ON THE TRUE NATURE OF "PER-ACIDS" AND THE ALLEGED "ACID NUCLEUS THEORY."⑴

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Several years ago, the present author commenced the researches to make clear the true nature of the "Per-acid." The results obtained in the researches have already been reported time to time in three former papers.⑵ In the present communication, the author proposes a new hypothesis concerning the structure of the "Per-acid," which explains the experimental results obtained by the author as well as those obtained by others.

"Per-acids" are "Acids" which are formed when "Oxy-acids" are treated with hydrogen peroxide or which turn into "Hydrogen peroxide" under suitable treatment. The "Permanganic" and "Perchloric" -acids, therefore, do not belong to this group although these are also prefixed with "Per-." When the "Oxy-acids" are "metallic," very sensitive and characteristic colorations are frequently produced. This is the reason why "Per-acids reactions are recommended for the detection of such metals in qualitative analysis. As for the other characteristics of "Per-acids," the unstability of these compounds may be mentioned. The literatures on this subject are so many and so divergent with each other that it is very difficult here to enumerate them briefly. The readers, however, may refer to the excellent book of T. Slater Price⑶ on this subject.

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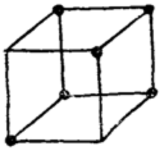
(1) Published in Japanese in the *Journal of the Chemical Society of Japan*, **50** (1929), 231.

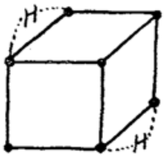
(2) Ibid., **48** (1927), 441; **49** (1928), 511; **50** (1929), 221.

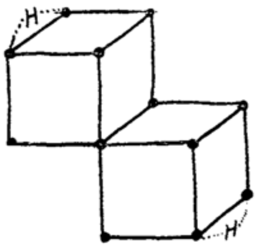
(3) "Per-acids and their salts", Longmans, Green & Co., London (1912).

The structure of the compounds should be considered very complicated but it can not be denied that it is related very closely in the fundamental aspects to that of the "Oxy-acids." Reflection upon the true nature of Oxy-acids," therefore, is required in order to make clear the true nature of "Per-acids." The present author here proposes a new hypothesis called "Acid nucleus theory" for these purposes. The theory starts from the following three postulates.

Postulate I. The natures of the elements which belong to the first, second and third short periods and the "Oxy-acid forming elements" are mainly determined by the arrangement of electrons of the outer shell as G. N. Lewis(1) suggested in his "Octet theory." Accordingly, for example, oxygen, water and hydrogen peroxide possess the following electronic configurations on the outer shells, the black dot showing an electron.







Postulate II. The valences are divided into the following three classes:

(1) Covalence, (2) Electrovalence, (3) Induction-valence.

Among these (1) and (2) have already been fully considered by G. N. Lewis(2) and are produced by the co-owning and locomotion of electrons respectively. Both of these are measurable with integral numbers. The combinations produced by (1) are stronger and firmer than those produced by (2), because, in the former cases, electrons are co-owned. The valence (3), is produced by the phenomenon of electric induction,(3) and is not measurable by integral numbers.

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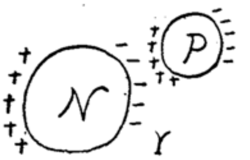
(1) G. N. Lewis, *J. Am. Chem, Soc.*, **38** (1916), 762.

(2) Loc. cit.

(3) Such conceptions as these may exist in everyman's thought implicitly. Cf. G.N. Lewis, *J. Am. Chem. Soc.*, **35** (1913), 1448. The author has attempted only to give a somewhat systematic external form to these conceptions with reference to the problem attempting the clearing up of the true nature of "Per-acid."



Assuming that N is a particle electrically neutral, P is a particle in a polarized state, and the latter approaches to the former, N is naturally polarized due to the electronic induction between the two, where P is called the "Inductor" and N, the "Acceptor."

The force F between them is given by

$$F=\frac{D_P\times D_N}{Kr^2}$$

where D_P denotes the electrical displacement in P, D_N the same in N, r the distance between the two, and K the dielectric constant of the medium.

