

The

EQUILIBRIUM CONSTANT

of the reaction between

LIQUID IRON

and

HYDROGEN SULPHIDE.

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T H E S I S

submitted to the

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by

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for the

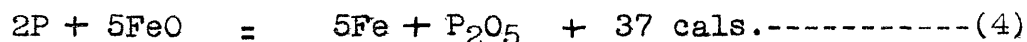
DEGREE OF DOCTOR OF PHILOSOPHY.

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INTRODUCTION.Balanced Reactions and Desulphurisation in the Basic Open-Hearth Furnace.

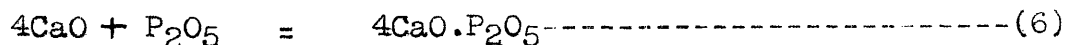
The reactions which bring about the removal of impurities from the bath of metal in the basic open-hearth furnace have been established in a qualitative manner. The following equations represent the principal reactions involved in the purification of the molten metal:



Besides these fundamental reactions, secondary reactions such as the following may occur:

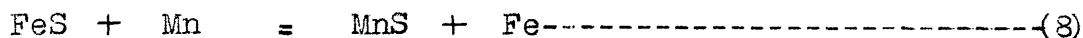


The different constituents of the slag also interact and produce compounds which may have a great influence on the process of purification. Thus the following reaction is possible:



The formation of tri-calcium phosphate is also possible, and the production of the tetra- or tri-calcium phosphate will probably depend on the amount of available lime in the slag. The removal of the impurities consists then essentially in the oxidation of the carbon, manganese, silicon, and phosphorus by means of iron oxide.

It is probable that the ferrous oxide also plays an important part in the removal of sulphur from the bath of molten metal. The chief desulphurising agents used are manganese and lime, and their actions may be represented by the equations:



Some of the MnS formed by reaction (8) rises into the slag where it is oxidised as follows:



The greater the amount of lime and the smaller the amount of ferrous oxide, the further will reaction (7) tend to go to completion towards the right. In other words, the larger the ratio CaO/FeO , the more sulphur will be transferred from the steel to the slag. Lime also combines with P_2O_5 to form $4\text{CaO} \cdot \text{P}_2\text{O}_5$, and the more lime there is the greater will be the amount of calcium phosphate produced. The P_2O_5 results from the oxidation of phosphorus by FeO, (equation (4)), and if there is an excess of lime in the slag, then the P_2O_5 will quickly combine with the lime to form $4\text{CaO} \cdot \text{P}_2\text{O}_5$. This will hasten the oxidation of the phosphorus and so the FeO content of the slag will fall. As the FeO also oxidises the manganese in the bath (equation (2)), then the amount of manganese in the bath will increase due to the decrease in the FeO content of the slag. Thus, it may be said that the effect of adding excess lime to the slag is to increase the amount of manganese in the bath. This manganese will then proceed to desulphurise as shown in equations (8) and (9). The transference of sulphur from metal to slag thus depends on the ratio $\text{CaO}/(\text{FeO} + \text{MnO})$.

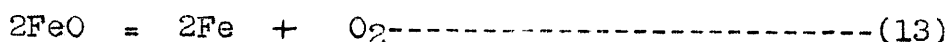
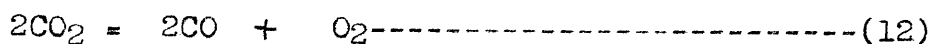
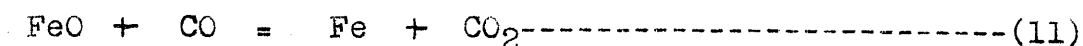
The active desulphurising agent then seems to be manganese which is present either as a direct addition or through the reduction of MnO from the slag. The ferrous oxide also plays an important part in the removal of sulphur, because the lower the FeO content of the slag, the less manganese will be oxidised and so there will be more of the latter available for desulphurisation. Moreover, when FeO is added to the bath it probably reacts with the MnS thus:



The FeS will remain dissolved in the metal, but the MnO will go to the slag and so the manganese content of the metal will decrease, with a consequent decrease in the process of desulphurisation.

Although the reactions which bring about the removal of impurities from the molten metal in the basic open-hearth process have been qualitatively established, much work has yet to be carried out on the physical chemical characteristics of these reactions. A wider and more accurate knowledge of the equilibrium constants of the balanced reactions is desirable, together with the effect on the reactions of various controlling factors, such as temperature and the constitution of the slag.

McCance⁽⁶⁾ has pointed out that different reactions which are interrelated have a characteristic property which can be used to derive values for the equilibrium constants. The following example is an illustration of McCance's technique. Consider the three equations:



If equation (11) is multiplied by two and added algebraically to (12), then equation (13) will result. A similar relationship will hold for the equilibrium constants of these reactions and therefore:

$$K_{13} = K_{11}^2 \cdot K_{12}$$

where K_{11} , K_{12} , and K_{13} are the respective equilibrium constants. Thus if K_{11} and K_{12} are known it is possible to derive a value for the equilibrium constant of the reaction representing the dissociation of ferrous oxide. This method cannot be used when the powers of the equilibrium constants on both sides of the equation are equal, because the equation then becomes an identity and is unsolvable.

The reaction between ferrous oxide and carbon is one of the most important in steel-making. It is the only one of the primary reactions (1) to (4) which is endothermic and some investigators have stated that it is confined to the higher temperatures of steel-making. The equilibrium constant of this reaction may be written:

$$K_1 = \frac{\text{Fe} \cdot P_{\text{CO}}}{\text{FeO} \cdot \text{C}}$$

where P_{CO} is the pressure of the carbon monoxide and is taken as a measure of its concentration. The concentration of iron in the steel bath will be little affected by the course of the reaction and it may be taken as constant. As the pressure of the carbon

monoxide will be limited to one atmosphere - above this pressure the excess gas will escape from the bath - then it may also be taken as being constant, and thus the following is obtained:

$$K'_1 = \text{FeO} \cdot \text{C}$$

Vacher and Hamilton⁽²⁾ obtained a value of 0.011 at 1620°C for this constant using weight percentages. The equilibrium stage of this reaction is influenced by the solution pressure of carbon monoxide and the dissociation pressure of ferrous oxide. Both of these are very low, and so the reaction proceeds until the carbon concentration is very small, as long as there is sufficient iron oxide available. The oxidation of the carbon by ferrous oxide has been discussed from the point of view of the bath only, but it is also necessary to consider the part played by the slag in this reaction. The ferrous oxide is dissolved in both the slag and the molten metal, and any variation in the iron oxide content of the slag will be communicated to the metal. The partition coefficient of the ferrous oxide between metal and slag may be represented by L_{FeO} and for practical purposes it can be taken as a constant depending only on temperature.

The equilibrium constant of reaction (2) may be written as:

$$K_2 = \frac{L_{\text{MnO}}}{L_{\text{FeO}}} \cdot \frac{(\text{MnO}) [\text{Fe}]}{(\text{FeO}) [\text{Mn}]},$$

where L_{MnO} is the partition coefficient of MnO between metal and slag, and () indicates the concentration of constituents in the slag, and [] the concentration of constituents in the metal.

The concentration of the iron may again be taken as constant and

thus:

$$K'_2 = \frac{L_{\text{MnO}}}{L_{\text{FeO}}} \cdot \frac{(\text{MnO})}{(\text{FeO}) [\text{Mn}]}$$

This equation indicates that the concentration of manganese in the metal is dependent on the ratio of the MnO to the FeO in the slag. Mc Cance⁽³⁾, by plotting many practical results, has shown that this theory is supported by experimental evidence. Körber and Oelsen⁽⁴⁾ give the following equation as representing the variation of the constant with temperature:

$$\log K'_2 = \frac{6234}{T} - 1.026$$

In basic open-hearth furnace practice it is found that silicon is the first element to be oxidised and this fact supports the thermochemical data. The equilibrium constant of the reaction (equation (3)) by which silicon is removed is as follows:

$$K_3 = \frac{\text{Fe}^2 \cdot \text{SiO}_2}{\text{Si} \cdot \text{FeO}^2}$$

The silica formed is probably insoluble in the steel bath, and its concentration in the steel may be taken as constant, as may also the concentration of the iron. Thus we have:

$$K'_3 = \text{Si} \cdot \text{FeO}^2 \propto \frac{1}{K_3}$$

Mc Cance⁽¹⁾ deduced theoretical values for this constant and obtained a value of $0.56 \cdot 10^{-4}$ for K'_3 at 1600°C on a percentage weight basis. The best experimental results are those of Körber and Oelsen⁽⁵⁾, whose value for K'_3 at 1600°C is $7.1 \cdot 10^{-4}$. Their equation for the variation of the constant temperature is as follows:

$$\log K'_3 = \frac{-32.360}{T} + 14.153$$

The phosphorus pentoxide formed through the oxidation of the phosphorus by the iron oxide (equation (4)) is unstable and may be attacked by carbon as shown by reaction (5). As carbon monoxide is formed as a result of this attack, the reaction is limited only by the low solubility pressure of the gas. Thus most of the phosphorus will return to the metal unless the phosphorus pentoxide is 'protected' from the action of the carbon. In the acid open-hearth process no such precaution is taken and the removal of phosphorus from the steel is impossible. However, in the basic process the lime which is added combines with the phosphorus pentoxide to form the calcium phosphate, $4\text{CaO} \cdot \text{P}_2\text{O}_5$, which is unattacked by the carbon. The oxidation and removal of the phosphorus to the slag can then proceed according to equation (4). The equilibrium constant of this reaction should be:

$$K_4 = \frac{\text{Fe}^5 \cdot \text{P}_2\text{O}_5}{\text{P}^2 \cdot \text{FeO}^5}$$

