CHAPTER VII.

PHLOGISTON PERIOD AND PROGRESS OF THE BALANCE.

In the 17th century innovations were beginning in chemistry, as we have already seen, but as usual, these did not all take one direction. Van Helmont put his little *archaeus*, a kind of intelligent agent, but with less independence than that of Paracelsus, into the stomach, to do the work which he could find no way of accomplishing by merely physical means. Thus things began a new mystical direction. Becher, in the *Physicae Subterraneae*, ridicules his archaeus and chimeras, and the whole host of "impudent chemists" also, who assert that they obtain salt, sulphur, and mercury, from all bodies, even animals and vegetables. He does not hesitate to call these the greatest falsehoods. He calls "elements the genuine and true things of which bodies consist, and from which others are made and prepared." * But as he held on by the four elements, we are not able to find in him much material.

He had the merit of raising inquiry in a high degree, and of bringing forward his great admirer, Stahl, who introduced phlogiston. In this chapter we have a class of men who have made another advance in experimenting, and whose works are the first which living chemists can, without difficulty, peruse. The advent of oxygen into science was preceded by a century of vague prophesyings. The use of the balance was becoming general, but men had no idea of the accuracy with which nature weighed, although they had long used the proper principle of making the earth the arbiter, by trying which side of the scale she drew most willingly towards her. They

* Phys. Sub. Lib. i., sect. iii., cap. i., No. 12.

had no idea of the fineness of her touch, and her absolute refusal to make any allowance for inaccuracy in the construction of instruments. It was not even known that all bodies could be compared by their weights; why should they not as well be known by their lightness? This plan had its fair trial. By a curious circle of reasoning, it was decided, that what we call oxygen, which makes an oxide, or calx of a metal, was sulphur; afterwards it was the principle of combustion; not such an erroneous idea. Now oxides or earths were, *of course*, simple bodies; when they were reduced to metals in the fire, they combined with phlogiston; they became lighter. Therefore phlogiston had the principle of lightness in it. The rule generally is, that we should begin wrong. We now say the metal is simple, and by uniting with oxygen, it becomes a compound, and is heavier. As the metal burns and gives out heat, they said it gives out its phlogiston, and loses its principle of lightness.* Stahl calls it sulphur. This would scarcely come under our view had it not been the cause of so many inquiries in the same direction, as to bring about a result, derived from an analysis of all the oxides, and a careful comparison of the weight of the metals, with the weight of the oxides, whether produced by combustion or oxidation in the fire, or precipitated from their acid solutions. Even this strange theory tended in the right direction, although at first threatening to take a mystical course. We could scarcely have anticipated this difficulty of proving that all bodies have weight and not lightness, but our forefathers encountered it, and it may yet come to the struggle again, renewed in a higher form, when we have to deal with those physical existences, now called *imponderables*.

I am not aware that any one went into the subject with care before Bergman. He may be said to have introduced modern analysis. Before him analyses were not superior to

* p. 277. "Traité de Soufre" Traduit de l'Allemand de Stahl. Paris, 1767.

those speculations about the constitution of bodies which in former chapters have been passed over. I may indeed cite here Roger Bacon's syntheses of bodies from the four elements, as the earliest examples of an endeavour to shew how so many bodies can be formed from few elements, and on the other side, as the fullest example I know of early analysis, and perhaps the very first in which numbers are used in connection with elements. They are intellectual strivings after quantitative analysis.

"There is, therefore, one different kind where fire and air are greater; 2ndly, where fire and air are less; 3rd, where fire and water are greater; 4th, where fire and water are less; 5th, where fire and earth are greater; 6th, where fire and earth are less; 7th, where air and water are greater; 8th, where air and water are less; 9th, where air and earth are greater; 10th, where air and earth are less; 11th, where water and earth are greater; 12th, where water and earth are less; and so you have two diversities. Next you have three diversities; 1st, where fire, air, and water are greater; 2nd, where fire, air, and water are less; 3rd, where air, water, and earth are greater; 4th, where fire, water, and earth are greater; 5th, where air, water, and earth are less; 6th, where fire, water, and earth are less; and in this manner, if you divide those methods, you obtain from the first 16, from the second 64, from the third 47, from the fourth 18, in all 145. I will now speak of the fourth diversity, fire much, air less, water much, earth less; second, air much, water less, earth less, fire less, and so being ingenious, you may draw out all these diversities to light."

A manuscript copy of Dr. Cullen's lectures in 1762-3 in the laboratory of Owens College, Manchester, from the late Dr. Henry's library, mentions four elements, which, by simple combination, could be formed into seven, but any proportionate combination to account for the number in nature, is not given.

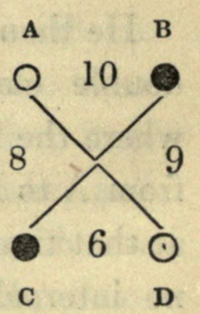
These lectures shew him to have been an exceedingly clear and rational expounder of science. With good common sense he waits for more knowledge when science fails, fully shewing why he became famous, although he published very little. Reasoning on the state of things at the time, he says, "It appears, then, that we know of no physical element, nor any chemical principle, nor are we acquainted with any body which has fixed and permanent qualities."

