the subject by such facts as he can acquire from treatises.

Unfortunately, works on Inorganic Chemistry are more or less of the nature of catalogues. They are very useful as books of reference. But the learning by heart of the lists of substances and their properties contained in those books has about as little educative value as the memorising of a tradesman's price-list, and is as uninteresting.

Study is to be encouraged rather than memorising, and is more congenial to the best type of student. Whilst a certain amount of memorising is unavoidable, it is very desirable that it should be reduced to the smallest possible proportions.

The Periodic Table as a basis of classification and the application of physico-chemical principles have been of enormous service in the propagation of chemical knowledge, and are to be found in most text-books on Inorganic Chemistry. Nevertheless, these books pay far too little attention to the classifying and correlating of the facts with which they deal. Consequently, they very often give the impression that chemistry forms a mysterious maze of intricacies in which it is impossible to trace a connection for most of the substances. There is so much absorption in the description of single substances that the wood cannot be seen for the trees.

What is wanted is some indication of the wonderful orderliness that prevails throughout the subject in spite of a few anomalies. A bird's eye view, giving at a glance the whole chemistry landscape, reveals the beautiful contour curves along which most of the neighbouring regions of substances merge gently into one another. By the tracing of this orderliness, the dull and uninviting drudgery of mere memorising gives place to a study that is fascinating and attractive.

It is hoped to help somewhat in bringing about this desirable end by means of the present work, which provides a clue to the labyrinth of chemical substances. It is intended to be a guide-book to the analogues and contrasts, the parallelisms and divergencies, the numerous gentle gradients and occasional abrupt cleavages, and the interplay of opposite polarities observable when we subject chemical substances to a proper classification.

In arranging and developing the present system I have been greatly indebted to the writings of Abegg, of Kossel, and of Langmuir. I have taken some of their best ideas and worked them into the present theory, together with some contributions of my own, and I am confident that what has proved very helpful to myself in systematising chemical facts will prove of service to many others and therefore be welcomed by them.

I have kept constantly in view the Periodic Table, so useful for the systematising of chemistry. A modification of this table has been called for, from time to time, owing to the steady extension of chemical knowledge. A satisfactory table should bring out clearly the use of the non-valent gases as the principal standards of atomic stability in the activation of valency, together with the use of certain other elements as sub-standards as proposed by Kossel. In order to show the connection between the position of an atom and its structure, the non-valent gases ought certainly to be placed at the end of the periods, instead of at the beginning where they usually are put. It is rather remarkable that Langmuir still adheres to the old method. His table is based on the use of the standards and sub-standards and is very suggestive but leaves room for improvement in the matter of clearness.

The present new form, which resembles somewhat Mellor's modification of Bayley's table and also that of Ivan Margary, is based on Langmuir's conceptions of atomic structure, and has, I believe, sufficient novel and useful features to warrant its publication.

Most chemistry text-books and books of reference classify the elements into the groups and sub-groups of the old form of periodic table. This classification can be easily traced in the present table.

FRANCIS W. GRAY.

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EXAMPLES SHOWING METHOD USED IN THIS BOOK FOR REPRESENTING CHARGES ON RADICALS.

Examples.	Meaning.		Total surplus charge.
	Number of radicals.	Formula of each radical.	
Cu_2^{+2}	2	Cu^{+2}	$+4$
$(SO_4)_3^{-2}$	3	$(SO_4)^{-2}$	-6
$(NO_3)_2^{-1}$	2	$(NO_3)^{-1}$	-2
$(N_3)^{-1}$	1	$(N_3)^{-1}$	-1
N_2^{-3}	2	N^{-3}	-6
Al_2^{+3}	2	Al^{+3}	$+6$

In referring to an element, its symbol is generally used in this work. The corresponding name will be found in the index.

CHAPTER I.

PERIODIC TABLE.

THE origin of the Periodic Table of the elements was due to the fact that when the elements were arranged in the order of atomic weights, almost every one fell into a place agreeing with its chemical properties.

For example, Newlands pointed out that when the fourteen elements known at that time (1864) beginning with lithium were written in the order of their atomic weights, the properties belonging to each of the first seven reappeared in the second seven.

He called this the "**Law of Octaves.**"

Mendeléeff (1869) extended Newlands' work and arranged the elements in a periodic table which in a more or less modified form has been generally adopted since his time.

Thus in the table :—

Li, Be, B, C, N, O, F,
Na, Mg, Al, Si, P, S, Cl.

properties that vary in passing along the top row from Li to F repeat themselves in passing along the bottom row Na to Cl : thus, Li and Na are both soft white solid metals, and have a strong tendency to act positively ; F and Cl are corrosive gases and have a strong tendency to act negatively. Again, Li and Na can both display a characteristic valency + 1, Be and Mg valency + 2, B and Al valency + 3, C and Si valency + 4, N and P valency − 3, O and S valency − 2, F and Cl valency − 1.

Note that in passing up Newlands' octave only seven steps are required.

At the present time, when the non-valent gases have to be included, eight steps are required in order that a property may reappear.

It has been the custom hitherto to place the non-valent gases at the beginning of the periods. Thus we have the short periods of eight elements each :—

He, Li, Be, B, C, N, O, F,
Ne, Na, Mg, Al, Si, P, S, Cl.

Farther on, above these elements in the atomic weight list, we have two periods of eighteen elements each :—

A, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br.

Kr, Rb, Sr, Yt, Zr, Nb, Mo, 43, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I.

In these two long periods we have properties reappearing after eighteen steps. Thus, Sr is eighteen steps farther up the list than Ca, and resembles it in being a metal and capable of activating valency + 2.

Several forms of Mendeléeff's periodic table are in general use all resembling more or less the following modification which is also of the older current type, and which indicates that difficulties occur after iodine with this method of classification, so that a number of blanks are provisionally introduced at this stage.

This older form, although unsatisfactory, is given here in order to show the arranging of the elements into the groups :—

0, I, II, III, IV, V, VI, VII, VIII,

and their sub-groups, a method of classification generally adopted in text-books on chemistry.

PERIODIC TABLE OF THE ELEMENTS. OLDER FORM.

Groups:	0	I.		II.		III.		IV.		V.		VI.		VII.		VIII.		
Rows.		A	B	A	B	A	B	A	B	A	B	A	B	A	B	X	Y	Z
1		H																
2	He	Li		Be			B		C		N		O		F			
3	Ne	Na		Mg			Al		Si		P		S		Cl			
4	A	K		Ca		Sc		Ti		V		Cr		Mn		Fe	Co	Ni
5			Cu		Zn		Ga		Ge		As		Se		Br			
6	Kr	Rb		Sr		Yt		Zr		Nb		Mo		43		Ru	Rh	Pd
7			Ag		Cd		In		Sn		Sb		Te		I			
8	Xe	Cs		Ba		La		Ce		—		—		—		—	—	—
9			—		—		—		—		—		—		—			
10	—	—		—		—		—		Ta		W		75		Os	Ir	Pt
11			Au		Hg		Tl		Pb		Bi		Po		85			
12	Nt	87		Ra		Ac		Th		UX_2		U		93				

Starting from the top left-hand corner of this older table and going through each row from left to right, we obtain the elements arranged in the order of their atomic weights.

The only misfits are :—

Argon, A, at. wt. 39·9, and potassium, K, at. wt. 39·10.

Cobalt, Co, at. wt. 58·97, and nickel, Ni, at. wt. 58·68.

Tellurium, Te, at. wt. 127·5, and iodine, at. wt. 126·92.

In each of these pairs, the first mentioned element, although it has the larger atomic weight, must be placed before the second, namely, argon before potassium, cobalt before nickel, and tellurium before iodine.

The modern theory of atomic structure throws light on this difficulty. The most generally accepted theory is that *an atom consists of a very small positively charged nucleus surrounded by negatively charged electrons.* The positive charge of an atom's nucleus is called the **atomic number** of the element. Now, the atomic number of the elements have been determined more or less directly from H, no. 1, up to U, no. 92, and it has been found that when the elements are arranged in the order of increasing atomic numbers instead of increasing atomic weights, then there are no misfits, the above mentioned pairs of elements falling now into their proper places.

Thus Li, the atomic number of which is 3, occupies place no. 3. Again, Mg, at. no. 12, occupies place no. 12.

Under the heading 0 we have the column He, Ne, A, Kr, Xe, and Nt, which are the non-valent gases. Row 2 beginning with He and ending with F a halogen, contains eight elements and is called the *first short period.* Row 3, containing the subsequent eight elements, is called the *second short period.* From He, eight steps are required along the atomic number scale to reach the next non-valent gas Ne; from Ne, eight steps to reach the next non-valent gas A; from A, eighteen steps to reach the next non-valent gas Kr, i.e. we have to pass along two rows, Row 4 and Row 5, which, arranged in one series of eighteen elements, A, K, . . . Mn, Fe, Co, Ni, Cu, Zn, . . . Se, Br, constitutes the *first long period.* Similarly, the subsequent eighteen elements from Kr to I form the *second long period,* namely, Row 6 followed by Row 7.

When there are two rows in a period, the three elements at the end of the first row (at the transition from the first to the second row) are called **Transition Elements** and are given in the table under the Heading VIII. They are also called Group VIII Elements. The Transition Elements are Fe, Co, Ni, in the first long period, and Ru, Rh, Pd in the second long period. Os, Ir, and Pt are also classified along with these, as in the atomic number scale they stand in the same relation to Au, Hg, Tl . . . as do Ru, Rh, Pd, to Ag, Cd, In . . . and as do Fe, Co, Ni, to Cu, Zn, Ga . . .

In the diagram some elements are given in Rows 8, 9, 10, 11, 12. These are assigned places which agree approximately with their properties.

However, the arrangement of the periods after Xe, as given in this old table, is not to be regarded as correct. A number of *rare earth metals* occur after Ce. These are not mentioned in the table, and cannot be readily assigned positions corresponding with their properties without introducing a new arrangement of the periods at this point in the table.

In the meantime we adopt the arrangement given in the diagram for Rows 8, 9, 10, 11, 12, for convenience of reference.

Whenever there are two rows in a period, the second row is placed more to the right so that the second rows help to form the B columns.

It will be observed that some of the elements of the two short periods are given in the B columns, some in the A columns. For example, in placing F and Cl we have to choose between putting them in the A column along with Mn or in the B column along with Br and I.

The decidedly greater likeness of F and Cl to Br and I than to Mn settles in favour of the B column. Similarly, there is no doubt that O and S should be classified along with Se and Te in the B column rather than in the A column with Cr, Mo, W, and U. Again, there is no difficulty about classifying N and P with As, Sb, and Bi rather than with V, Nb, and Ta.

On the other hand, Li and Na, column I, undoubtedly are to be grouped with K, Rb, and Cs in an A column rather than with Cu, Ag, and Au in a B column. Again, Be and Mg, column II, are grouped with Ca, Sr, and Ba in an A column.

The classification of C and Si presents the greatest difficulty. There is about as much reason for placing them in the A column with Ti, Zr, Ce, and Th as in the B column with Ge, Sn, and Pb. Similarly, B and Al may be put in the A or B column.

If any column contains the elements from Rows 2 and 3, that column is called a **Chief Group.** The Chief Groups contain the elements in the neighbourhood of the non-valent gases in the atomic number scale. In these Chief Groups, about the membership of which there is no doubt, the elements are never more than three places above or below a non-valent element in the atomic number scale.

If the Chief Group is an A column, the corresponding B column may be called a **Subsidiary Group.** If the Chief Group is a B column, the corresponding A column is then the Subsidiary Group.

Thus the following are Chief Groups :—

I. A : Li, Na, K, Rb, Cs.
II. A : Be, Mg, Ca, Sr, Ba.
VII. B : F, Cl, Br, I.
VI. B : O, S, Se, Te.
V. B : N, P, As, Sb, Bi.

The following are Subsidiary Groups :—

I. B : Cu, Ag, Au.
II. B : Zn, Cd, Hg.
VII. A : Mn.
VI. A : Cr, Mo, W, U.
V. A : V, Nb, Ta.

The following are given provisionally :—

III. B : B, Al, Ga, In, Tl.
III. A : Sc, Yt, La.

Also the rare earth metals are usually treated under Group III.

IV. B : C, Si, Ge, Sn, Pb.
IV. A : Ti, Zr, Ce, Th.
VIII. : Fe, Co, Ni ; Ru, Rh, Pd ; Os, Ir, Pt.
O. : He, Ne, A, Kr, Xe, Nt.

The number of the group is identical with at least some of the valencies of the elements in that group.

An important factor in the development of valency is the place of the element in the atomic number scale relative to the place of the nearest non-valent gases.

Cl, one place *below* A, can show *negative* character, as when it combines with H to form HCl, hydrogen chloride ; K, one place *above* A, can show *positive* character, as when it combines with the group OH to form KOH, potassium hydroxide.

All elements, that like Cl are one place below a non-valent element in the atomic number scale, can show decidedly negative character. Thus, F, Cl, Br, and I, one place below Ne, A, Kr, and Xe respectively can be very strongly negative.

All elements, that are two places below a non-valent element in the atomic number scale, can also indicate negative character. Thus, O, S, Se, and Te, two places below Ne, A, Kr, and Xe respectively, can all behave negatively. The negativeness of O, S, Se, and Te, however, is not so strong as that of F, Cl, Br, and I.

Again, N, P, As, and Sb, three places below Ne, A, Kr, and Xe respectively, can all display negative character; the negativeness of N, P, As, and Sb is weaker than that of O, S, Se, and Te.

Thus *the possible negativeness of an element depends upon its distance below the non-valent gas next above it in the atomic number scale.* The greater this distance, the weaker the possible negativeness. If this distance is very great the element may never display negative character.

All elements that like potassium are one place above a non-valent element in the atomic number scale can show decidedly positive character. Thus in Li, Na, K, Rb, and Cs the positiveness is very strong.

All elements that are two places above a non-valent element in the atomic number scale can also indicate positive character. Thus Be, Mg, Ca, Sr, and Ba, two places above He, Ne, A, Kr, and Xe respectively, can all behave positively. The positiveness of Be, Mg, Ca, Sr, and Ba, however, is not so strong as that of Li, Na, K, Rb, and Cs.

Again, B, Al, Sc, Yt, and La, three places above He, Ne, A, Kr, and Xe, can all display positive character; the positiveness of B, Al, Sc, Yt, and La is weaker than that of Be, Mg, Ca, Sr, and Ba.

Thus *the positiveness of an element depends upon its distance above the non-valent element next below it in the atomic number scale.* The greater this distance, the weaker is the positiveness. If the distance is very great the element may never display positive character.

Except in the case of the elements in Rows 1 and 12 in the old form of table, each element's position may be defined as being a certain number of steps above the non-valent gas next below it, and a certain number below the non-valent gas next above it.

The first position implies possible positiveness, the second possible negativeness. S is six places above Ne and two places below A; the first position corresponds with positiveness as seen in SO_3, the second with negativeness as seen in H_2S. Thus an element may sometimes behave positively, sometimes negatively. In other words, its polarity varies.

There are two polarity-determining distances, the one, the distance below a non-valent gas, determines negativeness, the other, the distance above a non-valent gas, determines positiveness.

In passing along the atomic number scale and approaching a non-valent element from below, we find the intensity of the negativeness gradually increasing and reaching its maximum one place below the non-valent element. Going on, and passing through the non-valent element and farther up the atomic number scale, we find that the decided negativeness of the halogens changes sharply to the decided positiveness of the alkali metals immediately above the non-valent element, the positiveness gradually falling in strength as we go still farther up the scale.

In the old form of periodic table, in passing along any row, as a rule, the intensity of positiveness diminishes from left to right and the intensity of negativeness increases; in passing down any column, the intensity of positiveness, as a rule, increases and the intensity of negativeness diminishes.

The distance of an element from the non-valent element nearest below it or nearest above it in the atomic number scale gives its maximum valency, and its polarity is positive or negative according as the element is above or below the non-valent element.

These two distances may be called the **Polarity Distances** of the element.

F, Cl, Br, and I, all can have valency -1; O, S, Se, and Te all can have valency -2; N, P, As, and Sb all can activate valency -3.

Similarly, the following maximum valencies are possible; $+1$ for Li, Na, K, Rb, and Cs, $+2$ for Be, Mg, Ca, Sr, and Ba.

S in SO_3 is displaying valency $+6$, and in H_2S valency -2; these are the two maximum possible valencies for S.

The *maximum positive valency plus the maximum negative valency of an element is equal to the difference between the atomic numbers of two non-valent elements of which the one is the next below and the other is the next above the given element.*

Example of a Short-Period Element :—

Maximum positive valency of S plus maximum negative valency of S equals the atomic number of A minus the atomic number of Ne. Or $6 + 2 = 8$.

Example of a Long-Period Element :—

Maximum positive valency of Fe plus maximum negative valency of Fe equals the atomic number of Kr minus the atomic number of A. Or $8 + 10 = 18$.

The above rule therefore gives :—

For a short-period element : sum of maximum valencies $= 8$.

For a long-period element : sum of maximum valencies $= 18$.

Abegg's rule, that the sum of maximum valencies equals 8, is therefore applicable strictly only to a short-period element. However, it is seldom that the larger maximum valencies for long-period elements are activated. Nevertheless, it is well to bear in mind the possibility of these maxima. They are useful, for example, in the study of metallic carbonyls.

N, three places below Ne, can activate valency -3. According to the above rule, this is the maximum negative valency and it is always shown by N when acting negatively ; N never has a less negative valency. We have NH_3 but not NH_2 nor NH. This is always the case when, as here, an element is near a non-valent element.

N, on the other hand, being five places above He, can show valency $+5$. This maximum positive valency is seen in N_2O_5. But N can also activate several lower positive valencies as in N_2O, NO, N_2O_3, NO_2.

This is characteristic of an element when the polarity distance is not small. In a case like this the maximum valency may not be reached and is nearly always variable.

Similarly, the valency of negative S is never less than 2 the maximum; on the other hand, the valency of positive S may be 6 the maximum, seen in SO_3, but it is variable; it may, for example, be 4 as seen in SO_2.

If the polarity distances of an element are very different, the smaller distance corresponds with the more characteristic polarity of the element, and the corresponding valency is never less than the maximum possible which is numerically equal to the polarity distance in the atomic number scale. On the other hand, the larger distance corresponds with a polarity towards which the element has not so great a tendency, and the corresponding valency may not reach the maximum, which is numerically equal to the polarity distance in the atomic number scale; also, the valency is nearly always variable.

If the two polarity distances are nearly equal, the element displays impartiality of polar disposition. The tendency to positiveness is about as great as the tendency to negativeness, both being weak. In this case, when the period is long, each distance must be great; therefore, the maximum valency is not to be expected, and the valency displayed will be nearly always variable.

In the old form of periodic table, the A columns to the left (chief groups) in accordance with their small "positive distances," contain elements of decidedly positive character and of constant positive valency. The B columns to the right (chief groups) in accordance with their small "negative distances," contain elements of decidedly negative character and of constant negative valency equal to the maximum.

The constant valency mentioned above is always small, being equal to the polarity-distance. The same elements when they display non-characteristic polarity (corresponding with the larger of their two polarity-distances) may show a larger valency, but it is nearly always variable and may never reach its maximum.

The elements not in the A columns to the left nor in the B columns to the right, i.e. the elements with neither of their polarity-distances small, cannot be relied upon to give the maximum valency. Their valency will often be variable, and their tendency will not be strong towards either positiveness or negativeness.

The formulæ of the highest oxides for each column give the actual valencies when union with oxygen takes place, assuming that oxygen itself is divalent.

Thus we have

Column . . .	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Formula of highest oxide . . .	R_2O	RO	R_2O_3	RO_2	R_2O_5	RO_3	R_2O_7	RO_4
Valency shown in highest oxide .	1	2	3	4	5	6	7	8
Positive distances of A columns . .	1	2	3	4	5	6	7	

The actual maximum valency obtained in this way is the same as the number of the column in which the element is placed.

The element united with oxygen in these oxides is to be regarded as positive. But only the elements in the A columns to the left are decidedly positive and have constant positive valency; only for these elements do the above numbers represent constant valency. These numbers less and less represent constant valency the farther we pass towards the right. For none of the B columns do these numbers necessarily refer to a constant valency. It is true that they are the actual maximum positive valencies for most B elements. These elements, however, are negative rather than positive, especially in the case of the B columns to the right. Thus even if the maximum is reached, the positive valency is often variable.

The formulæ of the highest hydrides for each column give the actual maximum valencies when union with hydrogen takes place, assuming that hydrogen itself is univalent.

Thus we have

Column . . .	I.	II.	III.	IV.	V.	VI.	VII
Formula of highest hydride . . .	(RH)	(RH_2)	(RH_3)	RH_4	RH_3	RH_2	RH
Valency shown in highest hydride . .	(1)	(2)	(3)	4	3	2	1
Negative distances of B columns . .	7	6	5	4	3	2	1

The element united with hydrogen in these hydrides is to be regarded as negative. But only the elements in the B columns to the right are decidedly negative and have constant negative valency; only for these elements do the above numbers represent constant valency. The formulæ and valencies in columns I, II, and III, are given in brackets on account of their lack of definiteness and precision, and the peculiar circumstances in which valency is activated in these cases.

It will be seen that the above maximum negative valencies for columns V, VI, and VII, are the constant negative valencies for the B columns.

It is therefore only in the case of the A columns to the left and the B columns to the right that we can assign to each element, from its position in the periodic table, a definite characteristic polarity and a definite constant valency.

Only the chief groups to the left of the periodic table can be relied upon to display as constant valencies the valencies obtained from a study of the oxides; and only the chief groups to the right to display as constant valencies the valencies obtained from a study of the hydrides.

Some Defects of the Old Form of Periodic Table.

The importance of the place of the element in the atomic number scale relative to the places of the nearest non-valent elements is not made sufficiently clear.

For example, although Li, Na, K, Rb, and Cs are only one place above He, Ne, A, Kr, and Xe respectively, and Cu and Ag are eleven places above A and Kr respectively, and Au is twenty-five places above Cs, all these metals are placed together in the same Group I.

From what has been said about valency, it is clear that elements ought to be classified according to their distances above or below the nearest non-valent elements.

The use of other elements as standards of stability in the activation of valency in addition to the non-valent gases should also be recognised.

There is no place for hydrogen in the old form of periodic table.

Hydrogen belongs to both group I and group VII.

The rare earth metals do not fit into the old and current form of periodic table.

All sorts of unsatisfactory make-shifts have been devised to get over this difficulty.

CHAPTER II.

SUB-ATOMIC STRUCTURE.

IT has already been pointed out that the use of atomic numbers instead of atomic weights avoids the occurrence of misfits with A and K, Co and Ni, and Te and I. So our knowledge of sub-atomic structure may be called in, to assist us in devising a periodic table on an entirely new plan. The improved table now published is based on Langmuir's conception of atomic structure, and is free from the above defects of the current forms of periodic table.

The usefulness of the present new form, however, depends, not upon the particular structure adopted by Langmuir, but rather upon the clear way in which the table shows how the atomic numbers of the various atoms are related to one another.

As already pointed out, the most generally accepted modern theory of sub-atomic structure is that the atom consists of a very small positive nucleus surrounded by negatively charged electrons. These electrons, according to **Bohr**, are moving in orbits, and, according to **Langmuir**, are located in more or less fixed positions in shells round the nucleus.

The **nucleus** consists of protons and electrons.

A **proton** has unit positive charge, an **electron** has unit negative charge.

The mass of a **proton** = 1850 times the mass of an **electron.**

The radius of an **electron** = 1850 times the radius of a **proton.**

Let W = the number of protons in the nucleus,
N = the number of electrons in the nucleus,
and S = the number of electrons in the shells.

W is always greater than N (as the nucleus is always positive) and for smaller atoms is equal to about $2N$ or $2S$.

W-N = surplus positive charge in the nucleus.
S = negative charge in the shells.
W-N = is called the **Atomic Number**.
W-N = S in a neutral atom.

If p is the symbol for a proton, and e is the symbol for an electron, then the formula for a neutral atom is

$$(p_W e_N) e_S$$

The part in the brackets is the formula of the nucleus.

