XXII. On the composition of caffenin, and of some its compounds

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to ascertain how far the mechanical equivalent of heat, as determined by my recent experiments on the friction of fluids, might be able to contribute to clear up this question.

The capacity of air at constant pressure, according to the experiments of De la Roche and Berard, is 0.2669. Consequently a quantity of heat capable of increasing the temperature of a lb. of water by 1° , will give 1° also to 3.747 lbs. of air, while the air will be expanded $\frac{1}{491}$; an expansion in which a force equal to 200.7 lbs. through a foot is expended in raising the atmosphere of the earth. The equivalent of a degree of heat per lb. of water, determined by the careful experiments brought before the British Association at Oxford, is 775 lbs. through a foot. Hence 200.7 lbs. through a foot is equal to $0^{\circ}.259$.

We see, therefore, that for every degree of heat employed by De la Roche and Berard in expanding and heating air, $0^{\circ}.259$ was occupied in producing the mechanical effect, leaving $0^{\circ}.741$ as that actually employed in raising the temperature of the air. Hence the actual specific heat (commonly called capacity at constant volume) is $0.2669 \times 0.741 = 0.1977$. Taking this as the specific heat of air and the equivalent 775, it follows that if a volume of air of 171.6 cubic inches be compressed to 170.6 cubic inches, it will be heated 1° , a quantity of heat which will occasion an increased pressure of $\frac{1}{491}$. So that the celerity of sound will be increased by this means in the subduplicate ratio of 491 to 661.6, or in the simple ratio of 2216 to 2572, which will bring it up from Newton's estimate of 943 to 1095 feet per ", which is as near 1130, the actual velocity at 32° , as could be expected from the nature of the experiments on the specific heat of air, and fully confirms the theory of Laplace.

Oak Field, near Manchester,
July 17, 1847.

XXII. *On the Composition of Caffein, and of some of its Compounds.* By EDWARD CHAMBERS NICHOLSON, Esq.*

CAFFEIN was first analysed by Professors Liebig and Pfaff† in 1832. The result of this investigation was confirmed by a subsequent analysis of Prof. Wöhler‡.

In 1838 Professor Liebig induced M. Jobst§ to analyse thein, who proved this body to be identical with caffein. His analyses gave the same results as his predecessors. The same remark applies to the experiments of Mulder|| on thein,

* Communicated by the Chemical Society; having been read Feb. 15, 1847.

† Liebig's *Annalen*, i. 17.

‡ Ibid.

§ Ibid. xxv. 63.

|| *Bulletin des Sciences Phys. et Nat. de Neerlande*. 1838, p. 32.

and also to an analysis which M. Martius * made of guaranin, a substance, the identity of which with caffein and thein had previously been pointed out by Berthemot and Dechastelus†. Lately Dr. Stenhouse‡, when examining Paraguay tea, has also made some analyses of thein.

The following table, in which I have recalculated these analyses according to the atomic weights, carbon 6 and hydrogen 1, allows a comparison to be made of the results obtained by these chemists.

Mean of the Analyses.

	Caffein.		Thein.			Guaranin.
	Liebig & Pfaff.	Wöhler.	Mulder.	Jobst.	Stenhouse.	Martius.
Carbon .	49.30	49.25	49.18	49.47	48.95	49.23
Hydrogen .	5.22	5.43	5.49	5.20	5.15	5.08
Nitrogen .	28.86		28.53	28.90		28.83

The most simple expression which can be deduced from these numbers is

Stenhouse's analysis however of the platinum compound proves that this formula must be doubled, and that the atom of caffein or thein is

The theoretical numbers of this formula are the following:—

16 eqs. Carbon . . .	96	49.48
10 ... Hydrogen . . .	10	5.15
4 ... Nitrogen . . .	56	28.86
4 ... Oxygen . . .	32	16.51
	194	100.00

From these numerous experiments the composition of caffein might have been considered as perfectly established. In a recent investigation of coffee, however, M. Payen§ states that he has obtained results which differ very sensibly from those obtained by his predecessors, and which he has translated into the formula

which contains 1 equiv. of oxygen less than the formula up to the present time admitted.

