

I have now remedied this defect, and made what I believe is an absolute standard barometer, by graduating the scale from the centre, and reading it off with two verniers to the  $\frac{1}{1000}$ th of an inch. The scale is divided from the centre, up and down, into inches, and subdivided into 20ths.

To ascertain the height of the barometer graduated in this way, take a reading of the upper surface of the column of mercury with the vernier, then of the lower surface in the same way, and the two readings added together will give the exact length of the column of mercury supported in the air, which is the height of the barometer at the time.

There is another advantage in this manner of graduating over the former, that if a little of the mercury drops out it will give no error, as the column will immediately rise out of the larger tube into the smaller, and become the same length as before; but by the former scale the barometer would stand too high, until readjusted, which could only be effected by putting the same quantity of mercury in again.

I have introduced Gay-Lussac's pipette into the centre of the tube, to prevent the possibility of any air passing up into the top.

The Society then adjourned over the Easter Recess to Thursday, April 7th.

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“On Mauve or Aniline-Purple.” By W. H. PERKIN, F.C.S. Communicated by Dr. STENHOUSE. Received August 19, 1863\*.

The discovery of this colouring matter in 1856, and its introduction as a commercial article, has originated that remarkable series of compounds known as coal-tar colours, which have now become so numerous, and in consequence of their adaptability to the arts and manufactures are of such great and increasing importance. The chemistry of mauve may appear to have been rather neglected, its composition not having been established, although it has formed the subject of several papers by continental chemists. Its chemical nature also has not been generally known; and to this fact many of the discrepancies in the results of the different experimentalists who have worked on this subject are to be attributed.

The first analysis I made of this colouring matter was in 1856, soon after I had become its fortunate discoverer. The product I examined was purified as thoroughly as my knowledge of its properties then enabled me, and the results† obtained agree very closely with those required for the formula I now propose. Since that time I have often commenced the study of this body in a scientific point of view, but other duties have prevented me

\* For abstract see vol. xii. p. 713.

† The substance I examined was doubtless the sulphate, of which I made two combustions:—

No. I. gave 71.55 per cent. of carbon and 6.09 per cent. of hydrogen.			
No. II. gave 71.60	“	“	5.77
Theory requires 71.5	“	“	5.5

from completing these investigations; but, although unacquainted with its correct formula, its chemical characters have necessarily been well known to me for a considerable time. When first introduced, commercial mauve appeared as an almost perfectly amorphous body; but now, owing to the great improvements which have been made in its purification, it is sent into the market perfectly pure and crystallized.

On adding a solution of hydrate of potassium to a boiling solution of commercial crystallized mauve, it immediately changes in colour from purple to a blue violet, and after a few moments begins to deposit a crystalline body. After standing a few hours, this crystalline product is collected on a filter, washed with alcohol once or twice, and then thoroughly with water. When dry, it appears as a nearly black glistening substance, not unlike pulverized specular iron ore.

This substance, for which I propose the name *Mauveine*, is a powerful base. It dissolves in alcohol, forming a blue violet solution, which immediately assumes a purple colour on the addition of acids. It is insoluble, or nearly so, in ether and benzole. It is a very stable body, and decomposes ammoniacal compounds readily. When heated strongly it decomposes, yielding a basic oil, which does not appear to be aniline.

The following analyses were made of specimens dried at  $150^{\circ}\text{C}$ . :—

I. .301 grm. of substance gave .8818 of carbonic acid and .162 of water.

II. .2815 grm. of substance gave .8260 of carbonic acid and .145 of water.

*Direct Nitrogen determination.*

III. .3435 grm. of substance gave 41.0 c.c. N at  $23^{\circ}\text{C}$ . and 766 mms. Bar.

$$V' = \frac{41.0 \text{ cub. centims. (766.0 millims. — } 20.9)}{824.1 \text{ millims.}} = 37.7 \text{ cub. centims.}$$

$$37.7 \times .0012562 \text{ grm.} = .04735 \text{ grm. of N.}$$

These numbers correspond to the following percentages:—

	I.	II.	III.
Carbon.....	79.9	80.0	—
Hydrogen.....	5.98	5.72	—
Nitrogen.....	—	—	13.75

The formula,  $\text{C}_{27}^* \text{H}_{24} \text{N}_4$ , requires the following values:—

	Theory.		Mean of experiment.
$\text{C}_{27}$ .....	324	80.19	79.95
$\text{H}_{24}$ .....	24	5.94	5.85
$\text{N}_4$ .....	56	13.87	13.75
	404	100.	