In the nucleus there is never less than one electron to every two protons.

This neat way of expressing the relationship is due to Aston and gets over the difficulty presented by hydrogen.

In physical and chemical transformations, S may change, but W and N and therefore W-N remain constant.

In radioactivity transformations, W and N may change.

If W and N diminish by different amounts, a new element is obtained, new chemical properties appearing.

If W and N diminish by the same amounts, a new species of the same element is obtained with a smaller atomic weight, but with the same chemical properties and the same atomic number. These two species of the same element are called **Isotopes**, this name being meant to indicate that they occupy the same place in the periodic table, i.e. they have the same atomic number.

The neutral atom of hydrogen is unique; it consists of one proton and one electron, its formula being *pe*. The nucleus of a hydrogen atom is thus a proton, and is much smaller than the nuclei of other atoms.

The number given in the new improved periodic table under each atomic symbol is the atomic number, or, for the neutral atom, the number of electrons in the shells of the atom. (See diagram at end of book.)

According to **Langmuir's theory**, for atomic numbers up to 86, the shell electrons may be located in as many as four spherical shells surrounding the nucleus of the atom.

These four shells may be numbered

	I.		II.		III.		IV.
the radii being as	1	:	2	:	3	:	4

II has two layers, IIa and IIb, of average radius 2.

III has two layers, IIIa and IIIb, of average radius 3.

Thus there are

6 layers	I.		IIa.		IIb.		IIIa.		IIIb.		IV.
the radii being as	1	:	2	:	2	:	3	:	3	:	4
the areas being as	1^2	:	2^2	:	2^2	:	3^2	:	3^2	:	4^2
or as	1	:	4	:	4	:	9	:	9	:	16
or, multiplying by 2, as	2	:	8	:	8	:	18	:	18	:	32

Thus if shell I is divided into two equal compartments, then there are

8, 8, 18, 18, and 32 compartments of that size in IIa, IIb, IIIa, IIIb, and IV respectively.

Langmuir supposes that each of the compartments may be occupied by one electron.

Thus 2, 8, 8, 18, 18, and 32, are the numbers of electrons that may be in layers I, IIa, IIb, IIIa, IIIb, and IV, respectively.

To obtain a structure for the atoms in Row 7 of the new table (atomic numbers 87 to 92) a seventh layer, IVb, not complete in any atom, may be postulated.

A layer cannot have an electron in any of its compartments unless all the compartments of the layers nearer the nucleus are occupied. In the case of the outermost layer, it may be that only some of the compartments are occupied. The only atoms that have their outermost layers complete are those of the non-valent gases :—

	He.	Ne.	A.	Kr.	Xe.	and	Nt.
of atomic numbers :	2	10	18	36	54	and	86
placed at the ENDS of the rows	1	2	3	4	5	and	6

in the new improved periodic table.

The numbers of electrons in the various layers of these atoms are :—

Layer :	I.	IIa.	IIb.	IIIa.	IIIb.	IV.	Total number of electrons or atomic number.
He .	2						2
Ne .	2	8					2+ 8 = 10
A .	2	8	8				2+ 8+ 8 = 18
Kr .	2	8	8	18			2+ 8+ 8+18 = 36
Xe .	2	8	8	18	18		2+8+ 8+18+18 = 54
Nt .	2	8	8	18	18	32	2+8+8+18+18+32 = 86

It will be noticed that in the new periodic table there is a parallelism between the number of rows and the number of possible layers, and between the number of elements in a row and the possible number of electrons in a layer.

The number of electrons in the incomplete outermost layer of any atom may be obtained from the new table by subtracting from the atomic number of the atom the atomic number of non-valent gas at the end of the row next above.

Thus for calcium,

20 (second in Row 4) - 18 (end of Row 3) = 2.

The layers of electrons in calcium are :—

I.	IIa.	IIb.	IIIa.
2	8	8	2

only two of the eighteen compartments of IIIa being occupied.

For rubidium, 37 (Row 5) - 36 (Row 4) = 1.

The layers of electrons in rubidium are :—

I.	IIa.	IIb.	IIIa.	IIIb.
2	8	8	18	1

only one of the eighteen compartments of IIIb being occupied.

The following table shows the structure of the various atoms :—

	Atomic Number.	Number of Electrons in Outer Layers.						
		I.	IIa.	III.	IIIa.	IIIb.	IVa.	IVb.
H	1	1						
He	2	2						
Li	3	2	1					
Be	4	2	2					
F	9	2	7					
Ne	10	2	8					
Na	11	2	8	1				
Mg	12	2	8	2				
Cl	17	2	8	7				
A	18	2	8	8				
K	19	2	8	8	1			
Ca	20	2	8	8	2			
Br	35	2	8	8	17			
Kr	36	2	8	8	18			
Rb	37	2	8	8	18	1		
Sr	38	2	8	8	18	2		
I	53	2	8	8	18	17		
Xe	54	2	8	8	18	18		
Cs	55	2	8	8	18	18	1	
Ba	56	2	8	8	18	18	2	
La	57	2	8	8	18	18	3	Rare earth metals.
Ce	58	2	8	8	18	18	4	
Ct	72	2	8	8	18	18	18	
Ta	73	2	8	8	18	18	19	
Nt	86	2	8	8	18	18	32	
Missing	87	2	8	8	18	18	32	1
Ra	88	2	8	8	18	18	32	2
U	92	2	8	8	18	18	32	6

CHAPTER III.

SUB-ATOMIC STRUCTURE AND THE ACTIVATION OF VALENCY.

THE atoms in the neutral state may be represented thus :—

H He Li Be . . . F Ne Na Mg . . .
(1) 1, (2) 2, (3) 3, (4) 4, . . . (9) 9, (10) 10, (11) 11, (12) 12, . . .

the number inside the brackets representing the inner or positive nuclear charge, and the number outside the brackets the outer or negative charge.

According to the view described here, negative electrons are detached from the neutral atom in the activating of positive valency and are attached to it in the activating of negative valency.

This activating of valency is the essential feature of chemical change and is associated with a change in the outer charge of an atom, i.e. in the number of outer electrons. On the other hand, chemical change is not known to be ever specifically associated with any change in the inner or positive nuclear charge of any atom, a radioactive transformation, for example, never resulting from a chemical reaction.

For example, in the activating of the negative valency of chlorine, whilst the outer 17 increases, the inner 17 remains unchanged. In becoming negatively univalent Cl changes thus : (17) 17 → (17) 18 gaining an electron, and in developing the positive valency 7, thus: (17) 17 → (17) 10, losing 7 electrons. The outer 17, then, may change to 18 on the one hand and to 10 on the other. What determines the 18 and the 10? We have a likely answer to this question when we recollect that the non-valent gas next above Cl is A, (18) 18, and the non-valent gas next below is Ne, (10) 10. The fact that these substances are always non-valent implies that there is great difficulty in changing the outer 18 in the one case and the outer 10 in the other. In other words, the (18) 18 and the (10) 10 configurations are very stable, and the natural inference is that Cl, (17) 17, in activating valency, is showing a tendency towards the more stable (18) 18 on the one hand and (10) 10 on the other. It is important to bear in mind that whilst this tendency may be allowed almost full play in the case of the outer 17, the inner 17 must remain constant. This constancy of the inner or nuclear charge will always impose more or less of a restraint on the change in the outer charge. Where the outer charges in the given atom and in the standard of atomic stability differ by little (e.g. in Cl and A), then the restraining influence of nuclear constancy is slight and the maximum valency which is small is easily activated. Where, however, the outer charges differ by much (e.g. in Cl and Ne), the maximum valency, which is large, is activated with difficulty, sometimes never. Thus, (17) 17 → (17) 18 takes place more easily than (17) 17 → (17) 10.

Similarly, Li, being near He, shows small maximum positive valency with easy activation, and being far from Ne should have large possible negative valency with very difficult activation.

In the middle of the first short period, at C, the positive and negative valencies become equal (C is four places from He and four places from Ne), and the tendency towards activation is about the same for both and is comparatively weak on account of the distance of C from the standards of atomic stability.

This absence in C of partiality for either positiveness or negativeness, coupled with the comparative feebleness of its atomic affinity and of its electro-affinity, together with the identity of its co-ordination number and its valency number, has given it a unique place among the elements.

Again, S can change thus: (16) 16 → (16) 18 or

(16) 16 → (16) 10

the second change being less easy of attainment, with the result that a smaller positive valency is often activated.

The *two standards for the first short period* are, then, He and Ne, and for the second short period, Ne and A; and the sum of the maximum valencies is 8 for both these periods.

Similarly, the *two standards for the first long period* are A and Kr, and for the second long period, Kr and Xe; and the sum of the maximum valencies is 18 for both these periods.

The reason for Abegg's rule thus becomes clear.

With regard to the connection between atomic structure and valency, it should be noted that the electrons in the shells will be the more easily removed the farther out their shell is. The electrons in the outermost layer are the most easily accessible and separable. The number of most easily separable electrons equals the positive valency. The maximum positive valency is activated by the complete removal of the electrons from the outermost layer.

Thus we have a periodic change in the number of electrons in the outermost layer as we pass up the atomic number scale, corresponding with the periodic change in valency. An arrangement of the outer electrons different from that of Langmuir and brought more into line with valency may yet be devised; but this will only slightly impair the usefulness of the improved new form of periodic table.

The continuity of the *K*, *L*, and *M* frequencies observed in X-ray work lead us to suppose that the arrangement of the inner shells does not undergo periodic change. Here again, however, we must bear in mind that various structures for the innermost layers have been devised by investigators to explain X-ray spectra.

We shall represent the subatomic structures of the atoms from H to Mn as follows:—

H (1) *1*
He (2) 2
Li (3) 2, *1*
Be (4) 2, *2*
B (5) 2, *3*
C (6) 2, *4*
N (7) 2, *5*
O (8) 2, *6*
F (9) 2, *7*
Ne (10) 2, 8

Ne (10) 2, 8
Na (11) 2, 8, *1*
Mg (12) 2, 8, *2*
Al (13) 2, 8, *3*
Si (14) 2, 8, *4*
P (15) 2, 8, *5*
S (16) 2, 8, *6*
Cl (17) 2, 8, *7*
A (18) 2, 8, 8

A (18) 2, 8, 8
K (19) 2, 8, 8, *1*
Ca (20) 2, 8, 8, *2*
Sc (21) 2, 8, 8, *3*
Ti (22) 2, 8, 8, *4*
V (23) 2, 8, 8, *5*
Cr (24) 2, 8, 8, *6*
Mn (25) 2, 8, 8, *7*

The number in the brackets gives the positive charge of the nucleus. The number of electrons (when detachable) in the outermost layer is in italics. This number gives the maximum positive valency in each case. There are no numbers in italics in the case of He, Ne, and A, **the standards of atomic stability.** The outermost numbers in these cases are 2 and 8. The 2 is the **stable pair** and the 8 is the **octet** of the **Lewis-Langmuir** structure. In He the only 2 electrons form a stable pair next the nucleus. In Ne there is again a stable pair next the nucleus, the remaining 8 forming a stable octet in the outermost layer. In A we have three layers surrounding the nucleus, the innermost containing a stable pair and the other two having stable octets. Thus, in these standards, as in each of the other structures represented above, there is a stable pair next the nucleus.

This tendency of electrons to form stable pairs and stable octets is the basis of a theory capable of wide application in chemistry.

Imagine a cube with two of its faces horizontal and an axis drawn through its centre perpendicular to these horizontal faces. Place a positive electrical charge of 10 at the centre, one negative charge at each of the eight corners of the cube and two negative charges inside the cube on the axis near the nucleus, the one above the nucleus and the other as far below. Then you have a picture of the Lewis-Langmuir structure for Ne. It is to be noted that in the actual atomic structures the octet cube is usually more or less distorted.

In Na, (11) 2, 8, *1*, the nucleus is surrounded by three layers, a stable pair, a stable octet, and an outermost electron. The maximum positive valency of Na is therefore 1. Cl may give up all the seven electrons in its outermost layer, when it will have the same system of outer layers as Ne. Thus, (17) 2, 8, *7* → (17) 2, 8.

Or Cl may take up an additional electron becoming (17) 2, 8, 8, and establishing the negative valency 1, when it will have the same outer system of layers as A.

We have seen how valency is activated in the case of a decidedly positive and a decidedly negative atom.

For example, in $Na + F \rightarrow Na^{+1} F^{-1}$
we have $(11)\ 2, 8, 1 + (9)\ 2, 7 \rightarrow \{(11)\ 2, 8\}\ \{(9)\ 2, 8\}$ Na losing one electron and F gaining one, Na becoming Na^{+1} and F becoming F^{-1}, these being separate particles held together by an electrostatic force.

Let us consider a case of union where the polarity is not so clear. For example, in

$$F + F \rightarrow F_2.$$

F is (9) 2, 7, and the tendency is for it to add one electron and form a stable octet. If each F atom forms an octet, then the two octets must share a pair of electrons. Neither atom is represented as positive or negative, although the force holding them together is really electrostatic. The two atoms in F_2 are not separate as in NaF, but are attached at the particular position occupied by the pair of electrons shared by the two octets.

When one atom unites with another there are thus two types of union, giving **polar** and **non-polar molecules**: (1) The atoms become radicals charged with opposite polarities, but they are separate particles, the outer layers of which do not share electrons. The valency depends on how many electrons have been transferred from one atom to the other.

(2) The atoms are not separate but share pairs of electrons. The relative positions of the atoms are fixed, the bond being at the position occupied by the pair of

electrons shared by the atoms. This corresponds with the fixed bond of Organic Chemistry.

(1) The valency here may be called **electro-valency.** To obtain its value what we count is *the number of electrons transferred from one atom to the other.*

(2) The valency here is called by Langmuir **co-valency.** To obtain its value what we count is *the number of pairs of electrons shared by the two atoms..*

Simple compounds containing not more than two elements e.g. H_2O, NaCl, SO_3, are called by Werner **compounds of the first order** and the valency acting in them he calls **primary valency.** This primary valency, then, is activated in the above two ways.

The last method is very useful in dealing with an element that is displaying neither decided positiveness nor decided negativeness, and is specially applicable to the union of negative atoms with one another.

The number of pairs shared may be obtained from the formula

$$e = 8n - 2p$$

where e = number of available electrons
n = number of octets
p = number of pairs shared by the octets.

Or $p = \frac{1}{2}(8n - e)$.

Example: CO_2 $e = 4 + 2 \times 6 = 16, n = 3.$
$p = \frac{1}{2}(24 - 16) = 4.$

This method is very useful in studying C compounds generally.

The application to compounds of N is of some importance. Consider the compounds of N and H.

For

NH NH_2 NH_3 NH_4 NH_5 NH_2NH_2

we have

$e =$	6	7	8	9	10	14
$n =$	1	1	1	1	1	2
$p =$	1	$\frac{1}{2}$	0	$-\frac{1}{2}$	-1	1

For the first five, p must be zero since there is only one octet. Therefore the only possible formula is NH_3.

In NH_2NH_2 the two N atoms share one pair of electrons.

For the oxides of N, since p must be an integer, e must be even; and since N has five available electrons and O has six, there will always be an odd number of electrons unless the number of N atoms is even. Therefore, the simplest general formula for an oxide of N is N_2O_x, The only possible values for x are 1, 2, 3, 4, and 5. If x is over 5, the number of electrons required becomes greater than can be found from the available electrons except on the supposition that rings or chains of O atoms are formed.

CHAPTER IV.

NEW FORM OF PERIODIC TABLE.

(*See diagram at end of book.*)

IN the new form of table, the dotted lines connect the odd-numbered elements and the other lines the even-numbered. *All atoms lying on any line passing downwards either vertically or towards the left have the same number of electrons in their outermost layer*, and so, except in the case of these elements that are themselves standards of atomic stability, by losing these electrons would develop the same maximum positive valency. Thus, with regard to positive valency, H, Li, Na, K, Rb, Cs, are all on the same equivalency line or on what may be called the same **positive equivalential**, and they can all activate the same valency + 1. Li, Na, K, Rb, and Cs tend to lose one electron and revert to He, Ne, A, Kr, and Xe respectively. *To what H tends to revert we do not know; here is an interesting point for speculation.*

Again, He, Be, Mg, Ca, Sr, Ba, and Ra are on the same **positive equivalential** and all contain two electrons in the outermost layer. He having an exceedingly stable configuration suffers no loss of its electrons. Be, Mg, Ca, Sr, Ba, and Ra lose their two outermost electrons, developing positive valency two, and tending to revert to the stable configurations of He, Ne, A, Kr, Xe, and Nt respectively.

Similarly, the other sets of elements on **positive equivalentials** are :—

B, Al, Sc, Yt, La, and Ac.
C, Si, Ti, Zr, Ce, and Th.
N, P, V, Nb, Pr, and UX_2.
O, S, Cr, Mo, Nd, and U.
F, Cl, Mn, and the missing elements 43, 61, and 93.
Ne, A, Fe, Ru, and Sa.
Co, Rh, and Eu.
Ni, Pd, and Gd.
Cu, Ag, and Tb.
Zn, Cd, and Dy.
Ga, In, and Ho.
Ge, Sn, and Er.
As, Sb, and Tm.
Se, Te, and Yb.
Br, I, and Lu.
Kr, Xe, and Ct.

Again, in the new periodic table, *all atoms lying on any line passing downwards either vertically or towards the right have the same number of unoccupied compartments in their outermost layer*, and by taking an electron into each of these vacant compartments would develop the same maximum negative valency. Thus, H, F, Cl, Br, I, and the missing 85 are all on the same **negative equivalential** and all can activate valency − 1. H, F, Cl, Br, I, and 85 tend to attach an electron, and to revert to the stable configurations of He, Ne, A, Kr, Xe, and Nt respectively.

Similarly, the other sets of elements on **negative equivalentials** are :—

O, S, Se, Te, and Po.
N, P, As, Sb, and Bi.
C, Si, Ge, Sn, and Pb.
B, Al, Ga, In, and Tl.
Be, Mg, Zn, Cd, and Hg.
Li, Na, Cu, Ag, and Au.
Ni, Pd, and Pt.
Co, Rh, and Ir.
Fe, Ru, and Os.
Mn, 43, and 75.
Cr, Mo, and W.
V, Nb, and Ta.
Ti, Zr, and Ct.
Sc, Yt, and Lu.
Ca, Sr, and Yb.
K, Rb, and Tm.

Factors affecting the Affinity of Valency.

We have seen how the quantity and the polarity of valency is determined by the "polarity distance" of the atom. We have now to consider what influences affect the affinity of the valency or the tendency towards activation of valency.

All atoms on the same **positive equivalential** have the same number of electrons in the outermost layer. The remaining part of the atom we may call the **Kernel.** The surplus positive charge of the kernel may be obtained from the positive charge of the nucleus together with the negative charges of the electrons in the shells apart from those in the outermost layer. This surplus kernel positive charge is the same for all atoms on the same **positive equivalential**; the effect, however, exerted by the kernel on the outermost electrons is not the same for all these atoms. It is not enough to consider merely the surplus positive charge of the kernel. *An algebraic summation of the positive and negative charges in the kernel does not give the real effect.* The repulsive action of negative electrons in the inner layers is not quite neutralised by the attractive action of the same number of positive charges in the nucleus. As the number of electrons in the inner layers increases with increasing atomic weight, *we find, as a rule, in a positive equivalential, that the electrons in the outermost layer are most easily removed in the case of those elements with highest atomic number.*

Thus, although the number of outermost electrons is the same for all elements on the same positive equivalential, and therefore the maximum positive valency is the same, yet the affinity or intensity of the valency increases with increasing atomic number.

Example: in the series: He, Be, Mg, Ca, Sr, and Ba, He is non-valent and the others display valency + 2, the positive character being greatest in Ba.

As we pass along a row from line to line of a series of positive equivalentials, towards the right, the surplus positive charge in the kernel increases. Although the effect of this charge is somewhat reduced by the relative positions of the positive and negative charges in the kernel, and by the action of the electrons in the outermost layer on one another, still, *as we pass along a row* in the new periodic table, *an electron in an outermost layer in a neutral atom becomes more and more firmly held.* Accordingly, it becomes more and more difficult to remove electrons from the neutral atom, in other words, to activate positive valency.

On the other hand, when extra electrons are attached to a neutral atom the energy obtained is greater the nearer the element is to the right-hand end of a row. In other words, the tendency to negative valency is seen most clearly in the last terms of the row, where on account of space relations it is expressed in definite valency numbers.

In the first terms of a row the number of electrons detached is never greater than the difference between the atomic number of the element and the atomic number of the non-valent element next below it in the atomic number scale. But this is to be expected from the fact that in the preceding row-end up to the non-valent element the electrons become more and more firmly bound.

The **effective kernel** of the atoms of a row increases from the beginning of the row right up to the end. The number of extra electrons that can be attached to a neutral atom should therefore increase also. In the initial atoms there are few electrons in the outermost layer. Therefore, there are several vacant places to be filled before the stability number is reached, so that space considerations impose no restrictions on the increase in the number of attachable electrons. Thus, at the beginning of a row, with increasing atomic number the valency shown in hydrides increases. On the other hand, towards the end of the row, although the effective kernel is still increasing, and accordingly the number of attachable electrons should be increasing also, yet the number of electrons in the outermost layer is nearing the stability value, and thus the number of attachable electrons is restricted to the number of vacant compartments and therefore diminishes instead of increasing, being 3, 2, and

1 in the third, second, and first place from the end respectively.

Accordingly, with rising atomic number the negative valency of the atoms of a row increases at the beginning of the row in a manner that is indefinite because there are no space restrictions and decreases at the end in quite definite steps, the last three negative valencies being 3, 2, and 1, these being the amounts by which, in the outermost layers, the number of electrons falls short of the stability number.

With regard to the hydrides of the elements at the beginning of the rows, it is quite possible that hydrogen is not acting positively here, as is assumed above, but negatively. Indeed some recent work seems to point to LiH being an analogue of LiCl; this is in agreement with the position of hydrogen at the top of the halogen negative equivalential.

The farther a positive equivalential is towards the right the less readily do the elements on that line activate the maximum positive valency belonging to the line, in other words, the less intense is the tendency for the atoms to revert to the configuration of the non-valent atoms next below them in the atomic number scale. The maximum positive valency increases, but the tendency towards that valency diminishes.

As a rule, the farther up a positive equivalential is the place of an element, the less readily does it activate the maximum positive valency belonging to the line.

For example, He at the top of the line, He, Be, Mg, Ca, Sr, Ba, Ra, is non-valent.

It is doubtful if F, at the top of the line F, Cl, Mn, ever activates positive valency at all; the only element that could from its position in the table be more negative than F, is H.

The farther a negative equivalential is towards the left, the less readily do the elements on that line activate the maximum negative valency belonging to the line.

In connection with the use of the non-valent gases as standards of atomic stability, we have, then, a series of positive equivalentials and a series of negative equivalentials. In passing along a row towards the right from line to line of the series of positive equivalentials, the positiveness decreases, but not at so great a rate as does the negativeness decrease in passing along a row towards the left from line to line of the series of negative equivalentials. Indeed the negative character may be lost before passing very far from the right-hand side of the diagram. Again, in passing down a positive equivalential, the positiveness, as a rule, increases, and in passing down a negative equivalential the negativeness decreases. Thus *the atoms having negativeness as a characteristic polarity are confined mostly to the top right-hand corner of the table.*

In accordance with this, *negatively charged atoms* (*ions*) *are far less common than positively charged.*

Further, in agreement with this again, *negative complex ions are more common than positive complex ions.*

An atom may occupy a position in the table at the intersection of two equivalentials which diverge downwards, namely, a positive equivalential and a negative. This atom is thus related on the one hand to a series of more positive atoms, and on the other hand to a series of negative or less positive atoms. For example, Na is related to the more positive K, Rb, and Cs on the one hand, and to the less positive Cu, Ag, and Au on the other. Similarly, the other atoms in Row 3 (in this new table) are related to two series of atoms. Thus, the difficulty of choosing whether the elements of the short periods should be in the A families or in the B families does not arise in this new form of table.

