

and bone char. The application of the tan polish is frequently preceded by the use of a cleaning solution to remove stains and discolouration.

A popular cleaner is a mucilage of gum tragacanth containing a small percentage of oxalic acid. So remarkable is the power of tragacanth to hold water that this article, in appearance a thick cream, is 97 per cent. water, gum and acid constituting the remainder.

## Liverpool Section.

Meeting held at the University, on Wednesday, February 12th, 1913.

PROF. F. G. DONNAN IN THE CHAIR.

### CHEMISTRY APPLIED TO COAL MINING.

BY DR. JOHN HARGER.

Coals are conglomerates of four classes of substances, humus bodies, resin bodies, carbon residuum, and hydrocarbons.

	Approximate composition.			Calorific power in Calories	Calorific intensity in air.
	C	H	O		
Humus bodies .	63	5.0	32	6470—6490	2670° C.
Resin bodies .	79	10.0	11	9120—9140	2250° C.
Carbon residuum	95.7	2.5	1.5	8670—8680	
Hydrocarbons .	n	2n+2	—	12,000	

The properties of a coal, and, to a certain extent, the danger or safety of a coal mine, depend upon the relative proportion of these four constituents. At present it is only possible to estimate each of these constituents approximately. An approximation to the humus bodies can be obtained by an estimation of the hygroscopic moisture in the air-dried coal, taken together with the amount of oxygen and other constituents. The true resin bodies can be estimated by extraction with pyridine.

The composition of firedamps and more especially of the inflammable part of them is of great importance, the present method prescribed by the Home Office being only correct when the inflammable gas is pure methane. The method is briefly as follows: The carbon dioxide is first estimated by absorption; the inflammable gas is then burnt by passage over a hot platinum spiral, the contraction is measured and the carbon dioxide formed is absorbed. The volume of inflammable gas is taken to be half the contraction and equal to the volume of the carbon dioxide formed.

The assumption that the inflammable gas is always pure methane is quite incorrect. It is true that most of it is methane and in some firedamps there appears to be no other inflammable gas. But gas is given off from coal for months after it is mined, and in mines where a large quantity of coal is left in the goafs a considerable quantity of firedamp comes off therefrom. In many cases the author has found large quantities of heavy hydrocarbons in this firedamp.

In a sample of air containing 2½ per cent. of inflammable gas, 5 per cent. of ethane in the latter might pass undetected by the present method of analysis. A mixture of equal volumes of hydrogen and ethane behaves on combustion with air in exactly the same way as pure methane, i.e., the contraction is twice the volume of the carbon dioxide formed. Also a mixture of two volumes of ethylene and 1.33 volumes of hydrogen gives exactly the same volume changes.

All these gases, methane, ethane, ethylene, and hydrogen, have been found in firedamps by Playfair, Bischoff, Wheeler,

and others, whilst from some coal dusts Bedson has sucked off inflammable gas in which the value for n in the formula  $C_nH_{2n+2}$  was as high as 4.4.

A mine atmosphere containing 2½ per cent. of pure methane, in the author's opinion, may be regarded as quite safe if coal dust is absent, but one with 2½ per cent. of firedamp containing hydrogen, ethylene, or heavy hydrocarbons may be explosive, even without dust.

A few examples of analyses of firedamp from the same mine on different days and from several different places are shown in the table. It will be seen that generally there is an indication of the presence of higher hydrocarbons, and in No. 12 of hydrogen. Recently results quite similar to those given in the table were found in another mine, while in a third (a new mine with practically no goaf) the figures agree for pure methane or for a mixture in which the higher hydrocarbons, if present, are balanced by some hydrogen.