The theoretical numbers of Payen's formula are—

16 eqs. Carbon . . .	96	51.43
10 ... Hydrogen . . .	10	5.35
4 ... Nitrogen . . .	56	30.34
3 ... Oxygen . . .	24	12.88
	186	100.00

* Liebig's *Annalen*, xxxvi. 93.

† Ibid. xxxvi. 90.

‡ Mem. Chem. Soc., vol. i. pp. 215, 237. [Phil. Mag., xxiii. p. 426.]

§ *Comptes Rendus de l'Académie*, tome xxiii. 8.

We observe here a difference of 2 per cent. of carbon, which M. Payen has obtained over the results of the above-mentioned chemists.

In order to elucidate this discrepancy, Dr. Hofmann induced me to make some experiments under his direction, partly with a quantity of beautiful caffein which he gave me* and partly with a specimen which I have prepared myself.

Caffein.

To ensure perfect purity of the substance it was crystallized three times from dilute alcohol, washed and dried. Thus purified, it formed very beautiful long white prisms, perfectly transparent when dried in the air, but which became opaque if exposed to a higher temperature. The crystals dried in the water-bath lost no weight when kept in an air-bath for four hours at a temperature of 130° C.

The specimen which I had prepared myself was obtained from Costa Rico coffee, by boiling the bruised fruit in water, precipitating the decoctions by basic acetate of lead and treating the filtrate with hydrosulphuric acid; after the whole of the lead had been removed, I evaporated the liquid to dryness in a water-bath, in order to get rid of acetic acid, and dissolved the residue in a small quantity of boiling water: upon cooling, the caffein crystallized out of a dark colour, and very impure. To purify it, it was washed and recrystallized three times from water, and finally from alcohol. It was then perfectly white, and had exactly the same appearance as the specimen which I obtained from Dr. Hofmann.

Analysis.

I. 0.3827 grm. of substance, dried at 100° C. and burnt with chromate of lead, gave 0.6948 grm. of carbonic acid, and 0.1800 grm. of water.

II. 0.417 grm. of substance, burnt with chromate of lead and chlorate of potash, gave 0.7552 grm. of carbonic acid, and 0.1965 grm. of water.

III. 0.3934 grm. of substance of my own preparation gave 0.7123 grm. of carbonic acid and 0.1878 grm. of water, which calculated in 100 parts gives—

	I.	II.	III.
Carbon . . .	49.51	49.39	49.37
Hydrogen . .	5.22	5.23	5.30

* I owe this specimen, of great beauty, to the well-known kindness of Mr. E. Merck of Darmstadt.—A. W. H.

which agrees with Professor Liebig's formula, as is seen by the following:—

		Theory.	Mean of experiments.
16 eqs. Carbon . . .	96	49·48	49·42
10 ... Hydrogen . .	10	5·15	5·28
4 ... Nitrogen . .	56	28·86	
4 ... Oxygen . . .	32	16·51	
	<u>194</u>	<u>100·00</u>	

Caffein and Bichloride of Platinum.

On precipitating a solution of caffein in hydrochloric acid with bichloride of platinum, as Dr. Stenhouse has shown, a precipitate of an orange-yellow colour is obtained. If the two solutions are mixed hot, the fluid on cooling deposits the compound in beautiful granular crystalline tufts, which, when thrown on a filter and washed with alcohol, are perfectly pure. This double salt is only sparingly soluble in alcohol, æther, and water. It does not alter when exposed to light, nor does it lose in weight when kept at 100° C. for a considerable time.

