

portion of sulphur as carbon disulphide present. This measurement of the volume of gas is effected by drawing the gas through the lead solution by running water from an aspirator, and measuring the volume of the water by means of the graduated measures—the smaller holding  $\frac{1}{16}$ , and the larger  $\frac{1}{8}$  of a cubic foot. By reference to a table, the amount of "sulphur" is then found, to which is added from 7 to 8 grains, as sulphur present in other forms than carbon disulphide, and therefore not indicated by the lamp. Sulphureted hydrogen in gas is estimated by means of the color standard by drawing the gas directly into the lead solution, without the use of the lamp; while carbonic acid is estimated by the use of a standard containing a known quantity of barium carbonate, and drawing the gas through a solution of barium hydrate until an equal degree of opacity is reached. Reference to a special table then gives the amount of carbonic acid present in the gas.

With regard to my own experiences in the use of the Harcourt tests, I will commence with the subject of heat. On this question my opinion is that a lamp comes more quickly into working order, and affords generally more reliable tests, where the heat is greater than that defined in the printed instructions as "a blue non-luminous ring" of flame. The temperature we generally use is reached by turning up the gas until a distinctly luminous ring of flame is obtained when the small clay pieces on the top of the chimney are in position. Then, as to the time to elapse before taking a test, the instructions state "a testing may be made five minutes after the burner is lit, except when the apparatus is first used, when the gas should be allowed to flow through the bulb for a quarter of an hour or a little longer." My experience of this has been (1) that it is advisable to allow a new lamp to be alight a considerable time before employing it for actual testing; and (2) that although a lamp, after the first time of using, will give a test five minutes after being lit, it will only give a reliable test where the sulphur in the gas being tested is in about the same proportion as in the gas upon which the lamp was last employed. I may here mention that in starting a new lamp a correct test is sooner obtained with gas containing a high proportion of sulphur than where the sulphur is small in quantity. Out of many experiments upon this branch of the subject, I will quote the following: Two new lamps, A and B, were started at the same time, A upon gas containing 18 grains of sulphur per 100 cubic feet, and B on gas containing only 9 grains. A gave a correct result in  $1\frac{1}{2}$  hours, while B was 30 hours before it gave a really correct return.

In order to illustrate the effect of transferring a lamp on to gas containing a markedly different quantity of sulphur to that upon which it had previously been used, the following experiments may be quoted: A lamp which was giving a correct result on gas containing 36 grains of sulphur per 100 cubic feet was transferred to gas containing 19 grains. After being on the 19 grain gas for five minutes, the sulphur indicated

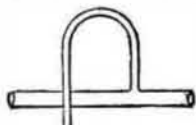


FIG. 2.

was 26.2 grains; after 15 minutes, 26.2 grains; after 30 minutes, 21.8 grains; and after 90 minutes, 19.5 grains. So that  $1\frac{1}{2}$  hours had to elapse before a correct test was obtained. In another case a lamp was taken from 23 grain gas and put on to gas containing only 8 grains, with the result that after one hour's interval it indicated 10.8 grains, and after two hours' interval 9.5 grains. The lamp was then turned out; but the experiment clearly shows that upward of two hours was here necessary to get a correct test. In fact, where a lamp is changed on to gas of different composition as regards the proportion of sulphur present, the interval which elapses before a correct test is obtained increases with the difference in the amount of sulphur in the two gases. The due appreciation of this fact is most important, and a knowledge of it has explained many anomalous tests made at an early period of my connection with the Commercial Gas Company, and when the conditions of accuracy were less understood. We now have a separate lamp on each purifier to be tested, instead of transferring a single lamp from one to the other; and by this means, and the observance of general conditions dictated by experience, the tests are rapid and reliable. Of these other conditions, temperature is entitled to the first place; while a proper rate of flow of gas through the lamps, and the maintenance of the platinized pumice in an active condition (by periodically removing any excess of carbon deposit), are also essential.

