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M. S. THESIS.

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HEAT OF FORMATION

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OF SOME

FERRO-CALCIC SINGULO-SILICATES.

BY

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Course III Option 2

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## INDEX.

# Part I.





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PART I.

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INTRODUCTION,

The investigation<sup>1</sup>of the heat formation of ferro-calcic silicates in general was begun in 1908. On account of many difficulties encountered both in the preparation of ferrous oxide and in the adjustment of the electrical apparatus and calorimeter, the experiments could not be brought to a finish with satisfactory results.

As this work is considered important, not only from <sup>a</sup> seientific, but also  $f$ rom a practical. point of view, the investigation was resumed in the latter part of <sup>1908</sup> and continued until the middle of 1SC9, The experiments were conducted according to the seme method as that of last year, the spperatus, however, was modified snd improved, and the former method of preparing ferrous oxide replaced by one that was better.

any methods have been proposed and recommended for the preparation of ferrous oxide. The leading ones are those of Wackerwoder, Sivert, Moissan, Debray, Berthier, Plattner, Mills, Vogel, Rirnie, Tissandier and Steffe, <sup>A</sup> brief history of their investigations appears to be interesting,

As early as 1843, Wackerwoder<sup>2</sup> began to prepare ferrous oxide by the reduction of ferric oxide at 300 deg. C by hydrogen. This experiment was later repeated by Sivert<sup>3</sup> and Moissan<sup>4</sup>, though at a higher temperature. The latter heated ferric oxide in <sup>a</sup> stream of hydrogen at

## 500 deg. C and proved that this method was not very satisfactory.

1. Wen, Thesis No. 352

Wackerwoder and Stromyer "Archiv f. Pharmacie" 1843 36 p. 27  $2.1$ Jahresberichte über die Fortschritte der Chemie 1864 17 p. 266  $3.1$ Annales de Chemie et de Physique 1880 21 p. 199  $4.1$ 

because of the fact that hydrogen, at that high temperature, reduced some ferrous oxide to metallic iron, Moissan, therefore, employed another method for the preparation, which consisted in reducing ferric oxide by a current of carbon monoxide. He found that the results were satisfactory and that the amount of total iron in the product approxinated the theoretical one,'

Of the work on ferrous oxide, that of Debray<sup>1</sup> should be mentioned. These experiments were conducted by passing a stream of equal rolames of carbon monoxide and carbon dioxide over ferric oxide at red heat. The results obtained proved unsatisfactory.

Another method used was that by Vogel<sup>2</sup>. Moissan<sup>3</sup> and Birnie<sup>4</sup>. It consisted in decomposing ferrous oxalate at an elevated temperature; the decomposition takes place according to the following equation:

FeC<sub>0</sub>0<sub>=Fe0+C0+C0<sub>0</sub>.</sub>

Vogel found that the product obtained was not free from metallic iron. Moissan pointed out that the decomposition did not take place exactly as the chemical equation given above, but that there was a secondary reaction, in which the carbon dioxide liberated converted the ferrous oxide first formed into magnetic oxide,

 $3Fe0+CO$  =  $Fe_0O_4+CO_6$ .

Phe results of Birnie agree in part with those of Vogel. He.

Comptes Rendus 1857 45 p. 1018  $1.$ 

- -. Liebig Annalen der Chemie und Pharmacie 1855 95 p. 116
- Annales de Chémie et de Physique 1880 21 p. 199  $3.5$
- $4.$ Am. Inst. Min. Eng'rs. Trans. 1899 29 p. 684 foot note.

found, however, that the product contained not only <sup>a</sup> little reduced iron, but also a small quantity of carbon and that the amount of carbon set free depended upon the mode of heating the ferrous oxslate and that the metallic iron was produced by the liberated carbon.

Berthier<sup>1</sup> and Plattner<sup>2</sup> prepared ferrous oxide by heating a mixture of metallic iron and magnetic oxide, or rather, hammer scale.

Tissandier<sup>3</sup>employed another method of making this oxide which zonsisted in passing carbon dioxide over heated iron wire at <sup>600</sup> deg. C The experiment was later repeated by Moissan<sup>4</sup> and Steffe<sup>5</sup>. They found that the method gave unsatisfsctory results, It was slso employed for the preparation of ferrous oxide in our experiment last year. the results obtained proving to be very unsatisfactory.

The best and most successful method is that which was first employed by Mills<sup>7</sup> and then by Steffe, being based upon the method of Berthier and Plattner. It consists in heating, in molecular proportions, a mixture of metallie iron and ferric oxide when FeO is formed according to the chemical formule:

 $Fe<sub>2</sub>O<sub>2</sub>+Fe=3FeO$ 



Steffe in 1908 made an investigation on this method and heated the mixture in a current of nitrogen. He found the product to be most satisfactory. Therefore, in our experiments of 1908-09, this method was adooted for the preparation of ferrous oxide. The preparation of FeO formed the first part of the thesis and the determination of the heat formation of ferro-calcic silicates of the second and main part.

The work of this investigation, as planned, was to consist in determining the heat formation of a series of singulo-silicates, and second, of a series of bisilicates of FeO and CaO. On account of the fact that much time was consumed in the adjustment of the electrical apparatus, and that many experimental difficulties were encountered, to overcome which it would have necessitated a new apparatus of larger capacity and a device for keeping the voltage constant, three concordant results of the singulo-silicate series were obtained.

 $4-$ 

For this experiment silica, calcium carbonate, iron powder, reduced by hydrogen, and ferric oxide were used.

The preparation and analysis of silica and calcium carbonate were given in my thesis<sup>1</sup> of last year.

### 1. Metallic Iron

Iron powder used in the preparation of ferrous oxide was that of Kahlbaum (C.A.L. Kahlbaum Chemical Supply Company, Berlin, S.O.) The iron was first dried in a steam chest at 110 deg. C for three hours, cooled and ground in an agate mortar until the whole passed through a bolting cloth. It was then analysed by the following method: A weighed sample, about 0.2 gm. is dissolved in 100 c.c. of dilute sulphuric acid, (5 parts H SO,, Sp.gr. 1.84:100 parts H O) and heated until the solution is complete. The solution is passed through Jones' Reductor<sup>2</sup> while hot, at a rate of not more than 50 e.c. per minute. The beaker in which the solution was contained and the reductor are carefully washed with 300 c.c. of the above sulphuric acid and then with 100 c.c. of hot water. The solution is titrated with potassium permanganate. Two analyses were made and the percentage of iron was found to be 99.10 and 99.08.

Analysis of hydrogen in the electrolytic iron. As Lupropen - whereod electro-depertted iron usually contains occluded hydrogen, it was therefore important to consider the analysis of this element. Its determination was made by the combustion method. The apparatus used is shown in Figure I.

1. Wen Thesis 1908 No. 352  $pp_{\bullet}$  4,  $5_{\bullet}$ 2. H.P. Talbot "Quantitative Analysis" N.Y. Wiley 1902 p. 96 <sup>A</sup> weighed sample of about <sup>2</sup> gm, of iron powder in

a porcelain boat is introduced into the combustion tube of the furnace. The Liebig potash-bulb L, containing potassium hydroxide and the U-tube **T** containing calcium chloride, are attached to one end of the combustion tube and the weighed Marchand U-tube <sup>M</sup> which also contains caleiam chloride to the other. The heating gas is then turned on and lighted. The oxygen before coming in contact with the iron is freed from carbon dioxide by the bulb L and from moisture by the tube T. The water vapor formed by the combustion of the hydrogen in the sample is absorbed and collected in the tube M. The time of combustion is twenty minutes. The amount of hydrogen from the increased weight is calculated as Follows:

18: 2=increase of wt. wt. of hydrogen.

 $nt<sub>e</sub>$  of hydrogen = increase of  $nt<sub>e</sub>$ 2

Percentage of hydrogen = wt. of hydrogen  $\overline{\text{wt}_{\bullet} \text{of}}$  samole  $\overline{\text{V}}$   $\times$  100. Three determinations were made and the percentages

sf 'hydroden 'in the samole were 0.018. 0.013. and 0.015

The determination of hydrogen was preceded by a blank test to find out whether the admission of oxygen and the amount of calcium chloride were rightly proportioned to have the oxygen free from  $H_0O_{\bullet}$ 

## 2. Ferric Oxide.

fhe ferric oxide used was that of Kahlbaum, It yas first dried in the steam chest at <sup>110</sup> des. <sup>C</sup> for three hours and

# $Fig. 7$ APPARATUS FOR

THE DETERMINATION OF HYDROGEN



to of original size

then analysed according to the following procedure: From 0.2 to 0.3 gm. of ferric oxide is weighed out, placed in a porcelain casserole and dissolved in 30 c.e. of hydrochloric acid (sp. gr. 1.12). It is heated to a temperature below boiling until the solution is complete. The solution is allowed to cool. Five c.c. of concentrated sulphuric acid (Sp. ar. 1.84) is then added carefully and the solution evaporated on the hot plate or on the steam bath, until it becomes nearly colorless. The casserole is covered and heated over the flame of the lamp until a heavy white fume of sulphuric anhydride is freely evolved, The casserole now is coole<sup>d</sup> 100 c.c. of distilled water is added. The solution is warmed until all the ferric sulphate is brought into solation. It is then passed through the Jones reductor, as described above and titrated with a potassium permanganate. The analyses gave the following percentages of Fe: 69.66, 69.72 and 69.71. Taking the average of these analyses we have 69.70 per cent of Fe = 99.57 per cent  $Fe_9O_8$ .