As has been indicated the reaction is greatly influenced by the presence of lime in the slag, and experimental results show that the ratio of phosphorus pentoxide in the slag to phosphorus in the metal increases as the lime content of the slag is increased. The results of the many investigations carried out on this reaction show great divergence and no quantitative conclusion can be deduced from them. It may be said that, as the reaction is exothermic, the value of the equilibrium constant increases with fall in temperature, and therefore more phosphorus will be oxidised at a low than a high temperature.

It has been pointed out that manganese is used as a desulphurising agent. An addition is made to the bath in the form of ferro-manganese and the manganese reacts with the iron sulphide as indicated in equation (8). The concentration of the iron may be again taken as constant and so we have:

$$K_8 = \frac{\text{MnS}}{\text{FeS.Mn}} .$$

If the iron is saturated with manganese sulphide at any definite temperature then the concentration of this compound may be neglected and we may write:

$$K'_8 = \text{S.Mn},$$

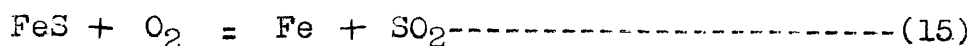
where the concentration of the sulphur is substituted for that of iron sulphide. Saturation of the metal with manganese sulphide must be assured in experimental work by having present high percentages of manganese and sulphur. By studying the results of various investigators of this reaction M^c Cance⁽³⁾ has derived the following equation for the variation of this equilibrium constant with temperature:

$$\log K'_8 = \frac{-6100}{T} + 3.67$$

This equation does not apply to steels which contain so little sulphur that they are far from being saturated with manganese sulphide. When the metal bath is covered by a slag which can dissolve manganese sulphide then the partition coefficient of the sulphide between metal and slag will largely influence K'_8 .

The problem of the desulphurisation of the bath in the open-hearth process has so far been discussed mainly from the point of view of the slag only, but the distribution of the sulphur between

metal and gas is an extremely important one in basic open-hearth furnace practice. The following reactions between gas and metal are fundamental sulphur reactions in the open-hearth process:



These reactions are reversible and, given, time, equilibrium will be reached in each case.

Investigations of the equilibrium of the reaction between iron and hydrogen sulphide have been carried out by Jellinck and Zakowski⁽⁶⁾, Britzke and Kapustinsky⁽⁷⁾, and Bierner⁽⁸⁾, respectively, but these were concerned only with equilibria at temperatures below the melting-point of iron.

Maurer and Bischof⁽⁹⁾ studied how the sulphur in the gas, in the form of hydrogen sulphide or sulphur dioxide, reacts with liquid steel containing sulphur. The equilibrium points of the two reactions and their dependence on the temperature were determined for sulphur contents in the molten iron of up to 30%. They circulated mixtures of known composition of $\text{H}_2\text{S}/\text{H}_2$, and SO_2/O_2 , respectively, over molten mixtures of iron and iron sulphide at different temperatures. The equilibria were approached from both sides of the equations. They evaluated a large number of practical operating analyses, and they concluded that the reaction with sulphur dioxide was the chief controlling factor of sulphur absorption or desulphurisation in the open-hearth process. The ratio of hydrogen sulphide to hydrogen in the fuel gas, they concluded, was of no aid in deducing any effect on the sulphur

content of the steel bath. Maurer and Bischof also made observations in practical operation concerning the dependence of the sulphur content of the bath on the ratio of the sulphur to the oxygen in the waste gas, and they claimed that these observations gave Chipman's history agreement with the test results.

Chipman has carried out an investigation of the condition of equilibrium in reaction (14). Values of the equilibrium constant were obtained for temperatures above the melting-point of iron. The iron was melted in a high-frequency induction furnace in a gaseous mixture of hydrogen sulphide and hydrogen of known composition. Chipman assumed that equilibrium had been established when the composition of the gas flowing from the furnace was the same as that entering it. At this stage the melt was quenched by suddenly cutting off the power supply of the furnace. The iron was then analysed chemically for sulphur. The equilibrium point was approached from the high-sulphur and low-sulphur sides. The experimental data obtained by Chipman are summarised by the equation:

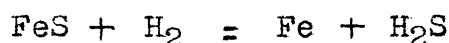
$$\log K = \frac{-4,500}{T} + 0.095,$$

where $K = \frac{H_2S}{H_2}$ (volume ratio) $\times \frac{1}{\%S \text{ in melt}}$.

Thus at 1535°C, $K = 0.0041$. It is worthy of note that Maurer and Bischof's values are about one hundred times as large as this. Chipman states that the free lime is the most important variable in the desulphurisation of liquid steel by slag in the open-hearth process. He also concludes that the desulphurising power of

metallic manganese is essentially equivalent to that of an equilibrium amount of manganese oxide in the slag.

At the present time the tendency in metallurgical research is toward the application of the methods of thermodynamics to metallurgical reactions. The use of thermodynamic methods can contribute greatly to investigations into the behaviour of sulphur in the basic open-hearth furnace, and may perhaps result in a better understanding of the methods of sulphur-control in open-hearth operation. An accurate determination of the value, and variation with temperature, of the equilibrium constant of the reaction:



may will enable the knowledge of desulphurisation to be placed on a more quantitative basis. As has been indicated, the equilibrium constant of this reaction has been investigated by Maurer and Bischof⁽⁹⁾, and Chipman⁽¹⁰⁾ at liquid iron temperatures. Unfortunately, the former's values for the constant are about one hundred times as large as Chipman's values. Because of this it seemed desirable to re-investigate the reaction. The following is an account of such an investigation.

PRINCIPLE OF METHOD

When pure iron is melted in an atmosphere of hydrogen sulphide and hydrogen the metal picks up sulphur from the gas mixture. The sulphur combines with some of the iron to form iron sulphide which is miscible in all proportions with liquid iron. The molten iron will continue to pick up sulphur until a state of equilibrium has been reached, which will be indicated by the percentage of hydrogen sulphide in the gas mixture remaining constant. At equilibrium, the total amount of sulphur in the iron will remain the same, providing that the temperature and the composition of the gas supplied are not altered. The reaction between the iron and the hydrogen sulphide will still be proceeding, but as the iron displaces hydrogen from some of the hydrogen sulphide so, simultaneously, some hydrogen will recombine with sulphur in the melt to produce an equivalent amount of hydrogen sulphide. This state of affairs can be aptly described as a state of "dynamic equilibrium". If the melt were quenched at this stage, then the resulting solid would contain the equilibrium amount of sulphur. Knowing the percentage of sulphur in the melt, and the composition of the gas mixture, it would then be possible to calculate the equilibrium constant for that temperature. This is an application of a well-known method of determining equilibrium constants, and the method is often referred to as "freezing the equilibrium"

This was the principle of the methods used by Maurer and Bischof⁽⁹⁾, and Chipman⁽¹⁰⁾, respectively.

If the iron could be weighed at intervals during the course of the reaction, it would be possible to record the rate of pick-up of sulphur and to note it decreasing progressively as equilibrium was approached. At equilibrium, the weight of the melt would remain constant and, as the gain in weight of the iron would be due to sulphur picked up, the equilibrium constant could be readily calculated. If necessary, the melt could be quenched and then weighed at room temperature in order to check the high-temperature weighing. This is the principle of the method which was used in the present investigation. It is the method of the "High-Temperature Balance", and was previously used to good effect by White⁽¹¹⁾ in research on equilibrium at high temperatures in systems containing iron oxides.