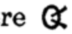
The author's "Induction valence" is nothing but such a force as represented by F. Now, consider a case in which a molecule formed by such a combination is moved to the gaseous space from an aqueous solution. Then the dielectric constant of the medium will continuously change, so also the force F. The valence, therefore, can not be equal in the aqueous solution and in the gaseous state.

Next, any arbitrary inductor is not always capable of inducing any arbitrary acceptor. As to this relation, the following postulate is given. Every inductor radiates its own characteristic electromagnetic wave say an inducing wave. And the wave-length of the characteristic wave is determined by the electronic configuration and the mass of the inductor. When the acceptor receives the wave, there are two cases in which an electrical displacement is either produced or not. The former case is nothing but a phenomenon called "Electrical induction."

When the electronic configuration of an acceptor is of unsymmetrical arrangement, electrical displacement will readily be accomplished and therefore, it is easily induced.

And when the mass of the acceptor is large or the domain occupied in the medium is accordingly large, the specific effects exerted over the mass will be comparatively small as though the same amount of electrical displacement is produced as in the case in which the mass is small. In this case, therefore, the acceptor is not easily induced.

Potulate III. The atom of the "Acid forming element" has so many electrons at the corners of a surface octet as is equal to the valency of the element as an acid. The element has a remarkable tendency to combine with oxygen by a co-valence, namely, by co-owning the electrons to fill the vacancy in the octets and thus makes the whole mass stable.

Such a mass of octets is called "Acid nucleus." For example, the "Acid nucleus" of hexavalent sulphur is given by: Where  shows an octet of oxygen combined with sulphur by co-owning two pairs of electrons. The "Acid nucleus" is not, however, to be hastily recognized at once as the same as the "Acid anhydride." The former is chiefly to be considered as a structural unit and the latter as a name of material.

Then, starting from the three postulates mentioned above, the "Acid nucleus theory" will be explained with reference to the data of a few "Oxy-acids" already existing.

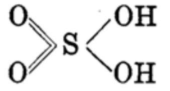
For the sake of convenience a part of the periodic table will be given below.

III		IV		V		VI	
B		**C**		**N**		O	
Al		Si		**P**		**S**	
Sc		**Ti**		**V**		**Cr**	
	Ga		Ge		As		**Se**
Y		**Zr**		**Nb**		**Mo**	
	In		**Sn**		Sb		Te
La (?)		Ce		—		—	
	—		—		—		—
Yb		—		**Ta**		**W**	
	Tl		Pb		Bi		—
—		Th		—		**U**	

In this table, those printed in Gothic type indicate the elements capable of forming "Per-acids." Glancing over the table, one will notice that all the elements capable of forming both "Oxy-acids" and "Per-acids" belong to the fourth, fifth and sixth groups in the table with a few exceptions.

For example, sulphur and phosphorus which form (A) sulphuric acid and (B) phosphoric acid, the most popular "Oxy-acid," belong to the sixth and fifth groups, respectively. They are explained here with the theory.

(A) *Sulphuric Acid.* The constitution of sulphuric acid is commonly represented as follows:



.... (1)

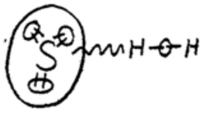
According to this formula, however, the two oxygen atoms out of four and the two hydrogen atoms must be of the same behavior. But in reality, the three oxygen atoms out of four are of the same behavior, e.g.

$$H_2SO_4 + PCl_5 = SO_3 + POCl_3 + 2HCl,^{(1)}$$

and one of the two hydrogen atoms dissociates more readily into an ion than the other.

The formula (1), therefore, is not pertinent to the real state of sulphuric acid molecule, regarding to even the above two points.

Now, according to "Acid nucleus theory," the "Acid nucleus" of sulphuric acid must be such that has been shown previously and be electrically neutral. In this case, a molecule of water, acting as an inductor, approaches to the "Acid nucleus," polarized the latter and combine with an "Induction valence." The above mechanism of the combination is shown schematically in the following figure, in which the wave line indicated the induction valence.