He afterwards adds, "Having laid down and demonstrated this fundamental proposition, viz., that the changes of the qualities of bodies are all of them produced by combination or separation, I now proceed to inform you that combination depends upon *attraction*, that is, the attraction of cohesion, whereby the small particles of bodies very near each other are disposed to approach, and in a certain contiguity to remain coherent together."

He then goes on to explain simple elective attraction and double elective attraction by diagrams, like those below, where the lines ought to be drawn straight from C to B, and from A to D. This appears to be earlier than Bergman, who at that time had published nothing on chemistry. I can find no internal evidence of their being written later than they profess to be, the binding itself being old.

Dr. Cullen was professor of chemistry at Glasgow, and Dr. Black attended his lectures, before being appointed his successor, on the removal of Dr. Cullen to Edinburgh, in 1756. In the Annals of Philosophy, Vol. III., p. 554, Dr. Thomson says:—"My knowledge of Dr. Cullen's opinions was derived from the late Professor Robison, of Edinburgh, who had the means of information, and, as he was a particular friend and great admirer of Black, is entitled to credit. Now, he informed me that Dr. Black's explanation of double decompositions, which he annually gave in his class, had been originally broached by Dr. Cullen. This was the circumstance that induced me to broach Dr. Cullen's name along with Black and Bergman.

"* * * As to Dr. Black, I consider myself as acquainted with his opinions, because I attended his lectures; and there are thousands in Great Britain who did the same, and who cannot but recollect the facts that I shall state. Dr. Black taught that bodies combine in definite proportions, and he explained double decomposition by means of diagrams, not, indeed, the same as those of Mr. Higgins, but much simpler and more elegant. I have been informed by Prof. Robison, that he employed these diagrams from the very beginning of his career, as a professor. One of them is given in page 554, Vol. I., of his printed lectures. I have no doubt that all similar diagrams, published in London, by Fordyce, &c., were derived from the same source. Now, could the doctrine of definite proportions be taught, and could double decomposition be explained in this way (I quote Dr. Black's explanation), let the bodies A and B be united with a force, 10; and the bodies C and D with a force, 6. Suppose the attraction of A for C to be 8, and that of B for D to be 9, if we mix these bodies, A will unite with C, and B with D. To me they conveyed just as much of the atomic theory as the perusal of Mr. Higgin's book did."

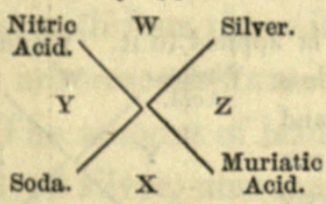


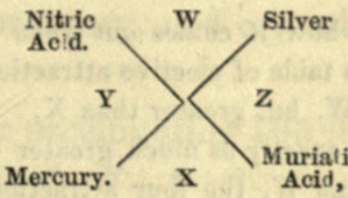
Dr. Robison edited the lectures of Black in 1803, and in a note gives the above diagram and some judicious remarks, shewing, at the same time, that although definite proportion was taken for granted, no general law to account for it had been given.

But the question cannot be as to whether Dr. Cullen discovered the atomic theory, (indeed, this extract might have been brought on somewhat later), but whether Dr. Cullen had so far advanced our knowledge of matter as to be the first who gave out the ideas of single and double elective attractions, such as have been attributed to Bergman.

A note gives a fuller account of Dr. Cullen's views; it was written in the year 1759. Elective attractions were in reality definitely laid down and presupposed in Geoffroy's tables; but the investigation and elaboration was needed.* At present we must consider Dr. Cullen as the first who used the words and explanations in the manner afterwards made so famous by Bergman.

* Note E., p. 45., Cullen's Life, by Thomson, p. 570. Appendix.—The following passages from a letter, written by Dr. Cullen to his friend and former pupil, Dr. George Fordyce, of London, in October, 1759, contains his own statement of his views with regard to double elective attractions. "I must give you the manner of considering the subject, which I fell upon last session, and shall continue to employ as the most easy and simple. I begin with your third and fourth cases, and to these one general rule applies, viz., that when two mixts (compounds) are applied to each other, if in each mixt there is a substance, that from the table of elective attractions, is by itself capable of decomposing the other mixt, the attractions between these substances and the substances they attract in the opposite mixt, must always be greater than the attractions subsisting in the mixts applied to each other; and therefore, &c. Thus, if *nitrum argenti* and common salt are applied to each other, as by the table of elective attractions, the nitric acid in nitrum argenti, is by itself capable of decomposing the other mixt, common salt; and the muriatic acid in common salt is capable of decomposing *nitrum argenti:* the attractions between the nitric acid and the soda, with the attraction of the muriatic acid and the silver must be always greater than the attractions subsisting in the mixts, nitrum argenti and common salt, that were applied to each other. This I illustrate by the diagram adjoined. Let there be two rods intersecting one another, and moveable on a common axis at the point of intersection. At the extremities of each let there be placed substances that have an attraction for each of the substances on the extremities contiguous to them, and let the attractions be expressed by the letters W, X, Y, Z. The rest of the illustration will readily appear from the diagrams.





$Y > X$ and $Z > W$ by table. $Y > X$ and $Z > W$ by table.
Ergo $Y + Z > X + W$ Ergo $Y + Z > X + W$

You see that the prevailing attractions are here determined from the table of single elective attractions.

We are now come to the only difficulty in the affair of double elective attractions in instance past. To this our general rule does not apply.