APPARATUS

Furnace and Balance

The source of heat was a molybdenum - wound alundum tube which was placed vertically inside a steel casing. This type of furnace has been described many times previously. The molybdenum wire was heated in an atmosphere of nitrogen and hydrogen, which was obtained by cracking ammonia over iron turnings heated to about 900°C in a nichrome furnace.

The actual melting and weighing operations were carried out inside a refractory tube which was fixed vertically in the furnace and projected out about 38 cms. at the top and about 18 cms at the bottom. The insertion of this tube in the furnace permitted the use of controlled atmospheres. The tubes used were of slightly smaller diameter than the alundum furnace tube, so that the top annular space between the tubes could be tightly packed round with asbestos wool. The bottom annular space between the refractory tube and the steel casing was plastered up with a mixture of alundum and asbestos. These precautions helped to prevent air escaping into the furnace casing and oxidising the molybdenum winding.

The refractory tubes used in the earlier experimental work were of Pythagoras composition, and, although it begins to soften above 1450°C, it can endure temperatures up to at least 1650°C. Furthermore, it is impervious to gases and it is not attacked chemically by hydrogen or hydrogen sulphide. However, if too

great a strain is placed on a Pythagoras tube at temperatures above 1450°C , then it is liable to crack. Great care had therefore to be observed when heating and cooling the tube. It was found that the best method of avoiding undue strain was to first suspend the tube inside the furnace so that it hung freely. The tube was suspended from two cords which were tied to a wooden board above the furnace. These cord suspensions passed through a steel ring which was screwed around the Pythagoras, near its top end. The bottom annular space between the outside of the Pythagoras and the steel casing was then plastered up as already mentioned. When the furnace was being heated, the cord suspensions were kept fairly taut and this prevented too heavy a load from bearing on the hottest, and therefore weakest, part of the tube. When the furnace was being cooled, the suspensions were slackened progressively, so that the tube cooled without being unduly strained.

Despite these precautions, breakages of tubes occurred owing to the embrittlement of the outside surface of the tubes, caused by many hours heating at over 1530°C . Some tubes also failed because of spalling. Pythagoras is a German product and latterly it was not possible to obtain the tubes. Morganite tubes, a British make, were therefore tried and they proved to be every bit as good. The same precautions were taken with the Morganite tubes as described for the Pythagoras tubes.

The balance for taking the weighings was placed on a wooden shelf which passed over the furnace. The arrangement of balance

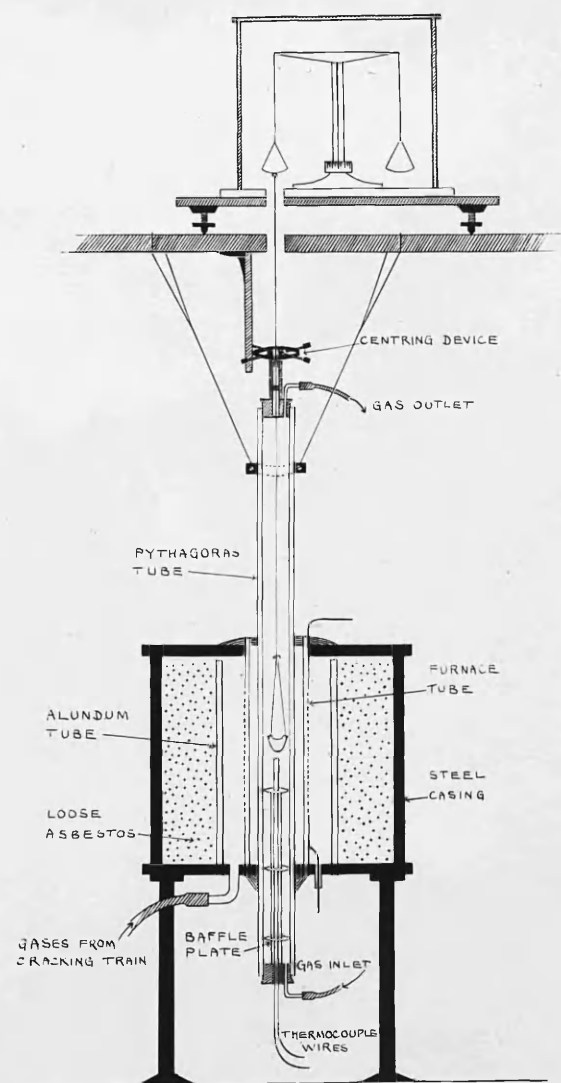


FIG. 1 - BALANCE AND FURNACE.

and furnace is shown in fig. 1. The balance used was a very sensitive assay balance which had been suitably modified.

Baffle plates made of alundum were fitted inside the lower part of the refractory tube in order to prevent draughts from affecting the weighings. These baffles also protected the lower rubber bung from excessive heat. The first baffle plates made were fitted to an alundum cylinder. This cylinder was made so that its external diameter was slightly less than the internal diameter of the refractory tube. The top end of the cylinder was closed by a baffle plate consisting of a thin disc of alundum. Another disc was fitted into the tube at the middle. A hole was cut in the centre of each of the baffles so that the Pythagoras sheath (which enclosed the thermocouple wires) could pass through them. This sheath projected about 3 cms. above the top of the cylinder, and the latter, which was open at the bottom, rested on the lower rubber bung. This type of baffle system was later altered in order to reduce the amount of alundum inside the reaction tube. In the new system, a long narrow tube of alundum was made so that it fitted loosely over the Pythagoras sheath. This tube was cut into three parts and each piece was used to support a baffle plate. This arrangement can be seen in fig. 1.

The crucibles used throughout all the experiments were made by the investigator. They were composed of a mixture of ten parts of coarse to one part of fine alundum. When alundum is mixed with water it becomes plastic and it is then possible to mould it. The crucibles were first moulded to the rough shape.



FIG.2 - CRUCIBLE WITH MELT.

The alundum was then dried, this being carried out slowly in order to prevent cracking. The roughly-shaped crucibles were next sand-papered down to the appropriate size, and were given a preliminary firing at 1000°C in a gas muffle. They were then fired at about 1600°C in an atmosphere of hydrogen in the molybdenum furnace.

The type of crucible used in the investigations is illustrated in fig. 2. The dimensions of these crucibles were approximately as follows: 2.5 cms. high, 3 cms. top diameter, and 1.5 cms. bottom diameter. The average weight of the crucibles was about 15 gms.

The greater length of the wire used to suspend the crucible inside the reaction tube was composed of platinum. The platinum wire was hooked to the left-hand pan of the balance, and extended to about 17.5 cms. from the top of the hot zone of the furnace. The remainder of the suspension consisted of two equal lengths of molybdenum wire (0.04 inch diameter) which were hooked through the two holes in the crucible. The platinum wire consisted of two different sizes; the lower part was 1.0 mm. diameter and 15 cms. long, and the remainder consisted of platinum wire of 0.5 mm. diameter. The suspension was made of such a length that the crucible which was hooked to it swung just clear of the top of the Pythagoras sheath (enclosing the thermocouple wires) when the left-hand pan of the balance was at the lowest part of its swing.

Weighing Device.

In previous work with the "high-temperature balance" (White^(u)) the balance was enclosed in a specially constructed bell-jar. The latter was connected to a Pythagoras tube by means of wide

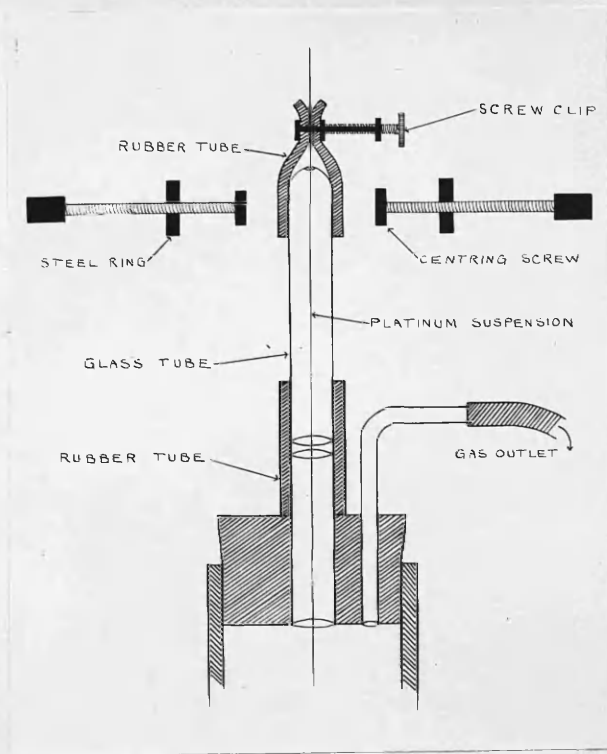


FIG.3 — CENTRING DEVICE (CLOSED).

