PRESENT STATE OF THE SUBJECT—"HEAT OF COMBUSTION OF COAL."

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The experiments of Dulong, Favre, Silbermann, Andrews and other distinguished scientists, have determined the heats of combustion of solid carbon and sulphur, and of hydrogen, olefiant, and marsh gases, within very close limits, the experimental discrepancies being quite inconsiderable. Now the combustible portion of coal is composed of these substances, and did they exist in it in their respective solid and gaseous states, there could be no question that the heat of combustion of coal, as a whole, would be the aggregate of the heats of combustion thus determined of its constituents multiplied by their relative weights. But the hydrogen, olefiant and marsh gases exist in the coal in the solid state, and as they gasify at lower temperatures than their temperatures of ignition, they are, when the coal is subjected to heat, first gasified and afterwards burnt. Now, as some heat is evidently converted into the work of this gasification, the heat of combustion of the coal, as a whole, composed of the aggregate of the heats of combustion of its constituents determined for their respective solid and gaseous states, must be less by that much. The problem is then to ascertain what portion of the heat of combustion of the coal as above determined, is expended in gasifying its volatile constituents; the remaining portion being its proper heat of combustion, that is to say, the heat available for external uses. I am not aware that any direct attempt has ever been made in this direction to solve the problem.

That the heat required to gasify the volatile constituents of coal is small, is evident from an examination of the results of the process of manufacturing illuminating gas. For example: Ordinary dry bituminous coal when retorted for this purpose leaves about 63 per centum of its weight as dry coke, which, sponge-like, rapidly absorbs a considerable amount of moisture from the air. This coke has a much less calorific effect than an equal weight of the coal from which it was derived, owing to its greater percentage of ash, and less percentage of hydrogen, so that the 63 per centum of coke has not more than 60 per centum of the calorific power of the coal from which it was made. Of this coke about three-eighths are consumed in volatilizing the gas from the coal, which makes the gasification cost *commercially* ($\frac{3}{8}$ of

60 $\Rightarrow$) $22\frac{1}{2}$ per centum of the heat of the coal. Now the temperature of the gases of combustion, which in the furnace is about 2,000 degrees Fahrenheit, is certainly not less than 1,700 degrees after passing the retorts, leaving only 300 degrees expended in gasification, or 15 per centum of the heat in the furnace; hence, of the heat of $22\frac{1}{2}$ per centum of the coal, only 15 per centum is converted into the work of gasification, so that the latter is equivalent to $(22\frac{1}{2} \times .15 \Rightarrow) 3\frac{3}{8}$ per centum of the heat of combustion of the coal. For different kinds of coal and different conditions of furnace, these figures will, of course, require corresponding modification, but they are probably nearly correct for the average of practice. Supposing them to be accurate for any given dry coal, then the heat of combustion of that coal can be calculated from the known percentage of its combustible constituents, and from their known respective heats of combustion. It will be the aggregate less $3\frac{3}{8}$ per centum of the sum of the products of these weights by these heats.

The celebrated chemists Dulong and Petit found that in the case of the combustion of cellulose, the heat obtained was only equal to what was due to the solid carbon constituent alone; the remaining constituents being hydrogen and oxygen, in the proportion in which they exist in water, it was assumed that these substances did exist as water in cellulose, the latter being chemically a hydrate of carbon, and that exactly the same quantity of heat was absorbed by their decomposition as was obtained by their recombination. On this hypothesis these chemists based their well known formula that in the combustion of dry vegetable matter (in which hydrogen is always somewhat in excess of what is required to form water with the oxygen) the heat evolved is that due to the carbon constituent and to whatever hydrogen may be in excess after saturating the oxygen constituent. This excess of hydrogen is very small in the case of wood, averaging about seven-tenths of one per centum of the wood. There is no reason for applying this formula to coal, even if it be of vegetable origin, for in that case it has been so changed chemically and physically by time, heat, pressure and its surroundings, that what may have been true of the wood cannot be properly predicted of the coal. Nevertheless, the formula of Dulong does give very close approximations to the total heat of coal, but this is probably owing to the facts:

1st. That the heat of gasification of the volatile constituents of the coal is very small; and

2d. That the weight of the hydrogen constituent of the coal required to saturate the oxygen constituent is also very small.

