

unable to detect a source of error in my analyses which would allow for a change from 39.16 per cent. of zirconium to 46.79 per cent., the amount needed for the oxychloride.

Still, as a necessary precaution, I made some determinations of the chlorine in the pure crystalline product and was greatly surprised to find only 35.5 per cent. of chlorine instead of 61.01, the amount required for the tetrachloride. The percentage in the oxychloride would be 36.63.

I regard the results as very singular. The substance must be an oxychloride, but what is its composition? The simplicity of its preparation and the constancy of its composition along with its stability would argue for a simple formula. No such formula can be calculated from the analysis. Probably the best formula suggested for this oxychloride, corresponding closely with the above analysis, is $Zr_3(OH)_3Cl_5 \cdot 5H_2O$.

UNIVERSITY OF NORTH CAROLINA,
August, 1895.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE ROSE POLY
TECHNIC INSTITUTE. NO. 7.]

THE DETERMINATION OF THE HEATING EFFECTS OF COALS.¹

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Received September 9, 1895.

MANY determinations have been made for the purpose of comparing the heating effect of coals as determined by the calorimeter with that calculated from analyses. Scheurer-Kestner, who seems to have been the first to show that the results obtained in the two ways do not agree, publishes results obtained with the calorimeter of Favre and Silbermann, which differ, in some cases, by ten per cent. from those calculated by Dulong's formula and are uniformly higher.³ In a later paper⁴ he states that he finds lower results with Bertholet's bomb but still results that differ from those calculated.

¹ Read at the Springfield meeting.

² The work of which this paper gives an account formed the basis of theses presented to the faculty of the Rose Polytechnic Institute for the degree of Bachelor of Science.

³ *Compt. rend.*, 106, 1092, 1160, 1230.

⁴ *Ibid.*, 112, 233.

Ferd. Fischer claims repeatedly in the *Zeitschrift für angewandte Chemie* and elsewhere that the calorimeter results differ from the calculated heating effect, but admits that the latter may answer for most technical purposes.

Hempel¹ states that the results calculated from careful analyses do not differ more than one or two per cent. from those of the calorimeter and considers that larger differences sometimes found have been due to careless work. He gives six cases of fair agreement, but one which shows a difference of six per cent.

Alexejew² gives one case in which the calorimeter result is three and eight-tenths per cent. higher than that calculated.

Scheurer-Kestner³ has compared the results obtained with Thompson's calorimeter (burning with potassium nitrate and potassium chlorate) with those given by the calorimeter of Favre and Silbermann and finds a maximum difference of three and a half per cent. In using Thompson's method, however, he applies a constant plus correction of fifteen per cent., which F. Fischer criticises as very unreliable.

W. Thompson⁴ describes a simple calorimeter which he has devised and gives results obtained with twelve samples of coal. In seven cases the results are lower, in two cases they are the same, and in three cases they are higher than those calculated. F. Fischer⁵ criticises these results, saying that the coals were probably not completely burned.

Barrus has described⁶ a calorimeter which he appears to have copied from that of W. Thompson.

C. v. John and H. B. Fuller⁷ have made a series of comparisons of Berthier's test (reduction of litharge) with the results calculated from analyses. The latter give, in some cases, 900 calories more than the former.

So far as we are aware, no comparisons of this kind have been made with American coals. The work here described was un-

¹ *Ztschr. angew. Chem.*, 1892, 393.

² *Ber. d. Chem. Ges.*, 19, 1557.

³ *Compt. rend.*, 106, 941.

⁴ *J. Soc. Chem. Ind.*, 5, 581, and 8, 525.

⁵ *Jahrb. chem. Tech.*, 1889, 9.

⁶ *Trans. Mech. Eng.*, 14, 816.

⁷ *Ztschr. angew. Chem.*, 1893, 285.

dertaken for the purpose of comparing the results obtained with Hempel's calorimeter with those calculated from analyses and those obtained by Berthier's test. Six specimens of representative Indiana coals were used, as follows: Brazil Block from Brazil, Lancaster Block from Clay Co., Shelburn coal from Shelburn, two samples from the mines of the New Pittsburg Coal Co. at Alum Cave, and a sample of mine screenings used in the shops of the Rose Polytechnic Institute. The first two are known locally as "block" coals and are non-coking. The others are known as bituminous and are coking coals.

ANALYSES.

The analyses were made as follows :

1. *Moisture*.—One gram of the coal was dried in a toluene-bath (about 105°) for one hour.