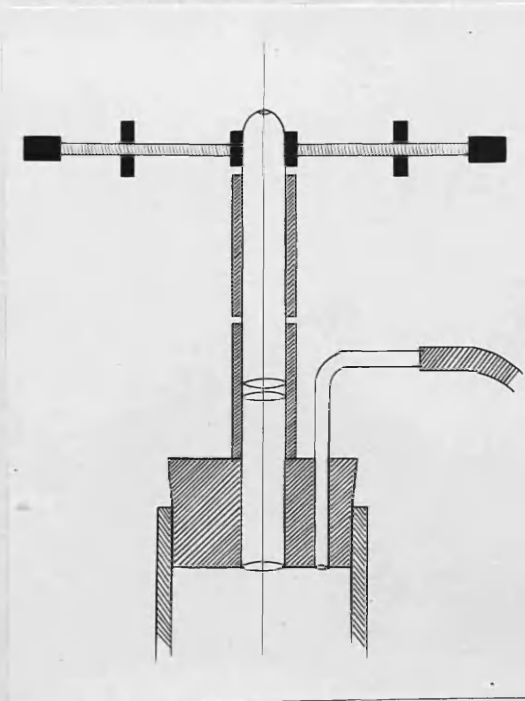


FIG.4 — CENTRING DEVICE (OPEN).

glass tubing down which the suspension hung. By this means, weighing at high temperatures in special atmospheres was comparatively easy. In this arrangement the balance was enclosed in the controlled atmosphere. This method was suitable for the present work provided that steps were taken to protect the balance from the chemical action of the hydrogen sulphide, which would be a component of the special atmosphere. At first, attempts were made to try and protect the balance by coating it with a thin film of collodion. A specially-constructed tube, containing copper phosphate for the removal of hydrogen sulphide, was also made for insertion between the balance and the furnace. However, it was not necessary in the present investigation to make the balance a part of the controlled atmosphere. It was decided, therefore, to confine the hydrogen sulphide/hydrogen atmosphere to the reaction tube, and to permit the gases to pass through an outlet tube fitted into the top bung of the tube. This introduced the difficulty of carrying out weighings when the iron was being heated at over 1530°C in a hydrogen sulphide/hydrogen mixture of definite composition. The difficulty was overcome by fitting a special device into the top rubber bung. This arrangement is illustrated in figs. 3 and 4. A glass tube of about 12 mms. diameter, with a very small hole at one end, was inserted centrally, with the orifice at the top, into a hole in the bung. The platinum suspension wire passed through this tube. The orifice could be sealed by slipping a short piece of tight-fitting rubber tubing over the glass tube and clipping the rubber by means of a

screw-clip, as shown in fig. 3. When the orifice was thus sealed, the gas mixture passed through the outlet tube. When a weighing had to be carried out the clip was undone and the rubber tube was slipped down the glass tube until it was clear of the orifice (see fig. 4). The gas mixture then escaped into the atmosphere but, as the amount of hydrogen sulphide in the mixture was always fairly low, there was never any strong smell of hydrogen sulphide in the air. Before an accurate weighing could be made, it was first of all necessary to centre the glass tube so that the suspension wire did not touch it at any point, especially at the orifice. This was readily accomplished by means of centring screws as illustrated in fig. 4. The centring device consisted of a steel ring, 8 cms. diameter, containing four equidistant holes through which passed steel screws, 6.5 cms. long. The ring was screwed to a wooden bracket which was fastened to the board above the furnace. This bracket can be seen in fig. 1 (facing page 16). To facilitate the removal of the bung and glass tube from the refractory tube, part of the steel ring was cut away. In order that the glass tube could be centred from extreme positions without any strain being put on it, it was cut in two and the two parts were connected together by a short piece of rubber tubing, as shown in the diagrams. It was found that when the orifice was sealed by the rubber tube and the screw-clip there was no leakage of gas through the weighing device.

Temperature Determination and Control

The temperature inside the reaction tube was determined by means of a platinum/platinum-rhodium thermocouple which was connected to a Tinsley vernier potentiometer. The thermocouple wires were enclosed inside a narrow sheath of Pythagoras composition in order to protect them from the action of the hydrogen sulphide and hydrogen. The sheath passed through a central hole in the rubber bung which was fitted into the lower end of the reaction tube. The Pythagoras sheath was 50 cms. long and 0.6 cm. diameter. It was fixed at such a height that the top of the thermocouple wires were just below the middle of the hot zone of the furnace.

The thermocouple was calibrated against the melting-points of silver, gold, and palladium, respectively.

In the method adopted for calibration, the "hot" ends of the thermocouple wires were connected by a short piece of silver, gold, or palladium wire. The thermocouple was then lowered through the top of the refractory tube until the ends of the wires were in the hot zone of the furnace. At the melting-point of the wire connecting the thermocouple wires, the ends of the thermocouple broke apart and the potentiometer ceased recording. The reading on the potentiometer was then noted. The thermocouple was calibrated before use and the calibration was checked at intervals during the course of the investigation.

When it was fixed in position inside the Pythagoras sheath the thermocouple was checked against the melting-points of silver, gold, palladium, and dicalcium ferrite, respectively. A small

stirrup, made of alundum, was lowered through the top end of the refractory tube, a small piece of silver wire having been laid across the stirrup. The alundum stirrup was lowered by means of a length of platinum wire until it was just touching the top of the Pythagoras sheath. The stirrup was then allowed to remain in that position. The furnace was heated very slowly as the temperature approached the melting-point of silver, and the wire was continually kept under observation. At the temperature of the melting-point the wire melted and broke and, at that stage, the reading on the potentiometer was noted. The process was repeated using gold and palladium wires. When using the dicalcium ferrite, a large crystal of the compound was selected and this was placed in a small platinum basket, which was lowered into the refractory tube. The melting of the crystal could then be clearly observed.

The temperature of the furnace was controlled by means of a variable resistance. By judicious use of this resistance, it was possible to maintain the furnace at a constant temperature.

Gas System

The gas mixtures of hydrogen sulphide and hydrogen were contained under pressure in a glass carboy with a capacity of about forty-five litres. This vessel was thoroughly cleaned and dried before starting to use it. It was contained in an iron basket and was packed round with straw. A rubber bung, containing two right-angled glass tubes, was fitted into the carboy.

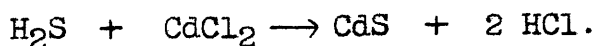
To prepare a gas mixture, the carboy was first of all evacuated by means of a Cenco-Hyvac pump which was capable of producing

a vacuum of 0.001 mm. mercury. A small amount of hydrogen sulphide, obtained from a Kipp's apparatus, was then passed into the vessel. Before passing into the carboy, the hydrogen sulphide was cleaned by bubbling it through water and it was then dried by passing it through a flask which contained calcium chloride. The rate of flow of the gas into the large evacuated reservoir would normally be very fast, but the flow was considerably reduced by inserting a fine glass jet into the rubber tubing which connected the reservoir to the drying-flask. The flow of the gas was controlled by means of a stop-cock which was also fitted into the rubber connection. It was thus possible to carry out an efficient cleaning and drying of the hydrogen sulphide before it finally entered the reservoir. After the requisite amount of hydrogen sulphide had been admitted into the carboy, hydrogen from a cylinder was passed in until the pressure inside the reservoir was about two atmospheres.

The carboy was connected by means of rubber tubing to a glass inlet tube which was fitted into the bottom bung in the reaction tube. The latter was connected to a manometer by means of a glass T-piece, and it was first evacuated before the gas mixture was admitted. After going through the reaction tube, the hydrogen sulphide/hydrogen mixture passed into a trap and then bubbled through a little water which was contained in a flask. The mixture was then allowed to escape into the air through a window. Between the trap and the flask containing water a T-piece was inserted so that the outgoing gas could be analysed as desired.

When the reservoir was being evacuated, the gas mixture was passed through a long glass cylinder which contained pumice-stone chips impregnated with copper phosphate. This removed the hydrogen sulphide and so prevented the pump from being damaged by chemical attack.

