ART. XLII.—*On the Determination of the Photometric Power of a rich gas by dilution with a poor gas of known value: the "method of mixtures;"* by B. SILLIMAN.

IN a paper on 'Farmer's Theorem,'* I have given several examples of the method of determining the intensity or photometric power of a rich gas by diluting it with several times its own volume of a poorer gas of known intensity, and then calculating its value from the increment of intensity. Having demonstrated in the paper before mentioned the worthlessness of all determinations of the intensity of gases of high illuminating power made by burning them in volumes less than five cubic feet, and then calculating their intensity by the rule of three up to that volume, I have shown how much more exact results were obtained when the results were calculated upon the theorem of Mr. Farmer; this greater exactness being predicated largely upon the confirmation drawn from parallel observations upon the same gases when measured by the method of mixtures. The results thus obtained having, however, been questioned by Mr. Stimpson,† on the ground that the method itself had not been experimentally demonstrated, I have undertaken lately, in connection with Mr. Farmer, to make some experiments calculated to test its accuracy.

The results which go to support the accuracy of the method were obtained with the use of a new photometric apparatus, constructed for the Manhattan Gas Co., under my direction, by Sugg of London, and which was designed to embrace all the best approved features which recent experience has indicated in photometry. A discussion of these details would be out of place in this connection. Before detailing our results, it will be proper to present the method of determination of intensity for gas of high illuminating power as practiced by Mr. Farmer at the Manhattan Gas Works in New York, and which I have called *the method of mixtures*.

To find the candle power of a gas having, for example, an intensity greater than 20 candles, mix the rich gas of unknown power with a poorer gas of known power in such proportions that the intensity of the mixture shall not be greater than 20 candles power, when consumed at the agreed rate of not over five cubic feet per hour. Then to compute the candle power (intensity) of the rich gas,—

* This Journal, II, xlix, 17; also Proceedings of American Association for Advancement of Science, Salem meeting, 1869, p. 149.

† See page 272, this volume.

Let a = the percentage or volume of gas of low intensity.

“ b = the intensity in candles of the gas of low intensity.

“ c = the percentage or volume of rich gas used in the mixture.

“ d = the intensity in candles of the mixture as observed.

“ x = the intensity in candles of the rich gas required.

$$\begin{aligned} \text{Hence, } \frac{ab + cx}{a + c} &= d & \frac{(d-b)a}{c} + d &= x \\ ab + cx &= ad + cd \\ cx &= ad + cd + ab. \end{aligned}$$

And this expression is stated arithmetically in the following

Rule:—Subtract the intensity of the poor gas from the intensity of the mixture; multiply the remainder by the volume of poor gas; divide the product by the volume of rich gas; add to the quotient the intensity of the mixed gas, and the sum is the intensity of the rich gas sought.

Now when we reflect that in any given illuminating gas we have always a certain volume of non-luminous combustible gas, as the substratum to which is added, according to its source and mode of treatment, a variable volume of illuminants, it is no unwarranted assumption to say that the illuminants (chiefly olefines) are *diluted* by the non-illuminants. It is agreed, on all hands, that hydrogen, marsh gas and carbonic oxyd, which together form the mass of the non-luminous substratum of all illuminating gas, have of themselves, when pure, no luminosity, and when burned at ordinary atmospheric pressures and corresponding temperatures, that they may in fact be called, as to luminosity, neutral. It can hardly be questioned that the intensity which these neutral gases may assume in a given mixture must depend, under the same ordinary conditions before mentioned, upon the amount and kind of olefines they may take up in the destructive distillation of the coal or other hydrocarbons used in making gas. If these assumptions are true, we ought to be able to demonstrate them by experiment, by commingling certain volumes of a gas of known intensity with a neutral gas of no intensity. These experimental conditions would be met by using carbonic oxyd as the neutral gas, or better still, the mixture of carbonic oxyd and hydrogen resulting from the decomposition of vapor of water at a high temperature in contact with highly ignited carbon, as in the hydrocarbon gas process. But in default of any convenient means of obtaining these gases, we had recourse to hydrogen gas evolved by the action of diluted sulphuric acid upon zinc in a large self-regulating generator of hydrogen. It is well known that hydrogen thus made is not absolutely non-luminous, but it is sufficiently so for photometric purposes. The avidity of hydrogen for all the olefines, however, renders it difficult to

obtain entirely satisfactory results with the use of this gas, provided it is passed through gas pipes and holders which have been previously used for the transmission of coal gas, since however carefully one may rinse out these tubes by hydrogen, there may yet cling, probably, some small trace of the condensed illuminants to the walls of the tubes, which imparts a trifling intensity to the hydrogen passing through them.

