II. "On the Existence of Multiple Proportion in the quantities of heat, or equivalent alteration of internal space of bodies, caused by definite changes of state as produced by Chemical Combination or otherwise." By THOMAS WOODS, M.D. Communicated by Prof. STOKES, Sec. R.S. Received November 28, 1855.

(Abstract.)

Gay-Lussac having shown that the combining proportions of gases and vapours are either equal in volume or some multiple of each other, and other chemists, particularly Playfair and Joule, having extended the same law to solids and liquids, it is evident that *specific volume* of its combining equivalent is characteristic of matter. But as every substance is composed of matter and space, or of particles with some distance between them, as is shown by expansion and contraction, whenever volume is altered there must be either an addition to or subtraction from the internal space of the body. This alteration of volume is evident in the case of bodies expanding or contracting by gain or loss of heat; but in chemical combination, where alteration of internal space must take place also (as shown by change of temperature, and because *specific* volume being characteristic of matter, this volume must change when the matter changes, by a substitution of a mixture of two kinds of matter for one), in chemical combination, I say, this alteration of internal space is not so plainly demonstrable. Still, in the change of temperature, we have not only an evidence, but a measure of the change of state of combining bodies. For, the phenomena of heat being produced by a *dual* force acting equally in opposite directions, one body cooling or contracting as another becomes heated or expands, it may be taken for granted that whenever heat or expansion is found in one body, the opposite change is occurring in some other. Now, regarding this proposition as true, it is intended to be proved from the combinations of oxygen that the internal space of a substance is lost and gained in multiple proportion, in the definite changes of state of bodies, such as in the condensation of vapours into liquids, and liquids into solids, and the reverse; and also in chemical combi-

nations and decompositions; and therefore that the *space* as well as the *matter* of which volume is composed can be only added to or taken away in what is called its combining equivalent.

In order to find whether the heat of chemical combination, which is taken as equivalent to the alteration of internal space, is equally produced by the same substance uniting with others, or if not, if it is given out in multiple proportion, oxygen is made to combine with several other simple bodies, and the alteration of temperature noted.

The method of oxidizing these substances, the details of each process being given in the paper, consisted in dissolving them in some suitable menstruum,—for instance, in sulphuric acid, liquor of potass, and nitric acid. When the two former are used, water is decomposed to oxidize the dissolved body; in the last case, the nitric acid is resolved into oxygen and binoxide of nitrogen, the former of which unites with the substance to be oxidized, the latter escaping. Other combinations and decompositions at the same time take place (as detailed in the paper), and being taken into account (decompositions absorbing as much heat as is produced by the combination of the constituents), the alteration of temperature by the oxidation alone is arrived at.

In this manner eighteen different metals were oxidized, but the heat of oxidation was obtained satisfactorily only with twelve. Other experimenters (Favre and Silbermann and Andrews) have, with a different object in view, found the heat of oxidation of fourteen other substances; their conclusions are added as being from unprejudiced sources, and the result of all the experiments is brought together in a table, in order to see whether the law of multiple proportion exists. The numbers found by the different experimenters are all calculated to the same standard. The unit of heat is the amount necessary to raise the temperature of 1000 grains of water 1° Fahr., and the quantity of the metal oxidized is an equivalent of each, oxygen = 1.

To find whether the law extends to change of state when no chemical combination takes place, the amount of heat given out by the condensation of an equivalent of steam, and by the solidification of an equivalent of water, is given. The following is the table giving the thermal equivalents of the several substances, the names of the experimenters, and the ratio of proportion. It is to be remarked,

that the condensation of steam being in multiple proportion with the other thermal equivalents, the expansion of all other bodies into vapour must be included; for I showed in the Philosophical Magazine for January 1852 (page 48), that all bodies expand into vapour in some multiple of their atomic volumes, and their atomic volumes being in ratio also, their expansion or gain of internal space in this definite change must be in multiple proportion.

Table showing the quantity of heat produced in 1000 grs. of water by the oxidation of an equivalent of each substance, O = 1.

Name of substance oxidized.	Units of heat.	Ratio.	Name of Experimenter.
Latent heat of ice ...	·1603	·1603	
Latent heat of steam	1·287	8 times ·1603	
Iodine..................	·8	5 times ·1603	Woods.
Chlorine...............	−1·6	....	Favre and Silbermann.
Nitrogen...............	1·6	twice ·8	Woods.
Silver	1·6	....	Woods.
Selenium	2·7	....	Favre and Silbermann.
Mercury..............	2·4	3 times ·8	Woods.
Palladium	2·42	....	Woods.
Molybdenum	3·38	4 times ·8	Woods.
Carbon	3·3		Favre and Silbermann.
Arsenic	4·8	....	Favre and Silbermann.
Antimony	4·8	....	Woods.
Copper	4·9	6 times ·8	Favre and Silbermann.
Cobalt	4·8	....	Woods.
Bismuth..............	4·82	....	Woods.
Nickel.................	6·5	8 times ·8	Woods.
Lead	6·2		Favre and Silbermann.
Hydrogen	7·8	....	Favre and Silbermann.
Tin	8·0	....	Mean of Andrews and Favre and Silbermann.
Phosphorus	8·1	10 times ·8	Favre and Silbermann.
Cadmium	8·18	....	Woods.
Iron	7·95	....	Mean of Andrews and Favre and Silbermann.
Zinc	9·6	12 times ·8	Favre and Silbermann.
Manganese...........	10·4	13 times ·8	Woods.
Barium	12·8	16 times ·8	Woods.
Aluminium...........	16·16	20 times ·8	Woods.
Sodium	17·5	22 times ·8	Favre and Silbermann.
Potassium	17·3		Favre and Silbermann.

Note.—I proved in a paper published in the Philosophical Magazine for October 1851, that "the decomposition of a compound body absorbs as much heat as the combination of the elements originally

produced." I believe I was the first to prove this as a general proposition, and, by so doing, laid the foundation of almost all the thermochemical researches since carried on; for, as far as I am aware, no process which took decomposition into account was used before my paper was published.

In a paper read to the British Association at Belfast, and published in the Philosophical Magazine for November 1852, I proved that the intensity of chemical affinity might be measured by the quantity of heat produced by the combination.

As regards the first of these papers, Mr. Joule published in the Philosophical Magazine for June 1852, a memoir proving exactly the same proposition, but giving me the merit of priority in a preliminary remark. It is, however, singular that Favre and Silbermann bring forward in 1853 (Annales de Chimie et Physique, vol. xxxvii. p. 507) the very same experiments to prove the same fact, and give it as their own.

As regards the second paper. In six months after its publication, Messrs. Favre and Silbermann (Annales de Chimie et Physique, vol. xxxvii. p. 484) prove the same truth with the same experiments, using exactly the same metals, and give their memoir as producing an original idea.

I notice these coincidences here as being remarkable, and because the propositions contained in the paper referred to are the groundwork of the present experiments, and also with a view to prevent an unconscious repetition on the part of Messrs. Favre and Silbermann.