# 8. Perrous Oxide.

The method of preparing ferrous oxide employed last year was that of Tissandier<sup>1</sup>, which consisted in heating metallic iron in a stream of carbon dioxide. This method, was found to give unsatisfactory results, because of the fact that the ferrous oxide first formed was peroxidized by the carbon dioxide and converted into magnetic oxide, according to the following chemical equation:

<sup>3</sup> Fe0+CO\_=Fe 0+CO.

1. Comptes Rendus 1872 74 p. 541.

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As the method of Tissandier failed to give good results, that of Steffe, discussed above, was adopted. The product formed was satisfactory, the results obtained agreed to those of Steffe. Preparation of Nitrogen. As the heating of the

mixture of iron powder and ferric oxide cannot take place in atmospheric air, it is necessary to heat the mixture in an inert gas. Nitrogen was used in this case and passed over the substance while heating and cooling. It was prepared by passing a mixture of air and ammonia gas over heated cupric oxide contained in the combustion tube. The heated cupric oxide and the free oxygen from the air decompose the ammonia gas; the chemical reactions taking place are represented by the following formulae.

> 2NH<sub>3</sub>+3Cu0=3H<sub>2</sub>0+3Cu+N<sub>2</sub>  $4NH_3 + 30.5 = 6H_2 + 2N_2$

Any remaining oxygen is absorbed by pyrogalate of potassium The apparatus for the preparation of nitrogen is shown in Plate 2

The air under pressure enters the 500 c.c. bottle A which contains concentrated ammonium hydroxide (sp. gr. ,90) After passing through the bottle, the air carries a certain amount of ammonium gas and enters the combustion tube K, 3 ft. long and 1/2 in. in diam., containing cupric oxide. B is the gas-heated combustion furnace in which the tube is placed. Bottles of 250 c.c. capacity contain oyregalate of potassium which is to absorb the oxygen. Bottles D contain potassium hydroxide which is to take away the carbon dioxide from the gas. Bottle E contains ammoniacal cuprous chloride which is to ab-

sorb the carbon monoxide that may be present in the air. F are bottles containing concentrated sulphuric acid (sp.gr. 1.84) which serves to remove any moisture. In order to obtain as pure nitrogen as possible, care was taken both in filling the combustion tube and in heating it, The tube was filled with eupric oxide uniformly, that the ammonia gas might not escape without being decomposed; it was heated barely to redness, for if heated to too high a temperature it would become soft and thus permit the ammonia gas to pass off andecomposed and contaminated.

The nitrogen thus prepared was not absolutely pure. but contained a trace of oxygen which could not be detected by the Orsat apparatus with which the gas was analysed. This trace of oxygen affected the results of ferrous oxide greatly. In order to prevent this, a boat (a) of metallic iron powder was introduced and placed in the tube F, near the end where the nitrogen gas entered (see eross seetion J. Plate 2). After an operation, part of the iron powder was found to have become oxidized, the color of the part near the entrance of the nitrogen was black, and the other part near the boat (b) remained unchanged,

As has already been said, the process of preparing ferrous oxide consisted in heating a mixture of metallic iron powder and ferric oxide in a current of nitrogen. The apparatus and its arrangement are shown in Plate <sup>2</sup> drawn enoroximately to seals. <sup>H</sup> is the dong<br>electric furnace 12<sup>-2</sup>×8<sup>--</sup> diameter and T the porcelain combustion tube  $25/8$ <sup>\*</sup> diameter in which the substance is introduced in a boat and

and heated. The nitrogen, after passing through bottles C, D, E and F, enters the tube at one end, as is indicated by an arrow, and leaves at the other end to which is attached bottle I containing concentrated sulphuric acid. This is to prevent any air from entering the tube. R is the rheostat which enables us to vary the current as desired. V is the millivoltmeter and P the thermo-junction which serves to measure the temperature of the electric furnace. Six lamps, two of 100 c.p. and four of 32 c.p., are connected in parallel in order that a larger current may be had.

The calculation of iron and ferric oxide necessary for the mixture was carried on as follows:

By analysis, the metallic iron was found to contain 99.10 per cent of Fe and the ferric oxide 99.57 per cent Fe O<sub>3</sub>. Let X-the wt. of Fe O required for 1 gm. of the sample of Fe.

> wt. of iron : X=mol. wt. Fe: Fe 0  $0.9910: X=56:160$

 $X = 160 \times 9910 = 2.8314$  gm. Fe  $0<sub>3</sub>$ But the Fe<sub>2</sub><sup>0</sup><sub>3</sub> was only 99.70 per cent pure; the weight of Fe<sub>2</sub><sup>0</sup><sub>3</sub> corresponding to one gram Fe was corrected as follows:

wt. of Fe  $0_2 = 2.8314 \times 100 = 2.8436$  gm. One gram of Fe requires 2.8436 gm. Fe 0 99.57

Mode of operating was as follows. The electrolytic iron powder was ground in the agate mortar until it passed through a bolting cloth. A portion of this fine metallic iron and a corresponding portion of ferrie oxide were weighed out in two one-inch watch

slasses, The iron and the ferric oxide were mixed and ground in the agate mortar for at least 15 minutes, so that the two substances might be in intimate contact with each other, The mixture was transferred to a piece of glazed paper and then to the iron boat in which the substance was going to be heated. This boat was of black sheet iron. Sin. long.  $3/8$  in. wide,  $1/4$  in. deep. It was made by folding a piece of the sheet over a semi-cylindrical piece of wood. The boat containing the mixture ves first introduced into the porcelain tube, Another iron boat eontaining metallic iron followed it, The ends of the porcelain tube were now closed, the gas for the ecombusticn furnace wes turned on and lighted, <sup>A</sup> streem of nitrogen, at <sup>a</sup> rate of not more than six bubbles per minute, was passed through the porcelain tube, The electric current was now ready to be turned on to heat the electric furnace. It took  $2 \frac{1}{2}$ =3 hr. to bring the electric furnace with a current of not more than 10 Amp. at 110 volt, to about 800 deg. C. The mixture was heated in the furnace at a temperature from 820 to 840 deg. C for two hours. After this period, the electric current wes turned off, but the stream of nitrogen was allowed to pass until the temperature had been reduced to the room temperature. The mixture was taken out, the air for the preparation of nitrogen shut off, and the flame extinguished. In order to make the experiment <sup>a</sup> successful one, the stream of nitrogen was adjusted and so regulated that not more than six, and not less than three, bubbles passed through the sulphuric acid bottle per minute. At the beginning of the operation, when the temperature of the electric furnace was below 200 deg. C, the current of nitrogen was allowed to pass more rapid-

lye: This was to drive out as soon as possible the air in the porcelain tube,

The temperature of the electric furnace was measured by means of the Le Chatelier thermo-electric pyrometer. The hot junction was placed in the middle of the tube and under the porcelain tube, as is shown in the cross section (Plate 2, Fig. J). The thermojunction was calibrated by means of the boiling points of distilled water, napthaline and sulphur and the freezing point of aluminum, and a temperature-millivolt curve plotted. In determining the total iron in the ferrous oxide, the method given on page 8 was first used. This, however, consumed much time and was replaced by the following method which consists in dissolving from 0.15 to 0.20 gm. of the sample in a 250 c.c Erlenmeyer flask with 75 c.c. of sulphuric acid,  $1 \text{ H } \text{SO}_4$  in 4 parts  $H_2^0$ , heating the solution until all the ferrous oxide is dissolved, dilating with 100 e.e. of  $H<sub>2</sub>0$ , warming, pouring through the Jones redactor and titrating with <sup>a</sup> potassium permanganate, The result obtained is tested by comparing with the theoretical value of ferrous oxide. which is 77.70 per cent of Fe.

The analysis of total iron is not, however, sufficient to show that the product is pare ferrous oxide. It is therefore important to find out whether the product contained any metallie iron or eant to find out methor the product contained any metallic from or<br>ferric oxide, or both. In testing for metallie iron, a small sample is was constructed in the college of the collect and product the compact of

C. L. Norton's Laboratory. "Notes on Heat Measurement" 1902 p. 9

boiled in <sup>a</sup> test-tube with distilled water to drive off any air that may be present, then a few drops of dilute hydrochloric acid are added. If metallic iron is present, small bubbles of hydrogen are set free and rise to the surface of the solution.

 $Fe+2HCl=FeCl<sub>2</sub>+H<sub>2</sub>$ .

In testing for ferric oxide, the substance is heated in dilute hydrochloric acid with exclusion of air, which is accomplished by passing a current of carbon dioxide into the tube while the product is being dissolved. If there is any ferric oxide, the solution hecores yellow; if not, it remains colorless. By the above qualitative methods, it is easy to ascertain the composition of the product.