From the above view, the correct answers to the two facts above mentioned will be readily made: The three oxygen atoms out of four are of the same behavior because the combination within the "Acid nucleus" is accomplished by covalence and is, therefore, stronger and firmer than in the other part; and one of the two hydrogen atoms dissociates more readily into an ion than the other because the part ∿∿H-O-H is itself polarized and the two hydrogen atoms are not to be of the same behavior, and as is clear from postulate II the valency exerted between the "Acid nucleus" and water is not always to be measurable by a definite integral number. The large dehydrating power and the large heat of dilution of sulphuric acid mean a large Coulomb's force exerted between the "Acid nucleus" and water molecule, that is the valency force is large.

(B) *Phosphoric Acid.* The peculier property of phosphoric acid is that there are several kinds which are derived from the same pentavalent phosphorus; for example, there are: (a) orthophosphoric acid, (b) pyrophosphoric acid and (c) metaphosphoric acid.

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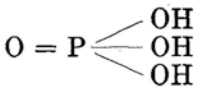
(1) Gerhardt and Chiozza, *Compt. rend.*, **36** (1853), 1050. In this case, SO_3 combines further with HCl and turns into SO_3HCl. Cf. Ostwald, "Grundlinien der anorg. Chemie", Leipzig (1922), 344.

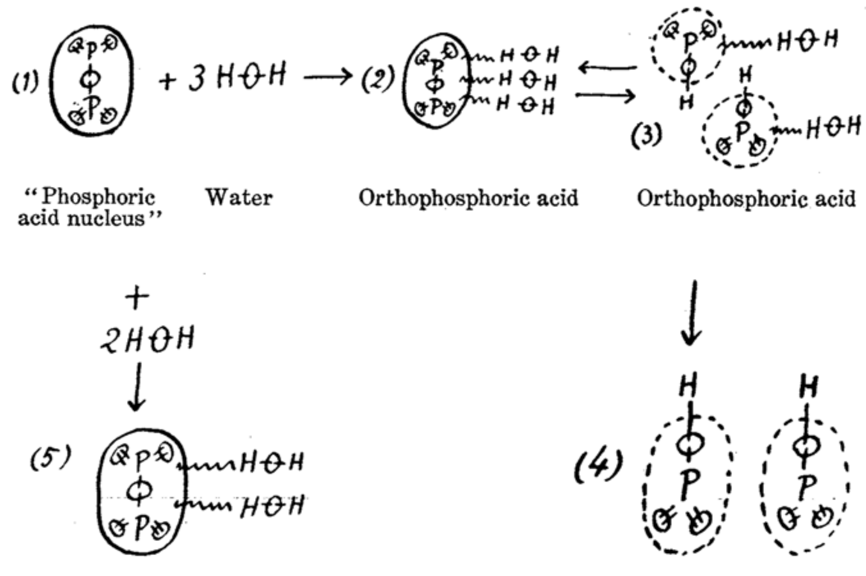
(b) is formed through dehydration of (a) by heating up to 213°C.; (c) is formed when (a) and (b) are thoroughly dehydrated by heating until no more water escapes or when phosphorus pentoxide is dissolved in cold water. These three substances are changeable with one another and the change is mainly controlled by the content of water. It is, therefore, most probable that, when the solution of any of them is boiled for a long time, it contains all three substances as the solutes. The constitutional formula for (a) is commonly represented as below:



$$O = P \begin{cases} OH \\ OH \\ OH \end{cases} \qquad \cdots\cdots\cdots\cdots\cdots\cdots \quad (2)$$

The formula (2) is not also pertinent to the real state of phosphoric acid just as the formula (1) is not so to that of sulphuric acid. From the "Acid nuleus theory," the "Nucleus" of phosphoric acid is given as below:

In this case, two atoms of pentavalent phosphorus gather together in order to render the "Nucleus" stable. But this "Nucleus" is not always the most stable, because it consists of octets of an odd number. It has, therefore, a tendency to separate itself further into two parts in order to form octets of an even number if possible and to combine with water by "Induction valence," as shown below:

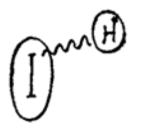


"Phosphoric acid nucleus" Water Orthophosphoric acid Orthophosphoric acid

Pyrophosphoric acid Metaphosphoric acid

As stated above, the "Acid nucleus theory" explains most conveniently the various properties of the "Oxy-acids." It must, therefore, be considered that, to explain the true nature of oxy-acid the present theory is more suitable than the commonly given formula.