Again, hydrogen falls naturally into a place at the intersection of two equivalentials, and the locating of this element presents no difficulty. It is related to Li, Na, K, Rb, and Cs on the one hand, and to F, Cl, Br, and I on the other.

The elements in Row 5 (Rb, Sr, Yt, Zr, Nb, Mo, 43, Ru . . .) are similarly situated at the intersection of two equivalentials. Note that the missing 43 is related to the missing 61 and 93 on the same positive equivalential on the one hand, and to the missing 75 on the same negative equivalential on the other.

In the use of the non-valent gases as standards of atomic stability, as already pointed out, *when the "polarity distance" of an element is large, the maximum possible valency may not be reached and the valency activated is usually variable.* Thus in the middle of a long row in the new periodic table, the positive valency is variable and is much less than the maximum, and the negative valency possibly does not appear at all. Accordingly, we find in the middle of Row 4 (new table) a series of elements all capable of displaying the same small valency +2 (in some cases together with other valencies); and similarly for Row 5. It is not surprising, therefore, to find in the middle of the much longer Row 6 a series of elements (**rare earth metals**) all displaying the valency +3. Their atomic numbers also agree very well with the positions assigned to them. Thus, the problem of the classification of these elements is to a large extent solved.

There is another factor, however, which tends to keep down the valency in the middle of the longer rows, and that is the influence of **sub-standards of atomic stability.** Just as the valencies + 1 for Li, + 2 for Be, + 3 for B, + 4 for C, and + 5 for N all point to He as a standard of atomic stability, and the valencies + 1 for Na, + 2 for Mg, + 3 for Al, + 4 for Si, + 5 for P, + 6 for S, and + 7 for Cl all point to Ne as a standard, and the valencies + 1 for K, + 2 for Ca, + 3 for Sc, + 4 for Ti, + 5 for V, + 6 for Cr, and + 7 for Mn all point to the standard A, so the valencies + 1 for Cu, + 2 for Zn, + 3 for Ga, + 4 for Ge, + 5 for As, and + 6 for Se all point to a form of Ni (called Niβ by Langmuir) as a standard of atomic stability. Similarly, the valencies + 1 for Ag, + 2 for Cd, + 3 for In, + 4 for Sn, + 5 for Sb, + 6 for Te, and + 7 for I all point to the standard Pdβ; and + 1 for Au, + 2 for Hg, + 3 for Tl, + 4 for Pb, and + 5 for Bi all point to the standard Ptβ; and the valencies + 3 for Lu, + 5 for Ta, + 6 for W, and + 8 for Os all point to the standard Erβ.

In the new periodic table broad lines show the connection between the standards. The relation between the **principal standards** is clearest of all. Note also the lines connecting the **substandards**: the line passing up from Er connecting it with Kr, and the line passing up from Pt connecting it with Pd and Ni and passing farther up from Ni to the left showing the connection with Ne.

The broad lines connecting these substandards are parallel to lines that are positive equivalentials relative to the substandards and that are negative equivalentials relative to the principal standards.

Thus, the line on which Cu, Ag, and Au are situated is a positive equivalential relative to the substandards Niβ, Pdβ, and Ptβ, but is a negative equivalential relative to the principal standards Kr, Xe, and Nt.

And so, when the substandards Niβ, Pdβ, and Ptβ are used we obtain the well-known groups :—

I. B : Cu, Ag, and Au.
II. B : Zn, Cd, and Hg.
III. B : Ga, In, and Tl.

There is another important substandard not specially indicated in the new diagram : the valencies + 1 for Tl, + 2 for Pb, and + 3 for Bi lead us to regard Hg as a substandard of atomic stability. This view also receives support from the resemblance of monatomic inactive mercury gas to the non-valent gases. Again, the valencies + 1 for In, + 2 for Sn, + 3 for Sb, + 4 for Te, and + 5 for I point to the standard Cd ; the valencies + 2 for Ge, + 3 for As, + 4 for Se, and + 5 for Br point to Zn ; the valencies + 2 for Si, + 3 for P, + 4 for S, and + 5 for Cl point to Mg ; the valencies + 2 for C and + 3 for N point to Be. Thus, Be, Mg, Zn, Cd, and Hg may be all connected as similar substandards, and these may be even further connected with He.

These substandards, together with other standards, may be used to bring out a remarkable feature in the **subatomic structure of the missing elements.** The missing elements, 43, 61, 75, 85, and 87, are seven places above the standards Kr, Xe, Er, Pt, and Hg respectively. Further, the first missing element above uranium, namely, 93, is seven places above Nt. The *occurrence of the number seven in every case* points to an important factor in determining the instability of these atomic structures.

Note also that the *atomic number of these missing elements is odd*, and that odd-numbered elements are, in general, more unstable then even-numbered. *All the standards of atomic stability above mentioned are even-numbered.*

Further, apart from the doubtful cases of potassium and rubidium, none of the elements up to mercury display radioactive disintegration. Mercury, thus, marks the end of the list of the non-radioelements. All the elements beyond this point, in some isotopic form, show radioactive properties. It is true that even-numbered lead is the end-product of several radioactive changes, but it has isotopic modifications that are radioactive. Thus, *the number* 80 *is of some importance in the study of atomic stability, as this is the highest number that an atom can have if it is to be free from radioactive disintegration.*

It is clear from the diagram that Ni has as many vacant compartments in its outermost layer as it has electrons in its next layer, namely, eight. The structure of Ni is (28) 2, 8, 8, 10, there being eighteen compartments in the outermost layer, ten of which are filled. According to Langmuir, in Ni eight of these ten are held by magnetic forces in positions above the eight in the next layer, the other two being at the poles. In passing from Niα to Niβ part of the atom turns round an axis so that the eight vacant compartments in the outermost layer come to be above the eight electrons in the next layer, the magnetic forces losing their predominance and the electric forces holding greater sway.

It is also clear from the diagram that a similar observation can be made regarding Er which has as many vacant compartments in its outermost layer as it has electrons in its next layer, namely, eighteen. The change from Erα to Erβ may be regarded as similar to that from Niα to Niβ.

The Ti, Zr, Ce, Th Equivalential.

It will be seen that the Ti, Zr, Ce, Th equivalential is indicated by a broad line. Its influence as a standard is not so clear as in the case of the others mentioned, although it is true that we have the valencies + 1 for V, + 2 for Cr, and + 3 for Mn pointing to the standard Ti. The importance of this equivalential, together with the equivalential Ni, Pd, Pt and the row Ti, V, Cr, Mn, Fe, Co, Ni, will be seen from the following:—

The elements on these lines and those within the diagram-space bounded by these lines are characterised by giving coloured cations in most cases, by having low values for atomic volume, compressibility, and coefficient of expansion and high values for melting-point, atomic frequency, cohesion, and magnetic susceptibility.

All these elements (with the doubtful exception of Zr) are paramagnetic. All elements to the left of this region either are feebly paramagnetic or are diamagnetic. All elements to the right are diamagnetic except Sn which is sometimes paramagnetic, but only feebly and only within a certain range of temperatures. As an example of this rule, it may be noted that of the rare earth metals the only diamagnetic elements are Sc, Yt, and La which are the only ones outside this region of the table.

There is a sharp change in the value of certain properties immediately to the right of this region. There is a sudden drop in melting point at Cu, Ag, and Au and a still sharper drop at Zn, Cd, and Hg; there is a sharp fall in electrical resistivity at Cu, Ag, and Au, these three metals being the best conductors of electricity; there is, however, a rise again in electrical resistivity at Zn, Cd, and Hg; Cu, Ag, and Au are diamagnetic, whilst the preceding elements Ni, Pd, and Pt are paramagnetic.

CHAPTER V.

SPACE RELATIONS OF ATOMS AND MOLECULES.

WHEN the atoms of elements, or when the simple Avogadro particles or gas molecules of a compound of the first order unite with one another to form a crystal, or unite with one another to form an associated molecule, or unite with simple molecules of another kind to form a molecular compound, the atoms tend to arrange themselves in space in symmetrical groups.

In this connection note the arrangement of symmetry in the five **regular solid figures of geometry.** In these figures there are points arranged symmetrically in space :—

In a group of 4 at the corners of a tetrahedron, or
at the face-centres of a tetrahedron, or
In a group of 6 at the corners of an octahedron, or
at the face-centres of a hexahedron (cube), or
In a group of 8 at the corners of a hexahedron (cube), or
at the face-centres of an octahedron, or
In a group of 12 at the corners of an icosahedron, or
at the face-centres of a dodecahedron, or
In a group of 20 at the corners of a dodecahedron, or
at the face-centres of an icosahedron.

Some of these symmetrical group numbers we find occurring frequently (I) in the groups of atoms and molecules in crystals, and (II) in the groups of atoms and molecules in molecules and in ions.

In addition to these group numbers, may be mentioned 2 and 3, the particles in these cases being, of course, in one plane.

For an arrangement of particles round a point any other numbers will not show so great symmetry as 2, 3, 4, 6, 8, 12, and 20 can give.

However, when a group of any of these numbers occurs, very often there is a distortion from the symmetry of a regular solid figure or of an equilateral triangle or of two points in the same straight line as the kernel and equidistant from it, this distortion being caused by differences in the grouped particles and by differences in the binding forces.

Nevertheless, in general, these numbers will correspond to greater stability than any others and even numbers will give more stable groups than odd.

I. Crystals.

The structure of crystals is of **three main types**:—

1. **In the first type the units are charged positive and negative particles,** which are separate from one another. The atoms are not arranged in groups of two or more, as they are in the molecules of most gases.

This is the structure in the crystals of **polar compounds** and in the crystals of **metallic elements.**

For example, the crystal of the **polar compound sodium chloride** consists of Na^{+1} and Cl^{-1} particles separate from one another and arranged so that each

Na^{+1} is surrounded by six equidistant Cl^{-1} atoms placed at the corners of an octahedron, and each Cl^{-1} is surrounded by six equidistant Na^{+1} atoms placed at the corners of an octahedron.

When the solid is fused the ions are more free to move so that the substance becomes a conductor of electricity.

When the salt is dissolved in water to form a concentrated solution the ions are again more free to move than in the crystal, so that the solution is a conductor of electricity.

In all these cases (the crystal, the fused substance, and the concentrated aqueous solution) there is complete dissociation into ions which are quite separate from one another.

If the sodium chloride is raised to a high temperature and evaporated the atoms leave the surface in pairs, each of the formula $Na^{+1}Cl^{-1}$. If the gas is liquefied or solidified and then evaporated again there will be a considerable rearrangement of atoms, only some of the Na^{+1} ions having the same partners as before.

The **concentrated aqueous solution** resembles the **fused salt.** Each Na^{+1} is being acted on not by only one Cl^{-1} but by several attracting it in different directions so that the attractions more or less neutralise one another. Accordingly, the movement of Na^{+1} in the conducting of electricity through the fused salt or through the concentrated solution is only very slightly influenced by the surrounding Cl^{-1} atoms.

In a **solution of infinite dilution,** there are no interionic attractions, either neutralised or not.

In a **solution of intermediate concentration,** the average distance between the ions is such that there are some interionic attractions that are not neutralised by others, and some of the Na^{+1} and Cl^{-1} ions come near enough to form pairs or Avogadro particles each of the formula $Na^{+1}Cl^{-1}$.

Thus, in the fused salt, in the concentrated aqueous solution, in the aqueous solution of infinite dilution, and in the crystal there are no molecules of the formula NaCl, or in other words there is complete dissociation into ions.

Another example of a polar compound is calcium carbonate. The positive and negative particles acting as units in the crystalline structure of this substance are Ca^{+2} and $(CO_3)^{-2}$. Each CO_3^{-2} is equidistant from six Ca^{+2} atoms. There are no separate groups of the formula $CaCO_3$.

In a polar compound, the bonds holding the units together may be weak when the ionic charges are small as in sodium chloride, or strong when the ionic charges are large as in ruby.

In the case of a **metal** the positive and negative particles acting as units in the crystalline structure are positively charged metallic atoms and electrons. The structure is analogous to that of a salt, and consists of a lattice of electrons and a lattice of metallic ions. In conducting electricity the electron lattice moves as a whole through the ionic lattice. The resistance offered to the passage of electricity is due to the movement of the electron lattice being hampered by the vibrations of the metallic ions. Therefore, the conductivity is increased by lowering the temperature.

2. In the second type the units are neutral atoms

held together by a force analogous to Langmuir's co-valency, so that probably they share some of their electrons. **Diamond** is an example of this type.

Each C atom is surrounded by four others equidistant from it and placed at the corners of a regular tetrahedron. The activation of the valency four which each atom seems to display in diamond, may be explained by the Langmuir electron-sharing method. Each atom is attached to four others by four electron-sharing bonds. The hardness of diamond is due to these bonds which are very strong.

3. **In the third type the units are neutral molecules,** held together by stray fields. **Organic substances** belong to this class.

This third kind of crystal is the only one in which separate molecules can be distinguished.

The following are examples of symmetrical groups:—

Groups of 4 : Diamond, ZnS.
Groups of 8 : S, CaF_2.
Groups of 6 : NaCl, KCl, KI.
Groups of 12 : Cu, Ag, Au.

The importance for the chemist of the study of crystals arises from the fact that vast numbers of chemical compounds exist in the solid state only, for example, $CuSO_4 5H_2O$.

The fact that definite and invariable proportions by weight are obtained, can be accounted for if the arrangements of the atoms are regular so as to constitute space lattices. But the arrangements do not bear any relationship to the primary valencies.

Nearly all molecular compounds decompose or dissociate when heated. For example,

$$\mathrm{H_2SO_4 \rightarrow H_2O + SO_3}.$$

Also, most of them do not even show a molecular weight in solution that agrees with the composition derived from an analysis of the solid substance.

Thus the study of the actual crystalline state is necessary, as usually neither the Avogadro gaseous particle is available nor the corresponding solute particle.

II. Arrangement of Atoms and Atomic Groups within a Molecule or within an Ion.

Here, again, we find the same symmetrical group numbers appearing. These are called by Werner **Co-ordination Numbers.**

The most common co-ordination numbers are 4, 6, and 8, which are the first three symmetrical group numbers observed in the five regular solid figures.

Very often an atom may be regarded as a kernel, round which a group of other atoms are situated. Round the central atom there is a maximum number of co-ordination positions, in each of which there may be an atom or an atomic group; an atom or an unsaturated atomic group occupying one of these co-ordination positions may have valency one or more than one. The maximum number of co-ordination positions is not determined by the valency or absence of valency in the atoms or atomic groups in these positions. Thus we have—

$$(\mathrm{V^{+3}F_6^{-1}})^{-3},\quad \left(\mathrm{V^{+5}}\begin{matrix}\mathrm{O^{-2}}\\ \mathrm{F_5^{-1}}\end{matrix}\right)^{-2},\quad (\mathrm{I^{+7}O_6^{-2}})^{-5},\quad \left(\mathrm{Os^{+6}}\begin{matrix}\mathrm{N^{-3}}\\ \mathrm{Cl_5^{-1}}\end{matrix}\right)^{-2}.$$

In all of these the co-ordination number is 6.

In the first group, each of the six positions is occupied by an F^{-1} atom. In the second group, one position is occupied by an O^{-2} atom. In the third group, each of the six positions is occupied by an O^{-2} atom. In the fourth group, one of the six positions is occupied by a N^{-3} atom. In the case of each of the above the complete group is stable though negative, the group being a complex anion. We may also have a stable positive group, as in the case of $(NH_4)^{+1}$. It is not necessary for stability that a group should be neutral.

$C^{+4}Cl_4^{-1}$, on the other hand, is neutral and stable. But more negative atoms cannot be added to this neutral group, because the co-ordination number is 4. Another O^{-2} can, however, be added to the neutral stable group $C^{+4}O_2^{-2}$ to give the negative stable group $C^{+4}O_3^{-2}$ or $(CO_3)^{-2}$.

The co-ordination number for most atoms is 6*; for some it is* 4*; and for others it is* 8. *It may also be* 2 *or* 3. Any other number does not give so great stability.

The co-ordination number expresses a space relationship, and is an indication of how many atoms can be fitted in round a central atom. It will depend both on the volume of the surrounding atoms and on that of the central atom. The smaller the volume of the central atom the less is the co-ordination number likely to be. This agrees with the fact that the co-ordination number for B, C, and N is 4. This is seen in HBF_4,CCl_4, and NH_4Cl. On the other hand, the smaller the volume of the atoms to be fitted in round the central atom the greater should the co-ordination number be.

The co-ordination number is 8 with Mo, Zr, Th, Ca, Sr, and Ba as central atoms. This is seen in—

$(MoCy_8)^{-4}$, $ZrCl_4(8NH_3)$, $ThCl_4(8NH_3)$, $CaCl_2(8NH_3)$, $SrCl_2(8NH_3)$, $BaCl_2(8NH_3)$.

It is interesting to compare C with Si and the others in the same family (or in the same equivalential). All these have the same valency 4, but only for C is the co-ordination number the same as the valency. Thus, with a molecule consisting of a C atom united to four univalent atoms, no addition compounds can be formed, such as we have with SiF_4, for example, which gives $2HF.SiF_4$ or H_2SiF_6 (co-ordination number 6).

CHAPTER VI.

ELECTRO-AFFINITY.

THE theory of positive and negative radicals and positive and negative ions implies that under certain conditions an atom or atomic group has a certain number of electrical charges. The polarity gives the sign of the charges and the valency gives the number of them. Thus when an atom has positive polarity and valency 3, it is charged with three positive charges.

When an atom M unites with an atom Z to form the compound MZ, we may in general regard the compound MZ as ionisable into two oppositely charged ions, for example, into a positively charged cation M and a negatively charged anion Z. Indeed, according to one view of chemical reactions, such ionisation of MZ is a necessary preliminary before any chemical interaction can take place between MZ and any other substance, every chemical reaction involving first ionisation and then either reuniting of ions with new partners, or destruction of the radicals. And, certainly, the quickest chemical changes are between molecules that most readily give ions. When chemical changes are slow, as in many organic reactions, the inference is that ionisation is very slight.

According to this view, then, every chemical compound such as MZ consists of two polarly opposite radicals; M the yielder of a positive ion being called positive, and Z the yielder of a negative ion being called negative.

Whilst, according to this view, every atom is capable of uniting with electricity and forming an ion, the tendency in some cases, for example, C and N, is so very slight that such atoms are not commonly regarded as yielding ions.

The existence of very minute traces of ions may be disclosed by various methods:—

1. In passing electricity through a solution, cations, even when present in exceedingly minute traces, may be discharged at the cathode, and anions at the anode.

Thus hydrogen is set free at the cathode from a normal solution of an alkali, though the number of molecules of H^{+1} per litre is only of the order of 10^{-14}.

Oxygen is liberated at the anode from many acid solutions.

Silver is liberated at the cathode from KCN solutions.

Sulphur is separated at the cathode from concentrated sulphuric acid solutions.

2. Liquids such as pure ammonia and pure sulphur dioxide are found to have a measurable conductivity; similarly, for such as the halides of groups 5 and 6.

At high temperatures electrolytic conductivity is obtained with the oxides of the Nernst lamp and SiO_2.

From the electrolytic nature of many compounds in non-aqueous solutions Walden assumed the existence of the cations Br^{+1}, Br^{+3}, I^{+1}, I^{+3}, P^{+3}, P^{+5}, As^{+3}, Sb^{+3}, Sb^{+5}, Sn^{+3}, S_2^{+2}, etc.

3. Quick chemical reactions with other ions show the presence of ionisation. Examples:—

OH^{-1} of water and of alkali acting on many of the chlorides gives the OH-compound of the element originally combined with Cl, therefore this element was present as a cation.

Some sulphides and water give H_2S, showing the positive nature of the element formerly united with S, e.g. B_2S_3, P_2S_3, etc. Some carbides and water give hydrocarbons.

According to the view explained here, then, every atom has a certain affinity for electricity varying from atom to atom. The greater the electro-affinity the more stable the ion or the more firmly is the electricity held by the atom, and therefore the greater is the difficulty experienced in discharging the ion. Accordingly, by measuring or calculating the voltage necessary *under standard conditions* in order to discharge cations, for example, and deposit them on the cathode, we obtain a means of expressing in actual numbers the electro-affinity of certain atoms. On the other hand, the electro-affinity of other atoms cannot be measured directly or accurately calculated; yet from their chemical and physical properties, and from their positions in the periodic table, we can classify most of the atoms according to their electro-affinities for positive electricity when we obtain the arrangement indicated in the diagram II. which is a modification of that given by Abegg.

It will be seen that elements placed in the same vertical line are in the same equivalential and that, in any of the equivalentials to the extreme left or right, elements of highest atomic number are the most positive. In the middle of the diagram, however, we find a tendency for this rule to be reversed.

The dotted straight lines indicate the positions of certain well-known elements relative to the others.

The present curves do not follow strictly those of Abegg. Where possible, the position of elements is determined by the electrochemical behaviour. Accurate data for this is very difficult to obtain in certain cases, especially when the metals display passivity, as, for example, do Cr, Mo, and W.

The behaviour of the metals V, Nb, and Mo agrees better with their position on the curves introduced here than on the curves as given by Abegg. Again, this would bring 43 much farther down, placing it among the noble elements, a position probably more suitable for a missing element.

The middle portion of the Cs curve is not given; there are not sufficient data for the rare earth metals. It may be, however, that although the La and Ce portion of the curve is high some of the remaining part may be low, so that the missing 61 comes into a lower and more noble region and the more magnetic rare earth metals may occupy a place analogous to that of Fe, Co, and Ni.

It is interesting to note that the missing 75 is assigned a place in the given curve analogous to that of the missing 43.

It must be understood that the places assigned to the elements in these curves are only approximate and in many cases by no means certain. These places also depend upon the conditions under which the elements were compared. It is possible so to change the concentrations of solutions of two competing metals that the conditions favour the positiveness of one metal compared with that of the other to such an extent that their positions in the scale of positiveness are reversed. This is analogous to the reversing of a chemical change by increasing the concentrations of the products of that change.

Thus the **action of mass** must be considered as well as the specific tendency of each single atom towards positiveness or negativeness.

The ionisation of an electrolyte when dissolved in a solvent is usually represented, for simplicity, as the formation of simple ions:—

$$MZ \rightarrow M^{+1} + Z^{-1}$$

whilst in reality in most cases there is formation of solvated ions, and probably, in every case, at least impending solvation. Hydrated ions would be (or would tend to be) formed when water is the solvent, thus:—

$$MZ + (x + y)\, H_2O = (M^{+1})\,(H_2O)_x + Z^{-1}\,(H_2O)_y.$$

It is possible, indeed, that the union of the solvent with the radicals of the undissociated molecule is a necessary factor in electrolytic ionisation.

Similarly, the dissolving of a metal at the anode involves not only the charging of the metallic atom but also the addition of water. Thus:—

$$M + xH_2O + \text{one positive charge} \rightarrow M^{+1}\,(H_2O)_x.$$

Factors Affecting the Value of Electro-affinity.

For the charging of a particle we have the **General Volume Law**: that the smaller the particle the less firmly is a given charge held. We have, however, to consider the effect of subatomic structure, and we find that in passing down an equivalential the atomic volume usually increases with rising atomic number and an electron becomes more easily removed or the positive electro-affinity rises, and on the other hand an electron becomes less easily attached or the negative electro-affinity falls. Thus the *general volume law is obeyed by positive electro-affinity but not by negative electro-affinity.*

The positive electro-affinity is less the greater the number of electrons detached, and the negative electro-affinity is less the greater the number attached. Thus both electro-affinities obey the **Quantity Law**.

Whilst, according to the Quantity Law, both electro-affinities diminish when the charge increases, the rate of diminution is greater for negative than for positive (**Polarity Law**).

In general, the formation of positively charged atoms is easier than that of negatively charged. Thus the first kind are far more common than the second.

In agreement with this, negatively charged complex ions are far more numerous than positively charged.

As pointed out above, the **General Volume Law** is obeyed by the positive electro-affinity, and it may be said to be obeyed also when the volume of the atomic particle is increased not by an addition to the subatomic structure but by an external attaching of other atoms. This increase in electro-affinity, however, is also favoured by the fact that the characteristic charge is reduced and, therefore, easier of attainment.