Treating these three conditions categorically, I have already stated the temperature which I consider best suited for efficient working. It may, however, be useful to show the effect produced by modifications of temperature; and I will therefore quote a few experiments bearing on the subject: Flame normal; grains of sulphur, 16. The flame was now turned up so as to be as high as possible without actually smoking, when the following consecutive tests were obtained, extending over a period of two hours: 27.8, 25.5, 23.7, 23.1, 21.3, 20.9, 19.3, and 18.9 grains. The flame was then turned down to its normal height, and gave 16.1 grains after the lapse of five minutes. In another experiment a lamp was giving 15.3 grains of sulphur with the normal flame; the referees' test on the same gas being 15.6 grains. When the flame was turned down to a "blue non-luminous ring," 12 grains was obtained. I need not quote any further experiments to show that temperature is an important factor in obtaining correct results. At the same time, those accustomed to the use of the test have no difficulty in adjusting the lamp to a proper temperature, judging simply, by the appearance of the flame.

The experiments next to be described were made in connection with the effect of velocity on the test. The normal rate is obtained when the passage of gas through the lamp is such as to give a flame about 1 inch high when the jet is lighted, and when during the use of the test the tap of the aspirator is turned on so as to give a slender stream which any check on the tap would break up into a succession of drops. I find this

corresponds to a mean rate of about 10 measures per minute. The following experiments illustrate the bearing of this part of the subject:

Time occupied in test.		Number of measures.	Grains of sulphur per 100 cubic feet.	Remarks.
Min.	Sec.			
1	28	15.0	40.3	Quick.
1	38	18.0	45.5	Normal.
1	12	14.0	42.7	Fast.
1	26	18.0	45.5	Normal.
2	40	10.0	57.0	Slow.
1	0	14.0	42.7	Fast.
2	30	10.5	54.7	Slow.
0	53	14.0	42.7	Fast.
1	30	18.0	45.5	Normal.
2	8	11.5	50.5	Slow.
1	25	12.5	47.1	Normal.

Mean normal time, 10 measures in 62 seconds; mean sulphur, 47.2 grains. Mean result slow... 10 " 126 " " 54.0 " Mean result fast... 30 " 49 " " 42.1 "

In another series of experiments the sulphur indicated was as follows, as a mean of a number of tests:

Normal rate.... 21.5 grains per 100 cubic feet.  
Slow..... 28.7 " " "  
Fast..... 18.0 " " "

With regard to the maintenance of the platinized pumice in an efficient condition, our custom since the year 1881 has been to aerate the lamps at intervals of about a month, by turning up the flame to considerably more than its usual height, and drawing a slow current of air through. About 0.1 cubic foot generally effects the desired result of burning off the deposited carbon. In addition to this, it is customary whenever a breakage occurs to thoroughly ignite the pumice for some time in a platinum crucible before using it to charge a fresh bulb. In order to illustrate the effect of aerating a lamp which has been in use for some time, the following experiments, made some years back, may be quoted: A lamp showing 12 grains of sulphur on gas which was giving 18 grains by the referees' test had 0.1 cubic foot of air drawn through, and was set to work. After an hour's interval, a test gave 19.2 grains of sulphur; and after a further period of 20 minutes, 18.3 grains—a practically correct result—was obtained. Another lamp, showing 12 grains on a 16.5 grain gas, was treated in a similar way; and, having been set to work, gave a correct result after the lapse of between one and two hours. An old lamp which has been used for some considerable period without aerating has been found to contain as much as 6.1 grains of deposited carbon; and it is obvious how seriously this would interfere with the proper action of the pumice.