No. of analysis.	Contraction on combustion.	CO <sub>2</sub> formed.	Ratio, contraction : CO <sub>2</sub> .
1	0.515	0.262	1.97
2	0.304	0.199	1.98
3	0.407	0.203	2.00
4	0.476	0.238	2.00
5	0.420	0.216	1.94
6	0.143	0.073	1.96
7	0.553	0.282	1.96
8	0.484	0.241	2.00
9	0.424	0.224	1.90
10	0.151	0.076	1.99
11	0.631	0.336	1.88
12	0.520	0.220	2.36
13	0.776	0.402	1.93
14	0.240	0.122	1.97
15	0.142	0.080	1.77
16	0.130	0.077	1.69
17	0.153	0.081	1.89
18	0.464	0.253	1.83
19	0.410	0.212	1.93
20	0.372	0.197	1.89

Numerous experiments have been made on gases sucked from coals from various seams. The coal in each case was put, at the fresh coal face, into a small bottle which was then closed by a rubber bung having a hole filled with a glass rod. At the laboratory the glass rod was pushed in by a tube having a mercury luted stop-cock; the tube was sealed on to a Töpler pump and after the rubber stopper, etc., had been luted with mercury the bottle was exhausted. The gas was pumped off from time to time until practically no more came.

In one experiment the first sample of gas obtained, after absorption of carbon dioxide, showed on combustion 28.3 per cent. contraction and 18.0 per cent. carbon dioxide formed. The gas was diluted with fresh air for analysis.

If it is assumed that the inflammable gas was methane the contraction would indicate 14.15 per cent., and the carbon dioxide formed 18.00 per cent.—a difference of 3.85. A later sample from the same experiment similarly indicated from the contraction 12.35 per cent. methane, and from the carbon dioxide formed 13.80 per cent.—a difference of 1.45.

By the following method it is possible with the Haldane apparatus to estimate the actual volume of inflammable gas without making any assumption as to its composition. First, in one portion of the sample estimate the carbon dioxide and oxygen, and note the volume of residual inflammable gas + nitrogen. Next, in a fresh portion of the sample, estimate the carbon dioxide; burn the inflammable gas, absorb first the carbon dioxide formed, and then the residual oxygen, and note the volume of the residual nitrogen. From (1) the inflammable gas + nitrogen and from (2) the nitrogen, the volume of inflammable gas is ascertained. By this method one also finds the amount of oxygen used, which is very important as a check on the other figures. The actual volume of the inflammable gas and the carbon dioxide formed having been ascertained, the average value of it in the formula  $C_nH_{2n+2}$ , or other formula, can be calculated, since two volumes of hydrocarbon give two volumes of carbon

dioxide on combustion, when it contains one atom of carbon in the molecule, four volumes when it contains two atoms in the molecule, etc.

An improved new method of estimating the inflammable gas which has been worked out is as follows:—The carbon dioxide and oxygen are first estimated and the residual mixture of nitrogen and inflammable gas is driven into the combustion pipette. The latter contains, instead of the simple platinum spiral, one covered with copper oxide. The spiral is heated by an electric current in the usual way, and the inflammable gas is thus converted into carbon dioxide and water. The volume is measured, the carbon dioxide is absorbed and the volume again noted. The reduced copper is re-oxidised by introducing some air and heating the wire. The air is then removed from the pipette which is washed out with nitrogen ready for the next test.

In gas analysis apparatus which is in regular use, all rubber connections between the cocks and pipettes should be done away with and the tubes sealed together. Such apparatus will be less troublesome in the end and more reliable, as numerous possible sources of leakage are removed.

A large number of experiments were made with various catalytic substances for the preparation of inert gas free from carbon monoxide. It was found that bog iron ore is a very strong catalyst, and in presence of a small quantity of oxygen effects the combustion of the last traces of carbon monoxide to carbon dioxide at a temperature of 200° C. or over. Below 200° there is some action but too slow to be of practical use. Incidentally it was found that a mixture of hydrogen and air, when passed over bog iron ore, burnt at a temperature of 100° C. and slowly at even lower temperatures. It is possible to use bog iron ore instead of palladium preparations in gas analysis.