The results obtained are shown in the following table:



+ The charge contained an amount of Fe203 allowed for the hydrogen in the metallic iron.<br># Here, an iron boat, was introduced into the percelain tube to absold any oxygen contained in the nitrogen before it came in contact with the mixture.

In sample 1 the product contained much metallic iron and ferric oxide and the percentage of total iron was therefore low. In sample 2 a small charge was used, but the product was no better than that obtained in Sample 1. In sample 3 the product, though heated to <sup>a</sup> high temperature, s180 contained much metallic iron and ferric oxide, The presence of these was chiefly due to the low temperature to which the mixture was heated. Quantitative analyses of samples 2 and 3 were not made. In sample 4, the mixture was heated to <sup>a</sup> higher temperature; it appeared to be much improved, but still it contained some metallic iron and much ferric oxide, for it colored the hydrochloric acid solution quite yellow. The presence of metallic iron and ferric oxide in the product and its low percentage of totel iron led us to think that this must be due to the emall emount of oxygen carried over by the nitrogen. To avoid this, an iron boat filled with metallic iron powder was introduced into the porcelain tube and placed at the end where the current of nitrogen entered, in order to remove e11 oxygen before the nitrogen came in contact with the mixture. Sample <sup>6</sup> was made under this condition. The product contained only <sup>a</sup> little metallic iron and sore ferric oxide and the percentage ef tetal iron became much higher end better, To further improve the results cf the product, <sup>a</sup> small amount of ferric oxide was taken away from the charge. The results obtained were satisfactory and the value of totel iron approximated the theoretical value which is 77.70 per cent, Samples 7, 8, 9, 10 and 11 show these satisfactory results.

In the preparation of ferrous oxide by this method, it appears that the temperature to which the mixture is heated plays an important part. If the temperature is too low, some metallic iron and some ferric oxide remain unchanged. In order to completely sonvert the mixture into ferrous oxide, it must be given the correct temperature and time, It is observed in the abcve table that, other conditions being the same, a small increase in the weight of the charge does not affect the character of the product.

It will be noted that the amount of ferric oxide required for the charge in this case is less than the theoretical, This is perhaps due to the fact that, as the percentage of iron is low (89.10 per cent), the iron is present to a small extent as oxide and consequently the amount of ferric oxide required for the formation of ferrous oxide is less than what it is expected to be.

# PART IT

DETERMINATION OF HEATS OF FORMATION.





SCALE  $\hat{I}$  IN. =  $\hat{Z}$  IN.





The method chosen for determining the quantity of heat set free or absorbed in the formation of a silicate consists in fusing the substances in a platinum boat by means of electricity in a calorimeter specially designed for this purpose. The difference between the quantity of heat developed by the electrical energy and the quantity of heat obtained by the rise of temperature of the water in the calorimeter when fusing a charge gives the heat of formation of the silicate or silicate mixture.

#### 1. The Apparatus

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The electrical apparatus used in the experiment and its general arrangement are shown in Plate III. It consists of: butcher, pair - cleane

Two concentric jackets, J, outer jacket 11 in.h. x8 3/4 in. diameter and an inner jacket 8 1/2 in. h. x 7 3/4 in. diameter, made of to anon - loute non-conducting material, the surfaces of which are burnished, so as to prevent the loss of heat by radiation, or gain of heat by absorption from the surrounding space.

A combustion chamber, C, of rolled brass.

A vessel, D, 6 in.h. x5 in. diam., of nickel-plated brass, which serves as a calorimeter. The calorimeter contains a weighed quantity of water into which the bulb of the thermometer, T, the stirrer, S, and the combustion chamber, C, are immersed. The thermometer permits reading to a precision of 0.01 deg. C, the stirrer is run by an electric motor mounted on top of it and is used to keep the water in the calorimeter at a uniform temperature.

The combustion chamber. Plate IV, consists of a cylindrical cover, c, and a circular bottom-plate, d, which rests on three

 $16<sub>z</sub>$ 

small legs, all made of rolled brass which has been treated with a solution of ammonia and cupricearbonate. This gives the surface a dark appearance and protects it from corrosion. Upon and through the bottom plate are fixed two brass poles, f, 1/4 in. diameter, insulated from the bottom plate by rubber washers, g, and set 2 1/4 in. apart, from centre to centre. These two poles are connected by a platinum boat h. 1 3/4 in. long, 5/16 in. high and 1/8 in. wide, made of foil 0.02 mm. thick, in which the charge is held and fused. The shape of the platinum boat is clearly seen in the figure. Vessel, c, and bottom plate, d, are connected to make a water-tight joint. For this purpose, vessel, c, has a rib, i, which rests on a rubber gacket, j, carried by rib, k, of the bottom plate, de The latter carries two rods, 1, each of which has <sup>a</sup> head, m, at the top, a lock-nut, n, near the bottom and a thread at the lower end to receive a nut, o. The two rods are connected by a cross<br>piece, p, and tightened by the set screw, q.

The electric current used to fuse the charge was furnished by a storage battery of light cells, B, plate III, four cells being connected in series and the two series are in parallel. Each cell had eleven electrodes, 8 in.x8 in. and furnished a current of 10 amperes at 2 volts. The current was measured by the **millivolt**meter, A, connected in parallel to the shunt, F, which is in series with the circuit, the instrument permitting to read to an accuracy of 0.1 amperes. The difference in potential was measured by the voltmeter, V, which could be read to 0.001 of a volt.

The disposition of the wire connection is shown in

plate III. The double-throw switch, E, serves to charge and discharge the storage battery, When the switch is in the position, P, the battery is being charged; the current from the supply-main passes along the dotted arrows through six 32 e.p. incandescent lamps, the switch, P, to the battery, B, and thence returns through the resistance wires,r, in the water-tank,  $K$ , back to, P, and the return-main.

When the switch is in the position,  $P_{f}$  the battery is being discharged. The current leaving the battery follows the fulldrawn arrows, passes through the right of the switch, P', the shunt, F, the connector,h, and enters the combustion chamber at the bottom through the + pole, passes through the platinum boat, leaves the com= bustion chember at the bottom through the -pole, passes throudh the left side of the switch, P", the two resistance wires, r, immersed in a large tank of water, K, returns to the battery. For measuring the difference in potential between the two terminals at the bottom of the combustion chamber where the current enhens and leaves, there sre attached two insulated copper wires which are connected with the voltmeter, V, to the two poles.

As <sup>a</sup> large current is required for the fusion of the charge, it is of much importance to consider the size of the copper wire used in the circuit. The wire should be large enough to carry 60 or more amperes without heating. With <sup>a</sup> smaller wire, the circuit vould become hested and an increment of resistance could not be avoided: and thus the current is not kept constant. The copper wire was  $4.06$  mm. diameter, equals No. 8 gauge.

1Q

It is a matter of great importance in this experiment to get a constant current. This was effected by the consideration of two points, first, the number of amperes drawn from the storage battery and, second, the external resistance of the circuit. If too large a current is drwan from the battery, this becomes over-discharged and a constant current can never be obtained even if the external resistance is kept absolutely constant. In the present case, a constant current was obtained only when not more than 10 amperes were drawn from [ each cell.

To get the proper and constant current for the fusion of the charge, a suitable external resistance of the circuit had to be provided. Three iron wires, No. 5 gauge, 2 ft., 8 in. long were first used and connected in parallel. It was found that these wires could not fulfil the required conditions because they offered too much resistance and then did not give either a proper current or a constant one. The iron wires were replaced by No. 14 I I wire of the Baker Co., Brooklyn, N.Y., which offered a resistance of only 73 ohms per 1000 feet. Two wires, 3 1/2 ft. long, connected in parallel were used, their ends were screwed into 2 brass blocks, b, 1/2 in. sq., 4 in. long. These were screwed onto the board, n, which was supported by two bricks, m. The wires were immersed in a large tank of water, k, to prevent their being heated and thus to obtain a constant current.

When the electric current is turned on, the platinum boat becomes heated; its resistance will increase and the electric current correspondingly decrease. In order to compensate for this, a

 $19<sub>o</sub>$ 

slider 0, was used and slid on one of the resistance wires. r. and the current kept thus constant by increasing or decreasing the external resistance of the circuit.

As the experiment was a delicate one, the operations were carried on with the greatest possible care. Every charge was preceded by a duplicate blank test in order to get the constant of the apparatus. In every blank- and charge-determination, the electric current, the quantity of water, 1200 grams, and the time were kept constant. The last was recorded by means of a stop-watch.