The analyses of salts, all prepared at different periods and dried at 100° C., gave the following results:—

I. 0·5382 grm. of substance, burnt with chromate of lead, gave 0·4765 grm. of carbonic acid, and 0·1387 grm. of water.

II. 0·4881 grm. of substance gave 0·1196 grm. of platinum.

III. 0·4779 grm. of substance gave 0·1172 grm. of platinum.

IV. 0·6022 grm. of substance gave 0·1482 grm. of platinum.

V. 0·5781 grm. of substance gave 0·1425 grm. of platinum.

VI. 0·5246 grm. of substance gave 0·1293 grm. of platinum.

VII. 0·3847 grm. of substance made of caffein of my own preparation, gave 0·0945 grm. of platinum.

Which give the following per-centages:—

	I.	II.	III.	IV.	V.	VI.	VII.
Carbon .	23·80						
Hydrogen	2·86						
Platinum ...		24·51	24·52	24·60	24·64	24·64	24·56

leading exactly to the formula given by Dr. Stenhouse, viz.

as is seen when placed in comparison with the calculated numbers.

		Theory.	Mean of my experiments.	Dr. Stenhouse's mean.
16 eqs. Carbon . .	96·0	23·97	23·80	24·22
11 ... Hydrogen . .	11·0	2·74	2·86	2·89
4 ... Nitrogen . .	56·0	13·98		
4 ... Oxygen . .	32·0	8·02		
3 ... Chlorine . .	106·5	26·59		
1 ... Platinum . .	98·9	24·70	24·58	24·49
1 ... Caffein and bichloride of platinum }	400·4	100·00		

The analysis of caffein, as well as that of the platinum compounds, agree so perfectly with the numbers of Professor Liebig's formula, that there can be no doubt about its accuracy.

Assuming 1 equiv. of oxygen less in the equivalent of caffein, as is proposed by M. Payen, the platinum compound should contain not less than 24·46 per cent. of carbon and 25·12 of platinum. Now three determinations by Dr. Stenhouse, and six which I have made, never gave more than 24·64 per cent., that is, 0·6 per cent. less of platinum.

Not satisfied, however, with these proofs, I have tried to find some other compounds by which the atomic weight of caffein could be determined with equal accuracy.

In what follows a description of several new double salts of caffein will be given, the analyses of which correspond equally well with the original formula of this substance.

Caffein and Nitrate of Silver.

This compound is obtained when a solution of nitrate of silver is added in excess to an aqueous or alcoholic solution of caffein. If the solutions are concentrated it falls down in white hemispherical nodules, which adhere firmly to the side of the vessel.

When washed with water and crystallized from alcohol it is absolutely pure. This compound is indistinctly crystalline, of a perfectly white colour, and if dry undergoes no change when exposed to light, but if moist acquires a purplish hue. It is very soluble in hot water and alcohol, sparingly soluble in cold, and may be boiled in either solvent without undergoing decomposition. It loses no weight in the water-bath, but at a higher temperature it is decomposed, caffein sublimes, and metallic silver is left.

Analysis.—When burnt with chromate of lead—

I. 0·4514 grm. of substance gave 0·4345 grm. of carbonic acid, and 0·1162 grm. of water.

II. 0·2500 grm. of substance gave ·0744 grm. of silver.

III. 0·2716 grm. of substance gave ·0810 grm. of silver,
which give the following per-centages:—

	I.	II.	II.
Carbon . . .	26·45		
Hydrogen . .	2·86		
Silver . . .	...	29·76	29·82,

and the formula— $C_{16}H_{10}N_4O_4 + AgO, NO_5$,

as may be seen by the following calculation:—

		Theory.	Found.
16 eqs. Carbon . . .	96	26·37	26·45
10 ... Hydrogen . .	10	2·74	2·86
5 ... Nitrogen . .	70	19·23	
10 ... Oxygen . .	80	22·00	
1 ... Silver . . .	108	29·66	29·79
	<u>364</u>	<u>100·00</u>	

The only analogues to this singular compound which I know are those of urea and nitrate of silver, analysed by Wether*: the formulæ of which are— $C_2H_4N_2O_2 + AgO, NO_5$, and $C_2H_4N_2O_2 + 2(AgO, NO_5)$.