There is no doubt that, however these opinions might be at the time floating amongst chemists, the works of Bergman were both the fullest and the most important on this subject. From them I shall give rather long quotations. *

"On the different amount of phlogiston in metals,† he says; calces (oxides) do not displace each other, as experience shows, at least, not in the same order as the metals do. May not therefore the quantity of reducing phlogiston in any metal be determined by a comparison of the weights of the precipitated and the precipitating metal? The following experiments will show the answer, but let us first examine, in a general way, those cases which may possibly occur:—

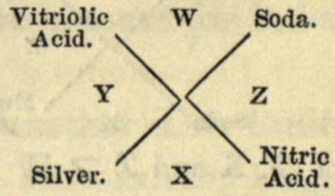
"Let A be the precipitating metal, m the weight of acid necessary for dissolving 100 of A, x the quantity of reducing phlogiston in 100 of A; B the metal to be precipitated, nm the weight of the solvent mentioned necessary for dissolving 100 B, and y the amount of reducing phlogiston in 100 B. n may be equal to unity, or it may be more or less than unity."

"Let, I., $n = 1$ then $m = nm$."

(In other words, if $n = 1$ the quantity of acid necessary for dissolving the precipitating metal, it will be equal to the quantity necessary for dissolving the precipitated metal.)

"In this case, if $x = y$ there is no difficulty, because the solvent of each dissolves an equal weight, and B is able to take from A as much of the inflammable material as is necessary for its reduction.

See how it comes out when my new scheme is applied to it. Y and Z are by the table of elective attractions each of them less than W, but greater than X. If, therefore, Y and Z are exactly as much greater than X, as they are less than W, the four attractions would be exactly balanced; but if Y and Z exceed in any degree more than they fall short of W, than Y + Z must be greater than W + X.



* Torberni Bergman, Opuscula Physica et Chemica, pleraque ante seorsim edita, jam ab auctore collecta, revisa et aucta. Holmiae, Upsaliae Aboae, &c. Vol. I., 1779, II., 1780, III., 1786, IV., 1787, V., 1788, VI., 1790.

† Vol. III., p. 136.

"If x is greater than y there appears still no obstacle to prevent complete precipitation.

"But if x is less than y, so that only a part of B can be displaced, a portion of the dissolved precipitant must be sensibly thrown down, so as to act anew, or some other assistance must be given.

"II. Let $n > 1$ et $m < nm$

"With respect to phlogiston, this is the same result as in case I., but the obstacles are less."

(That is, if the acid for dissolving the precipitating metal is less than the acid which dissolves the metal to be precipitated, as in this case, the precipitating metal would not cease its action for want of acid.)

"III.) Let $n < 1$ then is $m > nm$. In this case B cannot be entirely thrown down, unless $nx = y$ or $nx > y$, because only n 100 of the precipitant A is dissolved."

(That is, if it requires more acid to dissolve the precipitating metal than the one in solution, then the metal in solution cannot be quite thrown down, unless it should be found that the amount of phlogiston in the precipitant is equal to the amount in the precipitate, or greater than it.)

Then, after recounting experiments, the first of which are made with a nitric acid solution, he says, p. 139;

"Therefore 135 parts of mercury have reduced completely into the metallic form by means of their phlogiston, 100 parts of silver which had been dissolved and calcined. This had united with four times its weight of mercury, and crystallized in an arborescent form.

"The amount of lead necessary for precipitating 100 lbs. of dissolved silver, amounts to 234 lbs. * * * * * * *

"C. 375 lbs. of shining plates of copper were put into a solution of silver, and were soon covered with a crystalline silver coating. When all the silver had fallen, the copper plates, when well cleaned, were found to have lost 31 lbs. The precipitated silver was found to amount to a cwt. (100 lbs.)

"In order to examine into the power of different solvents, we precipitated with copper a hundredweight of silver, which was dissolved in vitriolic acid, but there were only 30 lbs. of copper used. This, then, enables us, to some extent, to measure the great avidity with which nitric acid seizes on phlogiston, so much excelling the vitriolic acid."

The amount of each metal needed to precipitate 100 lbs. of silver, is given with the experiments, but to save room, I add a list.

"135	lbs.	Mercury dissolve	100 lbs. of Silver.
234	,,	Lead	ditto.
31	,,	Copper (with nitric acid)........................	ditto.
30	,,	——— (with vitriolic acid).....................	ditto.
29	,,	Iron (with vitriolic acid)........................	ditto.
88?	,,	Tin...	ditto.
		Bismuth could scarcely be determined.	
64	,,	Nickel	ditto.
92	,,	Arsenic	ditto.
37	,,	Cobalt	ditto.
55	,,	Zinc	ditto.
83	,,	Antimony	ditto.
51	,,	Manganese	ditto.

Amounts of zinc used to precipitate 100 lbs. of metals.

217	lbs.	Zinc precipitated......................	100 lbs. of pure	Gold.
416	,,	,, ...	ditto	Platina.
44	,,	,, ...	ditto	Mercury.
26	,,	,, ...	ditto	Lead.
164	,,	,, ...	ditto	Copper.
68	,,	,, ...	ditto	Tin.
49	,,	,, ...	ditto	Bismuth.
70	,,	(the solution was difficult)	ditto	Antimony.

Scarcely any precipitation appears with Iron."