#### 2. Mode of Operating.

The substances were separately weighed out in oneinch watch glasses, mixed on a piece of glazed paper and transferred into the platinum boat beneath which a small piece of glazed paper had been previously placed, in order to catch any mixture that might fall from the boat. It was essential that the position of the boat in the poles should remain absolutely unchanged after the blank tests had been made, hence this method of filling the boat was adopted. The glazed paper was removed, the cover of the combustion chamber placed on the bottom plate and tightened by turning the screw. g. An experiment consisted of the following operations:

The room-temperature was read, that the temperature of the calorimeter-water might be adjusted so that at the end of a test the water-temperature should be the same as the room-temperature. or perhaps one degree higher, as in this way the cooling correction of the

calorimeter was reduced to a minimum. Usually the calorimeter water, at the start, was <sup>1</sup> degree <sup>C</sup> lower than ths room-temnerature,:

The combustion chamber was then placed in the weighed water, the stirrer inserted and set in motion by turning on the surrent, a branch from the suppcy main. The bulb of the thermometer was immersed, the voltmeter connected to the two poles. The circuit yas closed by connecting ths combustion chamber with the leads by means of two connections, h. The stirrer was allowed to run for at least five minutes and usually ten minutes, befors the preliminary readings of the temperature of the water in the calorimeter were taken. The temperature was read every minute for five minutes, then the surrsat was turned on and allowed to pass for one minate, being timed by a stop-watch. The temperature of the water would rise and continue to do so for three or four minutes more before it reached its highest point. After the current was turned off, readings of the temperature of the water were taken every 30 seconds and this continued until five minates after the temperature had reached its maximum.

During the passage of the current, readings were taken of the voltmeter and the millivoltmeter, the total current was kept constant by varying the external resistance, r. by means of a slide. O.

It will be observed, in this experiment, that the whole current did not pass through the flatinum boat, that a small part of it went through the voltmeter, v. Owing to the high resistance of the voltmeter, the low voltage of the storage battery:

only an inaporeciable part of the total current passed through the voltmeter and could be, therefore, neglected.

## 3. Cooling Corrections.

In ealorimetric work, one of the most troublesome sources of error is the gain or loss of heat caused by the surromdings. This is due chiefly to conduction and radiation. The conduction can be eliminated by supporting the calorimeter on three corks, but the srror dus to radiation is great and serious. To reduce this source of error to a minimum, the calorimeter should be enclosed within two concentric vessels of non-conducting material; further, the temperature of the calorimeter should not differ greatly from that of its surroundings, and the duration of the experiment should be as short as permissible.

The error due to radiation may be reduced to its pinimum by so adjusting the initial temperature of ths calorimetare water, that the room=tzmperabture lies about half way between its initial and final temosrabures. The duration of ths passage of the aurrsat was fixed at one minute.

The advantages of having such a short period are great and manifold. In the first place, the rise of temperature in the calorimeter is small; then, the initial temosrature can be more easily adjusted; further, the heat lost by radiation, or gained by absorption, is small and hence the amount of cooling correction is also small and of smaller influence. If, on the other hand, the duration of the passage of the current is long, the rise of temperature will be high and the initial temperature will have to be adjusted far below the room-temperature and the final temperature will rise far above it. The result is that the quantity of heat absorbed and radiated is large, and being irregular, makes the cooling correction uncertain.

In the experiments, the carrent was allowed to pass, at first, five minutes and the initial temperature was about the same as the room-temperature. The idea of doing this was to make the cooling correction a positive amount. The result was that the rise of temperature was far too great and the cooling correction correspondingly too large and therefore irregular. Table II will show the variations of the cooling correction varying from 0.20 to 0.27, average 0.235, with a rise of temperature of 13.30 to 13.99, average 13.645.

Next, the tims was reduced to three minutes and the initial temperature lowered, so that the final temperature was about the same as the room-temperature, Since, in this case, heat was absorbed from the surroundings, the cooling correction was negative. The amount of cooling correction, though greatly decreased, was still too large and irregular. Table III, No. 1 to 4, shows results. The correction gives an average 0.145 for a rise of temperature of 6.97.

In the two-minute runs shown in table III. No. 5 and 6, the amount of cooling correction was greatly decreased, amounting to  $0.09$  for a rise of temperature of  $4.95$ . This is still too large and too uncertain.

In the one-minute runs, the amount of cooling correction was reduced still further, as seen in table IV. Here the correction values are 0.05 for a rise of temperature of 2.71. But the results of the blank tests still varied greatly. The initial temperature was adjusted in such a manner that the surrounding temperature was about half-way between the initial and final temperatures. Jnder this eondition, the results proved to be much better and more satisfactory as seen in tables V, VI, VII and VIII.

### 4. Computation of Cooling Correction.

During the operation of a calorimeter, as has already been said, heat is either gained or lost by absorption or radietion, it is, therefore, of main importance to find out this amount of heat. As the conditions under which the experiments were performed were different in each series of runs, the values found will vary: they may be positive or negative. There are three possible cases.

1. The initial temperature of water in the calorimeter is about the same as that of the room.

9. The initial temoeratvre of water in the calcrimeter is sufficiently low, that at the end of the experiment the maximum temperature reached is equal to the room-temperature or little lower,

3. The room-temperature lies at half-way between the initial and final temperatures of the water in the calorimeter.

In Case 1, the temperature of water in the calorimeter begins to rise in the surrounding room-temperature and heat is lost by radiation. The corrected rise of temperature is expressed by

 $\mathbf{r} = \mathbf{t} - \mathbf{t}$  $r_1^+ r_2^{\left(\Theta_2 - \Theta_1\right)}$  No.

where t<sub>1</sub> denotes the temperature at the instant when the current is turned on, t<sub>2</sub> the temperature at the instant when the temperature, after having turned off the current, reaches its highest point; r, the rate of radiation per minute in deg. C before the current is turned on;  $r_{\alpha}$ , the rate of radiation per minute after the current is shut off;  $\theta$ , the time at which the current is turned on;  $\theta$  the time at which the temperature reaches its maximum. The following example will make clear the calculation of rise of the temperature and of cooling correction.




Since heat was radiated while the temperature of the water in the calorimeter was rising the correction will have to be added to the observed rise of temperature.

 $r_1 = 24.68 - 24.68 = 0$  deg. C

 $r_2$  = 38.19-37.83 = 0.36 = 0.072 deg. C; t = 38.19 deg. C; t 1 = 24.68

deg. C

 $\theta_1 = 5$ ;  $\theta_2 = 12$  1/2;  $\theta_1 = 38.19 - 24.68 + 0.072 \times 7$  1/2 = 13.78 deg. 0  $\overline{2}$ 

In Case 2, the initial temperature of the calorimeter was far below and the final temperature about the same as that of the room-temperature. Heat was gained, and the amount of cooling correction consequently negative. The general formula assumes this form in which the cooling correction is negative.

$$
T = t_2 - t_1 - r_1(\theta_2 - \theta_1) \quad (\text{No. B})
$$

The computation is shown by the following example:



 $27 -$ 



 $r_1 = 16.50 - 16.30 = 0.20 = 0.04$  deg. C;  $r_2 = 23.70 - 23.70 = 0$ ;<br>5  $t<sub>2</sub> = 23.70$ ;  $t<sub>1</sub> = 16.50$ ;  $\theta<sub>2</sub> = 12 \frac{1}{2}$ ;  $\theta<sub>1</sub> = 5$ ;  $T = 23.70 - 16.50 - 0.04 + 0 \times 7$  1/2 = 7.05 deg. 0

In Case 3, if the initial temperature of the water in the calorimeter could be brought to just as many degrees below the room-temperature as the final temperature of the water will rise above the room temperature, then the heat gained or lost would be balanced and a cooling correction become unnecessary. But it is practically impossible to so adjust the initial temperature, as the

conditions of the surroundings are changing all the time. The best that can be done in this case is to so adjust the initial temperature of the calorimeter water that the surrounding temperature lies about half-way between the initial and final temperatures of the water. The corrected rise of temperature is calculated by

$$
P = t_{2} - t_{1} \pm \frac{r_{1}r_{2}}{r_{1}} (\frac{\theta}{\epsilon} - \theta_{1}) \quad (\text{No. C})
$$

If  $r_1$  is greater than  $r_{22}$  the correction assumes a negative value and the negative sign of the formula is used. If  $r_{0}$  is greater than  $r_{1}$ , the positive sign, by arranging the conditions of the experiments to suit Case 3 and with it formula ( No. C), is used. It was found that the amount of cooling-corrections was greatly reduced and the results thereby improved. The following example will illustrate this method of computing the amount of cooling-corrections developed by electrical energy.



# Example continued



 $\overline{c}$ 

 $30.$ 



Table 1, charge-Tests without noting Difference in Potential.

The amount of cooling corrections in this case pust be added, as the quantity of heat which is radiated is larger than that which was absorbed.

#### 5. Nethod of Making Preliminary Fusions.

attempts were first made to determine the heat formation of silieates bv comparing the rise of temperature in the blank-test with that in the charge-test and to multiply the difference with the quantity of water. This was done by keeping the electric eurrent constant, the amount of water and the time constant, both in the blank-tests and in the charge-tests. The method did not give true values of the heats of reaction. The current passing through the platinum boat in a blank-test gives a certain value. Passing through <sup>p</sup> charse-test, the resistance is decressed by the conduction of the charge; if the current is to be kept constant, the voltage must be reduced, but the heat generated  $H = k$ , I,  $B$ , t, hence the rise of temperature of the water in the calorimeter will be smaller than the rise of temperature with the blank-test and the two are not comparable,

The results are given in the following table. I

By studying the table, it is found that in every determination the differences between the average rise of temperature of the blank-tests and of the charge-tests vary greatly from one ancther, and that the heat of formation of the silicates is negative, that is. that heat is absorbed.