Examples:—

$$Bi^{+3} \rightarrow (BiO)^{+1} \text{ and } C^{+4} \rightarrow (CO_3)^{-2}.$$

In passing along Row 2 of the periodic table (new form), the ionic charge commonly occurring increases:

$$Li^{+1},\ Be^{+2},\ B^{+3}$$

and in accordance with the **Quantity Law** the strength or stability of the ion diminishes; similarly, in the series:

$$\mathrm{Na}^{+1},\ \mathrm{Mg}^{+2},\ \mathrm{Al}^{+3}.$$

Again, in passing down a positive equivalential of the periodic table, for example, in going along the series Li, Na, K, Rb, Cs, the volume increases, and in accordance with the **Volume Law** the positive ion becomes stronger or more stable.

As will be seen from the diagram this law holds for the positive equivalentials at the right and left of the diagram, but certainly not for some and possibly not for others of the equivalentials in the centre. For example, for the three series:—

Cu, Ag, Au;
Zn, Cd, Hg;
and Ga, In, Tl;

in each of which, as the volume *increases* the positive electro-affinity *diminishes*.

Again, with these same atoms, in the three series

$$\mathrm{Cu}^{+1},\ \mathrm{Zn}^{+2},\ \mathrm{Ga}^{+3};\quad \mathrm{Ag}^{+1},\ \mathrm{Cd}^{+2},\ \mathrm{In}^{+3};$$
$$\mathrm{Au}^{+1},\ \mathrm{Hg}^{+2},\ \mathrm{Tl}^{+3};$$

as the charge increases, the strength of the ion increases, the **Quantity Law** being disobeyed.

The following is offered as an explanation of this apparent anomaly.

As already pointed out, hydration facilitates the formation of ions. Now the tendency towards hydration is increased by increasing the density of the field concerned in the hydration. This is brought about by increasing the charge of the ion or by diminishing its volume.

Increase of volume in itself would have the *primary* *effect* of *increasing* the positive electro-affinity, but increase of volume, producing as it does diminution of hydration, has the *secondary effect* of *diminishing* the electro-affinity.

Increase of charge in itself would have the *primary effect* of *diminishing* the electro-affinity, but increase of charge has the effect of increasing the hydration and therefore the *secondary effect* of *increasing* the electro-affinity.

Now, of the ions being considered those that are most hydrated are the ones that have the highest electro-affinity. Note in particular the case of Zn which is well known for its very positive character, being used as the anode in almost all primary cells; again, the salts of Zn are well known for their tendency to hydration, anhydrous zinc chloride being an important dehydrating agent.

Thus the above-mentioned secondary effect would appear to be at least one of the factors causing the anomaly.

CHAPTER VII.

ATOMIC AFFINITY.

CONSIDER a uni-univalent salt MZ formed by the union of a positive atom M and a negative atom Z.

When the neutral atom M is combining it becomes charged with one positive charge, and the neutral atom Z with one negative.

The union may be regarded as taking place in two stages:—

1. The charging of the neutral atoms.

2. The union of the charged atoms to give the neutral molecule.

1. is due to **electro-affinity**; 2. is due to **interionic affinity.** The whole is due to **interatomic affinity.**

Let the corresponding energies be E_e, E_i, and E_a.

then $$E_e + E_i = E_a$$

or work done by electro-affinity + work done by interionic affinity = work done by atomic affinity.

E_i is always positive.

Some indication of the value of E_a is obtained from the heat of formation. This is large and positive in a case like KCl where both elements are showing their characteristic polarity and where the polarity distances are short. Here E_e is also large. For all substances like this clearly atomic affinity and electro-affinity run parallel.

Sometimes the heat of formation is negative, hence E_a is negative. As E_i is always positive, it follows that in this case E_e is negative. In other words, if the work done by atomic affinity is negative, at least one of the works done by the electro-affinities is negative. Thus work has to be done to charge at least of the atoms, and to make the neutral atoms unite.

If the heat of formation is a large negative quantity then probably both the electro-affinities are negative.

If the heat of formation is a small negative quantity, then perhaps only one of the works done by the electro-affinities is negative.

On the other hand, if the heat of formation is positive but small, at least one of the works done by the electro-affinities may be a small negative quantity.

But if the heat of formation is positive and large, then both the works done by the electro-affinities are large and positive.

Negative work done by electro-affinity implies that the element is activating a polarity towards which it has no tendency.

For a compound between an element from the extreme left of the periodic table (from the positive chief groups) and an element from the extreme right (from the negative chief groups), e.g. for KCl, we should expect large heat of formation or large atomic affinity. *Here the parallelism between electro-affinity and atomic affinity is quite clear.*

When one of the elements is activating a non-characteristic polarity or has a feeble electro-affinity, the parallelism between electro-affinity and atomic affinity will not be so obvious. We shall, therefore, illustrate our theory mostly from elements of decidedly positive or decidedly negative character.

Sometimes, in passing from one member to another of a series of compounds, we find that when E_e rises, E_i falls. But E_i, for electrolytes in aqueous solutions, is of a much lower order of magnitude than E_e. Thus any fall in E_i is masked by a much greater rise in E_e. Therefore, with any series of decidedly positive and decidedly negative elements, the atomic affinity always rises when the electro-affinity rises even when the interionic affinity falls.

In some series of compounds, electro-affinity, interionic affinity, and atomic affinity all increase together.

When the neutral atom M comes into contact with the neutral atom Z, we shall suppose that an electron passes from M to Z, thereby making M positively charged and Z negatively charged. Thus the positively inclined atom M, both in its tendency to unite with the negatively inclined atom Z and in its tendency to become a positively charged atom (a cation), tends to lose an electron. Therefore, *the atomic affinity of the positively inclined atom M for negatively inclined atoms and the electro-affinity of the atom M for positive electricity ought to run parallel with one another.*

The atom M in the above is said to behave positively and the atom Z negatively. The terms positive and negative, however, refer to the particular compound MZ. It is possible that M may behave negatively towards some other atom. In other words, *the polarity of an atom varies according to the conditions.* The neutral atom M on account of its subatomic structure has a certain specific tendency to become positively charged, but this tendency will be modified by the external conditions, for example, by the nature of the element with which M may be united chemically. This modification may be so great that M behaves negatively instead of positively.

Thus, *every atom is amphoteric not only with regard to electro-affinity but also with regard to atomic affinity.* That is, its polarity in the ionic state, and also when chemically united to another atom, may be positive or negative according to the circumstances.

Illustrations of the above mentioned parallelism :—

The hydrogen halides increase in stability as we pass from iodine to chlorine and the anion-forming tendency increases in the same direction. The affinity for the positively inclined atom hydrogen is greater in the case of chlorine than in the case of bromine and greater in the case of bromine than in the case of iodine, and the affinity for negative electricity is greater in chlorine than in bromine and greater in bromine than in iodine.

Again we see a similar gradation of properties as we pass from left to right in the short rows in the periodic table. The strongest ion-forming tendencies are found at the extreme left and right where also are the strongest atomic affinities, and both the electro-affinities and the atomic affinities diminish as we pass from the extreme left and right towards the middle of the table. The diminution is at a less rate on the left (positive) side than on the right (negative) side (**Polarity Law**).

Consider the atoms Na, Mg, and Al. By the action of electro-affinity these atoms can combine with one, two, and three positive charges of electricity respectively. By the action of atomic affinity they can combine with one, two, and three atoms of chlorine respectively.

Just as in the case of electro-affinity the firmness with which electricity is held is greater the smaller the number of charges held, so in the case of atomic affinity the firmness with which chlorine is held is greater the smaller the number of chlorine atoms held. Thus among the three elements Na, Mg, and Al both the atomic affinity and the electro-affinity are strongest for sodium and weakest for aluminium.

In connection with atomic affinity we speak about polarity and valency. The polarity is the sign of the charges on a chemically combined atom and the valency is the number of the charges. Thus in $NaCl$, $MgCl_2$, and $AlCl_3$, Na, Mg, and Al have one, two, and three positive charges respectively.

When an atom displays in uniting with other atoms a varying active valency, then the affinity with which valency acts is weakest when the valency is greatest (**Quantity Law**).

When one chlorine atom per iron atom has been obtained from ferric chloride, the separation of the remaining two chlorine atoms is found to be more difficult. This is parallel with the fact that the three positive charges in the ferric iron cation are held less firmly than the two positive charges in the ferrous iron cation.

It must be borne in mind, however, that whilst the primary effect of the Quantity is as stated now, a secondary effect opposite to the primary is sometimes predominant, as pointed out in the study of electro-affinity.

Volume Law for Affinity of Positive Valency.

The volume law holding in general for positive electro-affinity, holds also for atomic affinity when the valency is positive.

In the series of atoms in an equivalential (new table), or in a group (old table), the greater the atomic volume of the central atom of a compound, the greater the atomic affinity when the valency is positive.

Examples :—

Cl Compounds of S, Se, and Te :—

SCl_4 gives off Cl_2 at ordinary temperature.

$SeCl_4$ is stable and a solid at ordinary temperature, and dissociated at 200° evaporating and giving Cl_2.

$TeCl_4$ can be evaporated without decomposition.

Br Compounds of S, Se, and Te :—

SBr_4 not known.

$SeBr_4$ prepared in solid form, but decomposes in air at 70° giving Cl_2.

$TeBr_4$ quite stable even as a gas.

I compounds of S, Se, and Te :—

S_2I_2 if it exists at all, decomposes giving I_2.

SI_4 not capable of existing.

SeI_4 loses I_2 on heating.

TeI_4 quite stable.

Halides of halogens :—

	Negative Elements.		
	F	Cl	Br
Positive Elements.			
Cl	no compds.	—	—
Br	BrF_3	BrCl ?	—
I	IF_5	ICl, ICl_3	IBr, IBr_3 ?

Cl Compounds of N, P, As, Sb, and Bi.

	m.p.	m.p.
NCl_3 liquid	—	——
PCl_3 liquid	− 115°	PCl_5 solid sublimes readily giving PCl_3 and Cl_2.
$AsCl_3$ liquid	− 18°	——
$SbCl_3$ solid	73°·2	$SbCl_5$ liquid − 6°.
$BiCl_3$ solid	225° − 230°	——

NCl_3 is so exceedingly unstable that it is not surprising that there is no NCl_5.

On coming, however, to PCl_3 the stability is increased so much that PCl_5 is also stable although its vapour readily dissociates into PCl_3 and Cl_2.

On the other hand, the non-existence of $AsCl_5$ would indicate that there is a fluctuation downwards again in the stability of the chlorides (though not so far down as NCl_3).

The existence of $SbCl_5$, which is quite stable, would indicate a rise again in the stability of the trichlorides, and the non-existence of $BiCl_5$ shows another fall.

Thus though the stability of the trichlorides shows a general trend upwards, there is an alternation of rises and falls at the different steps in passing along the list.

Stability of the trichlorides: $N \xrightarrow{\text{rise}} P \xrightarrow{\text{fall}} As \xrightarrow{\text{rise}} Sb \xrightarrow{\text{fall}} Bi$.

This fluctuation is sometimes called **Secondary Periodicity,** about which a fuller treatment will be given later.

Volume Law for Affinity of Negative Valency.

The volume law for negative electro-affinity is opposite to that for positive. *In a series of atoms in a family (or equivalential), the affinity for negative electricity increases when the atomic volume diminishes; parallel with this,* *the affinity of negative valency increases with diminishing atomic volume.*

Thus, the greatest stability in the hydrides of O, S, Se, and Te is at the O end of the list, whilst in the chlorides it is at the Te end.

Similarly, the greatest stability in the hydrides of N, P, As, Sb, and Bi is at the N end of the list, whilst in the chlorides it is at the Bi end.

Again, the greatest stability in the hydrides of F, Cl, Br, and I is at the F end of the list, whilst in the oxides it is at the I end. In this connection compare

$$2KI + Cl_2 \rightarrow 2KCl + I_2$$

and

$$2KClO_3 + I_2 \rightarrow 2KIO_3 + Cl_2.$$

In considering the effect of volume on atomic stability, we have to bear in mind not only the parallelism between atomic affinity and electro-affinity but also what are purely space relationships. Thus, in considering a positive tetravalent central atom surrounded by four univalent atoms, to which it is united, we see that the greater the volume of the central atom the more stable should be the compound not only because the atomic affinity of the central atom should be greater but also because it should be easier to place four univalent atoms in the space surrounding the central atom. On the other hand, from the point of view of purely space relationship, the smaller the volumes of the negative atoms the easier is it to place them in the space surrounding the central atom, and therefore the more stable is the compound.

The stability is also favoured by smallness of volume in the negative univalent atoms for another reason: because the negativeness is thereby enhanced.

On the grounds, therefore, both of purely space relationships and of subatomic structure, the stability of the compound is raised by increasing the volume of the central positive tetravalent atom and diminishing the volumes of the four negative univalent atoms.

On the other hand, when a central negative tetravalent atom is surrounded by four positive univalent atoms, the effect of subatomic structure is to increase the stability when the volume of the central atom is diminished and the volumes of the univalent atoms increased. This effect usually masks the effect of purely space relationships which acts in the opposite direction.

The **Polarity Law** for electro-affinity has also its analogue in atomic affinity.

In the periodic table positive trivalent boron is situated one place to the left of carbon and negative trivalent nitrogen one place to the right; positive divalent beryllium is two places to the left and negative divalent oxygen two places to the right; positive univalent lithium is three places to the left and negative univalent fluorine three places to the right. Similarly for the places to the left and right of silicon. The symmetry thus holding for valency does not also hold for the affinity of the valency. In accordance with the polarity law the fall in atomic affinity in the positive series Li → Be → B is less than in the negative series F → O → N.

Elements characterised by positive polarity may also sometimes be negative, and those characterised by negative polarity may sometimes be positive, but the activation of a non-characteristic polarity is easier for negative elements than for positive, this being in accordance with the polarity law.

Criteria of Polarity.

When two elements unite we regard one as positive and the other as negative. How can we tell which is positive?

The polarity of an element in a compound is indicated

1. By the polarity of the ions obtained from the element when the compound is dissolved.

2. By the action of water on the compound, i.e. by the nature of the hydrolysis.

3. By the place of the element in the periodic table compared with that of its partner.

4. By the formula of the compound, when the maximum valencies of the components come into play.

Example: P_3N_5.

1. Fails since insoluble P_3N_5 can be investigated in no solvent for its possible electrolytic nature.

2. Water gives ammonia and phosphoric acid, therefore N is negative since it unites to H of water and P is positive since it unites to OH.

3. In agreement with *2.* P occupies a more positive place in the periodic table than N.

4. P in the compound P_3N_5 cannot be negative part since according to our rule the maximum negative valency of P is 3; the maximum positive valency is 5, which is allowed by the formula if P is positive.

With regard to the relative position of two elements in the periodic table, note that compounds between two neighbouring elements in the same group (or equivalential) can show marked polarity only when the gradation of the electro-affinity is considerable. This, however, is always the case between two initial members of a group.

Therefore, we can have well-defined compounds of Al with B or of Si with C, not, however, of higher neighbours with one another.

How near to its maximum valency an atom can come will depend upon the electro-affinity of its partner. The valency of an atom will be higher the greater the polar difference between it and its partner.

The maximum positive valency of S is 6, which is reached only when S unites with O and F, i.e. with the most strongly negative atoms, in the compounds SO_3 and SF_6

The highest known halides of S are SF_6, SCl_4, S_2Br_2 (no compound of S and I is known definitely, the so-called sulphur iodide may be a mixture or a solid solution).

The highest halides of iodine are IF_5, ICl_3, IBr (IBr_3?).

CHAPTER VIII.

INTERIONIC AFFINITY.

We have already seen how the presence of separate ions in solution can be disclosed. The theory, that the neutral molecule itself contains charged atoms or atomic groups (i.e. radicals), is supported by the fact that this molecule can yield ions, but this is only indirect evidence. Methods, however, are available for proving more directly the presence of charged atoms in the undissociated molecules: the study of Refractive Index, Residual Rays, Magnetic Properties, and Crystal Structure (X-ray method).

Factors Affecting the Value of Interionic Affinity.

We shall suppose for simplicity that the total surplus charge on an atom acts as if at the centre of the atom supposed spherical in shape. Thus if two atoms are united chemically the distance between the charges equals the sum of the radii of the atomic spheres.

Thus the interionic affinity is greater the larger the charges and greater the smaller the volumes of the atoms.

Effect of Volume.

We are considering here the force acting between two particles one charged positively and the other charged negatively. This force increases as the atomic volumes diminish. The force is

$$\frac{E_1 \times E_2}{K \times D^2}$$

where E_1 and E_2 are the charges and D is the distance between them, and K is the dielectric constant of the medium.

On the other hand, whilst the electro-affinity for negative electricity increases when the atomic volume diminishes, the electro-affinity for positive electricity diminishes.

Then, again, interatomic affinity often runs parallel with electro-affinity, so that we may find that the volume effect in both electro-affinity and interatomic affinity acts in a direction opposite to that in interionic affinity.

Effect of Charge.

In general all uni-univalent salts are well ionised and to about the same extent; and all di-divalent salts are ionised to a less extent than uni-univalent ones and to about the same extent as one another. This is in accordance with the above law for the relation between charges and the interionic force.

Degree of dissociation.

uni-uni.		uni-di.		di-uni.		di-di.	
KCl	0·86 (*0·1 n*)	K_2CO_3	0·69	$BaCl_2$	0·77	$CuSO_4$	0·38 (*0·1 n*)
KBr	0·86 (*0·1 n*)	K_2SO_4	0·67	$Pb(NO_3)_2$	0·54	$ZnSO_4$	0·38 (*0·1 n*)
KI	0·86 (*0·1 n*)			CdI_2	0·56		
KNO_3	0·83 (*0·1 n*)						
NaCl	0·84 (*0·1 n*)						
$AgNO_3$	0·81 (*0·1 n*)						

$$\text{Compare } 2K + 2Cl \rightarrow 2K^{+1} + 2Cl^{-1} \rightarrow 2KCl.$$
$$\text{with } Ca + O \rightarrow Ca^{+2} + O^{-2} \rightarrow CaO.$$

The effect of electro-affinity in the first is greater than in the second, and the effect of interatomic affinity is also greater, but that of interionic affinity is less.

This shows that the effect of diminution of interionic affinity in the first case is masked by the increase of electro-affinity.

Thus 2KCl is more difficult to separate into atoms and more easy to separate into ions than CaO.

$$\text{Compare } K + Cl \rightarrow K^{+1} + Cl^{-1} \rightarrow KCl$$
$$\text{with } K + I \rightarrow K^{+1} + I^{-1} \rightarrow KI.$$

The effect of electro-affinity is greater in the first than in the second, and the effect of interatomic affinity and that of interionic affinity are also greater. Thus here the three effects all increase together. And so KCl is more difficult to separate into atoms than KI and also more difficult to separate into ions.

Compare $H_3^{+1}P^{-3}$, $H_2^{+1}S^{-2}$, and $H^{+1}Cl^{-1}$.

The chlorine atom with one negative charge holds a hydrogen atom with one positive charge much less firmly than does a sulphur atom with two negative charges. Thus a hydrogen atom can be separated from HCl in the ionic form more easily than from H_2S and similarly more easily from H_2S than from H_3P. HCl is a strong acid, H_2S is a weak acid, H_3P is not an acid.

It should be noted that the influence of volume differences is in the same direction :—

$$\text{Cl vol.} > \text{S vol.} > \text{P vol.}$$

The effect of volume and that of charge acting together intensify the difference between these hydrides.

Compare H_2F_2, HCl, HBr, and HI.

The volume relations of the halogen atoms are

$$I > Br > Cl > F.$$

The relative strengths of the acids should therefore be

$$HI > HBr > HCl > H_2F_2.$$

There is not, however, much difference between HI and HBr.

Similarly, we have the following order of acid strengths:—

$$H_2Te > H_2Se > H_2S > H_2O$$

the ionisation constants of which are

$$10^{-2},\ 1\cdot7 \times 10^{-4},\ 0\cdot97 \times 10^{-7}, \text{ and } 10^{-14}.$$

In $N^{-3}H_3^{+1}$, $P^{-3}H_3^{+1}$, and $As^{-3}H_3^{+1}$ electro-affinity, interionic affinity, and atomic affinity are all greatest at the N end of the list.

A stable group of atoms is not necessarily neutral. There may be a surplus of positive or negative electricity. N^{-3} combines with $3H^{+1}$ to form $N^{-3}H_3^{+1}$ which is a neutral molecule. But N^{-3} may combine with $4H^{+1}$ to form $N^{-3}H_4^{+1}$ which has a surplus positive charge of one, and may be written $(NH_4)^{+1}$ this being an ion obtained when NH_3 is dissolved in water.

Similarly, P^{-3} can attach $4H^{+1}$ to form $(PH_4)^{+1}$, but the fourth H^{+1} is held less firmly here than in $(NH_4)^{+1}$, this being because the volume of P is greater than that of N.

In the case of As the volume has increased by so much that AsH_3 cannot take up an extra H^{+1}, and thus AsH_3

does not function as a base in aqueous solutions but acts as a neutral. Similarly for Sb, the volume of Sb being greater than that of As.

BiH_3 has only recently been prepared.

It might be noted in passing that B and the four elements immediately preceding each nonvalent gas in the atomic number scale are the only elements that form volatile hydrides :—

i.e. B and C, N, O, F ;
Si, P, S, Cl ;
Ge, As, Se, Br ;
Sn, Sb, Te, I ;
Pb, Bi, Po, 85.

The hydrides of Sn, Pb, Bi, and Po have been discovered recently. Provisionally, 85 is put in the list.

In agreement with the above, we have :—

H_3N,	H_2O,	HF,
basic,	neutral,	acid of medium strength.

The separation into ions is most difficult at the N end.

The separation into atoms is most difficult at the F end.

H_3P,	H_2S,	HCl,
basic,	weak acid,	strong acid.

The separation into ions is most difficult at the P end.

The separation into atoms is most difficult at the Cl end.

HF, HCl, HBr, HI.

The separation into ions is most difficult at the F end.

The separation into atoms is most difficult at the F end.

H_2O, H_2S, H_2Se, H_2Te.

The separation into ions is most difficult at the O end.

The separation into atoms is most difficult at the O end.

H_3N H_3P H_3As H_3Sb.

The separation into ions is most difficult at the N end.

The separation into atoms is most difficult at the N end.

CHAPTER IX.

BASIC HYDROXIDES, ACIDIC HYDROXIDES AND ACIDIC HYDRIDES.

CONSIDER the hydroxide $M^{+x}(O^{-2}H^{+1})_x$.

An H^{+1} is attracted by O^{-2} and repelled by M^{+x}. M^{+x} and H^{+1} compete for O^{-2}. If M^{+x} obtains possession and H^{+1} is split off, the hydroxide is acid; if H^{+1} obtains possession and OH^{-1} is split off, the hydroxide is basic. Which of the two positive ions is predominant depends on the relative values of their charges and of their volumes. As H^{+1} has a vanishingly small volume, and the volume of M^{+x} is of atomic dimensions, H^{+1} may obtain possession even if M has as large a charge as 3.

In comparing a series of elements M for which x varies, we should find that the greater x the easier is H^{+1} detached, that is, the more acidic is the hydroxide. Thus, in passing along the row Li^{+1}, Be^{+2}, B^{+3}, C^{+4}, N^{+5}, we find that the hydroxide of the first element is basic only, that of the second, Be, is both basic and acidic, and the hydroxides of the other elements, B, C, and N, are acid. The transition point between the basic and acidic properties occurs at the *second* term Be.

Again in passing along the row Na^{+1}, Mg^{+2}, Al^{+3}, Si^{+4}, P^{+5}, S^{+6}, Cl^{+7}, we find that the transition occurs at the *third* term Al, i.e. one place farther to the right than in the previous row. This shift of one place is due to the fact that the volumes of corresponding atoms are greater in the second row than in the first.