With copper oxide, in the absence of air, carbon monoxide is burnt at temperatures below 100°; hydrogen at one or two degrees above 100° C. and rapidly at 150° C., while methane is apparently untouched at these temperatures. The use of copper oxide at 150° C. is suggested for removing hydrogen from methane when the latter is required pure and also for estimating hydrogen in presence of methane. The use of bog iron ore and copper oxide for removing traces of carbon monoxide on the large scale is described by the author in T.I.M.E., Vol. XLIV., Pt. 2 "Gob-fires and the Prevention of Gob-fires in Mines."

The temperature of ignition of methane and air mixtures is about 650°–700° C. (Dixon and Coward). If a calculation of the calorific intensity of 2½ per cent. methane in air is made the result is about this figure (650°–700° C.). But one cannot light such a mixture with a flame or make it burn with an electric spark; it is only when the percentage of methane reaches 5½ that the mixture becomes inflammable, when the percentage of methane reaches 13 the mixture again becomes non-inflammable *per se*. Although there is still over 18 per cent. of oxygen in the mixture, the excess of methane inhibits the reaction.

The presence of carbon dioxide in moderate amount does not appear to influence the combustion of liquid, gaseous, or solid combustibles, but in certain cases it does seem to exercise a profound influence on the *starting* of such combustions. The effect is far out of proportion to the dilution, and is not explicable by reference to specific heats or other similar data. It may be due, at least partially, to the property of absorption of radiant heat possessed by carbon dioxide and methane. Tyndall gives the relative absorptive powers for radiant heat of various gases as follows, viz.:—Oxygen 1, nitrogen 1, hydrogen 1, chlorine 39, carbon dioxide 90, methane 403, ethylene 970, ammonia 1195, water about 5000.

In some experiments with coal dust it was observed that 1 volume of carbon dioxide had as great a retarding effect on the starting of ignition as 12 volumes of nitrogen, but once combustion had started the carbon dioxide appeared to have very little, if any, more effect than an equal volume of nitrogen.

#### DISCUSSION.

Professor E. C. C. BALY said that the author had stated that the presence of hydrogen and higher hydrocarbons

in mine air would not be accurately estimated by the Haldane apparatus. If, however, one studied Dr. Harger's own figures, and worked out the difference which would result if the gas were pure methane or the mixture which gave the most divergent results, the percentage difference would only change from 3·1 per cent. to 2·89 per cent., a variation which did not seem to be very serious from the point of view of mine ventilation. A second point was that considerable discrepancies arose from the dirty state of the apparatus. In fact the dirtier the apparatus the greater the variation. From his experience of analysis of 300 to 400 samples of mine air, he found that the higher the methane content, the more nearly was the carbon dioxide absorption equal to half the contraction. With a perfectly clean apparatus and a high methane content one figure was almost exactly double the other. It did not seem to matter very much, so long as the gas was an explosive one, whether it was pure methane or methane mixed with some hydrogen or higher hydrocarbon. The only difference it might make in the working of the Act was that the limits of gas allowed might have to be modified. Finally, with regard to Dr. Harger's figures connecting absorptive power and radiant heat surely there must be more modern results than those given by Tyndall. Angström, Coblenz, and others must have used considerably more accurate apparatus and their results must be correspondingly more valuable. The figures, especially those for carbon dioxide and water, certainly seemed to require modification.

Mr. W. H. PATTERSON asked whether the pyridine used in the separation was the means of separating the two resinous products mentioned in the tables of coal analysis. What evidence was there for this separation taking place? Figures obtained by himself for extractions were inconsistent with a simple separation by the solvent action of pyridine, and a separation of two resinous products of which one combined with, and the other was dissolved by pyridine, would account for this.

Mr. A. CAREY asked whether Dr. Harger had done any work on the action of bog iron ore on flue gases in an actual boiler? Also if the respective catalytic actions of bog iron ore and bauxite had been compared?

Mr. H. B. STOCKS asked whether the action of phenol and terpineol as well as pyridine for dissolving out the resinous products of coal had been tried. Acetone might also be worth trying.

