GRÜNWALD'S MATHEMATICAL SPECTRUM ANALYSIS.

THE following interesting criticism of Dr. Grünwald's recent work on the mathematical spectrum analysis of various of the elements, by Joseph S. Ames, of the Johns Hopkins University, appears in the February number of the *American Chemical Journal*:—

"Dr. Anton Grünwald, Professor of Mathematics in the Technical High School at Prague, has given his theory of spectrum analysis in the following papers:—(1) 'Ueber das Wasser-spectrum, das Hydrogen-, und Oxygenspectrum,' *Astronomische Nachrichten*, No. 2797, 1887, and *Phil. Mag.*, xxiv. 354, 1887; (2) 'Math. Spectralanalyse des Magnesiums und der Kohle,' *Monatshefte für Chemie*, viii. 650, *Wiener Sitz. Berichte*, 2 Abth. xcvi., 1887; *Phil. Mag.*, xxv. 343, 1888 (abstract); and (3) 'Math. Spectralanalyse des Kadmiums,' *Monatshefte für Chemie*, ix. 956.

"His aim is to discover relations between the elements by tracing connections between their spectra, and thus to arrive at simpler, if not fundamental, 'elements.' He considers the lines in the spectra of two substances, say A and B. If he finds a group of lines in the spectrum of A, which, on multiplication with a simple numerical factor, give line for line a group in the spectrum of B, he assumes that A and B have a common component. This factor, which transforms the one group into the other, is, he says, the ratio of the volumes occupied by the common constituent in unit volume of the two substances. Thus, let *c* be common to A and B, and let it occupy the volume $[a]$ in unit volume of A, and $[b]$ in unit volume of B; then the factor which transforms that part of the spectrum of A due to *c* into that of B, also due to *c*, is $[b]/[a]$. It is not difficult to find relations between the spectra of different substances; and, accepting Dr. Grünwald's hypothesis as to the transforming factor, we can deduce formulas for the elements. For example, in the hydrogen spectrum there are two groups of lines, $[a]$ and $[b]$, which, when multiplied respectively by $\frac{19}{30}$ and $\frac{4}{5}$, give corresponding groups in the spectrum of water, and, since in water hydrogen occupies $\frac{2}{3}$ of the volume, we have the equations

$$[a] + [b] = 1$$
$$\tfrac{19}{30}[a] + \tfrac{4}{5}[b] = \tfrac{2}{3}$$
$$\therefore [a] = \tfrac{4}{5}, \quad [b] = \tfrac{1}{5}$$

which gives hydrogen the composition ba_4. For reasons which depend upon solar physics, Grünwald calls the substance *a* coronium, and *b* helium. Further, he says that all the lines in Hasselberg's secordary spectrum of hydrogen can be changed into water-line by multiplving by $\frac{1}{2}$; which shows, according to his theory, that the modified molecule H^1 occupies in H_2O half the volume it does in the free condition. He finds that oxygen has the composition $H^1b_4(b_4c_5)_5$, where *c* is a new substance. In his last paper, however, Dr. Grünwald states that he has proved *c* to be nothing but *a* in a different state of compression.

"He adopts the spectrum of water, *i.e.* of the oxyhydrogen flame, as a standard, and is then able to give various criteria by means of which the primary elements *a* and *b* may be recognized. Among them are the following: If λ is the wave-length of any line produced by *a* as it exists in hydrogen, $\frac{19}{30}\lambda$, $\frac{3}{4}\lambda$, $\frac{56}{75}\lambda$ will each be the wave-lengths of any line of the water-spectrum, and if λ is the wave-length of any line produced by *b* as it exists in hydrogen, $\frac{4}{5}\lambda$ will be the wave-length of a line of the water-spectrum. Applying his criteria to magnesium, carbon, and cadmium, he finds that they are made up entirely of *a* and *b* in various states of compression. For instance, one group of lines in the cadmium spectrum is transformed into a group of *b* by the factor $\frac{2}{3}$, another group is identical with a group of *b*, and so on. But the group of lines of *shortest* wave-length is transformed into a group of *b* by the factor $\frac{7}{6}$; and cadmium falls in the seventh row of Mendelejeff's table. Similarly, the group of lines of shortest wave-length of zinc is transformed into a group of *b* by the factor $\frac{5}{4}$, and zinc is in the fifth row of the table. Dr. Grünwald finds in this a general law which he verifies in the cases of Al, Si, Fe, Cu, Zn, As, Sr, Ag, Cd, In, Sn, Sb, Te, Ba, Au, Hg, Tl, Pb, and Bi. He farther connects the lines of greater wave-length with the substance *a*; and, as in all cases so far tried all the lines can be deduced from these two substances, he is led to believe that *all the so called elements are compounds of the primary elements a and b*.