The carboy was connected to a mercury manometer and, by noting the pressure readings during the preparation of a gas mixture, it was possible to obtain a good approximation of the composition of the mixture. The true composition was obtained by chemical analysis. For this purpose a gas-analysis apparatus was made and this was connected to the reservoir when it was desired to carry out an analysis. This piece of apparatus consisted of two boiling tubes, each containing an ammoniacal solution of cadmium chloride, which were connected to each other by means of glass and rubber tubing. One of the boiling tubes was connected to an aspirator containing water, and the other tube was connected to the reservoir. In carrying out an analysis, the gas mixture in the carboy was bubbled slowly through the cadmium chloride solutions. The rate of flow of the gas mixture was diminished by passing it through a fine glass jet, and it was controlled by means of a stop-cock. All the hydrogen sulphide in the gas mixture reacted with the cadmium chloride, and cadmium sulphide was precipitated according to the equation:



As the solution was strongly ammoniacal, the reverse reaction could not take place. The hydrogen alone then passed into the

aspirator where it displaced an equal volume of water into a measuring cylinder. Although two glass tubes containing cadmium chloride solution were used in the analysis apparatus, only the first one ever contained any precipitate of cadmium sulphide. This was because the rate of flow of the gases through the tubes was always maintained slow so as to ensure that all of the hydrogen sulphide reacted with the cadmium chloride. When a gas mixture containing a very low percentage of hydrogen sulphide was being analysed, a large volume of the mixture was used in order to give a sufficiently large precipitate of cadmium sulphide. The cadmium chloride solution consisted of 22 gms. CdCl_2 , $2\text{H}_2\text{O}$, 520 c.cs. distilled water, and 480 c.cs. ammonia (specific gravity, 0.90). 50 c.cs. of this solution were capable of precipitating approximately 0.175 gm. sulphur evolved as hydrogen sulphide.

When a sufficiently large precipitate of cadmium sulphide had been formed, the passage of the gas mixture was stopped. The precipitate was dissolved slowly in hydrochloric acid and the liberated hydrogen sulphide was titrated rapidly against standard iodine solution, using starch as an indicator. The strength of the iodine solution was in the region of N/60 and it was standardised at frequent intervals against tartar-emetic. Only freshly-prepared starch solution was used as an indicator.

The method of calculating the ratio of the volume of hydrogen sulphide to 100 c.cs. hydrogen in the gas mixture was as follows:

Let v = volume (c.cs.) of iodine solution used in the titration,

F = normality factor of the iodine solution,

T = temperature ($^{\circ}$ Absolute) of the hydrogen,

P = atmospheric pressure (mms.),

w = water-vapour pressure (mms.) at T $^{\circ}$ Absolute,

V = volume (c.cs.) of water displaced by the hydrogen.

Since one litre of normal iodine solution is equivalent to 11.2 litres of hydrogen sulphide at 0°C and 760 mms., then:

$$v \text{ c.cs. of } F - \text{normal iodine solution} = \left(\frac{11200 \cdot v \cdot F}{1000} \right) \text{ c.cs. H}_2\text{S},$$

at 0°C and 760 mms. pressure.

i.e.,

$$v \text{ c.cs. of } F - \text{normal iodine solution} = \left(\frac{11.2 \cdot v \cdot F \cdot T \cdot 760}{273 \cdot (P-w)} \right) \text{ c.cs. H}_2\text{S},$$

at T° Absolute and $(P-w)$ mms. pressure.

As this volume of hydrogen sulphide is present in the mixture for every V c.cs. of hydrogen, then:

$$\frac{\text{Volume of H}_2\text{S (c.cs.)}}{100 \text{ c.cs. H}_2} = \frac{11.2 \cdot v \cdot F \cdot T \cdot 760 \cdot 100}{273 \cdot (P-w) \cdot V}$$

By evaluating the various constants, this formula may be simplified to the form:

$$\frac{\text{Volume of H}_2\text{S}}{100 \text{ c.cs. H}_2} = \frac{3118 \cdot v \cdot F \cdot T}{(P-w) \cdot V}$$

PRELIMINARY INVESTIGATIONS

Before any exact determinations of the equilibrium constant were attempted it was necessary to carry out some preliminary investigations.

It was first of all desirable to investigate what would be the effect on the weight of an alundum crucible of heating it to over 1530°C in atmospheres of hydrogen, and hydrogen sulphide/hydrogen, respectively. On first heating in hydrogen the crucible lost weight appreciably but after about five or six hours its weight became constant. The total loss in weight of the crucible was about 0.05 gm. and practically all of this was probably water which was driven out of the alundum at the high temperature. When this crucible was heated in a gas mixture containing a larger percentage of hydrogen sulphide than was later to be used in the investigations, its weight remained practically constant after heating for about six hours at over 1530°C . Before a crucible was used it was heated in hydrogen at 1550°C - 1600°C until its weight had become constant.

In spite of these satisfactory results it was thought desirable to investigate the effect on the crucible of heating it with molten iron in a gas mixture. In such a circumstance there was a possibility that the alundum crucible could pick up sulphur through the iron sulphide in the iron fluxing with the crucible. To test this, a crucible which had been used in many runs with

molten iron was broken up and part of it was weighed. The broken part was then roasted in air, cooled, and re-weighed. The results showed that there had been a slight gain in weight. This pick-up was probably due to oxidation of iron, which is present in small amounts in alundum. No sulphur dioxide was detected during the roasting. Part of another crucible, which had also been used in many runs with molten iron in gas mixtures, was crushed to a fine powder. Part of the powdered alundum was boiled up with hydrochloric acid (equal volumes of concentrated acid and water) in a conical flask. In order to determine if hydrogen sulphide would be evolved, the flask was connected to a glass vessel which contained ammoniacal cadmium chloride solution. No precipitate of cadmium sulphide was formed after boiling for several minutes. A wet-analysis was carried out on another portion of the powder and no sulphur was found to be present. It was therefore concluded that there was no danger of the crucible picking up sulphur when heated, either alone or in contact with molten iron, in a hydrogen sulphide/hydrogen atmosphere. This meant that the total gain in weight of a crucible and melt, after heating in a gas mixture, could reasonably be attributed solely to sulphur picked up by the melt. Confirmation of this was obtained when melts were quenched and analysed for sulphur. The sulphur obtained from the analysis showed good agreement with the percentage sulphur calculated from the total gain in weight of crucible and melt.

Crucibles which had been used in many runs showed no sign of chemical attack. Frequently it was found that when the melt was

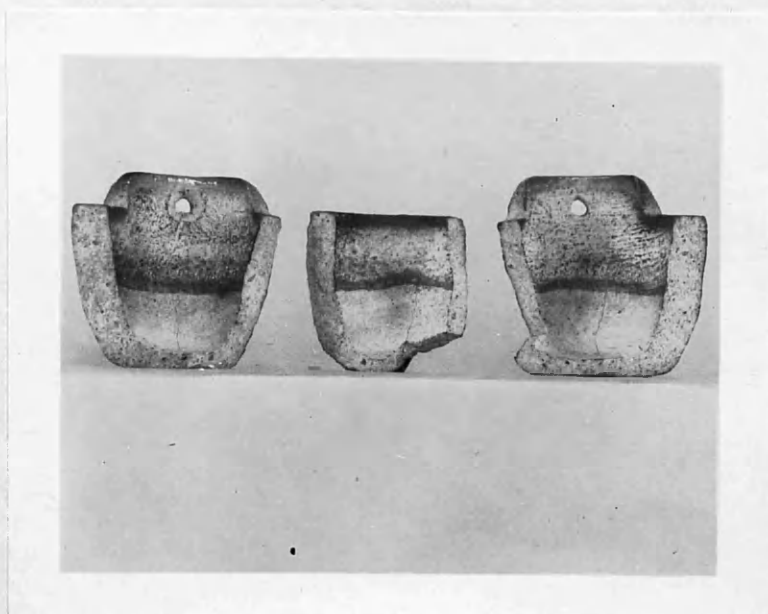


FIG. 5 - INSIDE OF CRUCIBLE AFTER USE.

taken out of the crucible, small particles of alundum adhered to that part of the melt which had been in contact with the crucible, but this was a physical action. The crucibles also remained clean; apart from a dark ring around the inner surface at a height corresponding approximately to the top of the melt. Fig. 5 is a photograph of a crucible which was broken purposely in order to illustrate the appearance of the crucibles after use. During the investigations it was often necessary to quench a melt by sharply pulling up the crucible from the hot zone of the reaction tube to the relatively cold top part. This sudden cooling put a strain on the crucibles, but they withstood it well and only showed signs of serious cracking after about four quenchings.

During the early investigations the suspension gave some trouble. The first suspensions used were composed entirely of platinum wire. The suspension was attached to the crucible by means of a stirrup of thick platinum wire, the crucible having two holes in it. On heating in hydrogen, the suspension frequently broke at a point inside the hot zone of the furnace when the temperature was only about 1200°C . To try and remedy this, thicker pieces of platinum wire were used for that part of the suspension in the hot zone but the breakages still occurred, although the thicker wire did endure a little longer. The breaking of the platinum was due to red-shortness, the grain boundaries having been weakened by absorption of hydrogen.