6. Final Method of Making Fusions.

In this method, the theoretical quantity of heat

developed by electrical energy is compared with the actual quantity of heat obtained in the calorimeter. In a blank-test, the theoretical quantity of heat should be equsl to the sctusl quantity, but in the experiments this was not found to be the case; as in almost every determination the actual quantity of heat was greater. This deviation was due to the constant error of the instruments and to error from other sources, such as cooling correction, personal factor in the reading of instruments, ete, In order to obtain reliable results, it is of great importance to determine the blank-constant. This was done by running two blank-tests before every charge-test.

The theoretical quantity of heat developed by electrical energy is

 $H = 0.2387$  I.E.t. Sm-cal.

in which I denotes the electric current in amperes, E, the difference of potential between two poles of the combustion chamber, in volts, and t, the time in seconds,

In the example given on page ... the electric  $\omega$  current was kept constant at 54 amperes, the average difference of potential was 4,009 volts, and the time during which the electric current was turned on was 60 seconds. Therefore the theoretical quantity of heat

 $H = 0.2387 \times 4.009 \times 60 = 3101$  gm-cal.

The actual quantity of heat is  $H_4$  = Q.T. in which Q denotes the quanity of water in grams including the water-cquivalent of the calorireter. the stirrer and the combustion chamber. and <sup>T</sup> the corrected

Table 2 Blank-Test

No. of	Time	current 117	Averaged Weight	difference of water		Temperature in degree Centigrade		Actual amount	Theoretical amount of heat	$D$ ifference		
tests	1 <sub>7</sub> Gecond	ampere	potential $V_0$ H.	117 $g$ m.	Ini <sub>ta</sub>	Final	Room temp.	$\begin{bmatrix} \text{Coling} \\ \text{correct,} \text{on} \end{bmatrix}$	Rise9f $tomp$ .	of heat $\int_{c}^{\infty}$	$gm-ca/$	
	300	53	4.502	1303	24.87	37.85	25	$+23$	13.30	17330	17090	240
$\mathcal{Z}$	300	53	4.527	1303	25.00	38.10	25	4.23	13.33		$17369$ $17180$	189
$\overline{3}$	300	53	4.547	1303	25.21	38.40	26	$+.22$	13.41		$17473$ $17260$	2/3
$\overline{A}$	300	53	4.564	1303	25.50	38.74	27	$+, 21$	13.45	17525	17330	195
$\mathcal{L}$	300	53	4.581	1303	25.77	39.08	27	$+.25$	13.56		17669 17390	279
6	300	53	4.576	1303	24.64	38.02	24	$+ .24$	13.62		17747 17370	377
$\tau$	300	53	4.582	1303	24.51	37.94	24	$+23$	13.66	17800	17391	411
$\mathcal{S}% _{M_{1},M_{2}}^{\alpha,\beta}(\mathcal{S})\equiv\mathcal{S}_{M_{1},M_{2}}^{\alpha,\beta}(\mathcal{S})\equiv\mathcal{S}_{M_{1},M_{2}}^{\alpha,\beta}(\mathcal{S})$	300	53	4.624	1303		$24.68$ 38.19	24	$+ .27$			$13.78$ $17955$ $17550$	405
9	300	53	4.696	1303		$19.24$ 32.99	22	$+24$	13.99	18229	17920	309
10	300	53	4.715	1303		$20.41$ 34.15	23	$+20$		$13.94$ 18164 17993		171

 $\sim 40$ 

×.

rise of temperature.

The water-equivalent is obtained by multiplying the sum of the weights of the calorimeter, the stirrer and the combustion chamber by the specific heat of the metal.

> Weight of calorimeter ..........  $211.0$   $\text{cm}$ . stirrer ...............  $-97$  $100.0$ 11 combustion chamber .... 836.0  $\overline{\mathbb{Y}}$

Taking the specific heat of the metal to be 0.09. the water-equivalent of metal parts is equal to  $(836+100+211)x0.09 =$ 

103 gm. water.

Then with 1200 gram water, Q= 1200+103=1303 gm. of water.

The actual quantity of heat

 $H_4 = 0$  T=1303×2.43=3166 gm-cal.

In order to ascertain the accuracy of this method, a series of blank-tests was first made. The duration of the operation proper of each test was five minutes; the initial temperature of the water was adjusted about the same as the surrounding temperature. The difference of potential between the two terminals was read every half minute. In this series of tests, heat was lost and the corrected temperature should be calculated as shown on page ...by the formula: A, viz:

$$
\mathbb{T} = t_2 - t_1 + \frac{r + r_2}{2} \left(\frac{\Theta - \Theta}{2}\right)
$$

The difference between the theoretical and the actual quantities, as shown in table II, are great and varied. These

Table 3

NO. of		Time	Current 1n		Averaged Weight of difference water in		Temperature of water in degree Cent.		Actual amount	Theoretical gmount $0 + heat$	Difference		
	Tebts	$\sqrt{n}$ Second	ampere	$\frac{potential}{in}$ $V$ o/t	gram	$ n_1 $	Final	Room temp	$\frac{1}{q}$ <i>Correction</i>	Rise of Tamp	of heat $q$ m - ca/	$qm-ca/$	
	$\alpha$	180	50	4.180	1303	16.70	23.79	23.5	$-0.09$	7.00	9121	8980	141
	$\ell$	180	50	4.168	1303	16.12	23.29	23	$-0.20$	6.97	9082	8954	128
	$\mathcal{C}$	180	50	4.196	1303	16.50	23.70	23	$-115$	7.05	9186	9004	182
$\overline{c}$	$\alpha$	180	50	4.374	1303	16.30	23.87	24	$-17$	7.40	9642	9396	246
	$\downarrow \downarrow$	180	50	4.386	1303	16.24	23.78	24	$-18$	7.36	9590	9416	22/
$\overline{3}$	$\mathfrak{c}$	180	50	3.853	1303	17.03	23.79	23	$-.17$	6.59	8587	8377	210
	$\mathcal{U}$	180	50	3.837	1303	15.73	22.47	23	$-20$	6.54	8522	8130	392
$4\overline{6}$	$\epsilon$ a	180	52	4.102	1303	15.01	22.39	23	$-17$	7.21	9395	9165	230
	$\iota$	180	52	4.100	1303	15.02	22.39	24.5	$-18$	7.19	9369	9,160	209
$\overline{\mathcal{F}}$	$\alpha$	120	50	4.202	1303	17.69	22.47	23	$-10$	4.68	6098	6018	80
	$\ell$	120	50	4.189	1303	17.63	22.50	23.5	$- \cdot \frac{1}{2}$	4.76	6202	6000	202
		120	50	4.195	1303	17.73	22.53	25	$-.11$	4.69	6111	6008	103
	ld	120	50	4.192	1303	17.96	22.79	23.5	$-10$	4.73	6163	6004	159
6	$\alpha$	120	54	4.217	1303	17.00	22.24	22	$-0.07$	5.17	6736 6525	6525	211
	$l\ell$	120	54	4.240	1303	16.50	21.80	23	$-07$	5.23	6824 6534	6534	290

discrepancies are due to many sources of error, but the greatest of all is perhaps the amount of the cooling corrections and the variations in the difference of potential. On account of these, another series of blank-tests was made in which the duration of the operation proper was reduced to three minutes and two minutes. In order to prevent a rapid loss of heat by radiation, the initial temperature was brought down to such a point that the final temperature was about the same as the roomtemperature. In these tests, heat was gained, hence the amount of cooling correction should be subtracted from the observed rise of temperature. The one marked "B" on p.27, is used for the correction.

$$
T = t_2 - t_1 - \frac{r_1(\theta_2 - \theta_1)}{2}
$$

The amount of cooling correction is seen to be greatly reduced and hence better, but the results are still unsatisfactory as shown in table III

By comparing tables II and III. it will be seen that the cooling correction in the three-minute runs is smaller than that in the five-minute runs, and that in the two-minute runs smaller then that in the three-minute runs. But even in the two-minute runs the difference between the theoretical and the actual quantities of heat are too great and varied to be of value, hence a fourth series of blank-tests was made in which the duration of the operation proper was reduced to one minute. The initial temperature was brought sufficiently below the surrounding temperature so that the final temperature was little below it. The difference of potential between the two terminals was read three times a minute, that is, at 15, 30 and 45 seconds. Two examples will show the details of the observations made in all the subsequent tests.

### First Example.



#### First Example Cont'd.



+ Current turned on. \* Current turned off.

The temperature correction is computed as shown

on page... as follows:

 $r_1 = 0.004$  deg. C;  $r_2 = 0.01$  deg. C  $t<sub>2</sub> = 21.59$ ;  $t<sub>1</sub> = 8.92$ ;  $\theta<sub>1</sub> = 5$ ;  $\theta<sub>2</sub> = 9$  1/2;  $T = 21.59-18.92+ 0.004+010 \times 4$  1/2 = 2.70 deg. 0

The cooling correction should, in this case, be added to the observed rise of temperature as the amount of heat radiated was greater than that which was a bsorbed.