Then, at p. 150, there are certain corollaries, of which the following sentences suit best the subject in hand:—

COROLLARIES.

"A. That dephlogisticated metals unite with different acids in a variable manner (*i. e.*, that different amounts of metal unite to different acids). Thus, 100 parts of silver, dissolved in nitric acid, are reduced by 31 of copper, but if united to vitriolic acid, they want only 30 of copper. In the same way 100 parts of copper, in a vitriolic solution, are restored *to a metallic form* by 146 pounds of zinc, but in a nitric acid solution, 164 lbs. of zinc are wanted. Therefore nitric acid dephlogisticates the metals most, vitriolic acid less, and muriatic acid still less.

"B. Since we added the solutions in a saturated state, it is clear that the mutual quantities of phlogiston in the precipitate and the precipitant are in inverse proportion to the weights. Let the quantity of the phlogiston in a hundredweight of silver be 100, and the amount in a hundredweight of mercury will be 74, in lead 43, in copper 323, in iron 342, in tin 114, in bismuth 57, in nickel 156, in arsenic 109, in cobalt 270, in zinc 182, in antimony 120, in manganese 196. * * * *

"D. Let us see then how those principles before-mentioned may be applied. With respect to silver, which answers to *B*, there is no precipitant or *A*, which acts so as to make $n = 1$. If mercury or lead is used, then $n \mathrel{7} 1$, but if copper, iron, tin, bismuth, nickel, arsenic, cobalt, zinc, antimony, or manganese is used, the case is $n \angle 1$. In the zinc precipitates $n = 1$ is also wanting. Gold, platinum, iron, and antimony, make $n \mathrel{7} 1$, all the rest $n \angle 1$.

"Page 155. According to the experiments produced, the metals richest in phlogiston, are platina, then gold, iron, copper, cobalt, manganese, zinc, nickel, antimony, tin, arsenic, silver, mercury, bismuth, and lead, so that, in some order, it approaches nearer to the first metal. The relative numbers designating the amount found in each, are to be sought by other methods. A trial of each of the metals, so as to obtain the attractions sought for, would be a great labour, if done with sufficient care and sufficiently repeated, but if the work were divided it would be easier. If one would choose for examination mercury, another lead, a third copper, and so on, so as to see their relation with respect to the others, then we should have a series of experiments, which, if rightly compared, would not only disclose the various properties of each, worthy of observing, but would determine also the relative quantities. In this way, if the absolute value of only one were diligently sought out, all the rest would follow.

Vol. ii., p. 373. " The calces of metals have not that amount of phlogiston which is necessary to the metallic condition, but they are still found not entirely deprived of it.

" Metallic precipitates, when properly examined, reveal to us various mysteries."*

" In the following table 100 parts of reguline metal are in all cases understood to be dissolved :— †

100 parts of	Gold	with the	aerated mineral alkali gave	106	of dry precipitate.
,,		,,	caustic	110	,,
,,		,,	martial vitriol	100	,,
,,	Platina	,,	aerated mineral alkali	34	,,
,,		,,	caustic	36	,,
,,	Silver	,,	aerated mineral alkali	129	,,
,,		,,	caustic	112	,,
,,		,,	phlogist. (pruss. of pot.)	145	,,
,,		,,	saline	133	,,
,,		,,	vitriolated	134	,,
,,	Mercury	,,	aerated mineral alkali	110	,,
,,		,,	caustic	104	,,
,,		,,	vitriolated	119	,,
,,	Lead	,,	aerated mineral alkali	132	,,
,,		,,	caustic	116	,,
,,		,,	vitriolated	143	,,
,,	Copper	,,	aerated mineral alkali	194	,,
,,		,,	caustic	158	,,
,,		,,	phlogisticated	530	,,
,,	Iron	,,	aerated mineral alkali	225	,,
,,		,,	caustic	170	,,
,,		,,	phlogisticated	590	,,
,,	Tin	,,	aerated mineral alkali	131	,,
,,		,,	caustic	130	,,
,,		,,	phlogisticated	250	,,

* Page 390. † Vol. II., p. 390.

100 parts of Bismuth	with the aerated mineral alkali	gave	130	of dry precipitate.
,,	,,	caustic	125	,,
,,	,,	phlogisticated	180	,,
,,	,,	pure water	113	,,
,,	Nickel ,,	aerated mineral alkali	135	,,
,,	,,	caustic	128	,,
,,	,,	phlogisticated	250	,,
,,	Arsenic ,,	phlogisticated	180	,,
,,	Cobalt ,,	aerated mineral alkali	160	,,
,,	,,	caustic	140	,,
,,	,,	phlogisticated	142	,,
,,	Zinc ,,	aerated mineral alkali	193	,,
,,	,,	caustic	161	,,
,,	,,	phlogisticated	495	,,
,,	Antimony	aerated mineral alkali	140	,,
,,	,,	caustic	138	,,
,,	,,	phlogisticated	138	,,
,,	Manganese	aerated mineral alkali	180	,,
,,	,,	caustic	168	,,
,,	,,	phlogisticated	150	,,

"Having compared the weights now produced, it is necessary, first, to inquire into the cause of such differences."

* * * * * Is it not then the matter of heat that is attached to the calx, and which is always united to the caustic alkali, for does it not excite heat when dissolved in the simple acids?