Passing along the list Be^{+2}, Mg^{+2}, Ca^{+2}, Sr^{+2}, Ba^{+2} we ought to find that the repulsive force on H^{+1} diminishes because the atomic volume increases. Only in the case of Be^{+2} is the volume small enough for an acidic hydroxide to be obtained, the other hydroxides being entirely basic and the basic character becoming stronger as we pass along the list towards Ba.

Thus in passing along a row of the periodic table towards the right, the basic character of the hydroxides diminishes and the acidic character increases. Again in passing down an equivalential (new form of table) or down a column (old form) in the periodic table, the basic character of the hydroxide increases (usually).

This holds with remarkable uniformity throughout the table. It must be borne in mind that we are dealing here with interionic affinity, the controlling factors of which are volume and charge, and that electro-affinity sometimes acts in an opposite direction. Thus, whilst volume shows its influence on electro-affinity at the left and right of the table by a primary effect and at the middle by an opposite secondary effect, the influence of volume on interionic affinity is always in the same direction. For example, compare the rows

$$Cu^{+1},\ Zn^{+2},\ Ga^{+3},\ Ge^{+4};$$
$$Ag^{+1},\ Cd^{+2},\ In^{+3},\ Sn^{+4};$$
$$Au^{+1},\ Hg^{+2},\ Tl^{+3},\ Pb^{+4}.$$

We find the transition to acidic character appearing at Zn in the first row, at In in the second row, and at Pb in the third row. The gradation is therefore exactly similar to what we observed in row two of new table (transition at Be) and in row three of new table (transition at Al). Similarly in the columns, we find the most acidic hydroxides at the top. We are here comparing valencies that are activated with reference to similar substandards (Ni, Pd, and Pt). Any other valencies would not be comparable; for example the charge in Au^{+3}, which is not comparable, is high enough to give an acidic hydroxide, whereas that in Au^{+1} is not.

The contrast between interionic affinity and electro-affinity in this part of the periodic table is very striking. For example, Zn, the element of highest positive electro-affinity in the equivalential Zn, Cd, Hg, is the only element of the three that gives an acidic hydroxide. There is, however, here nothing but what is to be expected if we distinguish clearly effects that are due to electro-affinity from those that are due to interionic affinity. *It is quite a mistake to suggest*, as is too often done, *that the formation of an acidic hydroxide is to be associated with negative character.* So far, indeed, is this from being the case, that an element in its acidic hydroxide is behaving positively. The error probably has arisen from the fact that the best known acidic hydroxides are formed by elements that have negativeness as their characteristic polarity, although it is not this polarity that they are displaying in their hydroxides. Sulphur is an example of such an element.

When the valency of an atom is variable, the higher the valency the more acidic and the less basic is the hydroxide.

Thus the lowest oxides of Mn are base-forming and the highest acid-forming.

Valency of Mn.	*Oxide.*	*Hydroxide.*	*Nature of Hydroxide.*	*Example Salt.*
2	MnO	$Mn(OH)_2$	Strong base	$MnCl_2$
3	Mn_2O_3	$MnO(OH)$	Weak base	—
4	MnO_2	$MnO(OH)_2$	Weak base or weak acid	—
6	MnO_3	$MnO_2(OH)_2$	Acid	K_2MnO_4
7	Mn_2O_7	$MnO_3(OH)$	Acid	$KMnO_4$

Similarly $Cr_2^{+3}O_3^{-2}$ is basic giving, e.g. $CrCl_3$.
and $Cr^{+6}O_3^{-2}$ is acidic giving, e.g. K_2CrO_4.

Again note the gradation in properties in passing along the series :—

N	P	As	Sb	Bi
N_2O_3 acidic.	P_2O_3 acidic.	As_2O_3 acidic and basic.	Sb_2O_3 feebly acidic mainly basic.	Bi_2O_3 basic.
N_2O_5 acidic.	P_2O_5 acidic.	As_2O_5 acidic.	Sb_2O_5 acidic.	Bi_2O_5 slightly acidic.

Comparison of Acidic Hydroxides and Acidic Hydrides.

Compare a series of elements of the same valency but differing atomic volume, e.g. S, Se, Te of which Te has the greatest atomic volume. In the acidic hydrides, SH_2, SeH_2, TeH_2, all these elements are negative and therefore attract the positive hydrogen atom, and the attraction is most in the case of S. Thus the hydride of S is the weakest acid and that of Te is the strongest.

On the other hand, in the acidic hydroxides, all three elements are positive and therefore repel the positive hydrogen atom, and the repulsion is most in the case of S. Thus the hydroxide of S is the strongest acid and and that of Te is the weakest. Therefore the direction of increasing acidic strength for hydroxides is opposite to that for hydrides in the case of a series of elements all of the same valency, i.e. when varying strength is due to varying atomic volume of the series.

On the other hand, when the varying strength is due to the varying charge of a series of elements,

e.g. P^{+5}, S^{+6}, Cl^{+7} and P^{-3}, S^{-2}, Cl^{-1}

the direction of increasing acidic strength is the same for the hydroxides as for the hydrides. In the given example the strength increases from P to Cl both in the acidic hydroxides in the first series and in the acidic hydrides in the second.

In other words, the directions of increasing acidic strength for hydroxides and hydrides are the same in a row of the periodic table, but different in a column or equivalential.

It is ambiguous to compare the acidic character of two elements unless it is specified whether the acidity refers to a hydroxide or to a hydride.

CHAPTER X.

HYDRATION AND HYDROLYSIS AND THEIR AMMONIA ANALOGUES.

WE have seen that we can compare a series of hydroxides of different atoms M of the general formula $M^{+x}(OH)_x^{-1}$ and observe how the H^{+1} becomes more detachable as x increases or as the volume of M diminishes. Further, when M remains the same atom and x increases we find that H^{+1} becomes more detachable.

Similarly, we can compare a series of salts $M^{+x}Z_x^{-1}$ for **hydrate formation and for hydrolysis.**

Suppose that water is attached to M^{+x} by means of the O^{-2} atom, a stray field holding the two together.

Consider for simplicity only one molecule of water and study $M^{+x}(O^{-2}H_2^{+1})Z_x^{-1}$.

Observe the changes that take place with increasing x.

At first if x is small, the binding power of M^{+x} may not be great enough to give a stable hydrate.

As x increases, however, the formation of stable crystalline hydrates or hydrated ions becomes possible.

As x increases further the repulsive force of M^{+x} upon H^{+1} becomes felt so that one of the H^{+1} radicals in OH_2 may be split off leaving OH behind and joining one Z^{-1} to form HZ. Thus, we may have—

$$M^{+x}(O^{-2}H^{+1})Z_{x-1}^{-1} + HZ.$$

In other words, hydrolysis ensues.

As x increases the repulsive force of M^{+x} upon the second H^{+1} appears and we obtain—

$$M^{+x}(OH)Z^{-1}_{x-1} \rightarrow M^{+x}O^{-2}Z^{-1}_{x-2} + HZ.$$

The successive steps with increasing x would be—

$M^{+x}Z^{-1}_x$.	
$M^{+x}(O^{-2}H^{+1}_2)Z^{-1}_x$	stable crystalline hydrate or hydrated cation.
$M^{+x}(OH)Z^{-1}_{x-1} + HZ$	hydrolysis.
$M^{+x}O^{-2}Z^{-1}_{x-2} + HZ$	hydrolysis.

Ammonia Analogues of Hydration and Hydrolysis.

We can compare a series of salts for the ammonia analogues of hydration and hydrolysis.

Suppose that ammonia is attached to M^{+x} by means of the N^{-3} atom.

Consider for simplicity only one molecule of ammonia and study—

$$M^{+x}(N^{-3}H^{+1}_3)Z^{-1}_x.$$

Observe the changes that take place with increasing x.

At first when x is small, the binding power of M^{+x} may not be great enough to give a stable **ammine.**

As x increases, however, the formation of stable crystalline ammines or ammoniated ions becomes possible.

As x increases further the repulsive force of M^{+x} becomes felt so that one of the H^{+1} radicals in NH_3 may be split off leaving NH_2 behind and joining one Z^{-1} to form HZ. Thus we have—

$$M^{+x}NH_3Z^{-1}_x \rightarrow M^{+x}NH_2Z^{-1}_{x-1} + HZ.$$

As x increases further the repulsive force of M^{+x} on a second H^{+1} appears so that we obtain—

$$M^{+x}NH_2Z_{x-1}^{1} \rightarrow M^{+x}NHZ_{x-2}^{-1} + HZ.$$

When the increase of x proceeds further, the third H^{+1} of NH_3 may be split off and there arises—

$$M^{+x}NHZ_{x-2}^{1} \rightarrow M^{+x}NZ_{x-3}^{1} + HZ.$$

Thus we have the following successive steps with increasing x;—

$$M^{+x}Z_x^{1}.$$
$$M^{+x}NH_3Z_x^{-1}.$$
$$M^{+x}NH_2Z_{x-1}^{-1} + HZ.$$
$$M^{+x}NHZ_{x-2}^{1} + HZ.$$
$$M^{+x}NZ_{x-3}^{1} + HZ.$$

We can obtain these transitions both for H_2O and for NH_3 when we pass along a row of the periodic table from left to right.

Whether we are dealing with the action of water or of ammonia, we obtain a similar series of steps, when we study a series of values of M^{+x} in which x remains constant but the volume of M diminishes.

We can obtain the latter transitions both for H_2O and and NH_3 if we pass up a column of the periodic table (old form), or up an equivalential in the new form.

We should also, of course, see the transitions due to change of charge, if we adhere to the same atom but change its valency.

Hydration and its Ammonia Analogue.

The trebly charged negative N^{-3} should be held more firmly by the M^{+x} than the doubly charged negative O^{-2}. Thus in a series of values of M^{+x} with increasing x (or in a series with constant x and diminishing atomic volume) the ammonia analogue of hydration should set in at least as early in the series as hydration if not before, and for the same values of M^{+x} ammoniates should be more stable than hydrates.

Thus if hydrates are known for a salt it should be possible to obtain ammoniates also. There are, however, several instances where crystalline ammoniates corresponding to known crystalline hydrates have not been observed hitherto, probably because the correct conditions for their preparation have not been found. But in certain cases where solid ammines are wanting there is evidence for the existence of ammines in solution.

The firmness with which the NH_3 molecules are held by the metallic atom in the ammines of metallic salts explains the remarkable stability of these compounds. This great stability led chemists at a comparatively early date to devote considerable attention to these compounds and allowed their constitution to be accurately studied.

Hydrolysis and its Ammonia Analogue.

If we assume that the grip of the H^{+1} on the N^{-3} in NH_3 is always firmer than that of the H^{+1} on the O^{-2} in H_2O and that both grips become weaker with increasing valency of the central atom (i.e. with increasing x in M^{+x}) or with diminishing volume of M (when x is constant), then hydrolysis should succeed hydration at an earlier point in the series than that at which ammoniolysis succeeds ammoniation.

These conclusions agree with the facts.

Examples of Hydration, Hydrolysis, and their Ammonia Analogues.

	NaCl	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_5	$(NoSCl_6)$
Hydration .	None at ordinary temperature	$MgCl_26H_2O$ Ordinary temperature	$AlCl_36H_2O$	None	None	
Hydrolysis .	None	None	On heating above hydrate	HCl and $Si(OH)_4$	HCl and $POCl_3$ or HCl and H_3PO_4	
Ammoniation	None (Slight in solution)	None	$AlCl_36NH_3$ Ordinary temperature	$SiCl_46NH_3$	PCl_58NH_3 In cold	
Ammoniolysis	None	None	None	$Si(NH_2)_4$ Heating $Si(NH)_2$	$PCl_3(NH_2)_2$	
	Cu^{ous} chloride	Cu^{ic}		Co^{ous}	Co^{ic}	
Hydration .	None	$CuCl_22H_2O$		$CoCl_26H_2O$ Easily loses water	Single Co^{ic} salts unstable	
Ammoniation	$Cu_2Cl_2(NH_3)_2$	$Cu(NH_3)_4Cl_2$		Ammines lose NH_3 at ordinary temperature	Ammines quite stable	
	$BaCl_2$	$SrCl_2$	$CaCl_2$	$MgCl_2$	$BeCl_2$	
Hydration .	$2H_2O$	$6H_2O$	$6H_2O$	$6H_2O$	$4H_2O$	
Hydrolysis .	None	None	None	None	$Be(OH)_2$ and HCl	

Hydration of Ions.

In estimations of molecular weights by the freezing point method, it has been found in certain cases that a result agreeing more closely with theory is obtained if account is taken of the presence of hydration in the solute. There is then, of course, less free water and therefore a higher solute concentration.

Again, in transport number measurements it is usual to assume that no water migrates; if, however, the ions are hydrated, there will be concentration changes at the electrodes due to the transport of water, the ions and a certain amount of water migrating together. It is the custom to measure the weight of salt per 100 grams (say) of water, in the neighbourhood of the electrodes, before and after the passage of electricity; if the ions are hydrated, this method is not available. If, however, there is added a substance such as sugar which will not migrate, then the weight of salt and of water also, per 100 grams (say) of sugar, can be measured and thus the migration both of salt and of water can be obtained, and hence the amount of hydration estimated.

In this way it has been found that the extent of hydration for the ions Cs^{+1}, K^{+1}, Na^{+1}, Li^{+1} increases in passing along the list being greatest for Li which has the smallest volume, this being in agreement with our theory.

Apart from hydration, we should expect the ionic mobilities to increase towards the Li end of the list, i.e. with decreasing volume and mass, whereas the reverse is the case; this apparent discrepancy is explained by the hydration just mentioned.

Comparison of the Action of Water and that of Ammonia.

Action of Ammonia on $PtCl_4$.—In $PtCl_4$ there are two vacant co-ordination positions. The first two NH_3 molecules occupy the two vacant places and thus obtain a position close to Pt. Neither of them has to force its way between the Pt atom and a Cl atom, and so do not change the linking of the Cl atoms to the Pt atom. However, for every additional NH_3 molecule added (beyond the first two) one Cl atom becomes capable of dissociation, i.e. responds to the usual ion reactions. The NH_3 molecule forces its way between Pt and one Cl. N^{-3} proves the stronger in competing with Cl^{-1} for attachment to Pt. Similarly,

$$NH_3 + HCl = NH_4^{+1} + Cl^{-1}.$$

Action of water on $PtCl_4$.—Similarly N^{-3} is superior to O^{-2}. *Only two molecules of water can be added to $PtCl_4$.* These occupy the two vacant positions. A third water molecule would have to force its way between Pt^{+4} and a Cl^{-1} atom and this it cannot do.

In $2H_2OPtCl_4$ the H^{+1} atoms are loosely held so that this substance behaves like an acid.

Comparison of the behaviour of H_2O and NH_3 when present together in the same molecule, i.e. in aquoammine metallic salts. For example, of $(Co(NH_3)_6)X_3$, $(CoCl(NH_3)_5)X_2$ and $(CoOH_2(NH_3)_5)X_3$ only the last shows an acid reaction.

Hydrated and ammoniated ions (present chapter) and multiplex ions (chapter XII) are sometimes called complex ions. It has been thought well, however, to reserve special chapters for these types. In all of these, as in the complex ions described in chapter XI, we have to consider the clustering capacity of a kernel atom. In hydrates and ammoniates or ammines there is generally a cluster of water or ammonia molecules round a kernel atom. As the present discussion shows, the formation of this cluster may be facilitated or made possible by reducing the volume or increasing the charge of the kernel atom.

The region of stability for ammoniates or ammines extends to higher valencies of the kernel atom than for hydrates (see page 85). Of the hexahydrates given by Werner the greater number are with kernels of valency +2, a much smaller number are with kernels of valency +3. On the other hand, whilst a number of hexammoniates or hexammines are known with kernel-valency +2, the best investigated are with kernel-valency +3, such as $(M^{+3}(NH_3)_6)Z_3$, and, further, there are well defined hexammines with kernel-valency +4, such as are obtained with Pt^{+4}. However, with some kernels of valency +4 processes set in with ammonia analogous to hydrolysis. Thus, neither hydrolysis nor ammoniolysis is observed with $PtCl_4$; both are obtained with $SiCl_4$.

CHAPTER XI.

FORMATION OF COMPLEX IONS.

Complex Anions.

To illustrate the formation of complex anions, consider the case of $H_2^{+1}O^{-2}$ and $S^{+6}O_3^{-2}$, which interact to form $2H^{+1}$ and $(SO_4)^{-2}$.

Here two types of positively charged atoms compete to have the negatively charged oxygen atoms grouped round them : the hydrogen atoms each with one positive charge and the sulphur atom with six positive charges. On account of the much larger charge in S^{+6}, the contested O^{-2} atoms tend to gather round the S^{+6}, the appearance of the group, when represented in a plane, being as follows :—

$$\begin{array}{ccc} O^{-2} & & O^{-2} \\ & S^{+6} & \\ O^{-2} & & O^{-2}. \end{array}$$

More likely, however, the cluster of O^{-2} atoms is arranged in space at the corners of a tetrahedron.

The group formed is stable though it has a surplus charge of $-8 +6$ or -2. This stable group forms the ion $(SO_4)^{-2}$. The two competing H^{+1} atoms are kept outside this group.

Again, $H^{+1}F^{-1}$ interacts with $B^{+3}F_3^{-1}$ to form H^{+1} and $(BF_4)^{-1}$. Here the competing atoms are H^{+1} and

B^{+3}, of which B^{+3} forms the stronger electric field and therefore gathers round it the contested F^{-1} atoms giving $(BF_4)^{-1}$ which is a stable group though not neutral. The other competing atom lies outside this group.

Complex Cations.

To illustrate the formation of complex cations, consider the interaction of $H_3^{+1}N^{-3}$ with $H^{+1}Cl^{-1}$ to form $(NH_4)^{+1}$ and Cl^{-1}. Here the competing atoms are N^{-3} and Cl^{-1} and there are four contested H^{+1} atoms. Of the competing atoms the one round which there is the strongest electric field (i.e. N^{-3}) will gather round it the four contested atoms, forming $(NH_4)^{+1}$ and the competing atom, Cl^{-1}, will be kept outside this group.

In a complex anion, therefore, *there is a positively charged atom acting as a kernel round which is clustered a group of negatively charged atoms ; and in a complex cation there is a negatively charged atom acting as a kernel round which is clustered a group of positively charged atoms. As the simple positive ion is commoner than the simple negative, the complex anion is commoner than the complex cation.*

The clustering capacity of the kernel atom of a complex ion depends upon its volume being smaller or its charge being larger than those of the competing atom. If, for any two competing atoms, there is not a sufficient difference between the volumes or the charges, then a complex will not be formed.

The clustering capacity of the kernel atom also depends upon the nature of the contested atoms to be clustered.

The entering of $M_y^{+x}Z_x^{-y}$ into a complex anion is hindered by hydrolysis of $M_y^{+x}Z_x^{-y}$. Hydrolysis will be increased by weakening of the base $M(OH)_x$ or by weakening of the acid H_yZ. These changes will be brought about by diminishing the volumes or increasing the charges of M and Z. These changes have, therefore, the secondary effects of diminishing the clustering capacity of M.

On the other hand, the diminution of the volumes or the increase of the charges of M and Z has the primary effect of increasing the clustering capacity of M, and also the effect of diminishing the ionisation of $M_y^{+x}Z_x^{-y}$, and thus further assisting the entering of this salt into a complex anion.

In a series of atoms M, the primary effect may not be seen at all until the diminution of volume or increase of charge has reached a certain figure, after which there may be a rise to a maximum followed by a falling off in clustering capacity due to the opposing secondary effect. Thus *for any series of atoms M of diminishing volume or increasing charge there is a certain* **optimum point** *for complex anion formation.* The position of this point will vary with the nature of Z. Above or below this point the tendency to complex anion formation diminishes.

Similarly, for a series of atoms Z of diminishing volume or increasing charge, there is a certain optimum point for complex anion formation, which depends upon the nature of the kernel atom M.

In the series $I^{-1} \rightarrow Br^{-1} \rightarrow Cl^{-1} \rightarrow F^{-1}$ we have falling volume, and the capacity to be clustered falls from I^{-1} to Cl^{-1} (due to the secondary effect masking the primary), and rises again at F^{-1} (due to the interionic affinity being so great in fluorides as to mask the secondary effect).

In the series: $BeCl_2$, $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$, where the atomic volumes run

$$Be < Mg < Ca < Sr < Ba$$

$MgCl_2$ is the only compound that forms a double chloride.

The optimum point may in some cases be at the end of the series, as in BeF_2, MgF_2, CaF_2, SrF_2, BaF_2, for double fluorides, and in BeO, MgO, CaO, SrO, BaO, for double oxides, where it is at Be.

Similarly, we find an optimum point or range for double oxides and double sulphides, the point for double sulphides being farther up, towards the positive end than for oxides.

Thus in	N	P	As	Sb	Bi
Double oxides	×	×	×	×	no oxy-salt
Double sulphides:	none	slight	×	×	×

The formations are at the points marked by crosses.

$Bi(OH)_3$ is not soluble in NaOH, and Bi_2S_3 is somewhat soluble in Na_2S although not in NaOH.

Oxides are poorly ionised, although O may be regarded as lying between F and Cl in the electronegative scale. This is because the interionic force in the oxides is great. Thus double oxides are common: oxyacids and oxysalts. The poorly dissociated oxide readily forms part of the complex anion.

Sulphides are not well dissociated but rather better than the corresponding oxides. Thus, double sulphides (sulpho-analogues of oxyacids and oxysalts) are formed but not so readily as double oxides. The tendency to be clustered in a complex anion is exceedingly slight with Se^{-2}, and is practically absent with Te^{-2}.

The optimum range in the above series may be put at N and P for double oxides and at As and Sb for double sulphides.

We are supposing that, when a compound is formed between two salts of the same anion, a complex anion is formed in every case, whether there is formed a "double salt" in which the kernel positive ion shows its original chemical properties in aqueous solutions, or there is formed a "complex salt" in the aqueous solutions of which the original chemical properties of the positive kernel ion no longer appear.

The "double salt" and the "complex salt" are two extreme types of a molecular compound formed between two salts. In some cases it may be difficult to place the molecular compound in one of these categories rather than in the other. In any case, however, the rules that we find to hold for the stability of molecular compounds between two salts will be applicable whether we agree to the presence of a complex anion in a "double salt" or not.

Examples of the Formation of Complex Anions.

Since the co-ordination number seldom exceeds 6, the highest positive valency to be expected in the kernel atom of the complex anion is 5, with univalent contested anions. With higher valencies in the contested anions, higher valencies would be obtained in the kernel.