For example, supposing the hydrogen constituent of bituminous coal to be five per centum and the oxygen constituent eight per centum, then the latter would be saturated by one of the per centums of the hydrogen, leaving four of the per centums to be utilized for heat. Now one of the per centums of the hydrogen thus withdrawn is equal to from three to four per centum of the heat of combustion of the coal calculated from the total heats of its constituents. But we have already seen that the heat required to gasify the volatile constituents of the coal is also from three to four per centum of the heat of combustion of the coal calculated from the heats of combustion of its constituents and their proportion by weight in the coal. The coincidence is doubtless purely accidental, and does not prove Dulong's law.

It is impossible to conceive that the heat of combustion of coal can be greater than what is due to the sum of the heats of combustion of its constituents multiplied by their proportional weights, less the heat absorbed by the gasification of the volatile constituents. After the gasification has taken place, the heats of combustion of the gases so formed can only be the same as those of the same gases formed in any other manner, and the heat of combustion of the remaining solid carbon must be the same as if it was derived in any other manner.

The subject was in this uncertain state when Messrs. Scheurer-Kestner and Meunier-Dolfus made their celebrated calorimetric experiments at Thann, in Germany, on the heats of combustion of the Alsatian and other coals, for the Industrial Society of Mulhouse, in Alsace, Germany; and their results, together with a complete description of their apparatus and methods, were published in its well known bulletins. These experiments have a great reputation, and were made by an improved Favre and Silbermann calorimeter with all the corrections and accuracy that the researches of modern science could furnish. The calorimeter employed was tested against that of Favre and Silbermann, by ascertaining with it the heat of combustion of dry charcoal. The Scheurer-Kestner apparatus gave for that heat 8,100 calories, while the Favre apparatus gave 8,080 calories.

From these experiments the startling facts were announced that the heat of combustion of the coals not only exceeded what was due to the formula of Dulong, but that it exceeded considerably the heat of combustion obtained by multiplying the relative weights of the ele-

mentary constituents of the coal by their respective heats of combustion and adding the products together. In other words, the heat of combustion of the coal exceeded the aggregate heat of combustion of its constituents considered as solid carbon and gaseous hydrogen, and exceeded it on an average by about four per centum. If the comparison be made with the heat of combustion due to Dulong's formula, then Scheurer-Kestner's determinations exceed it on an average about nine per centum.

In the calorimetric experiments of Favre and Silbermann on *organic* substances, the heat of combustion was always found to be less than what was due to that of the constituent carbon and hydrogen. In the single *inorganic* substance of the bisulphide of carbon, the reverse effect was found, and was left unexplained. Berthelot afterwards suggesting that the combination of the sulphur and carbon to form the bisulphide had been attended with absorption of heat, which heat was set free on the decomposition of the substance by combustion. It is remarkable in this connection that, in some calorimetric experiments on the heat of combustion of three Russian coals, made by Scheurer-Kestner after his experiments with the Alsatian coals, the heat of combustion as found by him averaged $2\frac{2}{3}$ per centum *less* than the heat due to the constituent carbon and hydrogen taken at their full values. These experimental heats averaged almost exactly the heats due to Dulong's formula.

The results of the calorimetric experiments made by Scheurer-Kestner and Meunier-Dolfus on the heat of combustion of the Alsatian coals, were never accepted by the British scientists, notwithstanding that no error was pointed out in either the apparatus or the method employed. Nor could the writer ever accept them although he bestowed the closest scrutiny and study upon them. He was therefore obliged to defer them until other experiments might be made that would either confirm or overthrow them. Experiments of this kind it appears have been in progress for several years in Munich, Germany, and with results which, though opposed to those of Scheurer-Kestner, are conformable to the general laws of chemistry and to common experience.

As much as is yet known of these later experiments will be found in the following note by Mr. Vingotte, which I translate from "The Proceedings of the 7th Congress of the Engineers-in-Chief of the Asso-

ciations of the Proprietors of Steam Apparatus," held at Bordeaux, France, in 1882.