These compounds, however, in consequence of the peculiar nature of urea, are not very stable, being decomposed when boiled with water into nitrate of ammonia and cyanate of silver. There likewise exists a compound of nitrate of silver and glycocoll, lately described by Horsford†, having the formula

and, according to H. Rose, a compound of nitrate of silver with ammonia, 3 eqvts. of this gas being absorbed by 1 equiv. of the former salt.

Chloride of Mercury and Caffein.

This beautiful compound is obtained when an aqueous or alcoholic solution of caffein is added to a solution of chloride of mercury; the latter being kept in excess, the fluid remains perfectly clear, but after the lapse of a few seconds solidifies into a mass of very small crystals, which when recrystallized from water or alcohol and washed on a filter, are quite pure.

When pure and crystallized from water it is very similar in appearance to caffein, the crystals not being however quite so large. It is very soluble in alcohol and water, hydrochloric, nitric, and oxalic acids, and seems to form with the latter a crystalline compound. It is nearly insoluble in æther. In reference to its constitution, it is distinguished from the dou-

* Liebig's *Annalen*, lvi. 262.

† *Ibid.* lx. 36.

ble salt of platinum, for in this instance the *cafein* is in direct combination with the chloride of mercury, and is exactly analogous to the corresponding compounds of leucoline and aniline investigated by Dr. Hofmann*. The mercurial compounds of this kind are generally easily decomposed, but the compound of chloride of mercury and *cafein* is so stable, that it may be boiled in water for a considerable time without undergoing the slightest change in its properties. It may be dried at 100° C. and loses no weight at that temperature.

I endeavoured to combine the determination of the carbon, hydrogen and mercury of this substance in *one* combustion, and have perfectly succeeded. The operation was conducted as follows:—The substance was mixed with chromate of lead and introduced into a combustion-tube of at least 26 inches in length. About 6 inches of copper turnings are placed above the mixture, leaving a space of 8 inches from the copper to the anterior end of the tube. A receptacle for the mercury is formed out of the tube itself by contracting it about an inch from the copper turnings, and again so as to leave an elongated bulb of an inch in length. At the close of the operation the tube is cut with a file at the posterior contraction. In order to separate the water from the mercury, the chloride of calcium tube (which has not been detached) is connected with an aspirator and air admitted through chloride of calcium, the bulb being kept at a temperature of 100° C.

I obtained in my analysis the following numbers:—0·7833 grm. of substance gave 0·5832 grm. of carbonic acid, 0·1639 grm. of water, and 0·3365 grm. of mercury, corresponding to the following per-centage, which I place in comparison with the theoretical numbers:—

		Theory.	Expt.
16 eqs.	Carbon	96	20·68
10 ...	Hydrogen	10	2·15
4 ...	Nitrogen	56	12·11
4 ...	Oxygen	32	6·89
2 ...	Chlorine	70	15·08
2 ...	Mercury	200	43·09
		464	100·00

Cafein and Terchloride of Gold.

This compound is formed when a solution of terchloride of gold is added in excess to *cafein* dissolved in dilute hydrochloric acid. If concentrated solutions are employed, the whole immediately solidifies into a mass of a most splendid lemon-yellow colour; this is to be washed with cold water

* Liebig's *Annalen*, xlvii. 37.

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and crystallized from alcohol, and finally dried in the water-bath.

The crystals from an alcoholic solution are in the form of long needles, of an orange-yellow colour and a very bitter metallic taste; they are soluble in alcohol and water. When boiled in water for a short time, the salt is decomposed, a yellow flocculent matter precipitating, which is insoluble in alcohol, ether and water, but soluble in hydrochloric acid. If an aqueous solution is kept on the sand-bath for some hours at a temperature of about 68°C . it is also decomposed, and metallic gold separates in shining scales.