In using the Harcourt test for sulphureted hydrogen and carbonic acid, there are also one or two little details conducing to correct results which I may mention. In any case, where the test cannot be taken directly off a leading main—and this is frequently inconvenient—the pipe used for conveying the gas from the main to the testing place should be as short as possible, should be of good diameter, and should be preferably of lead or composition metal. Before commencing, the gas should be allowed to "blow away" for a short time; and subsequently, when taking the test, I prefer to use a small glass tube like that shown in Fig. 2. The gas is connected to one end of the straight tube; the other end communicating with the outside air by a piece of rubber tubing. The inlet to the test glass containing the lead or baryta solution is connected by about an inch of rubber tubing to the end of the bent portion of the glass tube, and the test then taken. The object of this is to take the test always directly off an active current of gas. Where this is not done, my experience has shown that there is a tendency to obtain unduly low results, arising probably from a partial condensation of moisture, laden with sulphureted hydrogen and carbonic acid, in the pipe, when the velocity of the gas is not sufficient to prevent or mitigate such an effect. Contrary to the instructions issued with the test, it is also our practice to make carbonic acid tests directly on the gas, without the intervention of a small oxide vessel for the removal of the sulphureted hydrogen. It was found that the use of a moist porous mass such as was presented by the oxide purifier tended to absorb and retain a portion of the entering carbonic acid for a considerable time after being put on; and, on the other hand, that a clean oxide purifier, when first put on gas free from carbonic acid, showed distinct indications of carbonic acid at the outlet for about one hour. In order to avoid the possibility of errors of this kind, we pass the gas to be tested directly into the solution of barium hydrate. As the contents of the tube are thrown away after use, and as there is always a considerably larger quantity of barium hydrate present than is necessary to combine with both the carbonic acid and the sulphureted hydrogen in the volume of gas used for testing, the presence of the latter impurity does not affect the result.

In conclusion, I may describe some slight modifications in the construction of the apparatus used in the Harcourt tests which I have devised, with the effect of making the apparatus more portable and convenient. The lamp is shown in Fig. 8, where B is the bulb (supported by the arm and screw, K) containing the platinized pumice; C, the Argand burner; F, a solid metal stand; G, the gas inlet; and D and E, the taps—on to control the flow of gas to the burner, and the other to the bulb. D is a three-way tap made by drilling a small hole in the side of the tap right through to the center of the plug. While the gas supplying the burner is regulated by E, the tap, D, may be used either for controlling the gas to the bulb, or by being turned in a particular direction the gas supply is cut off and the bulb placed in connection with the air, so that by means of an aspirator air can be drawn through the pumice for the purpose of burning off any carbon deposit. The dimensions of the lamp are: Base,  $3\frac{1}{2}$  inches; extreme height,  $8\frac{1}{2}$  inches. The ordinary form of lamp stands about 18 inches high, with a base of about 3 by 5 inches. The top of the bulb is, of course, originally open; A representing where the tube has been sealed after the introduction of the pumice.

Instead of employing two measures—a large and a small one—and an aspirator, I use the glass vessel

shown in Fig. 4, in which measures and aspirator are combined. The water is run out by the tap into any vessel handy (an ordinary jug answering admirably); and the measures of gas used are read off direct. The upper part of the vessel is small in diameter, while the lower part is considerably larger; the object being to insure the greatest accuracy in reading where the volume of gas is smallest. The vessel stands about 27 inches high, with a base of a little more than 4 inches, and has a total capacity available for measurement of 1.20th of a cubic foot. Where extra portability is desirable, the vessel is made in two parts; the upper and narrower portion fitting into the lower and larger part by a ground-glass joint. The apparatus shown in Fig. 5 is also useful in judging of the respective intensities

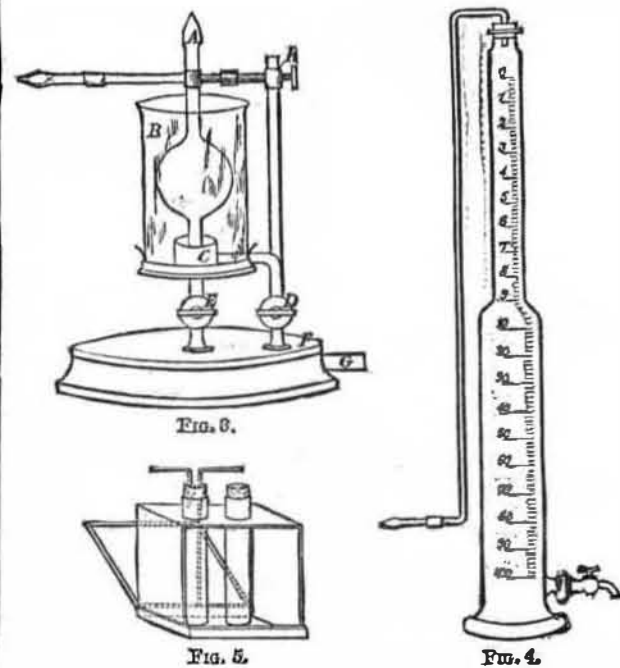


FIG. 3.