The theory of indicator will also be explained easily by the theory as follows. A definite colour change is produced when the concentration of hydrogen ions has a definite value. All indicators are, in the widest sense, acid. The "Acid nucleus" (I) of such an acid can, therefore, be considered.



The above explanation is nothing but an electrical phenomenon produced by a hydrogen ion, an "Inductor" upon the "Acid nucleus" (I), an acceptor. From the standpoint of "Induction valence," the definite hydrogen ion concentration means a definite "inducing" force which produces a definite amount of electrical displacement in (I), or in other word the definite tautomeric change and colour change.

As mentioned above, it has become clear that the "Acid nucleus theory" is most conveniently applied not only to the problem of "Oxy-acids" but also to the theory of indicator. From this same standpoint, a consideration will be given to the true nature of "Per-acids."

As is readily known from Postulate 1, both water and hydrogen peroxide are typical polar compounds. For example, the dielectric constant of the former is 80, the latter is 92.8. Both of these are, therefore, capable of playing the rôle as inductors. This is the reason why there is formed, on the one hand, water of crystallization and hydrogen peroxide of crystallization on the other. In other words, both of these are no other than compounds of the same type being reviewed from a standpoint of "Induction valence." As already stated, if the substance which is formed by combination of "Acid nucleus" with water by "Induction valence" is "Oxy-acid," then "Per-acid" is nothing but a substance which is formed by combination of "Acid nucleus" with "Hydrogen peroxide" by the same valence. The meaning of the above statement will be explained more fully in the following.

Now, by the readiness of formation of "Per-acids" it is perceived that, in the periodic table already given, the elements whose atomic weights are small show a remarkable tendency to form "Oxy-acids" rather than "Per-acids." The latter are formed only under special suitable conditions, as in the case of "Persulphuric acid." But when the atomic weights become larger such as in the case of Ti and V, "Per-acids" are formed most readily by the simple addition of hydrogen peroxide to the acid solutions of the ,,Oxy-acids" and the readiness with which "Per-acids" are formed reaches a maximum in the case of Cr. In all these cases "Per-acids" possess deep characteristic colourations. This is the reason why the "Per-acids reaction" is most frequently recommended in qualitative analysis for the detection of these elements. And finally, as the atomic weights increase further, the readiness of formation and the depth of the colourations decrease, but the stability of "Per-acids" increases. In the case of uranium we find the most stable metallic "Per-acids." In other words, in the case of those elements which readily form "Per-acids" by simple addition of hydrogen peroxide to the solution, the colourations produced are deep but the stability is small. On the contrary, in the case of those elements which form "Per-acids" only under limited conditions, the colourations produced are light but the stability is large. This is the fundamental rule which governs the formation of "Per-acids." The experimental results cited below clearly indicate that the above rule is valid.

No. of exp.	Atomic weight of the acid forming element	Initial conc. of H_2O_2 (mol.)	The ratio of metallic acid present and hydrogen peroxide 1:1	The rise in potential (V.)	The conc. of H_2O_2 in the presence of metallic acids as calculated from the rise in potential (mol.)	The approxim. partial vapor press. of H_2O_2 in the presence of metallic acids estimated from the photographic action (atm.)	The colours of "Per-acids"
1	U = 238	0.117	$UO_3 : H_2O_2$	0.0047	0.117×0.69	0.30×10^{-6}	yellow
2	Ti = 48	,,	TiO_2: ,,	0.0195	,, $\times 0.22$	0.7×10^{-7}	orange
3	Mo = 96	,,	MoO_3: ,,	0.1080	,, $\times 0.22 \times 10^{-3}$	no reducing action	yellow
4	V = 51	,,	V_2O_5: ,,	0.3107	,, $\times 0.3 \times 10^{-10}$	do.	reddish browh
5	Cr = 52	,,	CrO_3: ,,	0.4802	—	—	blue

