agrees well with such a supposition, for if 1 atom of sulphur belongs to a complex yielding all its sulphur as sulphide we would obtain 0.22 per cent. from this source, and if another atom belongs to cystein (Embden has obtained cystein from edestin), which according to Schulz yields about one-half its sulphur as sulphide, from this we would obtain about 0.11 per cent., making 0.33 per cent. in all, which agrees closely with the 0.347 per cent. found. The deficiency found for most of the proteins here represented as containing more than 1 atom of loosely bound sulphur is nearly equal to that which would occur if these contained 1 molecule of cystein, except for serum albumin, in which the deficiency corresponds to 2 molecules of cystein or 1 of cystin.

In conclusion, attention should be called to casein, which presents a marked contrast to all the other proteins examined, in the fact that only one-eighth of the total sulphur was obtained as sulphide. If the complex which contains this sulphur yields all its sulphur as sulphide, the molecular weight of casein cannot be less than 30,000; if, on the other hand, it yields only a part of its sulphur as sulphide, it presents a marked contrast to the other protein substances which contain but little loosely bound sulphur, for these yield almost exactly one-half of their total sulphur as sulphide, which strongly indicates that all the sulphur of the complex containing this is converted into lead sulphide. Of all the proteins examined, casein yields by far the smallest proportion of loosely bound sulphur.

RESEARCH LABORATORY OF THE CONNECTICUT
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THE PEROXIDE CALORIMETER AS APPLIED TO EUROPEAN COALS AND PETROLEUM.

BY S. W. PARR.

Received September 3, 1901.

AT the suggestion of Dr. Lunge, the calorimeter recently described in this Journal[1] has been subjected to a series of tests on European coals. The Zurich laboratory afforded especially good facilities for the work and I am indebted to Dr. Lunge for putting them at my disposal. Much credit is also due his assistant, Mr. Offerhaus, whose very efficient help made it possi-

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[1] This Journal, 22, 646.

ble to accomplish the large number of tests in the limited time available.

It was evident at the outset that the combustion of European coals offered a somewhat new and different proposition from that of the soft coals of the United States. Their anthracitic character and smaller percentage of bituminous matter made their combustion more difficult and in many cases incomplete. Experience had already shown that certain substances, as, for example, coke or sugar carbon, gave incomplete combustions when used alone with sodium peroxide. The two devices before suggested for overcoming the difficulty were fine pulverization and the addition of an accelerator in the shape of a weighed quantity of some good soft coal whose combustion factor had been carefully determined. Such soft coals in Europe, however, are the exception and the above expedient seemed impracticable as well as not altogether satisfactory in the very hard anthracites met with.

It was, therefore, necessary to increase the oxidizing power of the peroxide. From data already at hand it was evident that this could be accomplished in a measure by use of some free burning organic material as a good soft coal, sugar, etc. The effect of superoxides had also been tried, as barium peroxide, potassium chlorate, etc. Continuing along this line, the details of which are here omitted, it was found that a very intense oxidizing effect was secured by the use of a mixture of potassium persulphate and tartaric acid, 1 gram of the former to 0.5 gram of the latter, carefully weighed out ; this with about 12 grams of sodium peroxide and 0.5 gram of the coal to be tested gave very complete combustions. A soft iron wire, of No. 10 or 2.5 mm. gauge and 1 cm. long, was used for igniting. Other wire as of copper, nickel, silver, etc., will melt and burn to a greater or less extent, hence cannot be used. The factors already determined were found to apply also to these coals ; *viz.*, 73 per cent. of the total heat due to combustion and 27 per cent. due to the heat of combination of the products.

The results obtained in the table below are on samples kindly furnished by Professor Dr. Constam, Zürich, who had determined the Mahler factors and to whom we were further indebted for the use of his very exact thermometer carefully calibrated by himself.

TABLE I.

Coals.	Water.	Ash.	Calories by Mahler apparatus.	Calories by sodium peroxide.	Variations from Mahler.	Chemicals used in addition to 12.5 to 13.5 grams of sodium peroxide.
No. 277, Ruhr flame coal	2.6	7.1	7685	7695	+10	0.6 tartaric acid.
No. 278, Ruhr coal	1.3	6.6	8059	8075	+16	0.5 tartaric acid. 1.0 pot. persulph.
No. 282, Anthracite coal	1.5	6.7	7981	7990	+ 9	0.6 tartaric acid.
No. 285, Coke	0.6	13.0	6640	6687	+47	0.5 tartaric acid.
No. 289, Anthracite, Wales	2.0	4.2	8049	8021	−28	0.6 tartaric acid.
No. 308, English anthracite	2.4	4.6	8365	8326	−39	0.5 tartaric acid. 1.0 pot. persulph.
No. 312, Belgian "Braisettes"	2.4	10.7	7409	7394	−15	0.5 tartaric acid.
No. 324, Saar coal	4.9	11.7	6594	6634	+40	0.5 tartaric acid.
No. 326, Cardiff coal	2.2	7.2	7872	7936	+64	0.5 tartaric acid.
No. 331, Saar coal	3.5	8.4	7146	7184	+38	0.5 tartaric acid.
Brown coal	15.17	..	5037	5076	+39	1.0 of coal used, no extra chemical.