Competing cations.	*Contested anions, or anions to be clustered.*	*Compounds formed.*	*Remarks.*
Cs^{+1} and Sb^{+5}	Cl^{-1}	$CsSbCl_6$	The difference between the competing ions is greatest for Cs and Sb and least for Na and Sb, therefore the Cs salt should be the most stable. Vols. are as Cs > K > Na.
K^{+1} and Sb^{+5}	Cl^{-1}	$KSbCl_6$	
Na^{+1} and Sb^{+5}	Cl^{-1}	$NaSbCl_6$	
R^{+1} and Pt^{+4}	Cl^{-1}	R_2PtCl_6	Co-ordination number 6.
R^{+1} and Pt^{+4}	Br^{-1}	R_2PtBr_6	
R^{+1} and Ir^{+4}	Cl^{-1}	R_2IrCl_6	
R^{+1} and Si^{+4}	F^{-1}	R_2SiF_6	
R^{+1} and Sn^{+4}	Cl^{-1}	R_2SnCl_6	
R^{+1} and Fe^{+3}	F^{-1}	R_3FeF_6	
Na^{+1} and Al	F^{-1}	Na_3AlF_6	Cryolite.
K^{+1} and Au^{+3}	Cl^{-1}	$KAuCl_4$	Co ordination number 4.
K^{+1} and Cd^{+2}	Cl^{-1}	K_4CdCl_6	
K^{+1} and Cu^{+2}	Cl^{-1}	$KCuCl_3$	Co-ordination number 3.
K^{+1} and Cu^{+2}	F^{-1}	$KCuF_3$	
K^{+1} and Mg^{+2}	Cl^{-1}	$KMgCl_3$	Carnallite. Double fluorides of Mg also known.
K^{+1} and Cu^{+1}	Cl^{-1}	K_2CuCl_3	In these two cases the difference of field density in the competing atoms is due to difference of atomic volumes which runs.— Cu < K and Ag < Cs.
Cs^{+1} and Ag^{+1}	Cl^{-1}	Cs_2AgCl_3	
Fe^{+2} and S^{+4}	O^{-2}	$FeSO_3 3H_2O$	
Fe^{+3} and S^{+4}	O^{-2}	none	Difference between cationic field densities not sufficiently great.
Fe^{+2} and S^{+6}	O^{-2}	$FeSO_4 7H_2O$	
Fe^{+3} and S^{+6}	O^{-2}	$Fe_2(SO_4)_3$	Not so stable as ferrous sulphate; basic salts tend to be formed. Cationic difference not so great as in ferrous salt.
Fe^{+2} and C^{+4}	O^{-2}	$FeCO_3H_2O$	
Fe^{+3} and C^{+4}	O^{-2}	none	Cationic difference not enough. Compare Fe^{+3}, S^{+4} and O^{--2}.
Fe^{+2} and N^{+5}	O^{-2}	$Fe(NO_3)_2$	
Fe^{+3} and N^{+5}	O^{-2}	$Fe(NO_3)_3$	

Competing cations.	*Contested anions, or anions to be clustered.*	*Compounds formed.*	*Remarks.*
Fe^{+2} and P^{+5}	O^{-2}	$Fe_3(PO_4)_2$	
Fe^{+3} and P^{+5}	O^{-2}	$FePO_4$	
Na^{+1} and C^{+4}	O^{-2}	Na_2CO_3	Not dissociated by heat.
H^{+1} and C^{+4}	O^{-2}	H_2CO_3	Cationic difference not enough to prevent dissociation by heat. (Vol. of H^{+1} too small).
Ca^{+2} and C^{+4}	O^{-2}	$CaCO_3$	Cationic difference not enough to prevent dissociation by heat.
Ba^{+2} and C^{+4}	O^{-2}	$BaCO_3$	Substitution of Ba for Ca (Ba vol. greater than Ca vol.) increases cationic difference and dissociation by heat becomes impracticable. In most carbonates the cationic difference is not enough to prevent dissociation by heat.
Tl^{+1} and Tl^{+3}	Cl	Tl_3TlCl_6	Compare Na_3AlF_6.
Pb^{+2} and Pb^{+4}	O^{-2}	Pb_2PbO_4 $PbPbO_3$	Otherwise Pb_3O_4. Analogous to Na_2PbO_3.
Fe^{+2} and Fe^{+3}	O^{-2}	$FeFe_2O_4$	Compare spinel $MgAl_2O_4$, crystal struct. the same.
H^{+1} and N^{+3}	O^{-2}	HNO_2	Reduced by HI.
H^{+1} and N^{+5}	O^{-2}	HNO_3	Not reduced by HI. In dilute solution.
H^{+1} and S^{+4}	O^{-2}	H_2SO_3	Reduced by Zn and HCl.
H^{+1} and S^{+6}	O^{-2}	H_2SO_4	Not reduced by Zn and HCl.
K^{+1} and Cl^{+1}	O^{-2}	$KClO$	Reduced by As_2O_3 and by cold dil. HCl.
K^{+1} and Cl^{+5}	O^{-2}	$KClO_3$	Not reduced by As_2O_3 and partially by cold dil. HCl. Reduced by hot more conc. HCl and by $FeSO_4$.
K^{+1} and Cl^{+7}	O^{-2}	$KClO_4$	Not reduced by above conc. HCl nor by $FeSO_4$.

Some Complexes and Ammines obtained in Analytical Work.

$(NH_4)_2Pb^{+2}(SO_4)_2$ formed when $PbSO_4$ is dissolved in ammonium acetate.

$K_3Co^{+3}(NO_2)_6$ a yellow precipitate from a solution of a Co^{+2} salt containing acetic acid, when KNO_2 is added. Note that Co^{+2} has been oxidised to Co^{+3} which is the kernel.

Co^{+3} has a greater tendency to act as a kernel than Co^{+2}, as is seen in the complex cyanides of cobalt and in the cobaltammines.

There is no corresponding nitrite precipitate with Ni salts. Thus this reaction is used to test for Co in the presence of Ni. Another application is in a test for K, a solution of $Na_3Co^{+3}(NO_2)_6$ being the reagent.

An aqueous solution of ammonia contains NH_3 and NH_4OH.

1. The precipitation of the hydroxide of a metal by this solution will be prevented if NH_4Cl is present and forms with the metallic atom a complex chloride of the type $(NH_4)_2M^{+2}Cl_4$. This happens with Fe^{+2}, Co^{+2}, Mn^{+2}, and Mg^{+2}. Before iron is tested for, with NH_4OH, the solution is oxidised so that Fe^{+3} is present which is precipitated.

Co^{+2} gives a yellow solution of $(NH_4)_2Co^{+2}Cl_4$ which changes to red on exposure to air, owing to the greater tendency for Co^{+3} to become a kernel.

2. The precipitation of a metal as hydroxide by an aqueous solution of ammonia will also be prevented if the NH_3 present forms a soluble ammine with the salt of the metal. This happens with Ni^{+2} and Zn^{+2}, from

which the cations $(NiAm_4)^{+2}$ and $(ZnAm_4)^{+2}$ are formed, where Am is NH_3.

If NH_4Cl were not present, an aqueous solution of ammonia would give with Co^{+2} a precipitate of $Co(OH)_2$ which slowly goes into solution, the cation $(CoAm_6)^{+3}$ being formed. Here, again, is seen the greater tendency of Co^{+3} to act as a kernel.

If there is excess of ammonia, in the precipitation of the iron group, then the soluble ammine $Cr^{+3}Am_6(OH)_3$ is got, so that some Cr goes to form a violet solution.

$(AgAm_2)^{+1}$ is obtained in Analytical Group I. when AgCl is dissolved in ammonia solution.

$(CuAm_4)^{+2}$ giving a deep blue solution and $(CdAm_6)^{+2}$ giving a colourless solution are obtained in Analytical Group II.

Ammoniolysis is obtained with HgCl, in Group I., thus: $NH_3 + 2HgCl = NH_3Hg_2Cl_2 + Hg =$
$NH_2HgCl + HCl + Hg$.

Ammoniolysis is also the essential change in Nessler's reaction:

$$NH_3 + 2HgI_2 = NH_3 . 2HgI_2 = NHg_2I + 3HI.$$

The precipitate obtained may be regarded as a hydrate of NHg_2I.

In general, when the precipitate obtained with a reagent is soluble in excess of that reagent, a soluble complex or a soluble ammine is formed.

For complex cyanides in analysis, see the special section on these substances.

Langmuir represents complex anions such as $(SO_4)^{-2}$ and $(NO_3)^{-1}$ by the co-valency method.

Complex Cations. The -onium Compounds.

In the series N, P, As, Sb, and Bi we have, NH_3 and $(NH_4)^{+1}$; PH_3 and $(PH_4)^{+1}$, the fourth H of which is not so firmly held as in $(NH_4)^{+1}$.

Acidic properties begin to appear in AsH_3, which cannot function as a base in aqueous solution, nor of course can SbH_3 and BiH_3, the last of which is difficult to prepare.

We, however, have the alkylated cations

$$(NR_4)^{+1},\ (PR_4)^{+1},\ (AsR_4)^{+1} \text{ and } (SbR_4)^{+1}.$$

Similarly we have

Oxonium compounds, OR_3X, e.g. $O(CH_3)_2HCl$ corresponding to $OH_2 . HX$.

Sulphonium compounds, SR_3X corresponding to $SH_2 . HX$.

Selenonium compounds, SeR_3X corresponding to $SeH_2 . HX$, and

Iodonium compounds, IR_2X, e.g. $I(C_6H_5)_2OH$ corresponding to $IH . HX$.

Substitution of an alkyl for H increases the tendency to form -onium compounds.

The central atom (kernel) of the complex cation in an -onium compound must be negative and only moderately so, just as the kernel atom of a complex anion must be positive and only moderately. Thus, we do not have K^{+1} forming the kernel atom of a complex anion; similarly, we have I^{-1} but not F^{-1}, Cl^{-1} or Br^{-1} forming the kernel atom of a complex cation. Again, sulphonium compounds are more stable than the corresponding oxonium substances because O^{-2} is a little too negative.

Valency of the central atom of an -onium group :—

We are regarding the valency as negative :—
-1 for I, -2 for O, S, and Se, -3 for N, P, As, and Sb; whereas, according to an older theory, the assigned valencies were
3 for I, 4 for O, S, and Se, and 5 for N, P, As, and Sb.

A comparison of the degrees of dissociation of the bases is obtained from the molecular conductivities.

Mol. Conductivity at Various Dilutions.

(v = Dilution in litres.)

v =	16	64	256
$(CH_3)_4NOH$	219	226	228
$(CH_3)_4POH$	214	221	223
$(CH_3)_4AsOH$	211	216	218
$(CH_3)_4SbOH$	178	181	183
$(C_2H_5)_3SOH$	211	217	222
C_2H_5HgOH	1·2	1·4	1·9
v =	17·3	69·2	276·8
$(CH_3)_3SnOH$	0·4	0·63	1·37

N ^{3}, P ^{3}, As ^{3}, and Sb ^{3} repel OH ^{1} the strength of the repulsion varying thus: N > P > As > Sb.

The above Hg and Sn bases seem to be of quite a different type from the others. Working out the valency as for the others we should have to regard Hg as having valency zero.

It would be better to regard the charges as $+2$ for Hg and $+4$ for Sn. In the Hg and Sn compounds OH ^{1} would then be attracted, instead of repelled

CHAPTER XII.

MULTIPLEX ANIONS AND MULTIPLEX CATIONS.

Multiplex Anions.

A HYDROXIDE may be conceived as essentially a mixed oxide formed by the union of water molecules with molecules of another oxide.

An increase in the acidic character of the hydroxide may be produced

1. either by increasing the valency of the positive element in the other oxide,

2. or by increasing the number of the other oxide molecules per water molecule.

Examples: The relation of permanganic acid to manganic acid is not the same as that of dichromic acid to chromic acid.

1. In passing from H_2MnO_4 or $H_2O . MnO_3$
to $HMnO_4$ or $H_2O . Mn_2O_7$
the acidity is increased by raising the positive valency of Mn from 6 to 7.

2. In passing from H_2CrO_4 or $H_2O . CrO_3$
to $H_2Cr_2O_7$ or $H_2O . 2CrO_3$
the acidity is increased by increasing the number of CrO_3 molecules per water molecule or by increasing the **multiplexity** of the negative radical.

Thus where there is low valency of the kernel atom but *high multiplexity, the acidity may be comparable with some other case where there is high valency but low multiplexity.*

In the series

$H_2O . CrO_3$, $H_2O . 2CrO_3$, $H_2O . 3CrO_3$, $H_2O . 4CrO_3$,

as the multiplexity of the negative radical increases, i.e. as the number of Cr atoms in the molecule increases, the number of O atoms per Cr atom decreases. Therefore the O atoms become more firmly attached and the substance becomes less basic.

As the number of the Cr atoms increases the repulsive force on the two H atoms increases and the substance becomes more acidic.

Thus $H_2O . CrO_3$ is *basic* (seen in CrO_2Cl_2) and *acidic* (seen in K_2CrO_4)
$H_2O . 2CrO_3$ is only *acidic* (seen in $K_2Cr_2O_7$)
$H_2O . 3CrO_3$ is only *acidic* (seen in $K_2Cr_3O_{10}$)
$H_2O . 4CrO_3$ is only *acidic* (seen in $K_2Cr_4O_{13}$)

In passing down a column of the periodic table (old form) or down an equivalential (new form) we find that the basic character of the hydroxides (for corresponding valencies) increases. Therefore, the same degree of multiplexity will correspond to less acidity at the foot of the column or equivalential than at the top. In accordance with this, we find that although we have monochromates, monomolybdates, and monotungstates we have no monouranates. In the case of the hydrates of UO_3, the acidic character does not appear until the degree of multiplexity corresponding to dichromates is reached. Corresponding to $H_2O . CrO_3$ there are the important uranyl salts :—

UO_2Cl_2, $UO_2(NO_3)_2 6H_2O$, UO_2S, $UO_2SO_4 3H_2O$, etc.

and no monouranates, whilst corresponding to $H_2O . 2CrO_3$ there are diuranates, $K_2U_2O_7$, etc., but no salts containing oxybasic uranium radicals.

The radical UO_2 is more basic than the corresponding CrO_2, MoO_2, and WO_2. The stability of the dichlorides is in the order :—

$$UO_2Cl_2 > WO_2Cl_2 > MoO_2Cl_2 > CrO_2Cl_2$$

CrO_2Cl_2 is easily decomposed by water :—

$$CrO_2Cl_2 + 2H_2O = H_2CrO_4 + 2HCl$$

MoO_2Cl_2 and WO_2Cl_2 are not easily acted on by water.

UO_2Cl_2 withstands high temperature without decomposition and is not acted on by water.

CrO_2 resembles the oxy radicals in so-called acid chlorides, such as SO_2 in sulphuryl chloride, SO_2Cl_2, or PO in phosphoryl chloride, $POCl_3$. UO_2 on the other hand behaves as if it were a single metallic divalent atom. On electrolysis of uranyl salts, the group UO_2 migrates towards the cathode.

It was long supposed that the dioxide UO_2 was the free metal, and that the trioxide was a compound of one atom of the metal with one atom of oxygen.

In the case of an element like Cr, which for the valency concerned readily gives acidic hydroxides, the compounds with the basic oxy radicals (e.g. CrO_2Cl_2) must be prepared in the absence of water, otherwise the corresponding acids are got (e.g. $CrO_2(OH)_2$ and HCl would be got, even if CrO_2Cl_2 were primarily formed.)

When acidity appears with a certain degree of multiplexity, this does not mean that acidity is precluded with a higher degree. In fact, there may be a great variety in the degrees of multiplexity, such as is displayed, for example, with Mo and W each of which gives salts of about seven different types of multiplexity and in addition salts containing mixed multiplexes, of which the well-known phosphomolybdate is an example. With Cr there is a less variety of multiplexes and with U there is only one type.

The influence of multiplexing (or rather sub-multiplexing) appears with Cr_2O_3 also

$Cr_2O_3 3H_2O$ is *basic* (seen in $CrCl_3$, etc.).
$Cr_2O_3 2H_2O$ is *basic* (seen in Cr_2OCl_4).
$Cr_2O_3 H_2O$ is *acidic* (seen in $Zn(CrO_2)_2$, etc.).

Multiplexing appears with sulphates and tellurates, but not with selenates.

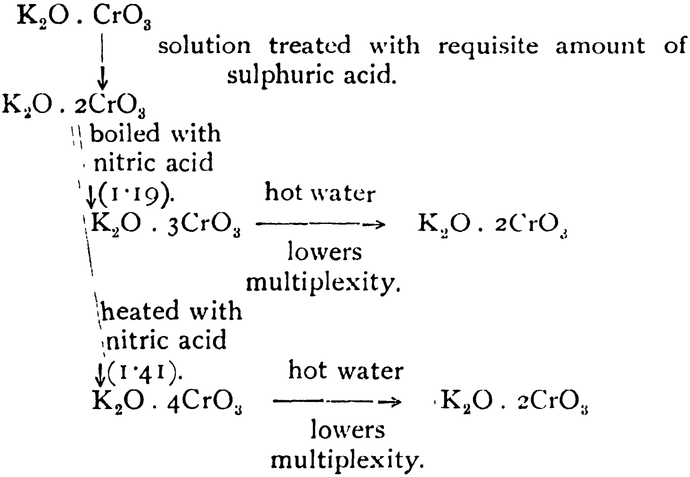
It also appears in sulphites and tellurites, in which the variety is greater than in sulphites, but is not seen in selenites except in the form of partial neutralisation. Here we have an instance of **secondary periodicity.**

The hydroxides from R_2O_5 show the following basic and acidic properties where R is one of the list As, Sb, Bi, V, Nb, Ta.—

Mols. R_2O_5 · Mols. H_2O	As	Sb	Bi	V	Nb	Ta
1 . 5	basic	basic	—	basic	basic	basic
1 · 3	acidic	acidic	—	basic and acidic	basic	basic slightly
1 . 2	acidic	acidic	—	acidic	acidic	—
2 . 3	—	—	—	—	acidic	—
3 : 4	—	—	—	—	acidic	acidic
1 : 1	acidic	acidic	acidic slight	acidic	acidic	acidic
3 : 2	—	—	—	acidic	—	acidic
2 : 1	—	—	—	acidic	acidic	acidic
3 : 1	—	—	—	—	—	acidic

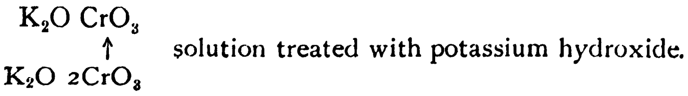
Whilst by multiplexing a better balance may be established between the positive and the negative side of the molecular compound, and there may in some cases be several multiplexes, there will always be a limit to the multiplexing otherwise the balance will be disturbed in the opposite direction. This restriction appears to a greater extent in some salts than in others.

Raising Multiplexity by Adding Acid.



CrO_3 formed by the action of strong sulphuric acid on the chromates.

Lowering Multiplexity by Adding Base.



A salt obtained by partial neutralisation of a polybasic acid is to be placed in the same category as a salt obtained by multiplexing.

Thus $NaHSO_4$, which may be written $Na_2O . 2SO_3 . H_2O$ or $Na_2S_2O_7 . H_2O$, is a hydrated multiplex.

Again, Na_2HPO_4, which may be written $2Na_2O . P_2O_5 . H_2O$ or $Na_4P_2O_7H_2O$, is a hydrated multiplex.

Both Na_2HPO_4 and $Na_4P_2O_7$ may be regarded as in a higher state of multiplexity than the normal salt Na_3PO_4 which is $3Na_2O\ P_2O_5$.

Accordingly the tendency towards partial neutralisation and the tendency towards multiplexing are associated properties.

The kernel cation of a complex anion may, then, be of so weak clustering capacity, that it is only by **multiplexing** *that it can prevail against the competing cation.*

On the other hand, the clustering capacity of the kernel cation may be so strong that it can prevail against several competing cations. We then have the **reverse of multiplexing**, *or what may be called the forming of a* **submultiplex.** The clustering capacity is greater the greater the difference between the charges in the competing cations, so that if this difference is increased the tendency towards formation of sub-multiplexes is increased. For example, with the competing cations M^{+1} and I^{+5} and the contested anion O^{-2}, that is, with iodates there are no submultiplexes, but with M^{+1}, I^{+7} and O^{-2}, that is with periodates there are several. We have

$M_2O + I_2O_7$	$M_2I_2O_8$ or MIO_4.
$2M_2O + I_2O_7$	$M_4I_2O_9$.
$3M_2O + I_2O_7$	$M_6I_2O_{10}$ or M_3IO_5.
$4M_2O + I_2O_7$	$M_8I_2O_{11}$ appears not to be definite compound.
$5M_2O + I_2O_7$	$M_{10}I_2O_{12}$ or M_5IO_6.

Partial neutralisation, which is the equivalent of multiplexing, is seen in KIO_3 but not in $KBrO_3$ nor in $KClO_3$. Thus we have KIO_3HIO_3 and KIO_32HIO_3 but no corresponding compounds with $KBrO_3$ and $KClO_3$, in agreement with the fact that the clustering capacity of the kernel weakens in the direction: $Cl^{+5} \rightarrow Br^{+5} \rightarrow I^{+5}$.

Another illustration is seen in the very common multiplexing among silicates.

Multiplex Cations.

When molecules of ammonia unite with those of another hydride to form a molecular compound, the clustering capacity of the N^{-3} is greater the greater the difference between it and the other competing anion. When this difference is reduced, the formation of a molecular compound should be made possible or facilitated by raising the ratio of the number of ammonia molecules to the number of molecules of the other hydride, i.e. by multiplexing.

Complex cations are not so numerous as complex anions, so that it is not so easy to illustrate the principles with cations. Any apparent exceptions are probably due to the data being incomplete.

Multiplexing with NH_3.

Mols. NH_3 to Mols. other hydride.

Other Hydride.		
HF	1 : 2	
	1 : 1	
HCl	1 : 1	
	4 : 1	low temperature.
	7 : 1	low temperature.

Other Hydride.		
HBr	1 : 1	
	2 : 1	low temperature.
	4 : 1	low temperature.
	7 : 1	low temperature.
HI	1 : 1	
H_2S	1 : 1	
	2 : 1	
	6 : 1	
H_2SO_4	1 : 1	
	3 : 2	
	2 : 1	
H_3PO_4	1 : 1	
	2 : 1	
	3 : 1	passes readily to 2 : 1.

Multiplexing with PH_3.

Mols. PH_3 to Mols. other hydride.

HCl	1 : 1	
HBr	1 : 1	
H_2SO_4	2 : 1	(never 1 : 1, anionic difference not enough).

Multiplexing with Hydrazine.

Two forms are known in the solid state :—

$N_2H_4 2HZ$ and N_2H_4HZ. N_2H_4HZ is the more stable.

Mols. N_2H_4 : Mols. other hydride.

Other Hydride.		Other Hydride.	
HCl	1 : 2	HNO_3	1 : 2
	1 : 1		1 : 1
HBr	1 : 2	H_2SO_4	1 : 1
	1 : 1		2 : 1
HI	1 : 2		
	1 : 1		

Multiplexing with Hydroxylamine.

Mols. hydroxylamine to Mols. other hydride.

Other Hydride.		
HCl	1 : 1	
	2 : 1	
HBr	1 : 1	
	2 : 1	
HI	1 : 1	formed under exceptional conditions.
	2 : 1	
	3 : 1	
$HClO_4$	1 : 1	
HNO_3	1 : 1	
H_2SO_4	1 : 1	
	2 : 1	
H_3PO_4	3 : 1	corresponding NH_3 compound readily passes to 2 : 1.

In general, the higher multiplexes in the case of NH_3 are the most unstable, and in the case of hydroxylamine the most stable.

Most of the above multiplexes with NH_3, PH_3, hydrazine and hydroxylamine are consistent with the relative strengths of the bases which run thus:

$$NH_3 > PH_3 \text{ ; and } NH_3 > N_2H_4 > NH_2OH.$$

The only anomalies are $NH_3 . 2HF$ and the general form $N_2H_4 . 2HZ$ which, however, is less stable than $N_2H_4 . HZ$.

CHAPTER XIII.

SECONDARY PERIODICITY.

IN passing down an equivalential of the periodic table, it frequently happens that the properties of the elements and their compounds do not vary steadily in one direction but show a fluctuation. There may be a general trend in one direction appearing in passing down from a row to another of the same length, but this very often receives a set-back in passing to another row of greater length.

For example in P, As, Sb,
S, Se, Te,
and Cl, Br, I,

the affinity for oxygen is least for the middle element in each case.

The heats of formation for the oxides of

	S,	Se, and	Te
are for RO_2	78,780,	56,160, and	77,180
and for RO_3	142,410,	76,660, and	98,380.

This fluctuation, however, does not appear in the hydrides:—

the heats of formation for the hydrides of

	S,	Se, and	Te
are	+ 2730,	− 5400, and	− 32000.

Again in	Cl,	Br, and	I
the heats of formation of the hydrides are	22,000,	8440, and	− 6040
and of the acids HXO_3	23,940,	5384, and	43,537.

The following are the oxides and oxyacids of Cl, Br, and I

	Oxides.	Oxyacids.			
Cl	Cl_2O ClO_2, Cl_2O_7.	$HClO$,	$HClO_2$,	$HClO_3$,	$HClO_4$.
Br	no oxides.	$HBrO$,	$HBrO_2$,	$HBrO_3$.	
I	IO_2 or I_2O_4, I_4O_9, I_2O_5	HIO, (In soln.)	—	HIO_3,	$HIO_4 2H_2O$.