Because of these breakages, it became necessary to find a suitable substitute for platinum. As the platinum always broke at a point inside the hot zone of the furnace, it was only necessary

to replace that part of the platinum inside the hot zone and, as a safety margin, two or three inches above it; the remainder of the suspension could be left as it was. Alundum was first thought of as a suitable substitute. It is a very refractory material and when fired at high temperatures it becomes strong and hard. It is also a very stable substance. It was decided therefore to try and make rods of alundum, about six inches in length. Normally, a mixture of ten parts coarse to one part fine alundum powder is used in making refractory articles. The coarse-grained alundum forms the main bulk of the mixture as it is much less liable to crack on drying than is the fine alundum. The latter is added because of its bonding power. In making the rods it was decided to use a mixture of equal parts of coarse and fine alundum. The success, or otherwise, of the rods would be determined by their ability to bear a load of about 40 gms. at temperatures up to 1600°C , and this would depend largely on the strength of the bonding agent used in making them. The coarse and fine alundum powders were thoroughly mixed up and then moistened with a little water. It was found that best results were obtained by adding only a small amount of water. The plastic mass was then put into a steel cylinder with a small hole in the bottom, and the alundum was extruded through this hole by means of a screw and plunger arrangement. As the rod of moist alundum came through the hole it was caught on a piece of cardboard which was held underneath the press. The cardboard was held horizontally and was gradually moved along as more of the alundum was extruded. The length of the rods varied from 6 to 8 inches and, while they were still damp, they were bent



FIG. 6—CRUCIBLE WITH LUGS.

at both ends. They were then slowly dried and fired at 1600°-1700°C in a carbon-granule furnace. The rods were next tested by using them in the suspension. It was found that, on heating in air, the rods broke when the temperature was much lower than 1530°C. They always broke at a point just above the hooked parts attached to the crucible. Because of this it was thought that the hooks were points of weakness and it was decided to eliminate the lower hooks. As the upper parts of the alundum rods were always relatively cool, it was thought unnecessary to alter them. Instead of bending the lower ends of the rods, small blobs of alundum were attached to them while they were still damp. A special alundum crucible with two pairs of lugs on it was made and the rods were slotted between the lugs, which then rested on the small blobs at the ends of the rods. This type of crucible is illustrated in fig. 6. The rods, however, continued to break when heated under load, and it was next decided to make thicker ones. In making the new rods about 5% of AlF_3 was mixed up with the dry alundum, and the rods were fired at 1800°C in the carbon-granule furnace. These rods did not break when tested and some of the earlier runs were carried out with them. The use of these rods, however, introduced some disadvantages: as the rods were heavier than wire, they increased the weight which the balance had to carry; the crucibles with lugs were also heavier than the normal crucibles, and were more difficult to centre inside the reaction tube when a weighing had to be taken, as the lugs left much less clearance; after each run the rods showed an appreciable gain in weight owing to sulphur deposition on those parts of the rods

outside the hot zone, and, because of the porous nature and relatively large diameter of the rods, this increase in weight was greater than it would be for wire.

Thus, although the alundum rods were satisfactory up to a point, it was thought desirable to try and improve on them. With this end in view, molybdenum wire was tested as part of the suspension. Although molybdenum oxidises readily on heating in air, this would not matter as the wires would always be heated in a reducing atmosphere. The wire chosen was of the same diameter (0.04 inch) as that used to make the furnace winding. Two lengths of about 8 ins. were hooked through holes in a crucible, and the lugs were thus eliminated. On testing under load it was found that the molybdenum endured temperatures over 1530°C without breaking. The wires also picked up much less sulphur than did the rods. Although the parts of the wires inside the hot zone became brittle with continual heatings, they never at any time broke during a run. As a precautionary measure, they were renewed from time to time. Platinum wire was of course used for the rest of the suspension, the thicker platinum wire being attached to the molybdenum.

In order to discover how much time was required for mixtures of hydrogen sulphide and hydrogen to become homogeneous, experimental mixtures were prepared for analysis. It was also necessary to test the gas-analysis apparatus to see if it gave consistent results. The first few analyses gave varying results but, after that, consistent results were obtained. The early inconsistencies were probably due to the absorption of the gases by different

parts of the apparatus until they became saturated. It was found that the gas mixtures became homogeneous after being allowed to stand overnight.

Accurate weighings at over 1530°C of the crucible and melt were found to be possible when a gas mixture was passing slowly through the reaction tube. The weighing operation was affected very little by draughts, and small changes in weight could be readily detected.

It was realised that the melt, crucible, and suspension weighed slightly more in a hydrogen sulphide-hydrogen atmosphere than in air but the difference was, at the most, about two in the third decimal place. Besides, the real criterion of the attainment of equilibrium was the weight constancy of the melt, and so this small difference was really immaterial.

EXPERIMENTAL METHOD

The iron used throughout the investigations was Armco ingot iron, which is the trade name for commercially pure iron manufactured by the basic open-hearth process. It is the purest commercial iron made and is surpassed in purity only by electrolytic iron. The pig iron, ore, limestone, fuel and scrap, used in the manufacturing process, are all carefully selected so as to keep the impurities at a minimum. The manufacturers guarantee less than 0.16% total impurities in the iron, and the following is given as a typical analysis:

Carbon	0.012%
Manganese	0.017%
Phosphorus	0.005%
Sulphur	0.025%
Silicon	trace
<hr/>			
TOTAL	0.059%
<hr/>			

0.16%

The first step in the determination of an equilibrium constant was to heat an alundum crucible to about 1580°C in an atmosphere of hydrogen, obtained from a cylinder. The crucible was heated until its weight was constant. It generally lost about 0.03 gm. after four hours heating, but the rate of loss in weight then rapidly diminished until, after about six hours, when it had lost about 0.05 gm., the weight of the crucible became constant. The weight of the crucible thus obtained was termed the "basic weight". This

process was carried out in the molybdenum-wound furnace, and the weight of the crucible during the firing was noted on the high-temperature balance. In the meantime, a piece of Armco iron of about 18 gms. weight was cleaned and then accurately weighed. Next, the crucible with the iron in it was lowered into the reaction tube and again heated to about 1580°C in a stream of hydrogen until the total weight was constant. It was found that there was always a small but decided decrease in the weight of the crucible and iron. This loss in weight was probably due to the purifying action of the hydrogen stream on the molten metal. When the iron had been thus treated it was allowed to remain in the crucible during the remainder of the investigation until it had to be analysed chemically. By subtracting the weight of the crucible from that of the crucible plus iron, the "basic weight" of the latter was obtained. The platinum suspension wire and the two molybdenum wires were each weighed also.

The next step was the preparation of a gas mixture. When the mixture had been made up it was allowed to stand until it had become completely homogeneous. It was then analysed as already described and the volume of hydrogen sulphide to 100 c.cs. hydrogen was calculated. The composition of the gas mixtures used varied between the limits 0.05 c.c.-1.50 c.cs. hydrogen sulphide in 100 c.cs. hydrogen.

The crucible and iron were carefully lowered into the reaction tube and suspended from the high-temperature balance. The suspension, crucible, and iron were then weighed. The orifice in the weighing device was sealed, the outlet tube was closed, and

the reaction tube was evacuated by means of the Cenco-Hyvac pump which was connected to the gas inlet. When evacuation was complete, the inlet tube was connected to the reservoir and some of the gas mixture was slowly admitted until the pressure inside the reaction tube was a few centimetres of mercury above atmospheric. The outlet was then opened and the excess gas escaped. The crucible and iron were thus suspended in a mixture of hydrogen sulphide and hydrogen of known composition.

The furnace was then heated up to a definite temperature which was maintained during the run. The temperatures chosen for the determinations were 1530°C, 1550°C, 1570°C, and 1600°C respectively. When the furnace was being heated up, the gas mixture inside the refractory tube expanded and the excess gas escaped through the outlet. When the temperature had been reached the connection between the inlet and the reservoir was carefully opened until a fast stream of gas mixture was passing through the reaction tube. During most runs the gas mixture was passed in at a rate of about 50 c.cs./min. but this was sometimes increased to 100 c.cs./min. In the early runs the rate of flow was about 30 c.cs./min. The effect of increasing the gas flow was to hasten the pick-up of sulphur by the melt and so shorten the time taken to reach equilibrium.