When the water content exceeds 2.5 or 3 per cent. it should be removed and the combustion made on the oven-dried sample. For example, the last number in the table, that of brown coal, has over 15 per cent. of water. A combustion with sodium peroxide in case of this sample without the water removed gives approximately 300 calories excess, or 20 calories for each per cent. However, not enough data is at hand to fully establish a correction for the water content.

Tartaric acid combining with sodium peroxide may be determined by mixing in the cartridge 0.5 gram of the finely ground acid with about 6 grams of peroxide, and igniting with a wire in the usual manner. The result of a number of such determinations indicated, for the material used in these tests, a factor for the tartaric acid, including the wire 0.85° per 0.5 gram and for the potassium persulphate 0.155° per 1 gram. Soft iron wire 2.5

mm. by 1 cm. long and weighing approximately 0.4 gram at an estimated temperature of 700°, carries into the mass 0.015° of heat. Hence, in using the combined chemicals above with but one wire the total correction factor is 0.99°. However, with any given set of reagents a blank determination should be made. Variations may arise from the potassium persulphate and tartaric acid employed and also from the moisture absorbed by the sodium peroxide. In the latter case, the effect of any hydrated sodium peroxide, $Na_2O_2 + 2H_2O$, may be measured or neutralized as may be desired by enclosing the usual amount alone in the cartridge and submerging in boiling water for five to ten minutes, cooling, opening, and adding the charge, then proceeding as usual.

With the above combination of persulphate and tartaric acid a complete oxidation of substances may be secured which, before, behaved indifferently with peroxide alone.

In illustration of this point a sample of crude oil from Beaumont, Texas, gave the results as follows, the Mahler determinations being made by Mr. Koch, of the Univerity of Illinois:

CRUDE OIL.

	Calories.
Mahler factor	10644
New method (*a*)	10654
" " (*b*)	10600
" " (*c*)	10637
" " (*d*)	10665
Average, last four	10639

The method while varying in no essential from that used for coals should, perhaps, be outlined, thus:

After preparing the cartridge and screwing the bottom on firmly, there is added about 1/4 measure (3 grams) of sodium peroxide. Upon this is dropped about 1/3 of a gram (30 drops) of petroleum, using a dropping pipette from a light weighing-flask, the exact weight of oil taken being determined by difference. There is now added the 1 gram of finely powdered potassium persulphate and 0.5 gram of powdered tartaric acid. This mixture is stirred with a wire to break up any lumps and make an even mixture. Now add one measure of sodium peroxide, clean the wire in this upper layer, jar off the adhering particles and remove the wire, screw on the top with valve, and shake thoroughly. Place in the calorimeter and ignite, using a soft iron wire.

The calculation is made by first subtracting the factor obtained by running the mixture of chemicals as above described, omitting the oil. The remainder r gives the rise in temperature due to the combustible ; 73 per cent. of this is due to the heat of combustion, and 27 per cent. to the heat of combination of the chemical products, hence,

$$\frac{r \times 0.73 \times \text{wt. of water}}{\text{wt. of oil}} = \text{calories per kilo.}$$

A homogeneous mixture may result from simply shaking, and without the use of the wire. Indeed, some of the above results were so obtained, but in general it is better to mix by stirring as described.

It is a convenience to have a thoroughly triturated mixture of potassium persulphate and tartaric acid carefully adjusted to the proportions above indicated. It is then necessary to make but one weighing and, of course, 1.5 grams of the mixture are taken.

ZURICH, July, 1901.

STUDIES IN NITRIFICATION.[1]

BY J. G. LIPMAN.

Received October 18, 1901.

IN undertaking the work submitted here it was intended to study nitrification in its bearing to practical agriculture. The aim was to investigate in how far certain conditions influence the production of nitrates in the soil, in how far the application of the various fertilizers promote or retard nitrification, and in how far the moisture conditions modify this. Much work has already been done on the subject, notably by the French investigators, and in the light of our present knowledge we have come to modify many of the older methods of husbandry, so as to bring them in agreement with recent facts. Yet great as is the service rendered to agriculture by the research of the last two decades, the conclusions reached are by no means final in every case ; nor have all of the questions raised by the work been satisfactorily answered. Much of our knowledge on nitrification is rather obscure ; many questions still await solution. We know now that plants take up most of their nitrogen in the form of nitrate ; we know that the conversion of organic nitrogen into ammonia, nitrite, and nitrate is effected by living organisms ; we know, to a great extent, what conditions are favorable or injurious to the development of these

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[1] Abstract from Master's Thesis, Cornell University, 1900.