2. *Ash*.—The residue of (1) was ignited over a Bunsen burner, at first with a very low flame, till the carbon was completely burned.

3. *Fixed Carbon*.—One gram of fresh coal was placed in a covered platinum crucible and heated with the full flame of a Bunsen burner for just seven minutes. The residue less the ash is the "fixed carbon."

4. *Volatile Combustible Matter*.—The loss of weight in (3) less the moisture is volatile combustible matter.

The above determinations are, of course, of no value for the calculation of the heating effect but give some indication of the character of the coal.

5. *Carbon and Hydrogen*.—About two-tenths gram of the coal was burned in a current of oxygen in a hard glass tube containing copper oxide and lead chromate.

6. *Nitrogen*.—This was determined with soda-lime.

7. *Sulphur*.—Determinations were made by Eschka's method, using potassium carbonate and magnesium oxide, by the method of Carius and by the use of sodium peroxide, as follows: one-half gram of the coal was weighed out in a platinum dish holding about fifty cc. and three grams of sodium peroxide and a little water were added. The whole was evaporated to dryness and ignited. After adding two grams of sodium peroxide and more water the evaporation and ignition were repeated. The mass was then

boiled with water, the solution filtered, acidified, and precipitated as usual. The barium sulphate was purified by fusion with sodium carbonate. The results obtained by this method agreed fairly well with those obtained by Eschka's method, but the results of Carius' method were mostly higher. As a comparison of methods was not part of our plan, the average of the results obtained by Eschka's method are given in the table.

8. *Oxygen*.—In most coal analyses the oxygen has been calculated by subtracting the other constituents, including the ash, from 100. Where the sulphur is low this introduces but a slight error. But with sulphur so high as in some of these coals the error is quite appreciable. The sulphur is mostly present in the form of pyrites and it has been assumed that this is burned to sulphur dioxide and ferric oxide. Accordingly, for the calculation of the oxygen, a correction has been applied to the ash by adding to it five-eighths of the weight of the sulphur present.

The quantities given in the following table are in every case, the average of at least two results obtained by different persons. Where the agreement was not fairly close, a larger number of determinations has been made, and results differing too far from the mean have been rejected. For the results finally used, the average variation from the mean is 0.08 per cent. for carbon, and 0.18 per cent. for hydrogen. These differences correspond to a difference of fifty-seven calories, or about nine-tenths per cent. of the calculated heating effect.

The heating effect is calculated for the coal burned to vapor of water by the formula $8080C + 28800(H - \frac{1}{8}O) + 1582Fe + 2162S$, where C, Fe, etc., are the amounts of each element present. As will be seen from the table, the heating effect of the iron and sulphur is quite important in some of these coals.

CALORIMETRIC DETERMINATIONS.

The calorimeter used was that described by Hempel.¹ The powdered coal was compressed into cylinders, through which a fine iron wire passed. This wire was weighed, and it was assumed that it gave one-fifth as much heat by its combustion, as the same weight of coal. The autoclave was filled with oxy-

¹*Ztschr. angew. Chem.*, 1892, 393. See also Hempel's Gas Analysis, translated by L. M. Dennis.

gen, by generating the gas from a mixture of potassium chlorate and manganese dioxide. The temperatures were read by means of a telescope, the thermometer being graduated into fifths. The highest point reached by the thermometer, was used for the calculation. As the rise in temperature was only about five degrees, and the same method was used in determining the water equivalent of the calorimeter, the error due to radiation must have been small. The water used was delivered from a measuring flask, and was found by direct weight to be 997.8 grams. The water equivalent of the autoclave and calorimeter was determined by burning pure sugar charcoal as directed by Hempel. Six determinations gave an average value for the whole, including the water used of 1337.5 grams, with a probable error of five and nine-tenths grams or 0.45 per cent.

At least three determinations were made with each coal. The average difference of the values obtained from the mean for a given coal, was thirty-two calories, or one-half per cent.

The water formed by the combustion in the calorimeter condenses, of course, to liquid water, and, assuming that the average temperature of the calorimeter is 26° , a correction of 610 calories per gram of water formed must be subtracted to find the heating effect when burned to vapor of water. The results given in the table have been corrected in this manner.

BERTHIER'S TEST.

This was made as follows: One gram of the coal was intimately mixed with forty grams of litharge and the mixture put in a Battersea C crucible, seven and a half cm. deep, and four and a half cm. internal diameter, and covered with a layer of salt. The covered crucible was then placed in a *hot* gas furnace and heated for fifteen or twenty minutes. The crucible was then taken out, tapped to collect the lead, cooled, broken, and the lead button cleaned and weighed.