*Hydrochlorate of Mauveine.*—This salt is prepared by the direct combination of mauveine and hydrochloric acid. From its boiling alcoholic solution it is deposited in small prisms, sometimes arranged in tufts, possessing

\* C = 12.

a brilliant green metallic lustre. It is moderately soluble in alcohol, but nearly insoluble in ether. It is also, comparatively speaking, moderately soluble in water.

Different preparations dried at 100° C. gave the following numbers :—

I. ·306 grm. of substance gave ·8255 of carbonic acid and ·162 of water.

II. ·308 grm. of substance gave ·8275 of carbonic acid and ·163 of water.

III. ·310 grm. of substance gave ·8345 of carbonic acid.

IV. ·3165 grm. of substance gave ·851 of carb. acid and ·16525 of water.

V. ·2447 grm. of substance gave ·6603 of carb. acid and ·1356 of water.

VI. ·627 grm. of substance gave ·205 of chloride of silver.

VII. ·560 grm. of substance gave ·195 of chloride of silver.

VIII. ·69 grm. of substance gave ·2266 of chloride of silver.

*Direct Nitrogen determination.*

IX. ·3497 grm. of substance gave 40 c. c. N at 20° C. and 777·2 mms. Bar.

$$V' = \frac{40 \text{ c. c. } (7772 - 17 \cdot 4)}{815 \cdot 8 \text{ millims.}} = 37 \cdot 2 \text{ c. c. at } 0^\circ \text{ C. and 760 millims. Bar.}$$

$$37 \cdot 2 \text{ cub. centims. } \times \cdot 0012562 \text{ grm.} = \cdot 04673 \text{ grm. N.}$$

These numbers correspond to the following percentages :—

	I.	II.	III.	IV.
Carbon . . . . .	73·5	73·27	73·4	73·3
Hydrogen . . . . .	5·88	5·88	—	5·8
Nitrogen . . . . .	—	—	—	—
Chlorine . . . . .	—	—	—	—

	V.	VI.	VII.	VIII.	IX.
Carbon . . . . .	73·59	—	—	—	—
Hydrogen . . . . .	6·16	—	—	—	—
Nitrogen . . . . .	—	—	—	—	13·3
Chlorine . . . . .	—	8·08	8·06	8·1	—

These numbers agree with the formula  $C_{27}H_{24}N_4HCl$ , as may be seen by the following Table :—

	Theory.		Mean of experiment.
$C_{27}$ . . . . .	324·	73·55	73·41
$H_{25}$ . . . . .	25·	5·67	5·93
$N_4$ . . . . .	56·	12·73	13·30
Cl . . . . .	35·5	8·05	8·07
	440·5	100·00	

I have endeavoured to obtain a second hydrochlorate containing more acid, but up to the present time have not succeeded.

*Platinum-salt.*—Mauveine forms a perfectly definite and beautifully crystalline compound with bichloride of platinum. It is obtained by mixing an alcoholic solution of the above hydrochlorate with an excess of an

alcoholic solution of bichloride of platinum; from this mixture the new salt separates as a highly crystalline powder. I have generally preferred to use cold solutions in its preparation; but if moderately hot solutions be employed, the salt will separate as crystals of considerable dimensions.

This platinum-salt possesses the green lustre of the hydrochlorate, but, on being dried, assumes a more golden colour. It is very sparingly soluble in alcohol. The following numbers were obtained from various preparations dried at 100° C. :—

I. .44125 grm. of substance gave .072 of platinum.

II. .4845 grm. of substance gave .079 „

III. .511 grm. of substance gave .083 „

IV. .510 grm. of substance gave .083 „

V. .6345 grm. of substance gave .1035 „

VI. .618 grm. of substance gave .101 „

VII. .31275 grm. of substance gave .60525 of carbonic acid and .118 of water.

VIII. .30675 grm. of substance gave .595 of carb. acid and .110 of water.

IX. .3795 grm. of substance gave .27 of chloride of silver.

These results correspond to the percentages in the following Table :—

	I.	II.	III.	IV.	V.	VI.
Carbon ....	—	—	—	—	—	—
Hydrogen ..	—	—	—	—	—	—
Chlorine ....	—	—	—	—	—	—
Platinum ..	.16.31	16.3	16.24	16.27	16.3	16.3