The subject is one of much importance to manufactures and commerce, and I have written this communication largely in the hope that the facts may be useful in inducing our government, in consideration of the enormous quantities of coal consumed in this country in the industrial arts, to direct that a commission of properly qualified scientists be appointed to make, together with an ultimate analysis of the coals and of their volatile parts, an exhaustive set of experiments on the heat of combustion of the different coals we produce, and on those of the more important foreign coals with which our own must commercially compete in the near future. Rightly interpreted, these heats of combustion give the relative calorific powers of the coals, and, of course, their respective commercial values.

Communication presented by Mr. R. Vingotte, Director of the Belgian Association for the Surveillance of Steam Boilers, to the 7th Congress of the Engineers-in-Chief of the Associations of the Proprietors of Steam Apparatus, held at Bordeaux, France, on the 10th, 11th, and 12th of September, 1882.

After having victoriously passed through a short period of criticism, the experiments of Messrs. Scheurer-Kestner and Meunier-Dolfus reached the position of a classic, and their results were considered absolutely certain; they were no longer even discussed. Further, they bore so striking a character of exactness that their verification was judged by other experimenters to be useless.

But to-day, on the contrary, the Experimental Station at Munich publishes results which contradict absolutely those of Messrs. Scheurer-Kestner and Meunier-Dolfus, and which I believe will interest the Congress, although I am not in possession of enough of the data of these experiments to enable me to pronounce a positive opinion on them.

The Station at Munich was established by the Bavarian government for the determination of questions relating to heating, for which purpose a boiler was constructed of such design that it could serve as a calorimeter without ceasing to be comparable as a boiler with the boilers employed in factories. It was so arranged that each portion of the heat utilized or lost could be measured separately; and that, at the same time, there could be ascertained the calorific power of a combustible and the distribution of this power in practice by a boiler.

Referring to the accompanying sketch: The furnace *H* is arrangeable at will for different kinds of combustibles, being adaptable for those giving a long as well as for those giving a short flame. The furnace and its masonry are entirely enclosed in two sheet-iron boxes, one within the other and separated by a water-tight space. The exterior of the outer box is prevented from radiating heat by a lagging of wood. The loss of heat due to the radiation from the masonry is

measured by means of the increased temperature of water circulating between the two sheet-iron boxes.

The hot gases of combustion, on leaving the furnace, traverse in succession two vertical tubular boilers *K*₁ and *K*₂, the latter being placed on top of the former. The exterior of both boilers is encased with Hasman's non-conducting covering.

The method of experimenting consists in first heating the apparatus until its temperature becomes stationary. Then the small quantity of ignited coal which remains in the furnace is drawn out, rapidly weighed, and thrown back, and the experiment is begun with all the observations made and all the precautions taken requisite in such cases.

The heat radiated from the masonry of the furnace is measured in

the water which constantly circulates between the iron boxes enclosing it, the temperature of the water being noted at its entrance and at its exit.

The loss of heat resulting from exterior radiation, and from the conductivity of the soil on which the furnace rests, is directly measured by heating with steam taken from a locomotive the water between the boxes to a temperature a little higher than what it had during the experiment, and then ascertaining the fall of this temperature during one hour. The loss will be equal to Q' ($t' - t_1'$); Q representing the weight of water between the boxes, and $t' - t_1'$ the fall of temperature.

I ought to say, in reproducing this calculation according to an article by M. Voit, that I do not believe such a process should have been adopted, because it entails a very great error since no account is taken of what the material of the boxes loses or gains at the sides of the furnace. Further, it does not appear at all easy to me to ascertain the exact value of the loss by the furnace due to radiation. The quantity of heat that the smoke abandons in each of the two boilers is measured separately and by the same method.

In the two reservoirs R and R_1 water furnished through lower orifices is kept at a constant level by an overflow, and this water, which is measured in advance, flows into a reservoir C divided into two compartments. The water in the small compartment of C is partly pumped into the boiler, and the remainder overflows into the other compartment.

The steam produced is condensed by the water entering R , and the sum of both, that is the whole quantity of water Q furnished by the two reservoirs, finally enters the calorimeter K where its temperature is measured.

The boiler's loss of heat by exterior radiation is measured directly, and *a priori*, by heating the water in the boiler by means of steam from a locomotive and then measuring the fall of pressure at the end of a given time. The heat usefully absorbed by the second boiler is measured in the same manner.

The gases of combustion are analyzed by a continuous aspiration across a series of absorption tubes and of a tube containing oxide of copper heated to redness.