Dr. A. HOLT asked, with regard to the gas which came off from coal, if the coal completely lost that gas or was there some left which could be pumped off afterwards? Did the coal dust re-absorb the gas to any extent, or in other words, could this be called a reversible process? Secondly, with regard to the dust itself, did the hydrocarbons condense on its surface? If so, was it this condensed hydrocarbon which started the explosion? Had any experiments been made on this subject?

Mr. R. E. SLADE said that he believed that if there were some gases which did not come off at 100°, probably these gases were adsorbed. Carbon would adsorb carbon dioxide at 500° and 600° C.

Dr. HARGER, in reply, thought Professor Baly had missed the point, because the behaviour of pure methane was so different to that of hydrogen and the higher hydrocarbons. Hydrogen, when present in comparatively small quantities, acted as a trigger and caused the mixture to ignite instantly. Methane was the most stable of all the paraffin hydrocarbons. Supposing that the limit allowed were 5½ per cent. of methane; this would be non-explosive, but a corresponding amount of ethane (2½ per cent.) was very dangerous. As to the extraction by pyridine, his figures were not from his own experiments, but other people's work, but he had no doubt that it was the resinous portion that the pyridine extracted. The difficulty was that the analyses were not to be relied upon, as the pyridine, besides extracting certain resinous matters, united with the residue, and until this product had been split up no very definite conclusions could be drawn. He believed that every other solvent had been tried, and apparently none were of any use. If, however, the action of terpineol had not been studied thoroughly Mr. Patterson might try this. The evolution of gas seemed to stop after a week, and then, if the coal were raised to 100° C., the gas came

off in volumes. The gases occluded by coal dust were of the greatest importance because it was the oxygen and the hydrocarbons which were the most readily occluded and which were the most dangerous. It did not really matter whether the absorption of the gases in coal were called adsorption or occlusion.

## London Section.

*Meeting held at Burlington House, on Monday, April 7th, 1913.*

PROF. W. R. E. HODGKINSON IN THE CHAIR.

## PRODUCTION OF HYDROGEN FROM WATER AND COAL FROM CELLULOSE AT HIGH TEMPERATURES AND PRESSURES.

BY DR. F. BERGIUS.

The progress of chemical knowledge has very often been caused by the progress of experimental possibilities and the improvement of experimental methods. Thus the chemistry of high temperature grew up after the introduction of electrical methods into the chemical laboratory. By electrical methods chemists were enabled easily to produce high temperatures. At the same time the electrical and optical methods of measuring these temperatures were so much refined that the handling of high temperature experiments ceased to be a difficult task.

The laboratory results were soon made use of in technical work and now we have a large industry, based upon the methods of electrical heating.

If we adopt this methodical point of view it will be observed that there is noticeable progress in every science, whenever new methods and a new instrument is introduced. I may refer to the combustion furnace in organic chemistry, to the optical methods, refractometry, and spectroscopy, to the measurement of electrolytic conductivity, to the method of producing high temperatures, to the liquefaction of gases and the production of low temperatures. One of the most recent methods introduced into the laboratory is that of handling very high pressures conveniently and without danger.

It is this subject to which I wish to call attention here, not merely because some very promising results have been obtained already during the last few years, but also because I am convinced that many important results will be obtained through this experimental method.

Chemical reactions under pressures higher than that of the atmosphere are not unknown in the laboratory and in chemical industry, but these efforts are characterised by their purely qualitative nature and the limited extent to which the pressure could be raised. The former was due to the lack of appreciation of the extent to which chemical reactions may be influenced by pressure, and this in general led to a mere attempt at raising the temperature of a liquid component of a chemical reaction above its boiling point. The second restriction lay in the inadequacy of technique and in the construction of the retaining vessels.