FIG. 5.

FIG. 4.

of the lead solution and the color standard. The two tubes stand close together in a small wooden frame, painted a dead black; the opaque sides preventing the effects of side light, which is apt, if present, to interfere with an accurate comparison of tint. The back is hinged at the bottom, and consists of a small metal frame fitted with a piece of thin opal glass. When inclined, the light reflected from the white surface enables the comparison tints to be clearly discriminated; and in different conditions of light the back may be closed up, and the tints judged by looking through the test tubes, with the diffused white semi-transparent screen behind.

The whole apparatus—lamp, measure aspirator, tubes, bottles for lead sirup and baryta—packs into a box 20 in. by 13 in. by 10 in., so that it is easily carried about; and I have no doubt, with a full knowledge of the conditions necessary to insure accuracy, a portable form of the Harcourt test that could be taken from place to place would be found a useful and reliable means for testing the condition of the gas in country works. From long experience in the use of the Harcourt tests, I can confidently recommend them as a good practical guide to gas purification. With care, results of sulphur compounds can be obtained within a grain or two of the results of the referees' test; and for carbonic acid and sulphureted hydrogen, the results, although not strictly accurate, are sufficiently correct to give an excellent guide as to the amount of work done by purifiers and scrubbers. The tests also have the great advantage of simplicity, which renders them capable of employment by an intelligent workingman. —*Journal of Gas Lighting.*

## THE PRESSURE AND COMPOSITION OF NATURAL GAS.

By Dr. H. M. CHANCE.

IN a paper discussing the "Anticline Theory" of Natural Gas,\* I have already shown that the pressure under which gas exists beneath the surface in Western Pennsylvania must be limited by the depth of the gas-producing stratum; it must, in other words, be less than the weight of the overlying rocks, which may be taken at one pound per square inch for every foot in depth. This determines the absolute maximum limit for any considerable area of gas-producing rock.

It is, perhaps, possible that the pressure is also limited by the hydrostatic head. We may distinguish two entirely independent hydrostatic pressures which might limit the gas pressure.

1. *Direct pressure* from stream level at the surface above the gas rock, acting through extremely narrow crevices, and thus sealing the gas within its porous sand rock reservoirs. When the gas pressure exceeds this water pressure, the gas must blow off. After the pressure is sufficiently reduced, the water might again seal up the vents. The gas pressure, if so limited, could not exceed  $\frac{1}{16}$  pound for each foot in depth of gas sand below surface water level. Thus for 1,500 ft. below water level, the gas pressure limit would be about 650 pounds per square inch, or somewhat less than half the ultimate maximum as limited by rock pressure (weight).

2. *Hydrostatic pressure* acting through each rock from its outcrop at water level in the northern part of Pennsylvania or Southern New York. If we could admit the possibility of such perfect continuity of porosity, or open crevices, or both, as would permit the pressure to be transmitted through eighty or one hundred miles of rock underground from the water level outcrop of the first oil sand near Titusville on Oil Creek, and below Tidioute on the Allegheny River, at an elevation above tide of about 1,100 ft., through and down the slope of the rock to Pittsburgh, where this rock lies about 800 ft. below tide, then the maximum gas pressure possible would be limited by this difference in elevation.

\* Read before the Bethlehem (1886) meeting of the American Institute of Mining Engineers.



The non-porous character of large areas of the rock, the clay luting of the rock joints (cleavage joints), render such an hypothesis improbable, but we have much stronger negative evidence in the salt water wells, many of which, when first struck, flow largely, but after a time, as the gas pressure (from dissolved gas) diminishes, they cease flowing, and in many cases the brine does not rise more than half way to the surface. If the hypothesis of open crevices or continuity of porosity were true, these wells should yield true artesian flows of constant volume.