	VII.	VIII.	IX.
Carbon.....	52.77	52.86	—
Hydrogen.....	4.19	3.98	—
Chlorine .....	—	—	17.6
Platinum .....	—	—	—

The formula,  $C_{27}H_{24}N_4H Pt Cl_3$ , requires the following values :—

	Theory.		Mean of experiment.
$C_{27}$ ....	324.	53.09	52.81
$H_{25}$ ....	25.	4.09	4.19
$N_4$ ....	56.	9.2	....
Pt ....	98.7	16.16	16.28
$Cl_3$ ....	106.5	17.46	17.6
	610.2	100.00	

*Gold-salt*.—This compound is prepared in a similar manner to the platinum-salt, only substituting chloride of gold for chloride of platinum. It separates as a crystalline precipitate, which, when moist, presents a much less brilliant aspect than the platinum derivative; it is also more soluble than that salt, and when crystallized appears to lose a small quantity of gold. The following results were obtained from a specimen dried at 100° C. :—

I. .47175 grm. of substance gave .1245 of gold.

II. .35525 grm. of substance gave .094 of gold.

III. .309 grm. of substance gave .495 of carbonic acid and .101 of water.

Percentage composition :—

	I.	II.	III.
Carbon	—	—	43·68
Hydrogen	—	—	3·6
Gold	26·3	26·46	—

The formula,  $C_{27}H_{24}N_4, H AuCl_4$ , requires the following percentages :—

	Theory.		Mean of experiment.
$C_{27}$ ....	324	43·53	43·68
$H_{24}$ ....	25	3·34	3·6
$N_4$ ....	56	7·44	—
Au ....	197	26·61	26·38
$Cl_4$ ....	142	19·08	—
	<hr/> 744	<hr/> 100·00	

*Hydrobromate of Mauveine*.—This salt is prepared in a similar manner to the hydrochlorate, which it very much resembles, except that it is less soluble in alcohol. Analysis of preparations dried at  $100^\circ C$ . gave the following numbers :—

I. .3935 grm. of substance gave .1515 of bromide of silver.

II. .450 grm. of substance gave .173 of bromide of silver.

III. .3265 grm. of substance gave .79675 of carb. acid and .158 of water.

IV. .35125 grm. of substance gave .86075 of carbonic acid and .1675 of water.

Percentage composition :—

	I.	II.	III.	IV.
Carbon	—	—	66·55	66·8
Hydrogen	—	—	5·37	5·29
Bromine	16·38	16·37	—	—

These numbers agree with the formula  $C_{27}H_{24}N_4, H Br$ , as shown by the comparisons in the following Table :—

	Theory.		Experiment.
$C_{27}$ ....	324	66·8	66·67
$H_{24}$ ....	25	5·15	5·33
$N_4$ ....	56	11·56	—
Br " ....	80	16·49	16·37
	<hr/> 485	<hr/> 100·00	

*Hydriodate of Mauveine*.—In preparing this salt from the base, it is necessary to use hydriodic acid which is colourless, otherwise the free iodine will slowly act upon this salt. It crystallizes in prisms having a

green metallic reflexion. It is more insoluble than the hydrobromate. The products used in the subjoined analysis were recrystallized three times, and dried at 100° C.

I. .5115 grm. of substance gave .22575 of iodide of silver.

II. .248 grm. of substance gave .549 of carb. acid and .10975 of water.

III. .2985 grm. of substance gave .663 of carb. acid and .1265 of water.

IV. .2765 grm. of substance gave .615 of carb. acid and .1145 of water.

Percentage composition :—

	I.	II.	III.	IV.
Carbon	—	60.46	60.57	60.65
Hydrogen	—	4.9	4.7	4.7
Iodine	23.8	—	—	—

The formula,  $C_{27}H_{24}N_4HI$ , requires the following values :—

	Theory.		Experiment.
$C_{27}$ . . . .	324.	60.89	60.56
$H_{25}$ . . . .	25.	4.69	4.7
$N_4$ . . . .	56.	10.54	—
I . . . .	127.1	23.88	23.8
	532.1	100.00	

*Acetate of Mauveine.*—This salt is best obtained by dissolving the base in boiling alcohol and acetic acid. On cooling, it will crystallize out; it should then be recrystallized once or twice. This acetate is a beautiful salt, possessing the green metallic lustre common to most of the salts of mauveine. Two combustions of specimens dried at 100° C. gave the following numbers :—

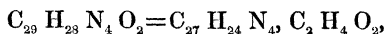
I. .28325 grm. of substance gave .778 of carb. acid and .153 of water.