The molten iron reacted with the H_2S to form FeS , which remained in solution in the iron. The melt thus gained in weight and this increase in weight was noted by taking weighings at regular intervals on the high-temperature balance. When a reading on the latter was being made the gas flow was reduced to

about 8 c.cs./min. so that the weighing operation was not affected to any great extent. In taking those weighings, use was made of the weighing device and it was found to work efficiently. After a weighing had been made, the orifice was closed and a fast stream of gas was again admitted to the reaction tube.

It was found that at the beginning of the reaction the rate of pick-up of sulphur by the iron was very rapid. Gradually, however, the rate slowed down until it became relatively small. The gain in weight recorded by the high-temperature balance was due mainly to the sulphur picked up by the iron, but the molybdenum and platinum wires of the suspension also gained in weight a little. When the high-temperature balance was registering only small changes in weight then it was assumed that equilibrium had been almost reached. The melt was then quenched by pulling it up sharply to the cool top part of the reaction tube, and the furnace was cooled.

When the furnace was cold the crucible, melt, and suspension were withdrawn. The platinum and molybdenum wires were weighed and their total increase in weight was obtained. This gain in weight was subtracted from the total gain in weight recorded on the high-temperature balance immediately before the melt was quenched. The pick-up of sulphur by the melt, denoted by the high-temperature balance, was thus obtained. The crucible and melt were also weighed at room temperature after they had been withdrawn from the reaction tube. The gain in weight of the crucible and melt at room temperature showed very good agreement with the gain in weight obtained from the high-temperature balance.

This increase in weight was, of course, due to the sulphur picked up by the melt. The method of quenching the melt thus showed itself to be quite efficient.

During the run, two analyses of the gas mixture were carried out. The gas was also sometimes analysed after it had passed through the reaction tube.

As the original weight of the iron was known, it was a simple matter to calculate the percentage of sulphur in the melt. A value for the equilibrium constant was then calculated using the equation:

$$K = \frac{H_2S}{H_2} \text{ (volume ratio)} \times \frac{1}{\%S \text{ in melt}}$$

In order to ensure that the gain in weight of the crucible and iron was due solely to the formation of iron sulphide in the latter some melts were analysed for sulphur, and good agreement was obtained. The method adopted for such analyses was as follows:

An accurately weighed sample was brushed into a conical flask which was then closed with a rubber stopper fitted with a thistle-funnel and a delivery tube. The stem of the funnel reached to near the bottom of the flask and the delivery tube extended from the flask to the bottom of a long glass cylinder which contained ammoniacal cadmium chloride solution. A mixture of equal proportions of concentrated hydrochloric acid and water was poured rapidly down the funnel until the end of the stem of the funnel was covered. The flask was then carefully heated. Hydrogen sulphide was liberated by the action of the acid on the sample, and the gas passed into the cadmium chloride solution where it

precipitated cadmium sulphide. Heating was continued until all the sample had been dissolved and all of the hydrogen sulphide had been driven out of the flask. The precipitate of cadmium sulphide was dissolved slowly with concentrated hydrochloric acid and the liberated hydrogen sulphide was titrated against standard iodine solution, using starch as an indicator. The cadmium chloride and iodine solutions were the same as those used in analysing the gas mixtures. The accuracy of this method was confirmed by carrying out analyses on standard samples of steel with known percentages of sulphur.

In analysing a melt, great care had to be observed in order to obtain samples which were representative of the entire melt. This was necessary, because micro-examination of polished specimens had shown that the iron sulphide was not always distributed uniformly throughout the iron. The procedure was to take borings through various parts of the melt. The turnings thus obtained were thoroughly mixed up, and at least three analyses were carried out on them. It was found that consistent results were obtained by this practice. Sufficient turnings were weighed out in each analysis to give a titration of about 15 c.cs. iodine solution.

The above is an outline of the technique adopted in the early runs. The first results obtained were rather inconsistent and, during some runs, the melt seemed to pick up more sulphur than was being passed into the reaction tube in the form of hydrogen sulphide. In these early runs the iron would pick up sulphur rapidly at the start, but after about three hours the rate of pick-up

would be very slow. This seemed to indicate that the equilibrium state was being approached. However, on quenching the melt and then continuing with the same run the following day, it was found that the rate of pick-up of sulphur increased instead of remaining at the previous low value. This seemed at first to indicate that the melt had not really been near the equilibrium point in the first instance, but this was not the full explanation. An analysis of the outlet gas from the reaction tube revealed the true reason for the inconsistency. During one run this gas was found to contain almost twice as much hydrogen sulphide as the inlet gas. It was obvious that the gas mixture, in its passage through the reaction tube, was picking up sulphur in some form. This extra sulphur could not have come from the melt as it had been gaining in weight during the run. The possibility of sulphur deposition in the tube was considered and it was decided to carry out an investigation. An examination of the reaction tube revealed that there was a thin deposit of sulphur on the surface a few inches above the hot zone. The hot zone itself was clean. The lower part of the tube contained the alundum baffle plates, and as the alundum was porous it would obviously provide a large surface for sulphur deposition. An examination revealed this to be the case. Because of this, the design of the baffle system was altered so as to reduce the amount of alundum. (See page 16)

There were two possible explanations for the presence of sulphur in the reaction tube. One was that the hydrogen sulphide was being decomposed - or perhaps dissociated would be a more

appropriate word - into hydrogen and sulphur during its passage through the tube. Part of this sulphur would then be deposited on those areas of the tube which were at a suitable temperature for condensation to occur. It was also possible that the hydrogen sulphide gas was being absorbed by the alundum and certain parts of the reaction tube. Although the sulphur deposition was continually being formed, some of the sulphur would also be given off when the tube was heated up and a gas mixture was passing through it.

It was necessary that this sulphur should be cleaned out of the reaction tube before an equilibrium run was started. The method adopted for cleaning the tube was to pass a rapid stream of hydrogen through it at about 1550°C . An analysis of the hydrogen after its passage through the empty tube showed that it contained as much sulphur as some of the gas mixtures used. This was definite proof of the existence of sulphur deposition. The hydrogen was passed in until the amount of sulphur it contained after going through the tube was negligible. This treatment solved the problem of sulphur deposition. It generally took about four hours to clean the tube and it was then possible to carry out a run with the knowledge that the gas in the tube was of the same composition as that being passed in from the reservoir. The reaction tube was cleaned with the hydrogen very frequently so as to keep the sulphur deposition so low that it could not interfere with the equilibrium determinations.

The time taken for the reaction to reach the equilibrium state, starting with pure iron, was rather long. It was possible

to shorten the time by increasing the rate of flow of the gas, but the gas rate could not be increased too much as the refractory tube was liable to crack if too fast a stream was passed through it. Besides, there was no real advantage in increasing the gas flow above a certain value, and the rate of flow of the gas was never greater than 100 c.cs./min. It was decided to try and hasten matters by first melting the iron in a mixture containing a comparatively high percentage of hydrogen sulphide. After melting the iron in this mixture for about two hours, the run was stopped. A gas mixture about half as strong in hydrogen sulphide as the previous one was then prepared and the melt heated in it. The iron picked up sulphur during those runs, and the process of reducing the concentration of hydrogen sulphide was continued until the iron either gained only a little, or started to lose sulphur in a gas mixture. The gas mixture in which this occurred was not altered and the run was continued until equilibrium had been reached in it. It was found that the melt was usually near equilibrium in the third or fourth mixture. The gas mixtures were not prepared indiscriminately; if it was thought that the melt was not very far from being in equilibrium with a mixture, the latter was not altered too much. This method worked quite well, but it had the disadvantage of causing larger sulphur depositions in the reaction tube, owing to the relatively strong gas mixtures used at the start. More time was taken up in removing those depositions.

When the value of K was known at least approximately, it was possible to calculate the composition of the melt which would be

nearly in equilibrium with a gas mixture, the composition of which was known from analysis. The first dependable values of K obtained were thus utilised. Melts which had already been used for equilibrium determinations were found to be convenient for preparing the synthetic melts. When the percentage of sulphur in a melt was known it was possible to prepare a melt with a smaller, but known, sulphur content. This was accomplished by adding a weighed amount of the melt, usually in the form of turnings, to a weighed piece of Armco iron. The usual procedure was to prepare a gas mixture of known composition and then a melt was made up containing the appropriate sulphur content. This process could also be reversed, the melt being made first and then the corresponding gas mixture. The former method was more favoured, as synthetic melts could be prepared more accurately than the gas mixtures.

Another method adopted for reaching the equilibrium stage more quickly was to melt in hydrogen a sample which had previously reached equilibrium in a known gas mixture. This treatment reduced the sulphur content of the melt. At the same time, the remaining gas mixture in the reservoir was diluted with hydrogen and so a gas weaker in hydrogen sulphide content was prepared. This gas was analysed. Knowing at least the approximate value of K and the gas composition, it was possible to calculate a value for the sulphur content of the melt at equilibrium. The melt could then be heated in the hydrogen until its sulphur content had been reduced to the appropriate percentage.