The Munich Station commenced operations in 1879, and published in the same year a first series of seventy-six experiments made during the first eight months, which experiments, in my opinion, ought to be

considered as only preparatory for the work to be undertaken. In fact, the results of these experiments are very discordant, and show that great accidental errors are possible with the Munich apparatus. Among them are nineteen determinations of the calorific power of the same coal, so divergent that the extremes differ six per centum from the mean. It is probable that the cause of these errors was discovered, because in a second series of one hundred and sixty-six experiments the different determinations for the same coal gave differences of only one and a half to two per centum. Nevertheless, I must add that, in a vigorous criticism, M. Luders, Professor in the school of Aix-la-Chapelle, points out that in addition to the one hundred and sixty-six experiments published, the second series contained twenty-nine which were rejected without any reason being assigned; and he believes they were omitted because their results differed too greatly from the mean. Be that as it may, I shall not here discuss the value of the methods employed, because I have been able to procure only a part of the publications by the Station. I limit myself therefore to stating the results obtained, according to which the calorific power of the coals is nearly always less than what is due to the formula of Dulong and Petit. The difference is mostly very small, but, in the case of the Louisenthal coal, it rose to ten per centum.

The following table contains the values found :

Name of Coal.	Calorific power in Fahrenheit units of heat.		Name of Coal.	Calorific power in Fahrenheit units of heat.	
	Observed.	Calculated by the formula of Dulong.		Observed.	Calculated by the formula of Dulong.
St. Ingbert, I a.....	13867·2	14365·8	Helnitz-Dechen.....	13402·8	13647·6
“ II a.....	13077·0	13287·6	Reden-Merchweiler.	12655·8	13174·2
“ III a.....	12717·0	13123·8	Dudweiler.....	14041·8	14288·4
Mittelbexbach.....			König I a.....	13114·8	13550·4
Bed No. 3.....	12803·4	12911·4	Friedrichsthal.....	12684·6	12742·2
Bed No. 6.....	12938·4	13444·2	Ziehwald II a.....	12110·4	12637·8
Bed No. 9.....	12978·0	13089·6	Louisenthal.....	10940·4	12119·4
Bed No. 10.....	12879·0	12729·6	Griesborn.....	10935·0	10638·0

[*Note by Translator.*—The means of the whole in the above table

shows that the observed calorific powers, or those obtained by experiment, averaged 2·352 per centum less than the calorific powers calculated according to the law of Dulong and Petit.]

The following table compares the calorific powers in Fahrenheit units of heat found by the Station at Munich, and by Messrs. Scheurer-Kestner and Meunier-Dolfus for the same qualities of coal. The figures of the latter gentlemen are for the pure coal, and in order to allow the comparison, I have placed by their side the values calculated according to the law of Dulong and Petit:

	Station at Munich.		Scheurer-Kestner and Meunier-Dolfus.	
	Observed.	Calculated according to Dulong.	Observed.	Calculated according to Dulong.
Dutweiler.....	14041·8	14288·4	15703·2	14349·6
Heinitz.....	13402·8	13647·6	15276·6	13714·2
Friedrichsthal.....	12684·6	12742·2	15222·6	13329·0
Louisenthal.....	10940·4	12119·4	14787·0	13260·6

The results obtained at the Munich Station were fiercely attacked, and they were declared false because they were in disaccord with those obtained by Messrs. Scheurer-Kestner and Meunier Dolfus. The Munich Station, before these criticisms were made, understood that their first experiments ought to be tested by comparative ones, and they recommenced the determination of the calorific powers of the same coals, requesting M. Stohman, Professor at the University of Leipzig, to make at the same time calorimetrical experiments by the ordinary method.

The results, given in the following table, vary but little, especially if there be taken into consideration the difficulty of obtaining a small sample for the calorimetrical trials, having the same composition as the mean of the coal burnt in the boiler.

M. Stohman in summing up says: You see by our figures that we have found some values in accord with the law of Dulong, and others greatly different, and these last in both directions, sometimes more and sometimes less. We have never found values as high as those of M. Scheurer-Kestner.

These figures suffice to show that if the experiments of Messrs.