The hypothesis of direct pressure from the surface is partly disproved by the experience of drillers throughout the oil region, that fresh water is found only to a certain depth—usually 300 to 500 ft.—and that below this, and until salt water is struck—commonly at 800 to 1,400 ft. in the oil regions—the slates and shales passed through are *extremely dry*. This dryness of the underground is not peculiar to the oil regions. In many mining districts the rocks at great depth are exceedingly dry, no water being met after passing below the limit to which the surface water penetrates. In some of our deep anthracite coal mines, and in deep coal mines in other countries, the absence of moisture is such that much inconvenience is experienced from the accumulation of large quantities of exceedingly dry dust.

This fact, that surface water finds its way down to only a limited depth, is sufficient proof that nearly all the cleavage joints and fissures are filled with a practically water-tight clay luting, and it is to this fact that we must attribute the possibility of the existence of large quantities of gas at great pressure. Without such a filling in of the cleavage joints and fissures, such accumulations would evidently be impossible.

Hence these hypotheses both seem to me improbable, and while they would, if true, establish pressure limits very nearly equal to the observed maximum pressures, I believe that this is merely a coincidence brought about in the following way:

We have no records of the gas pressure first shown by the larger wells. The recorded pressures have nearly all been observed after the gas had been blowing off for some weeks, months, or even years, and the pressure then shown by a gauge is evidently no measure of the pressure under which the gas exists in the rock, for the gas soon becomes exhausted from the immediate vicinity of the well, which then draws its supply from a considerable distance, and perhaps through bands of rock of such texture (and, perhaps, even through the clay filling of crevices) that the pressure shown at the well may be only a fraction of the actual pressure.

Hence, while recorded pressures range from about 600 down to 200 pounds per square inch, we have every reason to believe that the actual pressures are perhaps from 500 to 1,000 pounds per square inch, or even in some cases much greater, but must still be less than the maximum as limited by depth. In the paper above mentioned I have shown that this maximum is very much less than the pressure necessary to effect liquefaction, and that we must, therefore, abandon the supposition that the gas exists as a liquid.

One of the most interesting phenomena recently observed in natural gas is its variability. The analyses of Prof. Sadtler,\* made some nine years ago, told us that gas from wells located in districts not connected with each other was similar in composition, but that the percentages of the different gases present varied widely. We were, however, not prepared for the discovery that gas from wells in the same "pool" and that from the same well was subject to daily and even hourly variations in composition. When it was found that the calorific value of the fuel was subject to change from time to time, as shown by variations in temperature of the furnaces, and in the steam pressure of boilers under which it was burned, this was at first supposed to be due to differences in pressure, that is, in the quantity of gas delivered to the burners in the fire box. Automatic pressure regulators were introduced, and the producing companies perfected a system by which the pressures were maintained at a nearly constant figure, yet the same variations were observed. The chemists then began to examine the gas, and soon found that it was extremely variable in composition.

As the law of diffusion of gases should effect a thorough mixing of the gases throughout the limits of any gas pool or area of porous rock, we should naturally expect the gas from each such pool to be of uniform composition. Those who uphold the hypothesis of continuous manufacture underground quote this variation in composition as one of the strongest arguments in support of the theory, and as yet the geologists familiar with the phenomena of natural gas, who, almost without exception, have discarded this theory as untrue, have not furnished any explanation of this phenomenon. Two of our most noted scientists versed in the chemistry and geology of natural gas, and disbelieving any theory of continuous production (*pari passu* with consumption), have been disposed to explain this variability by asserting that the law of diffusion may become inoperative in gases under great pressure. As the diffusion of gases results from molecular activity, and as this cannot be destroyed or suppressed by pressure, and as it has never been shown that any of the laws of matter may be annihilated, this assertion appears to me to be entirely without support.

It seems to me entirely possible to account for the phenomena without doing violence to any natural law, and to explain how almost any and every possible variation in the composition of natural gas may, if indeed it must not, occur in the gas as yielded by the wells, while the gas throughout the porous area is of uniform composition. The first four of the following analyses were made from gas taken from the same well at different times. The remaining analyses are of wells in different districts.