To obtain a supply of rich gas of uniform intensity, 100 lbs. of Albertite were coked until 810 cubic feet of gas had been taken from it of a density of .498. This gas was purified, collected and preserved in a separate gas holder. Its intensity was determined,

- 1st. By Farmer's Theorem = 30.49 candles.
- 2d. " mixing with poor gas = 30.95 "
- 3d. " simple ratio = 26.20 "

In determining the intensity of this gas by the method of mixtures, 20 per cent by volume of Albert gas was mingled with 80 per cent of 10.6 candle gas obtained from a poor coal. The mixture had an intensity of 14.67 candles. Hence,

$$(14.67 - 10.60) \times 80 \div 20 + 14.67 = 30.95 \text{ candles}$$

for the intensity of the Albert Gas by the method of mixtures.

1st Experiment.

Taken	75	volumes of coal gas	=14.75	candles, obs'd.
"	25	" hydrogen	= ----	
"	100	" mixture	=10.22	" "
If hydrogen=0 this mixture should have given 11.06 " calc.				
Hence there is an error of observation of .84 of a candle,				
which makes the value of the hydrogen apparently below zero.				

2d Experiment.

Taken	75	volumes of coal gas	=14.25	candles, obs'd.
"	25	" hydrogen	= ----	
"	100	" mixture	=10.35	" "
If hydrogen=0 this mixture should have given 10.69 " calc.				
Hence there is an error of observation = .25 " which				
again makes the value of the hydrogen, apparently a little below zero.				

The want of sufficient storage room for hydrogen and the necessity of many repetitions, and much care in manipulation to avoid errors of quantity in the synthesis of mixtures make experiments of this sort tedious, and my other avocations have prevented my multiplying them as much as is desirable. I think, however, that most photometric observers will agree with me that it is safe to conclude, from these two experiments, that the action of hydrogen in gaseous mixtures is simply that of a

diluant. We might make a thousand observations by the means now at command, and not obtain one with an exact 0 for hydrogen. A very trifling error in the admeasurement greatly influences the result.

We may therefore safely conclude, as it appears to me—

1st. That in all illuminating gas we have a certain substratum of non-luminous gas, holding in solution a variable volume of luminous gas (olefines).

2d. That when a gas is too rich in illuminants to permit of accurate photometric admeasurement by the usual standards of intensity, it may be diluted with a poor gas of known value and volume to such a standard as is consistent with the accurate employment of the usual photometric apparatus, its true value being then calculated from the known values employed.

P. S. I find in the manuscript records of the Manhattan Gas Company, mention of four experiments made many years since by Mr. Schultz, chemist of that company, in which he mixed 5 per cent and 10 per cent of hydrogen with gas of very high illuminating power. The results are less satisfactory than they would have been, had the volume of hydrogen employed been much larger and the intensity of the coal gas not over 15 candles. Moreover at that time the means of admeasurement at the command of the observer in the laboratory of the Manhattan Company of small volumes of gas were much less exact than they now are. The results obtained are as follows:

1st Experiment.

Taken	90 volumes of coal gas	=22·53 candles, observed.
“	10 “ hydrogen	=----
“	100 “ mixture	=19·11 “ “
If the hydrogen is taken as 0	“	=20·27 “ calculated.
Showing apparent error of		=- 1·11 “ “

2d Experiment.

Taken	95 volumes of coal gas	=22·53 candles, observed.
“	5 “ hydrogen	=----
“	100 “ mixture	=20·35 “ “
If the hydrogen is taken as 0	“	=21·39 “ calculated.
Apparent error		=-1·04 “ “

3d Experiment.

Taken	90 volumes coal gas	=20·83 candles, observed.
“	10 “ hydrogen	=----
“	100 “ mixture	=19·44 “ “
If hydrogen is taken= 0	“	=18·29 “ calculated.
Apparent error,		+ ·15 “ “

4th Experiment.

Taken	95	volumes of	coal gas	=20·83	candles, observed.
“	5	“	hydrogen	= ----	
“	<u>100</u>	“	mixture	=20·52	“ “
If hydrogen is taken	=0	“		=19·79	“ calculated.
Apparent error,				<u>+ ·73</u>	“ “
New Haven, Sept. 1870.					