Theoretically, one gram of lead should correspond to a heating effect in the coal of 234 calories. The results calculated with this factor are, however, about twelve per cent. too low. The average of the results obtained, give an empirical factor of 268.3 calories per gram of lead. The results given in the table have been calculated with this empirical factor.

At least three fairly concordant determinations were obtained for each coal. A few results differing from this mean by more than one-half a gram of lead were rejected. The average difference of the results from the mean for a given coal, was 0.11 gram, which corresponds to twenty-nine calories or about 0.45 per cent.

The following table gives the results of the analyses and other determinations. The differences between the other determinations and those made with the calorimeter are given in per cents.

	New Pittsburg A.	New Pittsburg B.	Lancaster.	Brazil.	Shelburn.	Shop.
Moisture	6.83	5.89	12.66	8.98	8.63	2.36
Volatile combustible matter..	39.92	42.23	37.44	34.49	38.82	31.11
Fixed carbon	39.93	40.40	47.22	50.30	43.45	42.44
Ash	13.31	11.48	2.68	6.23	9.05	24.09
Carbon	62.88	65.26	71.41	70.50	66.86	57.32
Hydrogen	5.07	5.17	5.56	4.76	5.30	4.56
Nitrogen	1.01	1.17	1.54	1.36	1.50	1.44
Oxygen	13.06	13.25	18.42	16.29	15.69	9.93
Ash (corrected).....	17.98	15.15	3.07	7.09	10.65	26.75
Sulphur	7.46	5.88	0.62	1.39	2.57	4.25
Iron, calculated	6.53	5.14	0.54	1.22	2.25	3.72
Calories per gram, calc'ted	C 5081.	5272.	5770.	5696.	5402.	4632.
“ “ “ “	H 991.	1011.	939.	784.	962.	956.
“ “ “ “	S 161.	127.	13.	30.	55.	92.
“ “ “ “	Fe 103.	81.	9.	19.	36.	59.
	Total 6336.	6491.	6731.	6529.	6455.	5739.
Difference, per cent.....	+2.6	+1.2	+0.4	-4.6	-1.2	-1.2
Calories per gram, Berthier's						
test, factor 268.3.....	6307.	6471.	6831.	6689.	6461.	5726.
Difference, per cent.....	+2.1	+0.9	+1.9	-2.3	-1.1	-1.4
Calories per gram, calorimeter	6175.	6415.	6703.	6846.	6532.	5806.

In discussing the results, it is worth while to notice that, so far as indicated by the agreement of duplicate determinations, about the same degree of uncertainty attaches to the calorimetric determinations and to the litharge test, while the uncertainty of the analysis is about twice as great. It is noticeable that the results calculated from the analyses, and those given by

Berthier's test, agree better with each other than either agree with the calorimeter results.

On the average Berthier's test, when the empirical factor is used, appears to be more reliable than the results calculated from the analyses.

While the differences between the results obtained by different methods are not very great, they are certainly greater than can be accounted for by the errors of the work. In the case of two of the most important coals, the Lancaster and Brazil black, the relative value of the coals as given by the calorimeter, is reversed as given by the analyses and by Berthier's test. There can be little doubt that the calorimeter gives most accurately the relative heating value of these coals.

Attempts to make determinations with anthracite coals were unsuccessful, because it was found impossible to compress it into cylinders, and we have not yet been able to burn it in the form of a powder.

Some attempts have also been made to use the calorimeter of Barrus,¹ but a deposit of carbon was always formed, and the results appeared to be entirely unreliable. It is probable that the results would be more satisfactory with anthracite coals.

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TELLURIUM: ITS SEPARATION FROM COPPER RESIDUES WITH NOTES ON SOME NEW REACTIONS.²

BY CABELL WHITEHEAD.

Received Sept. 9, 1895.

TELLURIUM which a few years ago was classed as a rare metal, is now known to be distributed over a very wide area, not only in our western states, but also in the gold producing states of the east. It occurs in the free state, and also combined with gold, silver, bismuth and many other metals. In the state of Colorado, tellurium is found in combination with gold and silver to such an extent, that the ores in many districts are rendered unfit for amalgamation, and smelting and chlorination has to be resorted to. The separation of silver and gold from low grade

¹ Trans. Mech. Eng., 14, 316. See also W. Thompson, *loc. cit.*

² Read at the Springfield meeting