# Second Example.



Table 4

$NO.$ of	Time	Averaged difference	Current $1\pi$	Weightof water		Temperature of water in degree Centigrade		Actu amount	Theoretical amount $of$ <i>heat</i>	$\mathcal{I}$ ifference		
tests	1 <sub>H</sub> Second	potential rolt.	amp.	111 gram.	Initial	Final	$A$ oo $m$ $t_{em}$	$\begin{bmatrix} \cos(\pi a) \\ \cos(\pi a) \\ \cos(\pi a) \end{bmatrix}$	$Rise$ of temp.	ofheat	$qm-ca/$ $qm-ca/$	
	60	4.353	55	1303	18.69	21.46	23	$-07$	2.70	3518	3429	89
$\mathfrak{p}$	60	4.352	55	1303	19.25	21.98	23	$-.03$	2.70	3518	3428	90
3	60	4.374	55	1303	19.09	2181	23.5	$-0.05$	2.67	3479	3445	34
$\overline{A}$	60	4.371	55	1303	19.01	21.78	23	$-.05$	2.73	3557	3444	1/3
$\mathcal{F}_{0}$	60	4.351	55	1303		$18.93$ 21.64	23	$-.03$	2.68	3492	3427	65
6	60	4.354	55	1303	18.92	21.59	21.5	$+0.03$	2.70	3518	3430	88
$\tau$	60	4.367	55	1303	19.09	21.89	23	$-.05$	2.75	3583	3440	143
$\mathcal{B}_{0}$	60	4.384	55	1303		$19.48$ 22.29	25	$-.06$	2.75	3583	3453	130

Table 5

 $\mathcal{A}$ 



#### The tempersture correction is:

$$
r = 0.018 \text{ deg. 0; } r_2 = 0.004 \text{ deg. 0; } t_2 = 22.29; t_1 = 19.48; \theta_1 = 5;
$$
  
\n
$$
\theta_2 = 11 \text{ 1/2.}
$$
  
\n
$$
T = 22.29 - 19.48 - 0.018 + 0.004 (5 \text{ 1/2}) = 2.75 \text{ deg. 0}
$$

J 2)

The cooling correction, in this case, should be subtracted from the observed rise of temperature, as heat was gained from the surroundings.

The results obtained in this series of blanktests are given in table IV.

A perusal of the above results will show that there are still great discrepancies among them. These were due, in greater part, to two chief sources of error, first, that the initial temperature was brought too far below that of the surroundings, whieh rendered the amount of cooling correction uncertain and varied, and that. on account of the varistion of the difference of potential between the two terminals, three readings were not sufficient to give a fair average. In the next series, these two sources of error were nostly eliminated by adjusting the initial temperature just <sup>a</sup> little below the room-temperature, so that the final temperature was <sup>a</sup> little above it. and by reading the difference of potentisl between the two terminals as often and as accurately as possible

The results given in table V show the value of the change in the mode of operating as the duplicates check within the precision of measuring apparatus.

In this series, different platinum boats were employed in each pair of blank-tests. An inspection of the results

will show that the blank-constants, that is, the differences between the actual amount of heat and the theoretical amount of heat obtained in the blank-tests, agree in each case excellently, and that in every determination the actual amount of heat is greater than the theoretical. Four examples may serve to show the details of observation.

### First Example.



#### First Example Cont'd.



+ Current turned on # Current turned off

The corrected rise of temperature is calculated

as follows:

 $r_1 = 0.004$  deg. C ;  $r_2 = 0.006$  deg. C  $t_2$  = 26.03;  $t_1$  = 23.68;  $\theta_1$  = 5;  $\theta_2$  = 9 1/2  $T = 26.03-23.68 + 0.004+0.006 \times 4$  1/2 = 2.37 deg. 0  $\mathbf{2}$ 

 $40<sub>n</sub>$ 

# Second Example

 $\bar{\omega}$ 



+ Current turned on. \* Current turned off.  $r_1 = 24.51-24.49 = 0.02 = 0.004$  deg. C;  $r_2 = 26.90-26.89 = 0.01 = 0.002^{\circ}$ C<br>  $t_2 = 26.90$ ;  $t_1 = 24.51$ ;  $\theta_1 = 5$ ;  $\theta_2 = 9 \frac{1}{2}$ <br>  $\frac{5}{10}$  $r + r$ <sub>1</sub> × 4 1/2 = 0.014 deg. 0  $\overline{2}$ 

This amount should be subtracted from the observed rise of temperature, because the heat gained was greater than that which was lost.

# Third Example.



k

 $r_1$  = 0.006;  $r_2$  =0.000;  $t<sub>2</sub> = 23.60; t<sub>1</sub>=21.21; \theta<sub>1</sub>=5; \theta<sub>2</sub>=10$  $T = 23.60 - 21.21 - 0.006 \times 5 = 2.37$  deg. 0  $\overline{2}$ The amount of cooling correction should be added, for heat was gained at the beginning of the experiment.

# Fourth Example.



### Fourth Example Contrd.

 $r_1=0; r_2=0.002$  $t_2 = 26.00; t = 23.60; \theta_1 = 5; \theta_2 = 9$  $T = 26.00 - 23.60 + 0.002 \times 4 = 2.40$  deg. C  $\overline{2}$ 

#### 7. Fusion Tests.

It is seen that the conditions of the blank-tests have been greatly improved by the reduction of the amount of the cooling correction end by the more frequent readings of the voltmeter and that the results thus obtained were satisfactory.As in every blank-test there is <sup>a</sup> difference between the actual and the thecretical amount of neat. it is important to make <sup>a</sup> blank-test before <sup>a</sup> charge-test under the same conditions accurately. A duplicate blank-test was made in every case.

The heat formations of three singulo silicates of ferrous oxide and lime were determined and it was found that in every determination the formation evolved heat.

The results obtained in studying the heat formation of the singulo-silicate of the composition, 70.80 per cent FeO and 29.20 per cent SiO<sub>2</sub>, are given in table VI.

In every test, the charge was well fused, except in No. 1, where there was a small quantity at the two ends of the platinum boat which remained unfused. The result of Test No. 2 appears to be too high and should be discarded. Tests No. 3, 4, and 5 are in excellent agreement with one another. If the average of the last three results be taken, the amount of heat evolved by the formation of the silicate is 107 gram-calories per gram of charge.

Table 6<br>Singulo-Silicate



 $\tilde{\psi}$ 

### Details of the observations leading to the results

assembled in table VI are given in the following:

 $\lambda$ 

# Blank-Test No. 1 a.



#### Blank-Test No. 1 a cont'd.



# Current turned on. \* Current turned off.  $r_1$  = 22.07-22.05 = 0.02 = 0.004 deg. 0  $r_2 = 24.37-24.34 = 0.03 = 0.006$  deg. 0  $5$ 

Corrected temperature = 24.37-22.07 0.004+0.006 ×4=2.32 deg. 0  $\tilde{z}$ 

= 2.30 +,004 = 2.304 C

 $49 -$ 

# Blank-Test No. 1 b.



Blank-Test No. 1 b cont'd.



+ Current turned on. \* Current turned off.

 $r_1 = \frac{22.68 - 22.67}{5} = 0.01 = 0.002$  deg. C  $r_2$  = 24.98-24.94 = 0.04 = 0.008 deg. 0

Corrected temperature = 24.98-22.68+ 0.002+0.008 × 4.5 = 2.323 deg.C  $\tilde{2}$ 

= 2.30 +.018 = 2.318 C

#### Charge-Test No. 1



### Charge-Test No. 1 Cont'd.



+ Current turned on. \* Current turned off.

$$
r_{1} = \frac{23.12 - 23.11}{5} = \frac{0.01}{5} = 0.002 \text{ deg. } 0
$$
\n
$$
r_{2} = \frac{25.43 - 25.39}{5} = \frac{0.04}{5} = 0.008 \text{ deg. } 0
$$
\n
$$
5 = 54
$$
\nCorrected temperature = 25.43-23.12+ 01 × 5 = 2.335 deg. C

\n
$$
2 + 0.10
$$

 $25.43-23.12+\underbrace{0.002+0.008}_{} \times 5 = 2.335$  deg. C  $\overline{2}$ 

 $32.31 + .02 = 2.330$  C

#### Blank-Test No. 2 a.

 $\chi$ 

V.



÷,

 $\overline{r}$ 

### Blank-Test No. 2 a contide



Corrected temperature =  $27.48 - 25.28 - 0.003 + 0.002 \times 4 = 2.18$  deg. C  $\mathbf{c}$ 

 $5$ 

 $5$ 

= 2.20 = .012 = 2.188C
## Blank-Test No. 2 b.



### Blank-Test No. 2 b cont d.



+ Carrent turned on. \* Current turned off.