"This forms a triumphant foundation for assaying minerals and metals in the humid way, the mere weight of the precipitates being known. * * * * If the same mode of operating be used, the results of the experiments will be always the same. Let us say that a quantity of metal *a* in certain circumstances makes a precipitate of the weight of *b*; if the same method be used, it is obvious that *nb* may safely be allowed to correspond to *na* of the perfect metal, although in the fundamental experiment, the dissolved metal may not have been completely precipitated, or its weight may have been increased by foreign matter, still the same circumstances will produce always the same gain or loss, and the conclusion will remain unshaken. Let then the methods be exactly decided on, and no fallacy is to be feared." *

ON ELECTIVE ATTRACTIONS.

"Simple elective attractions.† Let *A* be the substance to which *a*, *b*, *c*, &c., are drawn; further, let *A* be added to *c* to saturation, this we shall call *Ac*, when again *b* is added, let the union take place to the exclusion of *c*; then *A* is said to attract *b* more than *c*, or *b* has a stronger elective attraction than *c*; then *Ab*, when *a* is added, gives up *b*, and *a* is united instead, then it is understood that *a* excels *b* in attractive force, and the order of the efficacy of the attraction forms a series *a*, *b*, *c*. What we here call attractions, others call affinity; we use either term promiscuously in future, although the latter being more a metaphorical expression does not appear so suitable in physics.

* * * * Page 318. "It has not escaped me, that some chemists have considered, as entirely without foundation, the doctrine which asserts that neutral or middle salts can receive a distinct excess of acid. That this sometimes takes place the experiments to be related most clearly shew, although naturally it *(the excess)* adheres with far less tenacity than that portion which is necessary to effect saturation.

* * * * Page 325. "From all that has been brought forward, I consider it clear, not only that the doctrine of a decided superfluity of either ingredient is not absurd, but that in reality this result is found in many cases. Certainly this superfluity attaches itself much more loosely than the portion necessary for saturation, so that frequently it is easily driven off, but this in no way causes it to be less real."

Here we find Bergman endeavouring to obtain the amount of oxygen in metallic oxides, or phlogiston in metals. He finds that the amount in equal quantities of metals is not the same. This could only be the case if the atomic weights of all metals were the same.

* Page 396. † Vol. III., page 294.

In agreement with this, he finds that the quantity of acid necessary for dissolving certain weights of metals, differs with each metal, and the amount which one metal precipitates from the solution, differs with each metal. This was promising fair for discovery; and in the first table we have the amount of various metals needed to precipitate 100 of silver, in fact, a table of atomic weights, if he could have seen it, although imperfection in experiment rendered it difficult, and the law seemed very intricate.

He drew the conclusion that some acids dissolve metals with more oxygen in their oxides than others, when he says, 100 of silver are reduced by 31 of copper in nitric, and 30 of copper in sulphuric acid. This helped to lead him wrong.

He seems to have most naturally thought that it would be needful to find the relation of the oxygen in a metallic oxide to that in every other, and was naturally surprised at the great labour needed. We know that this would be a most complicated relationship, and that the oxygen is constantly changing its per centage relation in every compound, to such an extent, that it would be impossible to follow it without constant recurrence to its atomic weight. We may look on this inquiry of Bergman as a search, acute although unsuccessful after that last step in simplicity.

He gives a valuable discovery in the establishment of the permanence of the amount of oxygen in precipitated oxides, the very foundation of analysis, and an important step towards the knowledge of permanence of constitution in all substances whatever. That the numbers need correction, need hardly be remarked.

At the same time it seems to be beyond doubt that he did not grasp with great clearness the doctrine of permanent constitution, or he would scarcely have made these remarks on neutral salts receiving a distinct excess of acid. Any indefinite amount added, becomes a mixture only.

He extended the tables of attraction to a great length, calling them elective attractions, preferring attraction to affinity. His tables are 59 in number, the first portion giving the wet way, and the second the dry. These were given in the old symbols, and have certainly a most formidable and unattractive appearance, in his original work. They have, however, been published in England, at an early period, in the form below.

SINGLE ELECTIVE ATTRACTIONS.

IN THE MOIST WAY.

SULPHURIC ACID.	NITRIC ACID.	MURIATIC ACID.
Potash	Potash	Potash
Soda	Soda	Soda
Baryta	Baryta	Baryta
Lime	Lime	Lime
Magnesia	Magnesia	Magnesia
Ammonia	Ammonia	Ammonia
Alumina	Alumina	Alumina
Oxide of Zinc	Oxide of Zinc	Oxide of Zinc
,, Iron	,, Iron	,, Iron
,, Manganese	,, Manganese	,, Manganese
,, Cobalt	,, Cobalt	,, Cobalt
,, Nickel	,, Nickel	,, Nickel
,, Lead	,, Lead	,, Lead
,, Tin	,, Tin	,, Tin
,, Copper	,, Copper	,, Copper
,, Bismuth	,, Bismuth	,, Bismuth
,, Antimony	,, Antimony	,, Antimony
,, Arsenic	,, Arsenic	,, Arsenic
,, Mercury	,, Mercury	,, Mercury
,, Silver	,, Silver	,, Silver
,, Gold	,, Gold	,, Gold
,, Platina	,, Platina	,, Platina
,, Water	,, Water	,, Water
,, Alcohol	,, Alcohol	,, Alcohol
,, Phlogiston	,, Phlogiston	,, Phlogiston

IN THE DRY WAY.

