ON THE RELATIVE INTENSITY OF CHEMICAL FORCE.

By L. H. Friedburg, Ph. D.

We are accustomed in chemistry to use the words "chemical attraction," or "affinity," without forming a distinct conception as to the manner in which this affinity may act.

The different degrees of readiness with which elements combine suggests the question : What is the cause of this difference in behavior? Some chemical compounds are less stable than others. Even the elements in their pure molecular state are split with greater facility in some cases than others into atoms before entering into new compounds. We are accustomed in this latter case to speak of a resistance which the molecule of an element offers before it enters into combination with other elements. We note that there is a force acting between the atoms of the same element and between those of different elements. We call this the chemical force.

Amongst the newer stereochemical conceptions there is one, expressed by Alex. Naumann[*] in the following words :

"The greatest possible effect of the attractive force between carbon atoms takes place when the directions of attraction coincide with the line which unites the centres of gravity of two such atoms. If the directions of attraction deviate from this line, only that component of the total attraction links the atoms, which lies in the direction of this line." If this be true, it follows naturally that even two carbon atoms may be held in combination by a greater chemical force than that which holds two other carbon atoms together. The reason is to be found in a different stereochemical arrangement.

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[*] Ber. d. Chem. Ges., **23**, 477, 1890.

In applying this idea to the chemical force in general, we find that this force is dependent upon the direction in which it is exerted. Older speculations, notably those of Berthollet, have impressed upon us the idea that the atomic weights have an influence upon this force, although not in such a general sense as Berthollet assumed it. We must add to this the principle of valency, which tell us that the atoms of some elements offer one point of attack to the chemical force while others offer two, three or four points of attack.

Thus we consider chemical force to be dependent upon atomic weight, valency and the direction in which this force acts between the atoms. From this standpoint we may explain chemical action with greater clearness than the mere use of the words affinity or chemical attraction admit of. For example, we find in the first place, that some elements are more ready to display chemical force than others. A hydrogen molecule is more easily split into atoms than a nitrogen molecule. We notice here that for a molecule of an element there is no difference of weight to be noticed, since these molecules are supposed to consist of two or more atoms of the same weight. But the difference of valency and of the direction of the action of force between such molecules need not be the exclusive cause of such difference in behavior as is displayed by hydrogen and nitrogen. The univalent hydrogen atom is bound by a chemical force acting in a straight line to another atom of hydrogen exactly equal to the first; this line evidently has the direction of the line which unites the centres of gravity of the two atoms. We purposely neglect here the theory of rotation of such a system. Two triatomic nitrogen atoms, forming a molecule, are supposed to represent the figure of a three sided double pyramid, the nitrogen atoms occupying two opposite corners.* The direction of any of these valencies which are supposed to act along the edges of the pyramids, certainly do not coincide with the line uniting the centres of gravity of the two atoms. We surmise, therefore, that although one single valency of the triatomic nitrogen atom is equivalent to one hydrogen valency, that the strength of chemical action within the nitrogen molecule cannot be exactly three times

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* Ber. d. Chem. Ges., **23**, 11, 1890.

as large as within the hydrogen molecule, but that it must be smaller to some extent.

It has been suggested above that the atomic weight might, in some way, come into consideration even when molecules of the elements were conceived of. If the chemical force is supposed to be the result of the vibrating ether coming into contact with elementary atoms, it is clear that this force will more easily join together the lighter atoms than the heavier, that consequently the heavier atoms are kept together by an absolutely stronger pressure. If we add that this force finds three points of attack in the nitrogen atom, and but one in the hydrogen atom, we see the possibility of the nitrogen molecule being less ready to display chemical force towards molecules of other elements than the hydrogen molecule.

We may extend this example to the *different* mono-, di-, tri- and tetratomic elements. We shall find, however, that oxygen and sulphur, for example, although both diatomic in *certain* compounds, show a difference in regard to readiness of combining with other elements. The influence of the atomic weight being perceptible in the above sense. Of course, we must allow for the different states of aggregation. Solid sulphur will be slower to react than gaseous oxygen; but we may consider both at the same temperatures in gaseous form, and thus eliminate this influence. As an example, we shall find that carbon dioxide is easier to prepare synthetically than carbon disulphide, water than hydrogen sulphide.

Concerning the *stability* of a chemical compound *formed* from atoms of different elements we find several cases possible.

Firstly, such compounds are more or less stable at ordinary conditions, and without being acted upon by other chemical elements or compounds. This is illustrated by ammonia gas and nitrogen chloride.

The hydrogen atom being fourteen times lighter than the nitrogen atom, it will not be able to bend the valency of nitrogen from its original direction, and the three hydrogen atoms may be considered as symmetrically arranged with reference to the nitrogen. The chlorine atom being two and a half times heavier than nitrogen, the three chlorine atoms representing a weight seven and a half times that of the nitrogen atom, may influence the directions of valency of this latter.