Now the principles of modern physical chemistry teach us that besides this application of pressure so often employed there are other ways of influencing chemical reactions by means of pressure. For instance, the law of mass action tells us when and in what direction an equilibrium will be changed by an increase of concentration, that is of pressure of any one component of a chemical reaction. Leaving aside reactions in condensed systems, that is in the liquid and the solid state, there remain those reactions with gaseous components, which are most easily affected by pressure.

Homogeneous gaseous reactions under the influence of pressure are forced in the direction in which a reduction of the number of molecules takes place. A chemical

reaction can therefore be carried further by an increase of pressure whenever the reaction is accompanied by a diminution of volume.

An excellent example of this sort is the synthesis of ammonia from its elements. A glance at the equation,  $N_2 + 3H_2 = 2NH_3$ , shows that four molecules of the mixture of nitrogen and hydrogen give two molecules of ammonia. The reaction thus leads to a diminution of molecules or a decrease of volume. The formation of ammonia must therefore be carried further by increased pressure. The utilisation of this fact made possible the technical method of synthesising ammonia from its elements. This achievement of highest economic value was obtained by the extraordinary and systematic researches in high pressure work carried out by Haber and Le Rossignol.

It may suffice to mention that this reaction is carried on at about 200 atmos. and at temperatures between  $500^\circ$ – $600^\circ$  C. in order to show that an entirely new experimental method had to be worked out. The many difficulties were overcome mainly through the extraordinary skill of Le Rossignol. To-day this process has left the experimental stage and is in the hands of the Badische Anilin und Soda Fabrik, by which it has been developed into a very large industry.

When a gas enters into reaction with a liquid or a solid with the formation of a new liquid or solid substance, it is evident that pressure must again further chemical combination as predicted by the law of Le Chatelier. Heterogeneous reactions under very high pressure have not yet been used on the large scale, but according to my own results it is possible to effect, for instance, the oxidation of calcium oxide to peroxide by means of gaseous oxygen. At atmospheric pressure no appreciable reaction takes place, not because reaction cannot take place, but simply because the speed of reaction is far too slow. Reaction velocities increase with higher temperatures, but at the same time the dissociation increases also. Now by subjecting lime in fused sodium hydroxide to the action of oxygen under pressures above one hundred atmospheres, it was possible to cause formation of the peroxide from ordinary limestone.

The dissociation pressure, that is the pressure of oxygen given off by the peroxide or pressure of oxygen remaining during the action of this gas on the oxide, was measured at various temperatures. The equilibria could thus be determined and were found to coincide by both methods. At temperatures at which the reaction velocity had sufficiently increased as to become measurable, for instance at  $300^\circ$  C., the pressure of oxygen was found to be 120 atmospheres. This is the pressure of oxygen necessary to cause the gas to combine with solid calcium oxide and to convert the latter completely into peroxide. Other examples of similar reactions are found in the extensive researches of Ipatow on the hydrogenation of various organic compounds in the presence of catalysts at high pressures. He was able, for example, to obtain alcohols from ketones and hexahydroaniline from aniline. He also succeeded in displacing some metals from aqueous solutions of their salts by hydrogen under pressure. Thus copper, silver, and mercury were precipitated from solutions of their sulphates under 100 atm. with formation of sulphuric acid, and so forth.

A third possibility of the application of high pressure for promotion of chemical reactions lies in the ability to retain the liquid state from the boiling point up to the critical point. The physical properties of a liquid may therefore be utilised at high temperatures, and thus reactions be caused to take place which at low temperatures cannot be carried out. Furthermore, the physical properties of a liquid may undergo remarkable changes between the boiling point and the critical point, as for instance the electrolytic dissociation of water. According to A. A. Noyes the dissociation of water increases between these temperatures nearly 2000-fold.

This suggests that water must act as a fairly strong acid or base at high temperatures provided it is kept in the liquid state. In the presence of a metal we may expect therefore a reaction with evolution of gaseous hydrogen. Led by this assumption, I have undertaken in collaboration with my assistant, Herr Specht, a series of experiments on the action of liquid water on metals, particularly