 $r_1 = 24.32 - 24.28 = 0.04 = 0.008$  deg.  $\circ$  $r_2 = 26.51 - 26.48 = 0.08 = 0.006$  deg. 0

 $+0075$  + Corrected temperature = 26.51-24.32- 0.008+0.006 x 4.5= 2.16 deg. C

=  $2.19 - 001 = 2.189$ 

 $\overline{2}$ 

### Charge-Test No. 2



 $\bar{z}$ 

### Charge-Test No. 2 cont d.

+ Current turned off # Current turned on.

$$
r_1 = 0
$$
  
\n
$$
r_2 = \frac{25.30 - 25.28}{5} = 0.02 = 0.004 \text{ deg. of}
$$

 $-1 - 2 + 1$ 

 $23.11$ Corrected temperature = 25.30-28.11 + 0.004+0 × 4.5 = 2.20 deg. 0  $\mathbf{2}$ 

# Blank-Test No. 3 a

 $\overline{\phantom{a}}$ 



×

#### Blank-Test No. 3 a cont d.

+ Carrent turned on \* Current turned off

 $r_1 = 23.50 - 23.47 = 0.03 = 0.006$  deg. C  $\overline{5}$  $r_2 = \frac{25.89 - 25.88}{5} = \frac{0.01}{5} = \frac{1}{6} .002$  deg. C

Corrected temperature = 25.89-23.50+0.002#0.006 × 4.5 = 2.37 deg. 0  $\mathbf{R}$ 

= 2.39 - 009 = 2.381 C

## Blank-Test No. 3b



#### Blank-Test No. 3 b Cont'd.

+ Carrent turned on # Carrent turned off.  $r_1 = 23.58 - 23.54 = 0.04 = 0.008$  deg. C 5 5  $r_2 = \frac{25.95 - 25.94}{5} = \frac{0.01}{5} = 0.002$  deg. C

Corrected temperature =  $25.95-23.58 - 0.008+0.002 \times 4.5 = 2.35$  deg. C  $\overline{c}$  $2.356C$ 

 $\sim 20$   $_{\odot}$ 



#### Charge-Test No. 3 Cont'd.

+ Current turned on. \* Current turned off.

 $\mathbf{r}$ 

$$
r_{1} = 23.51-23.48 = 0.03 = 0.006
$$
  
\n
$$
s_{2} = 25.91-25.90 = 0.01 = 0.002
$$
  
\n
$$
s_{3} = 5
$$
  
\n
$$
s_{4} = 5
$$
  
\n
$$
s_{5} = 5
$$

Corrected temperature = 25.91-23.51- $0.002+0.006 \times 5=2.38$  deg. C  $\overline{2}$ 

= 2.40 -.01 = 2.390 C



#### Blank-Test No. 4 a Cont'd.

+ Current turned on. # Current turned off.

 $r_1 = 22.40 - 22.41 = 0.01 = 0.002$  deg. C  $r_2 = 24.76 - 24.72 = 0.04 = 0.008$  deg. C  $5$  $5$ 

 $4.010$ Corrected temperature = 24.76-22.40+0.002+0.008 × 4.5 = 2.38 deg. C  $\mathbf{S}$ 

 $= 2.36 + .027 = .2.387C$ 

## Blank-Test No. 4 b

 $\sim$   $\star$ 

l.



 $\bar{1}$ 

### Blank-Test No. 4 b Cont'd.

+ Current turned on \* Current turned off N

$$
r_1 = \frac{23.59 - 23.58}{5} = \frac{0.01}{5} = 0.002 \text{ deg. C}
$$

 $r_{2} = 0$ 

Corrected temperature = 25.96-23.59-  $0.002+0 \times 4.5 = 2.37$  deg. C  $\overline{c}$ 

= 2.37 - .00' = 2.365 C

ł

## Charge-Test No. 4



### Charge-Test No. 4 a Contid.

x Current turned on # Current turned off

$$
r_1 = \frac{23.04 - 23.00}{5} = \frac{0.04}{5} = 0.008 \text{ deg. of}
$$

 $r_2 = \theta$ 

Corrected temperature = 25.50-23.04- $(0.008)$ ex 4.5 = 2.44 deg. C

## Blank-Test No. 5 a.



 $\overline{z}$ 



 $\frac{1}{2}$  ,  $\frac{1}{2}$  ,  $\frac{1}{2}$ 

# Charge-Test No. 5



The heat of formation of two other singulosilicates were next determined, their compositions were 12 per cent CaO+ 57.58 per cent FeO + 30.42 per cent SiO<sub>2</sub>, and 28 per cent CaO+  $40.30$  per cent FeO + 31.70 per cent SiO.

For the determination of the heat formation of these two silicates, calcium carbonate (CaCO<sub>2</sub>) was used, instead of calcium oxide (CaO), for the latter absorbs moisture and carbonicacid very readily. The amount of calcium carbonate required for the corresponding portion of calcium oxide was computed as follows: Mol. wt. of CaO: Mol. wt. of CaCO<sub>2</sub> = wt. of CaO: wt. of CaCO<sub>2</sub>. The amount of CaCO<sub>2</sub> corresponding 0.12 gm. CaO is

> $100.1 \times 0.12 = 0.2141$  gm. 56.1

The amount of CaCO<sub>2</sub> corresponding 0.28 gm. CaO is  $100.1 \times 0.28 = 0.4996$  gm.  $56.1$ 

The results of the heat formation of the above two silicates are given in the following tables VII and VIII.

Tables VII and VIII show show the quantity of heat evolved by the formation of these silicates. The amount of calcium carbonate used for the formation of the first silicate was 0.2141 gm. and the quantity of heat required to decompose it into CaO and CO<sub>2</sub> is 96<sup>\*</sup> gram-calcries. The amount of calcium carbonate for the formation of the sec-

\* J. W. Richards, Metallurgical Calculations Part I, p. 29  $Ed - 2$  Table 7



 $1 - 1$ 

 $1 - 1 - 1$ 

X

 $\lambda$ 

Table 8



# a small amount at the two ends of the boat remained unfused.

ond was 0.4996 gm. and the quantity of heat necessary to decompose it is 224 drem=calories, These quantities of heat should be added to the difference between the actual amount of heat and the theoretical amount obtained in the charge-tests, and the differences between the sums and the averaged blank constants give the heats of formation of the two silicates,

The amount of heat evolved by the formation of onegram mixture, 12 per cent CaO+57.58 per cent FeO+30.42 per cent SiO<sub>,</sub> is given in the last column of table VII. As the result of test No. 1 is too low and does not come within the precision of the method, it should be disregarded. Taking the average of tests No. 2 - 6, the heat of formation is 145 gram-calories for 1 gr. of mixture.

The quantity of heat evolved by the formation of one-gram mixture, 28 per cent Ca0+40.30 per cent Fe0+31.70  $SiO_{2}$ , is shown in table VIII. The result of test No. 3 is low; this was due largely to a portion of the charge remaining unfused. The results of tests No. 1. <sup>2</sup> and 4, appear to be satisfactory, and the average.of these results gives the heat of formation 192 gram-calories.

In performing the experiment, it often happened that when the fusion took place, the platinum boat fused at the instant when the charge became fused, This proved that the heat evolved raised the tempersture locally to above the melting point of platinum.

An inspection of tables VI, VII, and VIII will make it evident that:

76,

The actual amounts of heat in the blank- $1 -$ 

tests do not exactly agree with the theoretical, but are larger in every case.

2. The differences of these two quantities vary with the platinum boats used in making the blank-tests.

These discrepancies and variations are due to sources of error from various instruments. These sources, though eliminated as much as possible, may be caused by

> whe reading of the voltmeter  $1.$ The reading of the ammeter  $2.5$ The reading of the stop-watch  $3.1$ The reading of the thermometer  $4.$ The weighing of the water 5.

The specific heat of the calorimeter, the  $6.1$ combustion chamber and the stirrer.

7. The radiation of heat.

As the experimental errors may come in from numerous sources, exact agreement of results cannot be secured.

8. Conclusion.

The amount of heat evolved by the formation of the three ferro-calcic singulo silicates given in tables VI, VII and VIII, appears to increase with an increment of the percentage of CaO. and shows that a smooth curve would result if adequate data were obtained. On account of the fact that many difficulties were encountered and that the capacity of the apparatus was too small, data for the singulo silicates between 0 and 12 per cent CaO, and between 12 and 28 per cent

77.

CaO were not determined. In order to carry on such experiments with greater speed and accuracy, it would be necessary to have apparatus of larger capacity and instruments of greater delicacy, The charge night weigh <sup>5</sup> gm,as the amount of heat evolved would be sufficiently large to give characteristic values. This would require a larger platinum boat and a larger combustion chamber, hence also a larger namber of cells in the storage battery in order to farnish <sup>a</sup> larger sar»ant. The amount of water used is an imoortaat factor. In order to eliminate the loss of heat by radiation, the quantity of water ought to be such as to obtain <sup>a</sup> rise of tempsrature of only <sup>a</sup> few tenths of a degree C. This small rise of temperature will require a thermometer sensitive to 0.001 deg. C. Another important factor is that the current should be kept constant by an automatic device, instead of shifting the slider by hand. If the above conditions are fulfilled. this method used will give accurate results with ferro-calcic singulo silicates without including many failures, as was the case ia the oresent investigation.

Attempts were made to determine the heat of formation of the bi-silicate, 2FeO+SiO.. They were not successful, because the mixture required such <sup>a</sup> high temoeraturs for fusing, that the platinum boat melted in every case before the charge was completely fused. With another metal whose melting-point is a few hundred degrees hisher than that of the platinam and whose eondactivity is about the same, the determination of the heat formation of ths bi-silicate series ought to be carried to a successful end.