A compound is thus formed (assuming for brevity's sake that its formula be NCl_3) which gives us the conception that chlorine atoms in this case are more nearly in reach of and more likely to act upon one another to form chlorine molecules, and that nitrogen has a tendency in its valencies to spread out to their original direction, forming a nitrogen molecule with a similarly moving nitrogen atom. The whole compound is thus in a state of unstable equilibrium which is easily disturbed with the well known results. In *this particular case* it is difficult to decide whether the atomic weight of chlorine contributes more to the production of an explosion than the tendency of the curbed nitrogen valencies to spread back and to form an original nitrogen molecule. For the other explosive nitrogen compounds the case is a little more complicated, but it follows by analogy that the cause of the decomposition should not be ascribed to the above mentioned peculiarity of nitrogen alone. In all the explosives which contain *nitro* groups (potassium nitrate of gunpowder *not* excluded), it is just as much the tendency of oxygen towards new combinations which causes the explosion when oxidable elements are contained in the *same* compound, as the above peculiarity of nitrogen. Why does not nitric acid, when put upon copper, explode to form nitrogen, copper oxide and copper nitrate? The reason that nitro-products are so largely used for explosives is that they are practically manageable, that they are in other words, not the most explosive bodies. If it were possible to replace in nitroglycerine the three nitro groups by three ClO_2 groups, we should have a more explosive compound. A mixture of potassium chlorate and permanganate can only be pulverized together with the utmost care, as the dry salts may blow up during this treatment. There is no nitrogenized explosive substance known which does not contain oxygen as well as nitrogen.

There are many chemical compounds containing nitrogen in a semi-molecular state, the so called diazo compounds which contain the chromogene group N_2, some of which are beautiful and tolerably fast dyes and not explosive, while it is easily understood that if such diazo compounds do decompose under the influence of chemical reaction, the nitrogen is set free as such in the molecular state, simply because this molecule of nitrogen exists two-thirds preformed in the substance. Also here we see a marked difference between nitrogen and oxygen. Oxygen in a semi-molecular state, so to speak, often shows a tendency to reform its molecule under explosion. Peroxide of hydrogen and the chlorine or iodine compounds of oxygen illustrate this fact.

It must not be forgotten that the oxygen molecule and the sulphur molecule, its analogue in this sense, may be considered as containing dipolar atoms which allow of free rotation around an axis formed by one of their valencies. *This* rotation does not exist in the trivalent nitrogen. The explanation does not seem to be remote, if we admit that this rotation, when suddenly *stopped* by the beginning of combination of oxygen with other elements, causes the production of heat and light. As long as this rotation is partly existing, however, as in the peroxides, the tendency to return to the molecular state is noticeable, considering that oxidation takes place at the same time if the opportunity is offered.

We may note here the fact that phosphorus, antimony and arsenic, represent elementary conditions of molecules similar to that of nitrogen. A difference in the behavior of chlorine compounds of these, when compared with nitrogen chloride, strongly supports our surmise that the atomic weight is one factor which influences the intensity of chemical attraction between atoms. The greater atomic weights of arsenic, phosphorous or antimony as compared with nitrogen prevent the influence of the heavy chlorine atom upon the curbing of the directions of their valencies as we supposed this to take place in nitrogen chloride.

It does not help our purpose here to consider the peculiarity of tri- and pent- atomicity of these elements. It is sufficient to say, that under certain conditions a body may be prevented from offering all its points of attack to a certain force. If we take a horseshoe magnet and only allow one of its poles to attract a piece of iron while the other remains free, we should not be allowed to speak of a unipolar magnet. We may consequently settle this question here by assuming the higher number of valencies to be always shown when compounds exist at lower temperatures. If we surround phosphorus pentachloride with a heated mantle we attain a dissociation into chlorine and trichloride, similar to heated ammonium chloride which furnishes HCl and NH_3 gas.

In many of the cases so far mentioned we recognized reactions, which in a former chemical period were spoken and thought of as taking place between the atoms as between animate beings, by predisposition rather to combine with this than with that element. The mere word affinity, changeable as the sense was in which it was applied at different periods, indicates this animation. The tendency of modern chemistry is to attempt to reduce these reactions to general principles of physics starting from chemical phenomena and remaining upon the chemical standpoint.

We must finally consider another case, which illustrates our endeavor. It is the one examplified by chlorine, when acting upon bromides or iodides, when either bromine or iodine are liberated. We find here cases suggesting reversed conditions as we considered them in chloride of nitrogen and ammonia when compared. The chlorine atomically lighter than bromine is not able to influence the rotation of its unipolar ally hydrogen (as in hydrochloric acid) or of alkali metal in salts *as much* as the heavier bromine or the still heavier iodine. The compounds of iodine with metals show a remarkable tendency towards decomposition with formation of an iodine molecule, although the iodine compounds are still stable when compared to nitrogen chloride.

The *relative* intensity of the chemical force that acts between atoms to form molecules of elements or of chemical compounds must not be lost sight of in all our chemical views.

We have shown the strong points in favor of a more physical consideration of chemical phenomena from a chemical standpoint and it seems as if most chemical reactions might be satisfactorily explained in this way, even to-day.

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