It is not altered when exposed to light, and when dry may be heated to 100°C . without undergoing decomposition.

Analysis.—When burnt with chromate of lead—

I. 0.8530 grm. of substance gave 0.5525 grm. of carbonic acid and 0.1622 grm. of water.

II. 0.3224 grm. of substance gave 0.1197 grm. of metallic gold.

III. 0.3019 grm. of substance gave 0.1115 grm. of metallic gold, which give the following per-centages:—

	I.	II.	III.
Carbon . .	17.72		
Hydrogen . .	2.11		
Gold . . .		37.12	36.93

corresponding to the formula $\text{C}_{16}\text{H}_{10}\text{N}_4\text{O}_4\text{HClAuCl}_3$, as may be seen by the following table, where the calculated and quantities found are placed in comparison:—

		Theory.	Found.
16 eqs. Carbon .	96.00	17.98	17.72
11 ... Hydrogen .	11.00	2.06	2.11
4 ... Nitrogen .	56.00	10.50	
4 ... Oxygen .	32.00	6.01	
4 ... Chlorine .	142.00	26.60	
1 ... Gold . .	196.66	36.85	37.02
	533.66	100.00	

The caffein compounds which I have analysed are therefore—

Caffein	$\text{C}_{16}\text{H}_{10}\text{N}_4\text{O}_4$.
Platinum compound	$\text{C}_{16}\text{H}_{10}\text{N}_4\text{O}_4, \text{HCl Pt Cl}_2$.
Silver compound .	$\text{C}_{16}\text{H}_{10}\text{N}_4\text{O}_4, \text{AgO}, \text{NO}_5$.
Mercury compound	$\text{C}_{16}\text{H}_{10}\text{N}_4\text{O}_4, 2(\text{Hg Cl})$.
Gold compound . .	$\text{C}_{16}\text{H}_{10}\text{N}_4\text{O}_4\text{HCl}, \text{Au Cl}_3$.

There exist several other double compounds of caffein, which I have however not subjected to analysis.

On mixing a hot alcoholic solution of caffen with an alcoholic solution of cyanide of mercury, beautiful needles of a double salt are deposited upon cooling, which correspond most likely to the mercury salt I have just described. A solution of caffen in hydrochloric acid gives a beautiful brown precipitate with chloride of palladium; and the filtered solution deposits another compound in the form of yellow scales, very similar in appearance to iodide of lead.

Caffen gives no precipitate with solutions of sulphate of copper, chloride of tin, acetate of lead, and nitrate of suboxide of mercury. When boiled with sesquichloride of iron, a reddish-brown precipitate subsides upon cooling, which is perfectly soluble in water, and is most likely a double compound of caffen and sesquichloride of iron.

XXIII. *Note in reference to the extension of Euler's Theorem.*

By J. R. YOUNG, *Professor of Mathematics in Belfast College.*

To Richard Taylor, Esq.

DEAR SIR,

IN the Philosophical Magazine for June last a communication of mine was published respecting an extension of a certain theorem of Euler concerning the products of the sums of squares. At the time that notice was written, I was under the impression that the theorem admitted of an extent of generalization which a further investigation of the matter proves to me has not place. I am now prepared to show that the proposition does not hold beyond the case for eight squares, the formulæ for which I have already printed in the Proceedings of the Royal Irish Academy; in the Transactions of which body it is probable that the entire investigation of the theorem for eight squares, and the proof that it does not apply beyond that number, will hereafter appear.

It may perhaps be interesting to algebraists to find the real limits to this theorem demonstrably established; and thus to know—in any attempts that may hereafter be made to extend Sir W. R. Hamilton's remarkable and very fertile theory of quaternions—beyond what boundaries such attempts must prove fruitless.

I remain, dear Sir,

Very faithfully yours,

J. R. YOUNG.

Belfast, July 16, 1847.