II. .29275 grm. of substance gave .806 of carb. acid and .1645 of water.

Percentage composition :—

	I.	II.
Carbon	74.9	75.0
Hydrogen	6.0	6.2

These numbers lead to the formula



as shown by the following Table :—

	Theory.		Experiment.
$C_{29}$ . . . .	348	75.	74.95
$H_{28}$ . . . .	28	6.	6.1
$N_4$ . . . .	56	12.06	—
$O_2$ . . . .	32	6.94	—
	464	100.00	

*Carbonate of Mauveine.*—The tendency of solutions of mauveine to combine with carbonic acid is rather remarkable. If a quantity of its solu-

tion be thrown up into a tube containing carbonic acid over mercury, the carbonic acid will quickly be absorbed, the solution in the mean time passing from its normal violet colour to purple. To prepare this carbonate, it is necessary to pass carbonic acid gas through boiling alcohol containing a quantity of mauveine in suspension. It is then filtered quickly, and carbonic acid passed through the filtrate until nearly cold. On standing, this liquid will deposit the carbonate as prisms, having a green metallic reflexion. A solution of this salt, on being boiled, loses part of its carbonic acid and assumes the violet colour of the base. When dry this carbonate rapidly changes, and if heated to  $100^{\circ}$  C. loses nearly all its carbonic acid and changes in colour to a dull olive; therefore, as it cannot be dried without undergoing a certain amount of change, its composition is difficult to determine. However, I endeavoured to estimate the carbonic acid in this salt by taking a quantity of it freshly prepared and in the moist state, and heating it in an oil-bath until carbonic acid ceased to be evolved. The residual base was then weighed, and also the carbonic acid, which had been collected in a potash bulb, having been previously freed from water by means of sulphuric acid. The following results were obtained:—

I. 1.88 residual base obtained; .190 carbonic acid evolved.

II. 1.375 residual base; .1385 carbonic acid evolved. .190 of  $\text{CO}_2$  is equal to .268 of  $\text{H}_2\text{CO}_3$ ; this, added to the residual base, will give the amount of substance experimented with, viz. 2.148. The amount of  $\text{CO}_2$  obtained from this quantity, therefore, is 8.8 per cent.

Calculating the second experiment in a similar manner, the amount of carbonate operated upon would be 1.5702 grm.; the percentage of  $\text{CO}_2$  obtained is therefore equal to 8.8. A carbonate having the formula  $(\text{C}_{27}\text{H}_{24}\text{N}_4)_2\text{H}_2\text{CO}_3$  would contain 5.1 per cent. of  $\text{CO}_2$ , and an acid carbonate having the formula  $\text{O}_{27}\text{H}_{24}\text{N}_4\text{H}_2\text{CO}_3$  would contain 9.4 per cent. of  $\text{CO}_2$ .

Considering that this salt when prepared begins to crystallize before it is cold, probably the first portions that deposit are a monocarbonate, while the larger quantity which separates afterwards is an acid carbonate. Hence the deficiency in the amount of  $\text{CO}_2$  obtained in the above experiments. I hope to give my attention to this remarkable salt at a future period.

In the analysis of the salts of mauveine great care has to be taken in drying them thoroughly, as most of them are highly hygroscopic.

I am now engaged in the study of the replaceable hydrogen in mauveine, which I hope will throw some light upon its constitution. From its formula I believe it to be a tetramine, although up to the present time I have not obtained any definite salts with more than 1 equiv. of acid.

When mauveine is heated with aniline it produces a blue colouring matter, which will doubtless prove to be a phenyle derivative of that base. A salt of mauveine when heated alone also produces a violet or blue compound. These substances I am now examining, and hope in a short time to have the honour of communicating them to the Society.