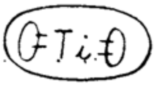
The above table shows that the concentrations of hydrogen peroxide in the "Per-acids" are gradually decreased in the order of U, Ti, Mo, V and Cr; the decreases of partial vapor pressure of the peroxide in these cases being also parallel to the quantity above mentioned. Considering from these points, it is clear that the degree of freedom of hydrogen peroxide in the "Per-acids" are restricted in the order above mentioned. In other words, the combinations of hydrogen peroxide with the "Acid nucleus" in the unstable "Per-acids" are firmer and stronger than those in the stable ones. And here exists, indeed, the key to the problem of clearing up the true nature of "Per-acids." The reason is that, from the above conjecture we know that the combining forces exerted between hydrogen peroxide and "Acid nucleus" are related very closely with the stability and colour of the "Per-acids."

G. N. Lewis⁽¹⁾ once published an opinion on the colour of the chemical substances that the compounds in which electrons are most firmly constrained have no colour; but when the constraints become gradually weaker, they begin to absorb the visible part of the spectrum, from longer wavelength to shorter and they show from yellow to orange or red; and finally, when the constrains reach its loosest condition, they absorb the red or ultra red part in the spectrum, and the colour of the compounds become blue. This theory also throws a light upon the true nature of " Per-acids."

As is clearly know from Postulate II, any arbitrary inductor is not capable of inducing any arbitrary acceptor. This is the reason why those elements situated in the early period of the periodic table show a more pronounced property as " Oxy-acids " than as " Per-acids." The " Acid nuclei " of C, N and S are readily induced by water as an inductor but not by hydrogen peroxide except under special conditions.

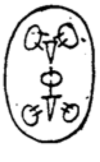
Next considerations will be given upon the case of Ti, V and Cr, whose atomic weights are larger than the preceding case. The " Acid nuclei " of these elements are as shown below:

(1)



" Titanic acid nucleus "

(2)



" Vanadic acid nucleus "

(3)

" Chromic acid nucleus "

Glancing at the configurations of the " Nuclei " of the acids, one will perceive that they well explain the gradual alterations manifested in the properties of these acids. The " Nuclei " which possess as much mass as in these elements are induced both by hydrogen peroxide and water as inductors. Among them (2) and (3) are coloured; the fact means that some electrons whose constraints are loose in some parts, and the " Nuclei " are readily inducable by inductors. This is the reason why V and Cr have a marked tendency to form " Per-acids." In the case of Ti, the loose combining force of hydrogen peroxide with the " Acid nucleus " is due to its comparatively stable configuration. Next in acid solutions, " Per-vanadic " and " Per-chromic "-acids decompose very rapidly and evolve oxygen, the blue and greenish blue colourations of vanadyl ion and trivalent chromium

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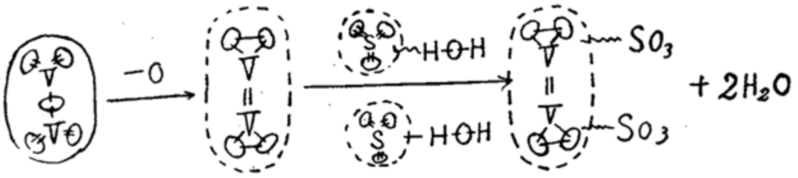
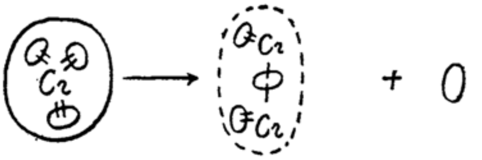
(1) Loc. cit.

respectively being finally produced. In these cases, the electrical displacement produced on the formation of "Per-acids" is so remarkable that the constraints upon some of the electrons are loosened over a definite range and the "Nuclei" suffer such fundamental alterations as mentioned above. The phenomena will most conveniently be represented by the following scheme.