SULPHURIC ACID.	NITRIC ACID.	MURIATIC ACID.
Phlogiston	Phlogiston	Phlogiston
Potash	Baryta	Baryta

SULPHURIC ACID.	NITRIC ACID.	MURIATIC ACID.
Soda	Potash	Potash
Baryta	Soda	Soda
Lime	Lime	Lime
Magnesia	Magnesia	Magnesia
Metallic Oxides	Metallic Oxides	Metallic Oxides
Ammonia	Ammonia	Ammonia
Alumina	Alumina	Alumina

He gave also two tables of his famous double elective attraction, or compound attraction. The examples given are numerous, and would take too much room. The form is exactly the same as given below as Elliot's, no numbers being used.

Elliot published Bergman's tables, with the addition of figures, to show the relative force which one bore to another. He says, "suppose that (see Encycl. Method. Dict. de Chymie, vol. i., p. 552) potash and sulphuric acid attract each other with the force of 9; that oxide of silver and nitric acid attract each other with the force of 2; that the affinity of nitric acid, with potash, is 8, and that of sulphuric acid, with oxide of silver, 4. As 8 + 4 is greater than 9 + 2, decomposition takes place, and two new compounds are formed, nitrate of potash and sulphate of silver."

He then made the symbols so:—

Nitre of Potash

	Potash	8	Nitric Acid	
Vitriol of Potash	9		2	Nitre of Silver
	Vitriolic Acid	4	Calx of Silver	

Vitriol of Silver

G. Morveau continued this *schema* or *symboles*, finding new numbers, and he has put into a short table his results. This is a more definite way of showing the relation of bodies to each other than we have yet seen.

*Table of the numerical expression of the affinities of five Acids and seven Bases, according to the constant relations indicated by the most familiar observations.**

	VITRIOLIC ACID.	NITRIC ACID.	MURIATIC ACID.	ACETIC ACID.	CARBONIC ACID.
Baryta	65	62	36	29	14
Potash	62	58	32	26	9
Soda	58	50	28	25	8
Lime	54	44	20	19	12
Ammonia	46	38	14	20	4
Magnesia	50	40	16	17	6
Alumina	40	36	10	·15	2

At the same time he says,† relating to the figures, "the numbers which I have employed have no certain basis, but because they agree with a sufficient number of the most familiar observations, they may be used without inconvenience, until we recognise the necessity of changing them, so as to make them agree with other results."

Fourcroy gave numbers also on similar principles, but Morveau objects to them as being so small that it was not easy to find intermediate ones, whilst he objects to Kirwan's numbers which gave the weight of the base as the amount of the affinity, because this did not agree with results.

In these schemes of double decomposition there seems to be a tacit agreement, that the acid which saturated one base, would saturate the second.

Kirwan experimented very much in the direction which Bergman had followed. He is another of those who nearly discovered the atomic theory, who laboured in a legitimate direction, but whose discoveries and theories on the subject are merged in the higher and simpler law.

A brief extract will give his results.

"The discovery of the quantity of real acid in each of the mineral acid liquors, and the proportion of real acid taken up by a given quantity of each basis at the point of saturation, led me, unexpectedly, to what seems to be the true method of

* Dict. de Chymie, Vol. I., p. 558. † Page 557.

investigating the quantity of attraction which each acid bears to the several bases to which it is capable of uniting; for it was impossible not to perceive, first, that the quantity of real acid, necessary to saturate a given quantity of basis, is inversely as the affinity of each basis to each acid. 2ndly. That the quantity of each basis, requisite to saturate a given quantity of each acid, is directly as the affinity of such acid to each basis. Thus 100 grains of each of the acids require for their saturation a greater quantity of fixed alkali than of calcareous earths, more of this earth than of volatile alkali, more of this alkali than magnesia, and more of magnesia than of earth or alum, as may be seen in the following table.

Quantity of Basis taken up by 100 *grs. of each of the Mineral Acids.*

	Veget. fixed Alkali.	Mineral Alkali.	Calcareous Earth.	Volatile Alkali.	Magnesia.	Earth of Alum.
	grs.	grs.	grs.	grs.	grs.	grs.
Vitriolic Acid...	215	165	110	90	80	75
Nitrous Acid ...	215	165	96	87	75	65
Marine Acid....	215	158	89	79	71	55

"As these numbers agree with what common experience teaches us concerning the affinity of these acids with their respective bases, they may be considered as adequate expressions of the quantity of that affinity, and I shall in future use them as such. Thus the affinity of vitriolic acid to fixed vegetable alkali, that is, the force with which they unite, or tend to unite, to each other, is to the affinity with which that same acid unites to calcareous earth, as 215 grs. to 110; and to that which the nitrous acid bears to calcareous earth as 215 grs. to 96," &c.* He adds a similar table of metals and acids. Kirwan gives here what would lead to the atomic weights of the bodies had he known the law which appears to have been first published by Richter; one obtained the atomic weights as the measure of affinities, the other reciprocal

* Philosophical Transactions Abridged, Vol. XV., p. 335-6, year 1783. This was read, I believe, in 1782.

affinities, but neither knew the other's results, and both were lost sight of. The one (Ritcher) did not know that he had got close upon a universal law, the other (Kirwan) did not know that he had got the mode of expressing that universal law, but used it for what it was little worth, an expression of affinity.