"It is unfortunate that Dr. Grünwald has not published a complete list of the lines characteristic of *a* and *b*, for until this is done his theory cannot be accurately tested. There are two distinct questions to be answered: (1) Are there any numerical relations connecting the spectra of the elements? and if so, (2) what is the meaning of the fact? Cornu, Deslandres, and others have long since answered the first question for us, but whether Dr. Grünwald's answer to the second is correct or not depends upon the completeness with which the numerical relations hold for the *entire* spectra of the substances. It is here that Dr. Grünwald's work can be criticized.

"As noted above, the spectrum of the oxyhydrogen flame is used to test the existence of lines belonging to *a* and *b*. By far the most accurate and complete determination of this spectrum is that of Liveing and Dewar (Phil. Trans. 1888); but this does not always answer Dr. Grünwald's purposes. In the B. A. Report for 1886 there is a provisional list of lines of the water-spectrum, which he often uses, although the wave-lengths have since been corrected. Further, if other lines are necessary, they are found by halving the wave-lengths of the secondary spectrum of hydrogen. Many lines thus determined are actually present in the water-spectrum; but why are not *all* there? Dr. Grünwald says it is because the amplitude of vibrations of parts of the molecule can be so changed, owing to the presence of other substances, that the intensity may increase or diminish, or become too faint to be observed. To this argument there is absolutely no answer. In some cases, too, the average of two wave-lengths is used as a criterion of a wave-length of *b* which falls between them! And as a last resort, if the necessary wave-length cannot be found in the water-spectrum by any of these means, it is put down as 'new,' and is called an 'unobserved' line. As just shown, Dr. Grünwald easily explains why the strongest lines in the spectrum of an element, cadmium for example, when 'transformed' into water-lines, may be faint, and *vice versâ*. But how does he account for the fact that double lines are not transformed into double lines? This seems to me a fundamental objection. The concave-grating gives the only accurate method of determining the ultra-violet wave-lengths of the elements; and, as a consequence of not using it, most of the tables of wave-lengths so far published are not of much value. So Grünwald's error here may be great. And, besides, when we consider that in the water-spectrum as given by Liveing and Dewar, without the help of the secondary spectrum of hydrogen, there is on the average one line for every two Ångström units, it would be remarkable indeed if any law could not be verified. This is strikingly shown in the first group of the cadmium lines. Here 6742 and 6740 are two readings for the wave-lengths of the *same* line, as made by two observers; yet Grünwald finds a water-line for each of them!

"The fact that there are exact numerical relations connecting the spectra of different elements does not afford a proof of Grünwald's hypothesis; and until the above difficulties are removed the evidence is against it. But, even granting it, how do we know that *a* and *b* are not themselves compounds? In the second group of cadmium lines there are nineteen lines which can be transformed into *b* lines; *b* has many other lines; so at the most this only shows that cadmium and *b* have a common constituent unless, of course, the absence of the other cadmium lines is accounted for in Grünwald's own way of varying intensity.

"The lines of the spectrum of any substance, as carbon or iron, seem to fall into definite series or groups; and the wave-lengths of the lines in these groups can be expressed by formulas, as is well known. All that the fact of there being a connection between the spectra of different substances seems to show is, then, that there may be a formula common to many elements, as Kayser and Runge have recently found. And all that this means is that the molecules of those elements vibrate in general according to a similar law."

ON THE FORMATION OF MARINE BOILER INCRUSTATIONS.[1]

IN the older forms of marine boilers, sea water was almost universally employed; but with the introduction of high-pressure tubular boilers the amount of deposit was so serious, and the difficulty of removing it so great, that it became imperative to use distilled water. It is found, however, that the trouble has

[1] A Paper read at the thirtieth session of the Institution of Naval Architects, by Prof. Vivian B. Lewes, F.C.S., F.I.C., Royal Naval College, on April 11, 1889.