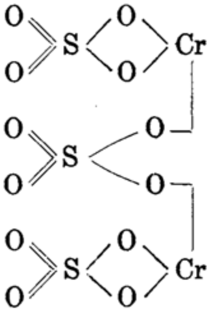
 .. (3)

"Vanadic acid nucleus" "Hypovanadic acid nucleus" Two molecules of sulphuric acid Vanadyl sulphate Water

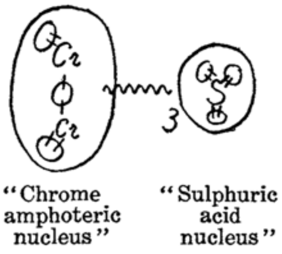
 .... (4)

"Chromic acid nucleus" "Chrome amphoteric nucleus"

Such group as is shown in the right hand side of (4) is called "Amphoteric Nucleus." Reviewing from the standpoint of "Induction valence," such a salt as chromic sulphate which is readily hydrolized must be considered from a different point of view. The constitutional formula commonly given to chromic sulphate is represented as follows.

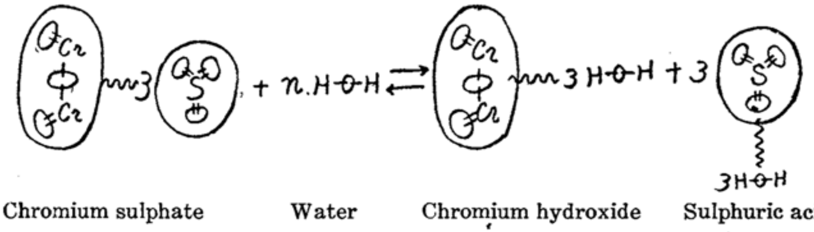
 .... (5)

But by (5), the readiness with which this salt is hydrolized can hardly be explained. The "Induction valence theory," therefore, substitutes (6) for (5)



.... (6)

Then the phenomenon of hydrolysis will be represented by the following,



.. (7)

It is clear that (7) explains the phenomenon very easily. The fact that Al and Cr are not readily deposited from its salt solution by electrolysis will also be conveniently explained by considering the presence of such a "Nucleus."

Now, a consideration will be given upon the case of Mo whose atomic weight is larger than the preceding case. In this case, the constraints upon the electrons is firm and strong as is known from the fact that MoO_3 is colourless. The electrical displacement due to "Induction" is accordingly small and the resulting "Per-acid" is yellow in colour and more stable than those of V and Cr.

The case of U will next be considered. As the mass of the "Uranic acid nucleus" is large, it is easily understood that the "Nucleus" will not be readily induced by the inductor as has been already explained in Postulate II. This is the reason why the freedom of hydrogen peroxide is largest in the case of "Per-uranic acid." The inertia to "Electrical induction" in this case, however, must be considered large, and the resulted "Per-acid" stable.

Finally, an explanation will be given upon the diversity of the compositions of "Per-acids" isolated. As has been mentioned already, the combination of "Acid nucleus" with hydrogen peroxide is accomplished by "Induction valence." It is, therefore, partly dependent on the dielectric constant of the medium, and a different medium will give a different dielectric constant. The diversity of the compositions is, therefore, nothing but a natural consequence of the above reason. This is also the case that there exist various kinds of phosphoric acid.

By the descriptions given above the present author believes that the true aspects of his "Acid nucleus theory" which explains the true natures of "Oxy-acids" or "Per-acids" have been rendered clear. He is also eager to extend his theory to the other problems in chemistry in the near future.

Summary.

1. Starting from three postulates, the presence of "Acid nuleus" has been considered and a new idea "Induction valence" also introduced.

2. That "Oxy-acids" and "Per-acids" are nothing but "Acid nuclei" combined with water or hydrogen peroxide by means of "Induction valence" has been rendered clear.

In conclusion, the author wishes to acknowledge his obligations to Profs. M. Kobayashi, F. Ishikawa and S. Mitsukuri in the Institute of Chemistry, Faculty of Science for their useful suggestions and Prof. T. Murakami, in the Institute of Metallurgy, Faculty of Engineering for the encouragement given to him.

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