We now come to Wenzel, one of those men whose names have been brought forward as a much neglected philosopher, and to whom almost every writer on the history of science, who has had occasion to mention him in later years, has been anxious to award the due honour. We see his book constantly quoted. Some writers give us his words, others give us what appears such a clear explanation of his ideas that we feel no more to be wanting. I had been long anxious to obtain his works, but after advertising in Germany, and inquiring in several towns and large libraries in this country, as well as in France and Germany, I did not obtain the volume, and proceeded without it. I afterwards found that a duplicate copy existed at the Munich Royal Library, and was fortunate enough to obtain it, duplicate copies being generally disposed of. Having read it carefully over, I found no such passages as are imputed to him; and, therefore, read it still more carefully again, and then a third time, but they did not exist. Having written to two eminent historians of science for an explanation, I find that neither had seen the volume; but one of them informed me that the mistake had been rectified in a supplement to the "Handwoerterbuch der Chemie u. Physik."*

The reciprocal saturation which results when two salts decompose each other, is the discovery, the honour of which has long been given to Wenzel. It is a curious fact that not only does he not see this, but he sees and explains the con-

* It is by Dr. J. S. C. Schweigger, and has been since published as a pamphlet (Ueber die Stoechiometrische Reihen im Sinne Richter's), &c., Halle, 1853.

trary, as he shews us that in double decomposition something always remains unsaturated; but generally very little remains. One is sorry that being so near a law, he had not the slightest conception of it. The most important part of his work, as far as our purpose is concerned, seems to me to be contained in the following sentences. The title of the work is "The Doctrine of the Affinity of Bodies."* I shall not give the original, although scarce, as the work, from the fact above stated, has lost its great importance.

In the Preface, he says, "at first my only intention was to make for my own use a treatise which should contain the order of the ascertained affinities and the circumstances under which they acted, lest I should not be able to remember them. But it occurred to me that others might find it useful also, if it were more worked out. For this end I endeavoured to explain the cause and the law of affinity on a good foundation, and the circumstances under which the bodies combine as well as the true relation of their weights towards each other.

Page 4. "It is of itself clear that any combination of bodies must have a constant unchangeable proportion, which can neither be greater nor smaller without some cause acting externally, because, otherwise, nothing certain could be decided on by comparing them. It therefore necessarily follows, that every possible combination of two bodies stands in the most exact relationship with every other, and this relation expresses the degree of combination.

Page 9. "These smallest particles of each body have at all times, in a natural state, a determinate figure; but the whole mass of the body takes a form according as chance or art gives it, without causing any change in the smallest particles, just as the tender fibres or tubes in a piece of wood remain always the same, although the whole piece may be in the shape of a ball or a cube."

* Carl Friedrich Wenzel, Lehre von der Verwandschaft der Koerper. Dresden, 1777.

Page 10. "I examine the natural structure of some metals, I see certainly nothing more than that they are hard solidly-united heavy bodies, which become liquid in the fire at different degrees of heat, and lose their former connectedness (or cohesion), and without being heavier take up a greater or less space than before. This is enough to enable us to conclude that the figure of the smallest particles of metals is changed by the fire, and that the fluid condition of the whole mass, and its altered specific gravity, are the necessary consequence of this alteration of figure. For when the mass of a body without change of weight takes up a greater or less space, it is certain that it can take place under no circumstances except a change of figure in the smallest portions of the bodies. A thousand small cubes may be put into a smaller space than the same number of spheres of the same mass and weight, and the heap made by the spheres is not so great as if they were converted into stars, and so on. When the specific gravity is altered, no matter by what means, the figure and situation of the smallest parts can no longer remain the same."

Page 20. "Besides change of figure, I know no sufficient reason for all that has been said; for if we completely banished the figure, and viewed the properties of the body as something substantial in matter, I know not how we could explain without contradiction the every-day experience; or we must, as Snellius with refraction, explain it by the will of God, which settles the matter at once; but if my understanding is to lay hold of the method by which anything acts, this explanation will not be satisfactory.

Page 28. "But we have remarked that any combination of bodies, on account of the figure of their parts, depends on static laws, and there it is proved that the motion of a weight is so much the slower the smaller the force is, in comparison with it. Let us apply this to the present case, and bodies will appear to us as so many weights, and their common solvent as a force, which acts more slowly or more rapidly on one or the other. It follows, then, that the more rapidly a common solvent unites with a body, the greater must be its degree of combination, and we obtain therefore this law.

" *The affinity of bodies with a common solvent is in the inverse ratio of the time taken to dissolve.*

Page 31. " We have now a universal law, according to which the affinity of bodies or their rank in the series is decided, and we obtain at once this important advantage, that we not only know that the union of a common solvent is greater or less with any body, but also how much greater or less it is, because the difference of the time of solution shews the difference of the combination. Therefore amongst a number of bodies, the combination of one with a common solvent may be considered as a quantity which may be expressed by a fixed number, if we take the smallest in such a series as *unity*; and by this means we are able to give a correct explanation of all phenomena.

Page 46. " This important question, then, remains, why a solvent, when it is only moderately diluted, does not in the least attack certain metals, but as soon as another metal is dissolved in it, with which it naturally has a less affinity, a ready solution of the first takes place. Page 47. Because here the powers meet which assist each other.