72,

The details of the observations leading to the results assembled in Table 7 are given in the following:

#### Blank-Test No. 1 a.



+ Current turned on. # Current turned off.

#### Blank-Test No. 1 a Con'd.

 $\sqrt{2}$ 

$$
r = \frac{20.41 - 20.39}{5} = .02 = 0.004 \text{ deg. } 0.
$$

 $r = 0$  $\mathcal{Z}$ 

Corrected temperature = 22.80-20.41-  $0.004 +0 x 5 = 2.38$  deg. 0

 $\circ$ 

 $\mathcal{I}$ 

 $\boldsymbol{I}$ 

 $\sqrt{}$ 

## Blank-Test No. 1 b.



 $\mathbf{C}$ .



 $\sim$ 

## Blank-Test No. 2 a.



# Blank-Test No. 2 b.



 $=2.43C$ 

deg. C

## Charge-Test No. 2



#### Blank-Test No. 3 a



Corrected temperature =  $23.27-20.90 + \frac{0.002+0.002}{2}x$  4.5 = 2.38<br>deg. 0

 $= 2.370$  C

#### Blank-Test No. 3 b.



 $\boldsymbol{z}$ 

Corrected temperature = 23.21-20.82-.004+0 x 4 = 2.38 deg. 0

## Charge-Test No. 3



## Blank-Test No. 4 a.


## Blank-Test No. 4 b.



 $\frac{2}{3}$ 

 $\bar{\ell}$ 

## Charge-Test No. 4.



## Blank-Test No. 5 a.



## Blank-Test No. 5 b.



 $\overline{C}$ 

## Charge-Test No. 5



 $94.$ 

 $\mathcal{C}$ 

 $=2.28C$ 

### Blank-Test No. 6 a.





u.

 $\sqrt{ }$ 

# Elank-Test 6b Cont'd.

+ Current turned on. \* Current turned off.

 $r_1 = 21.12 - 21.10 = .08$  = .004 deg. C

 $r_{2}$  = 0

Corrected temperature = 23.52 -21.12  $\neq$  .004 + 0  $\times$  5 = 2.39 deg C

## Charge-Test No. 6



 $\hat{\mathcal{C}}$ 

 $\lambda$ 

#### Charge-Test No. 6 Cont d.

+ Current turned on. \* Current turned off.

$$
r_1 = 21.22 - 21.20 = 0.02 = 0.004 \text{ deg. of } 5
$$
  

$$
r_2 = 0
$$

 $\mathbf{I}$ 

Corrected temperature = 23.55-21.22- 0.004+0 x 5.5 = 2.32 deg. C  $\overline{2}$ 

Details of the observations leading to the results assembled in table VIII.

### Blank-Test 1 a.



#### Blank-Test 1 a Contid.



+ Current turned on. \* Current turned off.

$$
r_1 = \frac{22.78 - 22.77}{5} = \frac{0.01}{5} = 0.002 \text{ deg. 0}
$$

$$
r_2 = \frac{25.20 - 25.18}{5} = \frac{0.02}{5} = 0.004 \text{ deg. 0}
$$

2.424 Corrected teperature = 25.20-22.78+  $0.002+0.004 \times 4 = 2.45$  deg. C  $\overline{a}$ 



102.

#### Blank-Test No. 1 b cont d.

+ Current turned on. \* Current turned off.

$$
r_1 = \frac{22.89 - 22.88}{5} = \frac{0.01}{5} = 0.002 \text{ deg. C}
$$

$$
r_{\circ} = 0
$$

Corrected temperature = 25.34-22.39-  $0.002+0 \times 4 = 2.45$  deg. C

 $\overline{2}$ 

### Charge-Test No. 1



 $104.$ 

 $\sqrt{}$ 

×,

#### Charge-Test No. 1 Cont d.

+ Current turned on. # Current turned off.

 $r_1 = 23.19 - 23.17 = 0.02 = 0.004$  deg. C  $\mathbf{r}_2 = \frac{25.50 - 25.49}{5} = \frac{0.01}{5} = \frac{1}{0.002}$  deg. 0 20305 Corrected temperature = 25.50-23.19- 0.004+0.002 × 5 = 2.395 deg. C  $\overline{2}$ 

 $105.$ 

 $\sqrt{}$ 

#### Blank-Test No. 2 a.



### Blank-Test No. 2 a Cont'd.

$$
r_1 = \frac{24.11 - 24.08}{5} = 0.03 = 0.006 \text{ deg. 0}
$$

$$
r_2 = \frac{26.63 - 26.61}{5} = 0.02 = 0.004 \text{ deg. C}
$$

 $\mathbf{1}$ 

Corrected temperature = 26.63-24.11  $\frac{1}{4}$  0.004+0.006 x 5 = 2.495 deg. C  $\overline{3}$ 

 $= 2.52 - 0.01 = 2.5152$ 

Blank-Test No. 2 b



 $\hat{\mathcal{A}}$ 

#### Blank-Test No. 2 b Cont'd.

$$
r_1 = \frac{23.59 - 23.57}{5} = \frac{0.02}{5} = 0.004 \text{ deg. of}
$$

 $r_2 = \frac{26.06 - 26.02}{5} = \frac{0.04}{5} = 0.008$  deg. 0

Corrected temperature =  $26.63 - 23.59 \times 0.004 + 0.008 \times 4.5 = 2.50$  deg. 0

= 2.47 + 009 = 2.479 C

## Charge-Test No. 2

 $\mathcal{A}$ 



# Charge-Test No. 2 Cont'd.

t Current turned on. # Current turned off.

 $r_1 = \frac{24.88 - 24.28}{1} = \frac{0.2}{1} = 0.004$  deg C  $r_2 = \frac{26.63 - 26.60}{5} = \frac{0.03}{5} = 0.006 \text{ deg } 0$ Conrected temperature = 26.68 - 24.23  $\frac{1}{4}$  0.006 x 5 = 2.4% deg C

 $2.35 + 105 = 2.355C$ 

# Plank-Test No. 3a.

 $\bar{\mathcal{A}}$ 



 $\sqrt{2}$ 

# Blank-Test No. 3a Cont'd.

Current turned on. \* Current turned off.  $^{+}$ 

 $r_1 = 22.63 - 22.67 = 0.01 = 0.002$  deg C

 $\bar{\nu}$ 

 $\frac{1}{\sqrt{2}}$ 

 $r_2 = 25.02 - 24.99 = 0.03 - 0.006$  deg C Corrected temperature = 25.02 -22.68 40.002 +0.003 x 4.5 = 2.36 deg C

= 2.34 + 0.9 = 2.35 C

Blank-Test No. 3b.



## Elank-Test No. 3b Cont'd.

+ Current turned on. # Current turned off.  $r_1 = \frac{22.30 - 22.73}{5} = \frac{0.02}{5} = 0.034 \text{ deg } 0$  $r_2 = \frac{25.19 - 25.13}{5} = \frac{0.01}{5} = 0.002$  deg C Corrected temperature =  $25.19 - 22.30 - 0.004 + 0.002 \times 4 = 2.38$ bdeg C



#### Charge-Test No. 3 Contid.

 $r_1 = 23.30 - 23.28 = 0.02 = 0.004$  deg. 0  $\overline{5}$  $5\overline{5}$  $\sqrt{}$ 

 $r_2 = 0$ 

Corrected temperature = 25.51 - 23.30 - 0.004+0 x 4.5 = 2.20 deg. C  $\overline{2}$ 



### Blank-Test No. 4 a Cont'd.

 $\overline{c}$ 

 $r_1 = 23.91 - 23.88 = 0.03 = 0.006$  deg. C<br>5  $r_2$  = 26.48-26.45 = 0.003 = 0;006 deg. 0  $5$ 5 Corrected temperature = 26.48-23.91  $\sqrt{0.006 \pm 0.006}$   $\times$  5 = 2.60 deg. 0

 $= 2.57 C$ 



## Blank-Test No. 4 b Cont'd.

$$
r_{1} = 24.21-24.18 = 0.03 = 0.006 \text{ deg. } 0
$$
  
\n
$$
r_{2} = 26.77-26.73 = 0.04 = 0.008 \text{ deg. } 0
$$
  
\n
$$
5 = 5
$$
  
\n
$$
6 =
$$

 $121.$ 

 $\mathcal{A}$ 

 $\mathcal{R}^{\text{max}}$ 



#### Charge-Test No. 4 Contid.

$$
r_1 = 24.71 - 24.70 = 0.01 = 0.002 \text{ deg. C}
$$
  
\n
$$
r_2 = 27.11 - 27.07 = 0.04 = 0.008 \text{ deg. C}
$$
  
\n
$$
5 = 5
$$
  
\n
$$
r_2 = 27.11 - 27.07 = 0.04 = 0.008 \text{ deg. C}
$$

Corrected temperature = 27.11-24.71  $\neq$  0.002+0.008  $\times$  5 = 2.48 deg. C  $\overline{2}$ 

= 2.40 + 015 = 2.415 C