Scheurer-Kestner and Meunier-Dolfus are exact, those of the Munich Station cannot be; and, in this connection, I ought to remark that the greatness of the errors necessary to be supposed astonishes me much, but in the absence of sufficient details, I cannot imagine how they could have been made.

Name of Coal.	Calorific Power of the Coal in Fahrenheit units of heat (ash inclusive).			
	Stohman.	Munich Station.	Differences.	
			Absol- ute.	Per cent.
Dutweiler.....	16852·8	13674·4	— 178·4	— 1·3
St. Ingbert.....	13777·2	13721·4	— 55·8	— 0·4
Mittelbexbach No. III.....	12956·4	12690·0	— 266·4	— 2·0
Louisenthal.....	12384·0	11970·0	— 414·0	— 3·3
Friedrichsthal.....	12879·0	12600·0	— 279·0	— 2·1
Thurn and Taxis.....	12600·0	12297·6	— 302·4	— 3·5
Gehenkinchen (gas making coal).....	13302·0	13582·8	+ 280·8	+ 2·0
Gehenkinchen (locomotive coal).....	14099·4	14475·6	+ 376·2	+ 1·5
Upper Silesia, Königsgrube, Sattelflotz.....	12844·8	12648·6	— 196·2	— 1·5

It appears evident to me at first sight that the Munich apparatus should furnish results more closely concurrent than 12 per centum. Well made experiments on ordinary boilers come closer than that. It seems to me that once familiar with the method of experimenting, figures should be obtained not diverging more than one or two per centum. I have not, however, any reason for rejecting the figures of the second series of experiments: there is no case here of accidental errors. If the general result is erroneous, it must be due to a general error in common for all the experiments. In this connection we encounter in the first place, the determinations of the constants which represent the cooling by radiation from the furnace, from the boilers, and from the calorimetrical apparatus. It seems to me very difficult to determine these constants exactly by the method of cooling during a given time, for the apparatus cannot then be under the conditions of the experiment. It appears to me, therefore, that these constants are strongly subject to inexactness, but, on the other hand, the probable error made under this head is not enough to explain the figures obtained.

Remarks on the above by Mr. E. Cornut, Engineer-in-Chief of the Association of the North of France.

I have had occasion to specially examine the calorimetical investigations of Messrs. Scheurer-Kestner and Meunier-Dolfus, and, for my part, have the greatest confidence in the results obtained by those able experimenters. I will remark that in a problem of this kind, the errors are in general of two perfectly distinct classes :

1st. A sensibly constant error due to the imperfection of the apparatus and of the methods employed.

2d. Error of observation which, by its very nature, can reach in one direction or the other, such or such an experiment.

This second cause of error does not seem to me to have been in action from a comparison of the results of the calorimetical powers obtained by the method of Messrs. Scheurer-Kestner and Meunier-Dolfus and those obtained by the German laboratory at Munich ; we perceive, in fact, that the case is one of a constant of from about ten to fifteen per centum applying to all the results.

Is there, then, an error of the first category in the experiments at Thann ? I will remark that Messrs. Scheurer-Kestner and Meunier-Dolfus took the precaution to test their process by obtaining the calorific power of wood charcoal, and they found its value the same which had been previously ascertained by Messrs. Favre and Silbermann. Have the experimenters at Munich taken that precaution ? and, if they have, what figure did they find for the calorific power of wood charcoal ?

As our colleague, M. Vinçotte, promises us for the next year more details on this subject, I will leave it for the present ; but I believe the experiments of Messrs. Scheurer-Kestner and Meunier-Dolfus to have been made with all possible guarantees for exactness, and in the most disinterested manner.

LOW TEMPERATURES.—Wroblewski has tried to measure the temperature of boiling oxygen. For that purpose he applied a system of thermoelectric measurements, which, in addition to being extremely sensitive, may be made to register all the sudden changes in the temperature of the medium. The indications of the apparatus have been compared with those of a hydrogen thermometer, between 100°C. and —130°C. (212°F. and 202°F.) The nature of the function which unites these indications is such as to permit an extrapolation, which indicates —186°C. (—302.8°F.) as a first approximation to the temperature which is produced in the liquification of oxygen. Compressed nitrogen, at this temperature, solidifies and falls, like snow, in crystals of remarkable size.—*Les Mondes*, Jan. 6, 1884. C.