Page 72. " The circumstances under which this metal (iron) is dissolved by vitriolic acid are these, that the acid must not be strong. When both unite, iron vitriol is formed, which loses the most of its acid in the fire, as well as by frequent solution in water. A small bored cylinder of Styrian steel of 102 grains was put into half an ounce of the spirit of vitriol, diluted with an equal quantity of water, exactly as with the zinc experiments; there remained 46¾ grains of steel, and 55¼ grains were dissolved in the half ounce of the spirit of vitriol.

"Therefore the relation of the hardest steel to the strongest vitriol is 175 : 240.

"*Application of the doctrine of affinity of bodies.** "This will best be shewn by examples.

"Is it possible by Beguin's spirit of sulphur (a sulphide of ammonium chiefly) to decompose the *luna cornua*, or to separate the muriatic acid entirely without loss?"

"To settle this question we require only the following experiments. Muriatic acid has a smaller degree of affinity with silver than with the volatile salt. Sulphur, on the other hand, unites with silver in preference to the volatile salt. The silver is not separated from the muriatic acid by the volatile salt, on account of accidental circumstances, but this separation follows the moment any other body unites with the silver, if it has not the property of dissolving the silver. But sulphur is just such a body, and is, therefore, fitted for the purpose. If, then, the spirit of sulphur of Beguin is poured on finely powdered luna cornua, it is easily seen that the muriatic acid in the luna cornua must unite with the volatile salt in the spirit of sulphur, and the sulphur will unite with the silver. The new products that are formed by this separation, can consequently be nothing more than common sal ammoniac and sulphuretted silver.

Page 452. "Another similar question arises by which the proportions of the mixture must be considered. How much cinnabar must be mixed with the *luna cornua*, so as completely to separate the silver?

"The possibility of this decomposition may be shewn in the same way as in the first case. If no particular experiment is made, it depends on the comparison only of the following propositions. Half an ounce of *luna cornua* contains $180\frac{9}{10}$ grains of fine silver. Half an ounce of fine silver takes up $35\frac{1}{2}$ grains of sulphur. We may then calculate that for $180\frac{9}{10}$ grains of fine silver, $26\frac{3}{4}$ grains of sulphur are required. We know besides,

* Page 450.

that cinnabar contains sulphur in the proportion of 65 to 240 of quicksilver, or 65 grains of sulphur united with 240 of quicksilver, are to be met with in 305 grains of cinnabar, therefore $26\frac{3}{4}$ grains of sulphur are contained in $125\frac{1}{2}$ of cinnabar. This quantity of cinnabar, as regards its sulphur, will be sufficient for the decomposition of half an ounce of *luna cornua*.

"But we must inquire if $125\frac{1}{2}$ grains of cinnabar contain as much quicksilver as will be sufficient to take in the muriatic acid which is saturated with the silver. Half an ounce of luna cornua contains $53\frac{7}{16}$ grains of muriatic acid of greatest concentration. In half an ounce of the caustic sublimate there are $58\frac{1}{3}$ grains of the strongest acid, which is saturated with 174 grains of quicksilver. From this proportion it is found that $53\frac{7}{16}$ grains of the strongest muriatic acid are required for $159\frac{2}{5}$ grains quicksilver. Now as there are in cinnabar 240 grains of quicksilver united with 65 grains of sulphur, $159\frac{2}{5}$ grains of quicksilver require $43\frac{1}{8}$ grains of sulphur. Both together give nearly $202\frac{1}{2}$ grains of cinnabar. Consequently, from $125\frac{1}{2}$ grains of cinnabar, all the muriatic acid found in the luna cornua is not separated. We see from this that the muriatic acid of the lunar caustic rises in sublimation with the quicksilver out of the $202\frac{1}{2}$ grains of cinnabar as a caustic sublimate, whilst the silver remains united only with so much sulphur as it found in $125\frac{1}{2}$ grains of cinnabar."

His *smallest parts* of bodies are not atoms, but molecules rather, or particles, as they change their form.

He has made a theory of affinity, and attempted to represent the force by a number. To attempt to give the numerical or dynamical ratio of every body to each other was an object of the very highest kind, and we must look on him as one of those less fortunate men who, when search was required in every direction, has had the misfortune to have the wrong one assigned to him. He searched in the direction of time, and obtained a manifest fallacy; as bodies are constituted abstractly he might be correct, but his theory cannot be introduced into science at present, and in the way he introduced it, it was entirely a mistake. But he has done great service in early times in seeking for the distinct constitution of bodies, and in asserting the constancy of combination; whilst he obtained numbers representing the constant relation of bodies to each other, he failed to see that they would be reciprocal. This failure at once removes him from the great discoverers, and places him among those honourable and valuable labourers in science whose names are read with respect by students, but who cannot be recognised by mankind generally, because the capacities of our minds are too small to retain more than the lives of a few of the most eminent.

The doctrine of reciprocal proportion must be taken from him, and he can now no longer hold a place in the history of the atomic theory other than as the author of an intelligent attempt which has entirely failed.

I feel sorry to leave him in this state, and a few kind words will do little good. I believe he would have preferred the truth; the honour he received was not required by him; the discovery was not claimed by him; he died in 1793, before it was known to be worth making. In his works he appears an honest, earnest man.