The first four analyses show marked variations in hydrogen and ethane. In the gas from the well near Greensburg, from which the Cambria Iron Company is to get its supply, Mr. John Fulton informs me that nitrogen is contained in considerable quantity, and that it is subject to marked and rapid variations.

All rocks are traversed by cleavage joints and fissures. They may be seen in every quarry, in every railroad cut, tunnel, and mine. The rocks of western Pennsylvania are no exception, but the fact that gas exists under great pressure in the porous rocks is sufficient

	1	2	3	4	5	6	7	8	9	10
Carbonic acid, CO <sub>2</sub> .....	0.80	0.60	.....	0.40	0.34	0.35	0.66	2.28	.....	0.30
Carbonic oxide, CO.....	1.00	0.80	0.58	0.40	trace	0.26	trace	.....	1.00	0.60
Hydrogen, H.....	20.02	26.16	29.08	35.92	6.10	4.79	13.50	22.50	9.64	14.45
Marsh gas, CH <sub>4</sub> .....	72.18	65.25	60.70	49.58	75.44	89.65	80.11	60.37	57.85	75.16
Ethane, C <sub>2</sub> H <sub>6</sub> .....	3.60	5.50	7.92	12.30	18.12	4.39	5.72	6.80	5.20	4.80
Propane, C <sub>3</sub> H <sub>8</sub> .....	.....	.....	.....	.....	trace	trace	.....	.....	.....	.....
Nitrogen, N.....	.....	.....	.....	.....	.....	.....	.....	7.32	23.41	2.89
Oxygen, O.....	1.10	0.80	0.78	0.80	.....	.....	.....	0.83	2.10	1.20
Illuminating hydrocarbons.....	0.70	0.80	0.98	0.60	.....	0.56	.....	.....	0.80	0.60
Ratio, C to H (weight).....	2.72	2.59	2.64	2.59	3.08	3.00	2.88	2.70	2.91	2.84

1, 2, 3, 4. From well supplying Edgar Thomson Steel Works, by S. A. Ford.  
5. Burns well, Butler Co., Pa., by Sadtler.  
6. Luckburg well, Armstrong Co., Pa., by Sadtler.  
7. Harvey well, Butler Co., Pa., by Sadtler.  
8. Cherry Tree well, Indiana Co., Pa., by Sadtler. Small flow through fresh water.  
9, 10. Two wells near East Liberty, Allegheny Co., Pa., by S. A. Ford.

evidence that these cleavage joints are sealed with a luting of clay and perhaps calcareous material from percolating water, and the fact that the waters do not now percolate from the surface to a greater depth than 300 to 500 ft. is evidence that these narrow crevices are impervious below that depth. The word crevice or fissure is not exactly applicable to many of these openings, which are merely joints or cleavage planes, and in a few cases only do they have a width entitling them to be termed crevices or fissures.

If these joints in the rocks above the gas sands are luted with clay or calcareous material, then we have every reason to believe that the cleavage joints of the gas rock itself are also partially closed by similar material, and we may, therefore, conclude that every gas area is divided into many subdivisions by diaphragms of clay or calcareous material, through which the gas must diffuse in passing to the well. As the rate of diffusion of gases through porous diaphragms is inversely as the square root of their densities, the gases will diffuse in ratios proportional to the following figures:

	Density.	Rate of Diffusion.
Hydrogen, H.....	1	1
Marsh gas, CH <sub>4</sub> .....	7.985	$\frac{1}{2.81}$
Ethane, C <sub>2</sub> H <sub>6</sub> .....	14.97	$\frac{1}{3.87}$
Nitrogen, N.....	14.01	$\frac{1}{3.74}$

If the diffusion is from an inclosed area, the hydrogen percentage will be largely increased, and the percentages of the other gases decreased. If the diffusion is through a plane along which a current of gas is constantly flowing to find its way by a circuitous route to the well, the diffused gas will contain a still larger percentage of hydrogen, and nearly equal percentages of marsh gas, ethane, and nitrogen. If the diaphragm of clay or calcareous material permits transfusion as well as diffusion, we will have still different percentages.