The regular change with the hydrides of N, P, As, Sb, and Bi and the fluctuation with the chlorides have already been referred to. There is a similar fluctuation with the heats of formation of the oxides.

In all the above when there is regularity of variation of properties, the elements are activating a valency of characteristic polarity. On the other hand, when there is fluctuation, the valency is of non-characteristic polarity.

As sub-standards of atomic stability usually control the activation of valency of non-characteristic polarity, the structure of these sub-standards is probably to be associated with secondary periodicity. The set-back producing the fluctuation is not observed in passing from any row to another row of the same length but in passing to a longer one. The structures of the controlling standards for two rows of the same length are similar, but for two rows of different lengths they are probably quite different and therefore the nature of the control will be quite different also.

CHAPTER XIV.

UNIQUE PROPERTIES OF HYDROGEN.

WHEN we compare the behaviour of acids with that of corresponding salts, we see that the properties of hydrogen are unique, especially when we compare univalent hydrogen with other univalent positive radicals.

We can account for the unique properties of hydrogen if we bear in mind that in the atomic structure of a neutral hydrogen atom there is one central positive charge with one outside negative electron. When this negative electron is detached, the hydrogen kernel remaining is the hydrogen nucleus and therefore very different from the kernel of any other atom.

The kernel of any other atom obtained by detaching the electrons in the outermost layer is atomic in dimensions (diameter about 10^{8} cms.), whereas the kernel of hydrogen is of the dimensions of about 10^{16} cms. in diameter and thus is smaller than even an electron although of course of much greater mass. H^{+1} can, therefore, approach very much closer to the outside shell of another atom than can any other element.

Thus *on account of its small volume the hydrogen univalent positive radical exerts an influence equivalent to that of an atom with a polyvalent positive charge.*

H^{+1} has no surrounding shell of electrons, and the tendency is for it to form a stable pair of electrons; in the case of H^{-1} this pair is the outermost shell, and corresponds to the outermost shell of eight, present in many atoms, for example, in F^{-1}. This tendency of neutral hydrogen to attach another electron and form a stable pair becoming H^{-1} is, therefore, analogous to the tendency of neutral F to attach another electron and form a stable octet becoming F^{-1}. In one sense, H is the most electronegative of all the elements. This association of H^{+1} with a stable pair is seen in the structure of the diatomic molecule H_2 which consists of two H^{+1} nuclei with a stable pair of electrons between them. This is an exceedingly stable configuration with very little stray field, and in forming these diatomic molecules, H resembles other extremely negative elements like N, O, and the halogens all of which tend to form diatomic molecules, with very little stray field. These substances are, therefore, very volatile. This tendency of hydrogen to form these diatomic molecules accounts for the volatility of the gas and the ease with which the hydrogen of an acid can be replaced by a metal.

When H forms part of a molecule it may be regarded as sharing a pair of electrons with another atom. Thus in HCl, H^{+1} when not actually dissociated may be regarded as associated with one of the pairs of electrons in the outermost octet of Cl. H^{+1} on account of its small volume can come exceedingly close to the pair of electrons.

H compounds in the pure state are all very non-polar. Pure liquid HCl, for example, is a non-conductor of electricity like H_2O. Even when dissolved in water the ionisation of many acids is much more difficult than that of the corresponding salts.

When H^{+1} does split off, it is very unlikely that it is present free in solution; it probably is merely transferred from one molecule to another.

Illustrations of the Unique Properties of Hydrogen.

Acids and their Salts compared.

Although acetic acid is poorly dissociated, i.e. is a weak acid, sodium acetate is well dissociated.

In acetic acid the H^{+1} radical being of vanishingly small volume is bound much more firmly to the negative radical than is Na^{+1} bound to the negative radical in sodium acetate in which Na^{+1} has a volume of normal atomic size.

Crystalline form of Ammonium Salts.

Ammonium salts can be isomorphous with salts of K, Rb, and Cs. If all the atoms of NH_4 had normal atomic volumes, the group would have a volume about five times the volume of K, or of Rb, or of Cs. It would then be difficult to see how K could be replaced in a salt by NH_4 and at the same time the same space lattice be retained, i.e. the same crystalline form be obtained in the new salt as in the old. If, however, the group NH_4^{+1} has volume equal to one atomic volume then the isomorphism becomes more intelligible.

Hydroxides.

In a series of hydroxides of the general formula $M^{+1}O^{-2}H^{+1}$, O^{-2} is always held far more firmly by H^{+1} than by the other univalent atom M^{+1} and, therefore, MOH is always basic, H^{+1} remaining attached to O^{-2}.

In the hydroxide of a divalent metal, other things being equal, it is to be expected that univalent H^{+1} competing as it is with a divalent positive metal atom would not be able to retain possession of the O^{-2}. This is actually what happens in certain cases, as for example in $Be(OH)_2$ which can behave as an acid. On the other hand, all the other members of the alkaline earth metal group give hydroxides that are distinctly basic.

In the hydroxides of the series Na^{+1}, Mg^{+2}, Al^{+3}, Si^{+4}, P^{+5}, S^{+6}, the transition point from basic to acidic character does not occur until the charge $+3$ is reached, i.e. at Al^{+3} the hydroxide of which is both basic and acidic. Raising the charge to 4 and more enables the atom to prevail against hydrogen so that the hydroxide is acidic.

Salts formed by Partial Neutralisation.

$KHSO_4$ is analogous to KHO. In both cases H^{+1} remains attached to a divalent negative particle and K^{+1} is split off. $KHSO_4$, therefore, behaves as an "acid salt" in this dissociation.

Similarly, $CaHPO_4$ can dissociate thus :—

$$CaHPO_4 \rightarrow Ca^{+2} + (HPO_4)^{-2}.$$

The part of an atom left after removing the electrons in the outermost layer, we have been calling the **kernel of the atom.**

The compounds—

CH_4, NH_3, OH_2, and FH may be written

$$\underset{\times}{C}{}^{-4}(H^{+1})_4,\ \underset{\times}{N}{}^{-3}(H^{+1})_3,\ \underset{\times}{O}{}^{-2}(H^{+1})_2 \text{ and } \underset{\times}{F}{}^{-1}H^{+1}.$$

The atoms undercrossed have the following charges in their kernels—

C	N	O	F
+4	+5	+6	+7.

There is a greater stray positive field from these kernels the larger their charge. Therefore, although all the above molecules are neutral, H^{+1} is most easily removed at the F end of the list and the difficulty of removal increases towards the C end.

Inorganic Acids.

H_2SO_4 may be written thus—

$$\begin{array}{c} O^{2} \\ H^{+1}\ O^{2}\ S^{+6}\ O^{2}\ H^{+1} \\ O^{2}. \end{array}$$

In S^{+6} all the outermost electrons we suppose to be removed so that the charge +6 is the charge of the kernel.

H_2SO_3 may be written thus—

$$\begin{array}{c} H^{+1}\ O^{2}\ S^{+4}\ O^{2}\ H^{+1} \\ O^{2}. \end{array}$$

In S^{+4} the kernel is +6 and two electrons are still in the outermost layer. In the development of valency +4, we have—

$$(8)\ 2,\ 6 \rightarrow (8)\ 2,\ 2.$$

H^{+1} is more easily repelled by S^{+6} in H_2SO_4 than by S^{+4} in H_2SO_3. Thus H_2SO_4 is a stronger acid than H_2SO_3.

H_2CO_3 may be written thus—

$$\begin{array}{c} H^{+1}\ O^{2}\ C^{+4}\ O^{2}\ H^{+1} \\ O^{2}, \end{array}$$

a formula analogous to that of H_2SO_3.

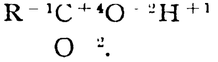
However, the charge +4 in S^{+4} is obtained by supposing that the +6 of the kernel is reduced to +4 by two positive charges being neutralised by the pair of electrons in the outermost layer. In reality the neutralisation is not quite so much as this.

Thus in H_2SO_3 the effective charge on S is in reality greater than +4, whereas in H_2CO_3 the effective charge is +4, which is the kernel charge.

Thus H_2CO_3 is a weaker acid than H_2SO_3.

Organic Acids.

The acid RCOOH may be written thus—



$$R^{-1}\underset{O^{-2}.}{C^{+4}}O^{-2}H^{+1}$$

C^{+4} repels H^{+1}. R^{-1} counteracts this effect to a certain extent, but this counteraction will be less the greater the stray positive fields from the positive kernels of the atoms in R. In general, therefore, the greater the charge of the positive kernels of the atoms in R the stronger is the acid.

We find the following order of acid strengths—

$CH_2ClCOOH > CH_2OHCOOH > CH_3COOH$ which contain in R the corresponding kernels :—

$$Cl^{+7} > O^{+6} > H^{+1}.$$

On the other hand, CH_3COOH is stronger than CH_3CH_2COOH, or H^{+1} is more effective than C^{+4}. Thus H^{+1} in its effect comes between O^{+6} and C^{+4}; thus is shown the unique nature of H^{+1} on account of its volume.

Again we have the acid strengths running thus—

$$CH_2ClCOOH > CH_2BrCOOH > CH_2ICOOH$$

the effects being in the order

$$Cl^{+7} > Br^{+7} > I^{+7}$$

because the volumes are in the order—

$$\text{Vol. Cl} < \text{Vol. Br} < \text{Vol. I.}$$

The effect of the various atomic positive kernels in increasing the strengths of the acids seems to be in the order—

$$Cl^{+7} > Br^{+7} > I^{+7} > O^{+6}(\text{in } OH) > H^{+1} > C^{+4}(\text{in } CH_3)$$

i.e. we find the strengths of the acids in the order—

$$CH_2ClCOOH > CH_2BrCOOH > CH_2ICOOH$$
$$> CH_2OHCOOH > CH_3COOH > CH_3CH_2COOH.$$

Bases.

The base RNH_2 may be written—

$$R^{+1}\,N^{\ 3}\,H_2^{+1}.$$

N^{-3} attracts the $2H^{+1}$. R^{+1} counteracts this effect to a certain extent, but this counteraction will be greater the greater the stray positive fields from the positive kernels of the atoms of R. Thus, in general the greater the charge of the positive kernels of the atoms of R, the less firmly is H^{+1} held in NH_2, i.e. the less is the strength of the base RNH_2.

Thus we have the following order of strengths—

$$NH_2OH < NH_2NH_2 < NH_2CH_3.$$

Or, the effect in reducing the strengths of the base is for the given kernels in the order—

$$O^{+6} > N^{+5} > C^{+4}.$$

On the other hand, H^{+1} in accordance with its unique nature comes in between N^{+5} and C^{+4}.

Thus, we find the strengths of the bases—

$$NH_2OH < NH_2NH_2 < NH_2H < NH_2CH_3.$$

CHAPTER XV.

HOMOGENEOUS COMPLEX ANIONS.

Hydrazoates.

In so-called hydrazoates or salts of hydrazoic acid, HN_3, one of the N atoms may be represented as the kernel of a complex anion. KN_3 would be $K^{+1} N^{+5} N_2^{-3}$.

CsN_3, RbN_3, KN_3, NaN_3, $LiN_3 H_2O$ are arranged in order of stability. CsN_3, in which the cationic difference is greatest, is the most stable, being melted easily without explosion. Similarly, we have the series:

$$Ba(N_3)_2 H_2O, Sr(N_3)_2, Ca(N_3)_2, Mg(N_3)_2, Be(N_3)_2.$$

$Ba(N_3)_2 H_2O$ is the most stable; $Be(N_3)_2$ is known only in aqueous solution.

The acid, HN_3, is very unstable, as is to be expected from the smaller cationic difference. It sometimes explodes at ordinary temperatures. The interionic affinity is weak, so that HN_3 behaves like a strong acid in aqueous solution.

The salts of the alkalies and alkaline earth metals are more stable than those of the heavy metals which are extremely explosive.

E.g. AgN_3, HgN_3, and $Cu(N_3)_2$, all of which are insoluble, are very explosive.

The constitution of the anion $(N_3)^{-1}$ may also be explained by Langmuir's co-valency method, the three atoms sharing four pairs of electrons, corresponding to two single bonds and one double.

Polysulphides and Polyoxides.

For the lowest members of these types, it is impossible to give a kernel constitution like the above without assuming for O and S a higher negative valency than 2.

However, Langmuir's co-valency method can be applied. In $(O_2)^{-2}$, for example, the two O atoms can be represented as sharing a pair of electrons. In $(O_4)^{-2}$, the four O atoms would be in a chain, every two adjacent atoms sharing a pair of electrons, there being in all three shared pairs.

For higher members, such as Rb_2O_4 we can, however, have a kernel constitution.

Rb_2O_4, K_2S_5, and Rb_2S_6 would be $Rb_2^{+1}O^{+4}O_3^{-2}$, $K_2^{+1}S^{+6}S_4^{2}$, and $Rb_2^{+1}S_2^{+3}S_4^{2}$ respectively.

Polyhalides.

In these salts at least one atom of I or Br is always present, and may be regarded as forming the positive kernel of the complex anion. Cl has not a sufficient tendency to positiveness to act in this way.

CsI_9 is $Cs^{+1}I^{+7}I_8^{1}$. This is the highest polyiodide because I is showing here its maximum positive valency. The co-ordination number is 8.

Similarly we have

$$Cs^{+1}I^{+3}I_4^{1},\ Cs^{+1}I^{+1}I_2^{1},\ Cs^{+1}I^{+3}Cl_4^{1},$$
$$Cs^{+1}Br^{+3}Br_4^{-1},\ Cs^{+1}Br^{+1}Br_2^{-1},\ Rb^{+1}I^{+7}I_8^{-1},$$
$$Rb^{+1}I^{+5}I_6^{-1},\ Rb^{+1}I^{+1}I_2^{-1},\ Rb^{+1}I^{+3}Cl_4^{-1},$$
$$Rb^{+1}I^{+1}Br_2^{1},\ Rb^{+1}I^{+1}Br^{-1}Cl^{-1},$$
$$Rb^{+1}I^{+1}Cl_2^{-1},\ Rb^{+1}Br^{+1}Br_2^{-1},\ \text{etc.}$$

Polyhalides are more stable and numerous at the Cs end of the list of alkalis.

Note that the clustered halogen atoms have the negative valency 1, characteristic for halogens, whilst the kernel halogen atom has one of the positive valencies: 1, 3, 5, or 7, an odd number in every case, as is usual with an odd numbered element.

There is always an odd number of halogen atoms in the complex anion of a polyhalide. When one halogen atom is regarded as kernel, the co-ordination number is therefore even, being 8, 6, 4, or 2.

CHAPTER XVI.

COMPLEX CYANIDES.

IN the anion of the complex cyanides, $(CN)^{-1}$ or Cy^{-1} ions are clustered round a positive kernel. Each ratio given below is the ratio of the number of molecules of $M^{+1}Cy^{-1}$ to the number of molecules of $Q^{+v}Cy_v^{-1}$ in the complex cyanide, where Q^{+v} is the kernel.

Example: for K_3FeCy_6, the ratio is 3 : 1 and Q^{+v} is Fe^{+3}.

There is a certain ratio characteristic for kernels in the same equivalential or group of the periodic table, with additional ratios for some of the atoms.

Ratios Characteristic of Group.	*Additional Ratios.*
1 : 1 for Cu^{+1}, Ag^{+1}, and Au^{+1}.	1 : 2, 2 : 3, 2 : 1, and 3 : 1 for Cu^{+1}. 1 : 1 for Au^{+3}. None for Cu^{+2}.
2 : 1 for Zn^{+2}, Cd^{+2}, and Hg^{+2}.	1 : 1 for Zn^{+2}, 4 : 3 for Cd^{+2}. 1 . 1 and 4 : 3 for Hg^{+2}. None for Hg^{+1}.
4 : 1 for Fe^{+2}, Ru^{+2}, and Os^{+2}.	3 : 1 for Fe^{+3}.
3 : 1 for Co^{+3}, Rh^{+3}, and Ir^{+3}.	4 : 1 for Co^{+2} less stable than 3 : 1 for Co^{+3}.
2 : 1 for Ni^{+2}, Pd^{+2}, and Pt^{+2}.	

The following ratios also occur:—

4 : 1 for Cr^{+2} (very unstable) and 3 : 1 for Cr^{+3}.

4 : 1 and 1 : 1 for Mn^{+2} (less stable) and 3 : 1 for Mn^{+3}.

4 : 1 for Mo^{+4}.

4 : 1 for V^{+2} (easily oxidised) and 3 : 1 for V^{+3}.

1 : 1 for Tl^{+3}.

Pb^{+2} has too large a volume to act as a kernel of a cyanide complex.

As with other complexes, the complex cyanides are, as a rule, more stable the smaller the volume and the larger the charge of the kernel.

Zn, Cd, and Hg have all larger atomic volumes than Ni, and H_2S precipitates the heavy metal as sulphide from K_2ZnCy_4, K_2CdCy_4, and K_2HgCy_4 but not from K_2NiCy_4. Again, H_2S precipitates the sulphide of the heavy metal from K_2CdCy_6 but not from K_3CuCy_4. The smaller volume in Cu^{-1} makes its complex more stable although the kernel has a smaller charge than Cd^{+2}.

This property of the complex cyanides of Cu and Cd is applied in analysis to separate these metals, the less noble metal being precipitated first, contrary to the usual order.

$K_3Co^{+3}Cy_6$ with the larger charge in its kernel is more stable than $K_4Co^{+2}Cy_6$.

$NiCy_2$ is precipitated from a solution of K_2NiCy_4 by dilute hydrochloric acid even after boiling the solution exposed to the air ; and NaOBr forms $Ni(OH)_3$.

$CoCy_2$ is precipitated from a solution of K_4CoCy_6 by dilute hydrochloric acid, but not after boiling the solution exposed to air, which changes K_4CoCy_6 to K_3CoCy_6 which gives a precipitate neither with dilute hydrochloric acid nor with NaOBr.

This property of the complex cyanides of Co and Ni is used in qualitative analysis.

When an atom can activate more than one valency, it should have its greatest clustering capacity with its highest valency. With lower valencies, either a complex should not be formed, or a less stable one. A striking exception to this rule is the formation of several cyanide complexes with Cu^{+1} and none with Cu^{+2}. Again, the numerous ferrocyanides, which are complexes with a lower-valency kernel (Fe^{+2}), have remarkable stability, even the acid, H_4FeCy_6, not being decomposed by dilute hydrochloric acid.

CHAPTER XVII.

DOUBLE DECOMPOSITION.

CHEMICAL changes involve the formation of new substances, but not necessarily of new radicals.

In **Double Decomposition** the positive and negative radicals of the reactants remain intact and are merely interchanged to form the resultants.

In **Oxidation-and-Reduction** there is destruction of some of the radicals of the reactants and the formation of some new radicals.

A Double Decomposition involving univalent radicals may be represented thus :—

$$M^{+1}Z^{-1} + Q^{+1}R^{-1} \rightarrow M^{+1}R^{-1} + Q^{+1}Z^{-1}.$$

The radicals M^{+1}, Z^{-1}, Q^{+1}, and R^{-1} have remained intact and have merely interchanged partners.

Suppose, for simplicity, that all the four substances are in solution. The back reaction takes place to a certain extent, so that ultimately the equilibrium

$$M^{+1}Z^{-1} + Q^{+1}R^{-1} \rightleftarrows M^{+1}R^{-1} + Q^{+1}Z^{-1}$$

is established, the condition for equilibrium being

$$\frac{(M^{+1}R^{-1})(Q^{+1}Z^{-1})}{(M^{+1}Z^{-1})(Q^{+1}R^{-1})} = \text{Reaction Constant},$$

where $(M^{+1}R^{-1})$, $(Q^{+1}Z^{-1})$, $(M^{+1}Z^{-1})$, $(Q^{+1}R^{-1})$ are the concentrations of $M^{+1}R^{-1}$, $Q^{+1}Z^{-1}$, $M^{+1}Z^{-1}$, $Q^{+1}R^{-1}$ respectively.

The original double decomposition is checked by an accumulation of either of the resultants, and is therefore favoured by removing from the field of activity one of the resultants as fast as it is formed. This happens when one of the resultants is insoluble or very volatile.

Double decomposition cannot take place until each participating positive radical of the reactants is detached from its negative partner. The separation is opposed by the interionic affinity binding the positive radical to its partner. Therefore double decomposition is hindered when one of the reactants is a weak electrolyte, and, of course, favoured when one of the resultants is a weak electrolyte.

Thus double decomposition is helped

(*a*) when one of the resultants is a weak electrolyte, or
(*b*) when one of the resultants is very insoluble, or
(*c*) when one of the resultants is very volatile.

(a) Double decompositions in which one of the resultants is a weak electrolyte.

Example : *The neutralisation of a base by an acid.*

E.g. $$\underset{\textbf{base.}}{M^{+1}(OH)^{-1}} + \underset{\textbf{acid.}}{H^{+1}Z^{-1}} \rightarrow \underset{\textbf{salt.}}{M^{+1}Z^{-1}} + \underset{\textbf{water.}}{H^{+1}(OH)^{-1}}.$$

The resultant, H_2O, is the electrolyte the weakness of which has a great influence in bringing about the neutralisation.

If MOH is a weak base, then the neutralisation is checked and the reverse change, or hydrolysis, is favoured.

Hydrolysis is the action of water upon the salt MZ giving the base MOH and the acid HZ.

The weaker the base the greater will be the proportion of MOH in the equilibrium mixture.

When a weak base MOH and a strong acid HZ are mixed in equimolecular proportions, the M^{+1} radicals retain most of the $(OH)^{-1}$ radicals as partners, giving up only a small portion to the H^{+1} radicals. The weaker MOH the larger the share of $(OH)^{-1}$ radicals that it retains. Thus there is a balance between neutralisation or salt formation and hydrolysis ·

$$MOH + HZ \rightleftarrows MZ + H_2O.$$

Therefore, a solution containing equimolecular (i.e. in this case formally equivalent) proportions of MOH and HZ, contains excess of H^{+1} ions and therefore reacts acid, when MOH is weak and HZ is strong.

Again, the normal salt $M^{+1}Z^{-1}$ is formally neutral or contains formally equivalent amounts of M^{+1} and Z^{-1}. But if MOH is a weak base and HZ is a strong acid, then when MZ is dissolved in water, the solution reacts acid. Examples: soluble salts formed by the union of the following positive radicals with strongly negative radicals:

$$Hg^{+1},\ Hg^{+2},\ Cu^{+2},\ Al^{+3},\ Cr^{+3},\ Fe^{+3},\ Sn^{+2},\ Sn^{+4},\ Sb^{+3},\ Bi^{+3}.$$

Similarly, if MOH is a strong base and HZ is a weak acid, then an aqueous solution of MZ reacts alkaline, because it contains an excess of $(OH)^{-1}$ ions. Examples: soluble salts formed by the union of the following negative radicals with strongly positive radicals:

$$(BO_3)^{-3},\ (CO_3)^{-2},\ (CrO_4)^{-2},\ (ClO)^{-1},\ (NO_2)^{-1},$$
$$(PO\ )^{-3},\ (SiO\ )^{-2},\ S^{-2},\ (SO\ )^{-2}$$

We have supposed in the above that there are equimolecular proportions of M^{+1} and Z^{-1}, but we can shift the equilibrium in any direction we please by varying the proportions of the different substances. Thus we can diminish the amount of hydrolysis by adding excess of the base or of the acid, and we can increase the amount of hydrolysis by adding more water, that is, by diluting the solution.

The Great Influence of Interionic Affinity on Double Decomposition.

The action of difficult solubility and of easy volatility in removing one of the resultants of a double decomposition is very obvious, but the action of a strong interionic affinity in bringing together radicals of opposite polarity and thus forming one of the resultants is apt to be overlooked, doubtless owing to the fact that very often the resulting substance remains in solution. Apart from any question of solubility or volatility, double decompositions in which interionic affinity is the driving force are of so frequent occurrence in chemical analysis, that the importance of this factor cannot be too much emphasised. With strong interionic affinity, the substance, a weak electrolyte, may for convenience be regarded as not ionised at all, and with weak interionic affinity, the substance, a strong electrolyte, may be regarded as completely ionised, in aqueous solutions of suitable concentrations.