Again, the gas dissolved and held by salt water contains less hydrogen, nitrogen, and marsh gas, and more ethane, than the free gas. Gas given off from the salt water as the pressure diminishes will, therefore, constitute another variety. If this gas diffuses through a diaphragm on its way to the well, the diffused gas will have a composition dissimilar to any of the mixtures already described, being lower in nitrogen. If this gas flows past a diaphragm while diffusing through it, the diffused gas will contain nearly all the hydrogen, nitrogen, and ethane, and the gas flowing past and around the diaphragm will consist almost entirely of marsh gas.

Hence we have the following varieties:

1. Normal mixture of gas.
2. Gas diffused through diaphragm.
3. Gas left behind diaphragm.
4. Gas diffused through diaphragm while flowing past it.
5. Gas flowing past diaphragm, not diffused.
6. Gas from salt water.
7. Gas from salt water, diffused through diaphragm.
8. Gas from salt water, left behind diaphragm.
9. Gas from salt water, diffused while flowing past diaphragm.
10. Gas from salt water, flowing past diaphragm not diffused.

And, in addition to these varieties, we may have an infinite number of minor variations resulting from the combined action of diffusion and varying rates of transfusion, and from mixtures of these variations with the normal gas mixture we can readily conceive a well so located with reference to a salt water area and to a number of cleavage joint diaphragms that the mixture of gases flowing into it from different directions would be subject to such constant changes that uniformity of composition, even for short periods, would be exceptional and variability the rule.

The solubility of these gases in salt water is not accurately known. The following coefficients of solubility (by volume) in fresh water for a temperature of 20° C. (68° F.) were calculated from the formulæ given by Roscoe and Schorlemmer.\*

H	Hydrogen.....	0.01930	1.93 per cent.
CH <sub>4</sub>	Marsh gas.....	0.03449	3.45 "
C <sub>2</sub> H <sub>6</sub>	Ethane.....	0.049	4.90 "
N	Nitrogen.....	0.18	1.80 "

By Dalton's law of partial pressures the composition of the dissolved gas is found by multiplying the percentage of each gas by its coefficient of solubility, and dividing each product by the sum of all the products, the results showing the percentage of each gas in the mixture.

The influence of unequal pressures underground caused by the unequal action of several wells drawing gas from the same rock, and the movements of salt water through the rock, will sufficiently account for varying flows of gas toward any one well from different directions. Under such conditions, it is evident that more abrupt changes in composition would occur than in the case of a single well drawing gas from a pool in

which water movement could not occur, for in this case the gas flowing toward the well from each direction would maintain a constant ratio to the total flow, and the resulting mixture in the well would remain more nearly constant in composition, except as the mixture coming from any one direction might become exhausted (or slowly change by diffusion) and be replaced by the gas left behind a diaphragm, through which the first mixture had diffused.—*Proc. Eng. Club, May, 1886.*

## ON THE DETERMINATION OF ALUMINUM IN PRESENCE OF LARGE PROPORTIONS OF IRON.

By ROBERT T. THOMSON.

HAVING lately had occasion to test for and determine a minute proportion of aluminum in presence of a large proportion of iron, I was led to try the capabilities of the two best-known methods, namely, by boiling with a large excess of caustic soda or potash and subsequent precipitation in the filtrate from the peroxide of iron, and by direct precipitation with thiosulphate of sodium. In the latter case only about 90 per cent. of the total aluminum present was obtained, when working on a solution containing 100 parts of iron to 1 part of aluminum. But the failure of the caustic alkali method was more striking, as not a trace of alumina could be detected in the sodafiltrate. The solution operated upon contained 2 grms. of iron and 0.02 gm. of aluminum. It was nearly neutralized, and slowly added to a quantity of caustic soda solution heated to boiling in a nickel basin. The mixture was thoroughly boiled, filtered, and tested for alumina, with a negative result, as already stated. The excess of caustic soda used was more than 10 grms. Both of these processes had to be rejected, but I at last hit upon the following method, which gives excellent results:

The iron, if in the ferric state, is first reduced to the ferrous condition by passing a current of sulphurous acid through the solution. The excess of sulphurous acid is boiled off, the mixture cooled, and at least as much phosphoric acid, or phosphate of ammonium or sodium, added as will be equivalent to the alumina present. It is advisable to use a large excess of phosphoric acid, as the alumina may not be completely precipitated if it has not at least its own equivalent of the former. One drawback to the unlimited use of phosphoric acid is that if manganese is present it will be thrown down; but if the quantity of the former is limited, the latter will remain in solution. Where manganese is present in quantity, it is advisable to employ the alternative method of precipitation to be described further on. Ammonia is now added until a faint permanent cloudiness is formed; then excess of ammonium acetate, which throws down the alumina as phosphate. The precipitate always contains some ferric phosphate, which forms from any traces of ferric iron salt which may have escaped reduction, and from the oxidizing action of the air during filtration. The great bulk of the iron, however, remains in solution in the ferrous condition. The precipitate is now collected on a filter, washed two or three times with water, and dissolved by passing dilute warm hydrochloric acid through the filter. If it does not seem sufficiently free from iron, the solution thus obtained should be put through the same process as has been just described, beginning at reduction with sulphurous acid. When filtered rapidly I have had as little as 0.1 gm. of peroxide of iron in the aluminum phosphate, and in no case have I required a reprecipitation. It is well to reduce the iron as much as possible.

An alternative method of getting rid of the great proportion of the iron is to add ammonia to the reduced solution till a slight cloudiness is formed; then excess of ammonium acetate, and boil for a few seconds. The whole of the alumina and a portion of the iron are precipitated, and are collected on a filter. No phosphoric acid is added in this case, and manganese remains in solution. More iron is brought down than in the first described cold method, and, when only minute quantities of alumina are expected, a second reduction and precipitation will most likely be necessary.

After obtaining a satisfactory precipitate (whichever method has been adopted), it is dissolved in hydrochloric acid, boiled with a little nitric acid to oxidize any protosalt of iron, nearly neutralized with pure caustic soda, and added to a considerable excess of the latter in a nickel basin. The mixture is boiled for a short time, filtered, the filtrate acidified with hydrochloric acid, and a large excess of phosphoric acid or phosphate of ammonia or soda added. I have found that the presence of at least two equivalents of P<sub>2</sub>O<sub>5</sub> to one of Al<sub>2</sub>O<sub>3</sub> are necessary to give rise to the normal phosphate of aluminum (Al<sub>2</sub>P<sub>2</sub>O<sub>7</sub>). The latter is now precipitated by adding ammonia till a slight cloudiness is produced, and then excess of acetate of ammonium. Or the precipitation may be effected by simple neutralization with dilute ammonia till a red reaction ceases to be obtained with blue lakmoid paper. The aluminum phosphate is now collected on a filter, washed thoroughly with a hot 1 per cent. solution of ammonium nitrate containing about 0.1 gm. of the diacid ammonium phosphate (NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>) per liter, dried, ignited, and weighed. If the aluminum phosphate is washed with water it partially loses its gelatinous form, and becomes tedious to filter. But besides this the precipitate is decomposed to a considerable extent, and a portion of the phosphoric acid passes into solution. For these reasons the precipitate must be washed in the manner described, when pure Al<sub>2</sub>P<sub>2</sub>O<sub>7</sub> is weighed, and may be calculated to alumina or aluminum as required.

The following are results obtained by the above process in solutions containing 3 grms. of metallic iron. To the iron solution a weighed quantity of pure ammonia alum was added.

Grm. of Al <sub>2</sub> O <sub>3</sub> added.	Grm. of Al <sub>2</sub> P <sub>2</sub> O <sub>7</sub> obtained.	Grm. of Al <sub>2</sub> O <sub>3</sub> obtained.
0.0340	0.0800	0.0336
0.1135	0.2695	0.1132
0.1135	0.2703	0.1136

The presence of titanium is not injurious in the above process, as only slight traces of titanous acid are dissolved by strong caustic soda.

City Analyst's Laboratory, Glasgow.

—*Chem. News.*

\* Report L, Pennsylvania Geological Survey.

\* Organic Chemistry, vols. i. and iii., pt. 1.