Thus, in the equilibrium

$$M^{+1}Z^{-1} + Q^{+1}R^{-1} \rightleftarrows M^{+1}R^{-1} + Q^{+1}Z^{-1}$$

in aqueous solution, if the interionic affinity in $Q^{+1}Z^{-1}$

is strong and in the other three substances is weak, then we may write the equilibrium thus:

$$M^{+1} + Z^{-1} + Q^{+1} + R^{-1} \rightleftarrows M^{+1} + R^{-1} + Q^{+1}Z^{-1},$$

or $$Q^{+1} + Z^{-1} \rightleftarrows Q^{+1}Z^{-1}.$$

With originally equimolecular proportions of MZ and QR there will be practically complete displacement of the equilibrium towards the right.

Bearing in mind that a salt is usually well ionised, even when formed from a weak acid or a weak base, for aqueous solutions we may write

$$MOH + HZ \rightleftarrows MZ + H_2O$$

thus

$$M^{+1} + (OH)^{-1} + H^{+1} + Z^{-1} \rightleftarrows M^{+1} + Z^{-1} + H_2O$$

or $$H^{-1} + (OH)^{-1} \rightleftarrows H_2O,$$

the mixture reacting neutral when MOH is a *strong* base and HZ is a *strong* acid; and thus:

$$MOH + H^{+1} + Z^{-1} \rightleftarrows M^{+1} + Z^{-1} + H_2O$$

or $$MOH + H^{+1} \rightleftarrows M^{+1} + H_2O,$$

the mixture reacting acid when MOH is a *weak* base and HZ is a *strong* acid; and thus:

$$M^{+} + (OH)^{-1} + HZ \rightleftarrows M^{+1} + Z^{-1} + H_2O$$

or $$(OH)^{-1} + HZ \rightleftarrows Z^{-1} + H_2O,$$

the mixture reacting alkaline when MOH is a *strong* base and HZ is a *weak* acid.

So great is the influence of the interionic affinity between H^{+1} and $(OH)^{-1}$, that salt formation may be obtained when an acid is added even to an insoluble base, although the insolubility of the base checks the change, e.g.

$$\underset{\text{insoluble.}}{Zn(OH)_2} + 2HCl \rightarrow ZnCl_2 + H_2O.$$

Action of a strong acid on a salt of a weak acid.

Example:

$$\underset{\text{sodium acetate.}}{Na^{+1}(CH_3COO)^{-1}} + \underset{\text{hydrochloric acid.}}{H^{+1}Cl^{-1}} \rightarrow \underset{\text{sodium chloride.}}{Na^{+1}Cl^{\ 1}} + \underset{\text{acetic acid.}}{H^{+1}(CH_3COO)^{-1}}$$

The strong interionic affinity in $H^{+1}(CH_3COO)^{-1}$ is the force that brings about this change.

When equivalent amounts of sodium acetate and an acid are mixed, the amount of acetic acid formed will be the greater the greater the difference between the interionic affinities in the two acids, i.e. between the strengths of the acids. Acetic acid is so much weaker than hydrochloric acid that nearly all the $(CH_3COO)^{\ 1}$ radicals of sodium acetate unite with H^{+1} radicals to form acetic acid.

Thus the influence of the weak electrolyte acetic acid in this change is exactly analogous to that of water in neutralisation.

If, instead of sodium acetate in the above, we used the sodium salt of an acid of about the same strength as hydrochloric acid, then about equal amounts of the two acids would be in the equilibrium mixture. Thus the formation of an acid from its sodium salt by the action of another acid is favoured by the first acid being very much weaker than the second.

The solution of an insoluble salt of a polybasic acid in an acid.

H_2SO_4 may be regarded as dissociated in two stages:—

$$H_2^{+1}(SO_4)^{\ 2} \rightarrow H^{+1} + (HSO_4)^{-1} \quad . \quad (1)$$

and

$$(HSO_4)^{\ 1} \rightarrow H^{+1} + (SO_4)^{-2} \quad . \quad . \quad (2)$$

There is a greater tendency towards dissociation (1) than (2). In other words, the interionic affinity causing the back reaction in (2) is stronger than in (1).

The dissolving of $PbSO_4$ in hydrochloric acid or in nitric acid is due to the strong interionic affinity which leads to

$$H^{+1} + (SO_4)^{-2} \rightarrow (HSO_4)^{-1}.$$

Thus

$$\underset{\text{insoluble.}}{Pb^{+2}(SO_4)^{-2}} + H^{+1} + Cl^{-1} \rightarrow Pb^{+2} + Cl^{-1} + H^{+1}(SO_4)^{-2}$$

H_3PO_4 may be regarded as dissociated in three stages :—

$$H_3^{+1}(PO_4)^{-3} \rightarrow H^{+1} + (H_2PO_4)^{-1} \qquad . \quad (3)$$
$$(H_2PO_4)^{-1} \rightarrow H^{+1} + (HPO_4)^{-2} \qquad . \quad (4)$$
$$(HPO_4)^{-2} \rightarrow H^{+1} + (PO_4)^{-3} . \qquad . \quad (5)$$

It is clear that the interionic affinity runs thus :—
That between H^{+1} and $(PO_4)^{-3} >$ that between H^{+1} and $(HPO_4)^{-2} >$ that between H^{+1} and $(H_2PO_4)^{-1}$.

In other words, the tendency towards the back reaction :—

$$\text{in } (5) > \text{in } (4) > \text{in } (3).$$

So great are the interionic affinities in (4) and (5), that salts of the types $BaHPO_4$ and Ag_3PO_4 are soluble in acetic acid :—

$$Ba^{+2}(HPO_4)^{-2} + H^{+1}(CH_3COO)^{-1} \rightarrow Ba^{+2} + (CH_3COO)^{-1} + (H_2PO_4)^{-1}$$

$$Ag_3^{+1}(PO_4)^{-3} + H^{+1}(CH_3COO)^{-1} \rightarrow 3Ag^{+1} + (CH_3COO)^{-1} + (HPO_4)^{-2}$$

$$Ag_3^{+1}(PO_4)^{-3} + 2H^{+1}(CH_3COO)^{-1} \rightarrow 3Ag^{+1} + 2(CH_3COO)^{-1} + (H_2PO_4)^{-1}.$$

As explained in Chapter XIV, the interionic affinity in an acid is often greater than that in one of its salts. For example, Na_2HPO_4 and NaH_2PO_4 give more of the ions $(HPO_4)^{-2}$ and $(PO_4)^{-3}$ than does H_3PO_4. This explains why solutions of disodium hydrogen phosphate and sodium dihydrogen phosphate give precipitates with the ions Ba^{+2}, Pb^{+2}, and Ag^{+1}, whilst a solution of phosphoric acid does not.

With NaH_2PO_4, not only is dissociation in the first stage greater than with H_3PO_4, but, there being no H^{+1} ions formed in this stage with the salt, the dissociation in the second and third stages is made easier.

(b) Double decompositions in which one of the resultants is insoluble.

This type is of very common occurrence in chemical analysis.

Insoluble salts :—

e.g. $Na^{+1}Cl^{-1} + Ag^{+1}(NO_3)^{-1} \rightarrow Na^{+1}(NO_3)^{-1}$
$+ Ag^{+1}Cl^{-1}$
insoluble.

$Ba^{+2}Cl_2^{-1} + H_2^{+1}(SO_4)^{-2} \rightarrow 2H^{+1}Cl^{-1}$
$+ Ba^{+2}(SO_4)^{-2}$
insoluble.

Insoluble hydroxides :—

e.g. $Zn^{+2}(SO_4)^{-2} + 2Na^{+1}(OH)^{-1} \rightarrow Na_2^{+1}(SO_4)^{-2}$
$+ Zn^{+2}(OH)_2^{-1}$
insoluble.

$Cu^{+2}Cl_2^{-1} + 2Na^{+1}(OH)^{-1} \rightarrow 2Na^{+1}Cl^{-1}$
$+ Cu^{+2}(OH)_2^{-1}$
insoluble.

The precipitation of hydroxides is usually represented in this way as merely a case of double decomposition.

Probably it is better to regard the change as one consisting of two steps: hydration followed by hydrolysis, the hydrolysis being facilitated by the presence of the NaOH. Thus :—

$$Zn(OH_2)_nSO_4 \rightarrow Zn(OH)_2 + (n - 2)H_2O + H_2SO_4.$$

(c) **Double decompositions in which one of the resultants is volatile.**

$$Na^{+1}Cl^{-1} + H^{+1}(NO_3)^{-1} \rightarrow Na^{+1}(NO_3)^{-1} + \underset{\text{volatile.}}{H^{+1}Cl^{-1}}$$

NaCl is completely changed to $NaNO_3$ and HCl if HNO_3 is kept in excess.

$$Na^{+1}(NO_3)^{-1} + H^{+1}Cl^{-1} \rightarrow Na^{+1}Cl^{-1} + \underset{\text{volatile.}}{H^{+1}(NO_3)^{-1}}$$

$NaNO_3$ is completely changed to NaCl and HNO_3 if HCl is kept in excess.

$$(1)\ Na^{+1}Cl^{-1} + H^{+1}(HSO_4)^{-1} \rightarrow Na^{+1}(HSO_4)^{-1} + \underset{\text{volatile.}}{H^{+1}Cl^{-1}}$$

$$(2)\ Na^{+1}Cl^{-1} + Na^{+1}H^{+1}(SO_4)^{-2} \rightarrow Na_2^{+1}(SO_4)^{-2} + \underset{\text{volatile.}}{H^{+1}Cl^{-1}}$$

Note that the $(SO_4)^{-2}$ required for $Na_2^{+1}(SO_4)^{-2}$ is more easily obtained from $NaHSO_4$ than from H_2SO_4 and that the change in equation (2) requires a higher temperature than that in equation (1).

$$Fe^{+2}S^{-2} + 2H^{+1}Cl^{-1} \rightarrow Fe^{+2}Cl_2^{-1} + \underset{\text{volatile.}}{H_2^{+1}S^{-2}}$$

If solutions of an acid and of the sodium salt of another acid are mixed in equivalent proportions then double decomposition will proceed until each acid has a share of the sodium proportionate to that acid's relative strength. But if, as in the present section, the acid resulting from the double decomposition is volatile, then the other acid obtains a greater share of the base than that to be expected from the relative strengths of the acids. Thus the tendency of the one acid to evaporate prevails against the interionic affinity of the other.

Similarly, the method of shares is not available for comparing the strengths of acids if one of the resultants of the double decomposition is insoluble.

Accordingly, with regard to double decomposition, conclusions derived from consideration of competing interionic affinities will not be correct unless these affinities are competing under comparable conditions. If one of the substances participating in the reaction is insoluble or volatile, then "mass action" joins forces with the interionic affinity of that substance.

CHAPTER XVIII.

OXIDATION-AND-REDUCTION.

WHILST in **Double Decomposition** the positive and negative radicals of the reactants remain unchanged, in **Oxidation-and-Reduction** there is destruction of some of the radicals of the reactants and the formation of some new radicals.

The charge of a radical may vary in quantity and in polarity. Thus we have

$$S^{+6}O_3^{-2},\ S^{+4}O_2^{-2},\ \text{and}\ H_2^{+1}S^{-2},$$

in which the atom S has 6 positive, 4 positive, and 2 negative charges respectively.

The change $S^{+6} \rightarrow S^{+4} \rightarrow S^{-2}$ is called Reduction and the reverse change Oxidation.

Reduction takes place when a positive radical has its charge reduced or a negative radical its charge increased, oxidation when a positive radical has its charge increased or a negative radical its charge reduced. The reduction of one radical is always accompanied by the oxidation of another.

Reductions Involving Complete Loss of Positive Charge.

If a piece of iron is dipped in a solution of copper sulphate, some metallic copper is separated and forms a red coating on the iron, while at the same time some of the metallic iron enters into the solution forming ferrous sulphate :—

$$Fe + Cu^{+2}(SO_4)^{-2} = Fe^{+2}(SO_4)^{-2} + Cu.$$

iron. copper sulphate. ferrous sulphate. copper.

Of the radicals of this reaction, one is unchanged, another is oxidised, and the third is reduced :—

Unchanged	$(SO_4)^{-2}$.
Oxidised	$Fe \rightarrow Fe^{+2}$: gain of 2 positive charges.
Reduced	$Cu^{+2} \rightarrow Cu$: loss of 2 positive charges.

Thus, *the reduction of one radical supplies the electricity required for the oxidation of another.*

Again, a piece of copper dipped in a solution of mercuric nitrate, which is colourless, becomes coated with mercury and the solution turns blue, due to the formation of copper nitrate :—

$$Cu + Hg^{+2}(NO_3)_2^{-1} = Cu^{+2}(NO_3)_2^{-1} + Hg.$$

copper. mercuric nitrate. copper nitrate mercury.

In this reaction, $(NO_3)^{-1}$ is unchanged and the reduction of Hg^{+2} to Hg yields the electricity required to oxidise Cu to Cu^{+2}.

The change $Fe + Cu^{+2}(SO_4)^{-2} \rightarrow Fe^{+2}(SO_4)^{-2} + Cu$ may be written $Fe + Cu^{+2} \rightarrow Fe^{+2} + Cu$

where we see competing the two tendencies :—

$$Fe \rightarrow Fe^{+2} \text{ and } Cu \rightarrow Cu^{+2}.$$

The first proves the stronger, with the result that the second is reversed. In other words, the positive electro-affinity of Fe being greater than that of Cu, Fe displaces Cu from a solution of a Cu salt.

Similarly,

in $Cu + Hg^{+2}(NO_3)_2^{-1} \rightarrow Cu^{+2}(NO_3)_2^{-1} + Hg$,

or $Cu + Hg^{+2} \rightarrow Cu^{+2} + Hg$,

$Cu \rightarrow Cu^{+2}$ is seen to be stronger than $Hg \rightarrow Hg^{+2}$, or the positive electro-affinity of Cu is stronger than that of Hg.

As already pointed out (see Chapter VI and Diagram II) for solutions of standard concentration, which is chosen to be ionic normal, metals may be arranged in the order of their electro-affinities for positive electricity. Thus, we have the following, beginning with the highest, Mg, Al, Zn, Fe, Pb, Sn, H_2, Cu, Hg, Ag, Au. This list is arranged for a charge of + 2 on the corresponding ions except for Al (charge + 3) and H, Ag, and Au (charge + 1).

Any given metal will be displaced by all those having a greater electro-affinity and will displace all having a less. Fe, for example, should displace Pb, Sn, H_2, Cu, Ag, and Au, and should be displaced by Mg, Al, and Zn. H_2 is displaced from one of its salts, i.e. from an acid, by any metal standing before it in the above list. Thus, $Zn + H_2^{+1}(SO_4)^{-2} \rightarrow Zn^{+2}(SO_4)^{-2} + H_2$.

Similarly, we can arrange radicals in the order of their electro-affinity for negative electricity. Thus, $Cl > Br > I$. Accordingly, Cl will displace Br and I from a bromide and an iodide respectively, and Br displace I from an iodide :—

Oxidations Involving Complete Loss of Negative Charge.

In $Cl_2 + 2Na^{+1}Br^{-1} \rightarrow 2Na^{+1}Cl^{-1} + Br_2$

or $Cl_2 + 2Br^{-1} \rightarrow 2Cl^{-1} + Br_2$

we see competing the two tendencies : $Cl_2 \rightarrow 2Cl^{-1}$ and $Br_2 \rightarrow 2Br^{-1}$. The first proves the stronger, with the result that the second is reversed.

	Oxidised.	Reduced.	Unchanged.
$Cl_2 + 2Na^{+1}Br^{-1} = 2Na^{+1}Cl^{-1} + Br_2$	$2Br^{-1}$	$2Cl$	$2Na^{+1}$
Similarly :			
$Cl_2 + 2Na^{+1}I^{-1} = 2Na^{+1}Cl^{-1} + I_2$	$2I^{-1}$	$2Cl$	$2Na^{+1}$
$Br_2 + 2Na^{+1}I^{-1} = 2Na^{+1}Br^{-1} + I_2$	$2I^{-1}$	$2Br$	$2Na^{+1}$
$Cl_2 + H_2^{+1}S^{-2} = 2H^{+1}Cl^{-1} + S$	S^{-2}	$2Cl$	$2H^{+1}$
$Br_2 + H_2^{+1}S^{-2} = 2H^{+1}Br^{-1} + S$	S^{-2}	$2Br$	$2H^{+1}$
$I_2 + H_2^{+1}S^{-2} = 2H^{+1}I^{-1} + S$	S^{-2}	$2I$	$2H^{+1}$
$2Cl_2 + 2H_2^{+1}O^{-2} = 4H^{+1}Cl^{-1} + O_2$	$2O^{-2}$	$4Cl$	$4H^{+1}$
$O_2 + 2H_2^{+1}S^{-2} = 2H_2^{+1}O^{-2} + 2S$	$2S^{-2}$	$2O$	$4H^{+1}$

Reductions Involving Partial Loss of Positive Charge.

In $2Fe^{+3}Cl_3^{-1} + Sn^{+2}Cl_2^{-1} \rightarrow 2Fe^{+2}Cl_2^{-1} + Sn^{+4}Cl_4^{-1}$
or $2Fe^{+3} + Sn^{+2} \rightarrow 2Fe^{+2} + Sn^{+4}$

there is partial loss of the charge in Fe^{+3}.

Here we see competing the two tendencies :—

$$2Fe^{+2} \rightarrow 2Fe^{+3} \text{ and } Sn^{+2} \rightarrow Sn^{+4}.$$

The second proves the stronger, with the result that the first is reversed.

	Oxidised.	Reduced.	Unchanged.
$2Fe^{+3}Cl_3^{-1} + Sn^{+2}Cl_2^{-1} = 2Fe^{+2}Cl_2^{-1} + Sn^{+4}Cl_4^{-1}$	Sn^{+2}	$2Fe^{+3}$	$8Cl^{-1}$

Similarly:

	Oxidised.	Reduced	Unchanged
$2Fe^{+3}Cl_3^{-1} + H_2^{+1}S^{-2} = 2Fe^{+2}Cl_2^{-1} + 2H^{+1}Cl^{-1} + S$	S^{-2}	$2Fe^{+3}$	$6Cl^{-1}$ and $2H^{+1}$
$2FeCl_3 + 2H_2O + SO_2 = 2FeCl_2 + 2HCl + H_2SO_4$	S^{+4}	$2Fe^{+3}$	$4O^{-2}$, $6Cl^{-1}$, and $4H^{+1}$
$2Cr^{+6}O_3^{-2} + 3S^{+4}O_2^{-2} = Cr_2^{+3}(S^{+6}O_4^{-2})_3$	$3S^{+4}$	$2Cr^{+6}$	$12O^{-2}$
$K_2Cr_2O_7 + H_2SO_4 + 3H_2SO_3 = Cr_2(SO_4)_3 + K_2SO_4 + 4H_2O$	$3S^{+4}$	$2Cr^{+6}$	$20O^{-2}$, $8H^{+1}$, $2K^{+1}$ and S^{+6}
$K_2Cr_2O_7 + 3H_2S + 8HCl = 2CrCl_3 + 2KCl + 7H_2O + 3S$	$3S^{-2}$	$2Cr^{+6}$	$8Cl^{-1}$, $7O^{-2}$, $2K^{+1}$ and $14H^{+1}$

Oxidation-and-Reduction in the Dry Way.

	Oxidised.	Reduced.	Unchanged.
$Pb^{+2}O^{-2} + C \rightarrow Pb + C^{+2}O^{-2}$	C	Pb^{+2}	O^{-2}
$2Pb^{+2}O^{-2} + C \rightarrow 2Pb + C^{+4}O_2^{-2}$	C	$2Pb^{+2}$	$2O^{-2}$
$Fe^{+2}Fe_2^{+3}O_4^{-2} + 4H_2 \rightarrow 3Fe + 4H_2^{+1}O^{-2}$	8H	Fe^{+2} and $2Fe^{+3}$	$4O^{-2}$
$Sn^{+4}O_2^{-2} + 2C \rightarrow Sn + 2C^{+2}O^{-2}$	2C	Sn^{+4}	$2O^{-2}$
$Cu^{+2}O^{-2} + H_2 \rightarrow Cu + H_2^{+1}O^{-2}$	2H	Cu^{+2}	O^{-2}
$C^{+4}O_2^{-2} + C \rightarrow 2C^{+2}O^{-2}$	C	C^{+4}	$2O^{-2}$
$Cu^{+2}O^{-2} + C^{+2}O^{-2} \rightarrow Cu + C^{+4}O_2^{-2}$	C^{+2}	Cu^{+2}	$2O^{-2}$
$Fe_2^{+3}O_3^{-2} + 2Al \rightarrow 2Fe + Al_2^{+3}O_3^{-2}$	2Al	$2Fe^{+3}$	$3O^{-2}$
$Cr_2^{+3}O_3^{-2} + 2Al \rightarrow 2Cr + Al_2^{+3}O_3^{-2}$	2Al	$2Cr^{+3}$	$3O^{-2}$
$Si^{+4}O_2^{-2} + 4Na \rightarrow Si + 2Na_2^{+1}O^{-2}$	4Na	Si^{+4}	$2O^{-2}$
$B_2^{+3}O_3^{-2} + 6Na \rightarrow 2B + 3Na_2^{+1}O^{-2}$	6Na	$2B^{+3}$	$3O^{-2}$
$Ba^{+2}S^{+6}O_4^{-2} + 4C \rightarrow Ba^{+2}S^{-2} + 4C^{+2}O^{-2}$	4C	S^{+6}	Ba^{+2} and $4O^{-2}$

The standard scale of electro-affinities and oxidation-and-reduction potentials have been obtained with reference to aqueous solutions. Nevertheless, reactions carried out under other conditions such as by the "dry way" will be found to agree very well with the relative positiveness of the elements, as shown in Diagram II, unless "mass action" is allowed to mask the effect of electro-affinity.

Self-Oxidation-and-Reduction.

	Oxidised.	Reduced.	Unchanged.
$6Na^{+1}O^{-2}Cl^{+1} \rightarrow 4Na^{+1}Cl^{-1} + 2Na^{+1}Cl^{+5}O_3^{-2}$	$2Cl^{+1}$	$4Cl^{-1}$	$6Na^{+1}$ and $6O^{-2}$
$4K^{+1}Cl^{+5}O_3^{-2} \rightarrow 2K^{+1}Cl^{+7}O_4^{-2} + 2K^{+1}Cl^{-1} + 2O_2$	$4O^{-2}$ and $2Cl^{+5}$	$2Cl^{+5}$	$4K^{+1}$ and $8O^{-2}$
$8H_3^{+1}P^{+3}O_3^{-2} \rightarrow 2P^{-3}H_3^{+1} + 6H_3^{+1}P^{+5}O_4^{-2}$	$6P^{+3}$	$2P^{+3}$	$24O^{-2}$ and $24H^{+1}$
$4H_3^{+1}P^{+1}O_2^{-2} \rightarrow 2P^{-3}H_3^{+1} + 2H_3^{+1}P^{+5}O_4^{-2}$	$2P^{+1}$	$2P^{+1}$	$8O^{-2}$ and $12H^{+1}$
$6H^{+1}N^{+3}O_2^{-2} \rightarrow 2H^{+1}N^{+5}O_3^{-2} + 4N^{+2}O^{-2} + 2H_2^{+1}O^{-2}$	$2N^{+3}$	$4N^{+3}$	$12O^{-2}$ and $6H^{+1}$
$3Na^{+1}O^{-2}H^{+1} + 4P + 3H_2^{+1}O^{-2} \rightarrow 3Na^{+1}H_2^{+1}P^{+1}O_2^{-2} + P^{-3}H_3^{+1}$	$3P$	P	$6O^{-2}, 3Na^{+1}$ and $9H^{+1}$

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Students are advised to begin by reading 6, 11, 12, 32, and the little book 35.

Special attention should be given to number 27 among Langmuir's papers and number 20 among Harkins'.

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DIAGRAM I.

PERIODIC TABLE OF THE ELEMENTS. NEW FORM.