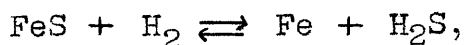
By the judicious application of these various techniques, it was possible to reach the equilibrium state from both the

high-sulphur and low-sulphur sides. All but one of the following results were obtained by using these methods. That is, in only one case was there no sulphur in the iron at the start of the equilibrium run.

EXPERIMENTAL RESULTS.

The results of the investigation may be divided broadly into two groups: the early results, which were inconsistent because of sulphur deposition, and the results obtained when provision was made to eliminate the sulphur deposition. The samples used in the early investigations are referred to as Sample I, Sample II, etc. The melts from which more reliable data were obtained are denoted by a letter thus, Sample A, Sample B, etc. Runs with the same melt in different gas mixtures are numbered Run 1, Run 2, etc. For example, the first run with Sample A in a gas mixture is termed as Sample A Run 1, and the next run with Sample A in a different gas mixture is called Sample A Run 2. Similarly, the first run with Sample B is denoted as Sample B Run 1, and so on with the other melts.

The first results were obtained for the temperature 1550°C and the starting material was Armco iron. As has been previously explained, the early results were inaccurate because of the sulphur deposition in the reaction tube. This caused the iron to pick up more sulphur than it would have if the sulphur content of the gas in the tube had been the same as that of the gas in the reservoir. The equilibrium constant of the reaction:



may be represented as:

$$K = \frac{\text{H}_2\text{S}}{\text{H}_2} \text{ (volume ratio)} \times \frac{1}{\% \text{S in melt}}$$

SAMPLE II RUNS 1 AND 2

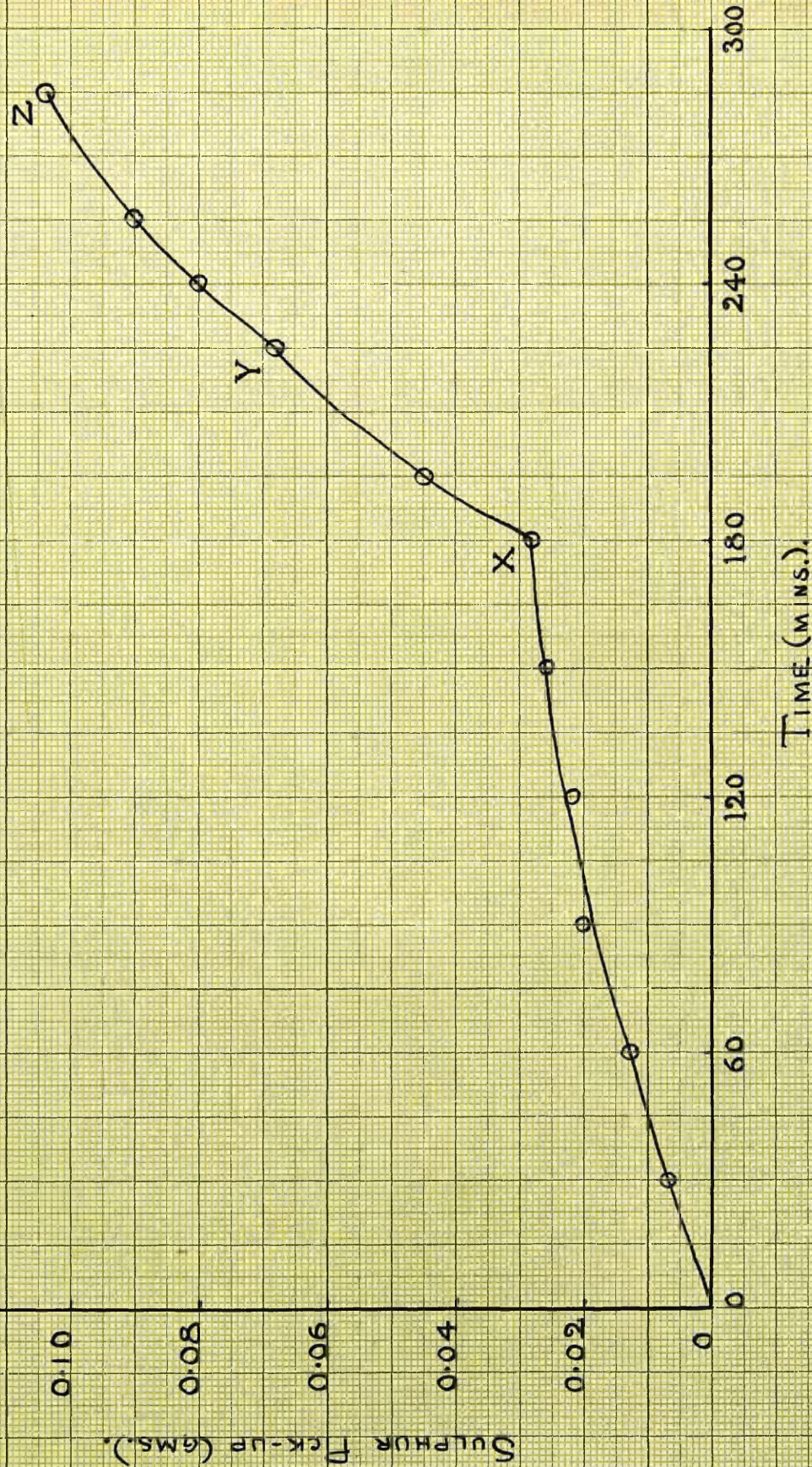


FIG. 7- VARIATION OF SULPHUR PICK-UP WITH TIME.

The effect of the sulphur deposition was that on calculating K a value which was too low was obtained, because the percentage of sulphur in the melt occurs in the denominator of the above equation.

Fig. 7 is a good illustration of the effect of sulphur deposition. In this graph the weights of sulphur picked up by the iron (Sample II) have been plotted against the corresponding times. The run was started with 19.920 gms. Armco iron and the composition of the gas in Run 1 was 0.203 c.c. hydrogen sulphide to 100 c.cs. hydrogen. The flow of the gas mixture through the tube was maintained at about 30 c.cs./min., except of course when it was reduced while a weighing was being made. The rate of pick-up of sulphur by the melt decreased progressively as the run was continued until, after about three hours, the pick-up was very slow. At this stage Run 1 was stopped. (Point X on the graph) The melt had then gained in weight by 0.028 gm. sulphur after three hours at 1550°C. A mixture consisting of 0.072 c.cs. hydrogen sulphide to 100 c.cs. hydrogen was prepared, and on the following day the melt was reheated to 1550°C in this new atmosphere. This was Run 2 with Sample II. The flow of the gas through the reaction tube was maintained at the same rate as in Run 1, and it was expected that the rate of pick-up of sulphur by the melt would at the most be the same as at the conclusion of Run 1. As the melt had seemed to be approaching equilibrium in the first run, and as the second run was in a gas containing a much smaller content of hydrogen sulphide, it was thought possible that the melt would lose sulphur in this new run. It was found, however, that the melt picked up sulphur, and at a much greater rate than before (X→Y on the graph).

Whereas previously it had taken three hours to gain 0.028 gm. sulphur, it now picked up 0.040 gm. sulphur in 45 mins., after which the run was stopped. On continuing the run the following day, with the same gas mixture, there was an additional pick-up of 0.036 gm. during 60 mins. (Y→Z on the graph). The evidence indicated that the melt was not yet at the equilibrium stage, but a value for K was calculated by taking the total pick-up of sulphur as 0.104 gm. This represented 0.52% sulphur in the melt, and thus:

$$K = \frac{0.072}{100} \times \frac{1}{0.52} = 0.00138$$

But, as the sulphur content of the melt was still increasing, then K was really less than 0.00138. It was in this manner that the sulphur deposition resulted in the values obtained for K, in the early investigations, being too small. This particular investigation was carried out using freshly-made alundum rods as part of the suspension for the crucible, and, during the runs, the alundum picked up an appreciable amount of sulphur. However, in drawing the graph in fig. 7, a correction was applied for the sulphur picked up by the suspension, and the sulphur gains recorded in the graph were those of the melt alone. The time occupied in taking a weighing on the high-temperature balance was only about two minutes, during which time the gas flow was reduced to 8 c.cs./min.

As the results of these early runs proved to be false, they will not be discussed in detail. They were all carried out at 1550°C and the values obtained for K varied from about 0.00130 to 0.00250. Later, new values for K were re-determined at 1550°C.

One point which is well illustrated by fig. 7 is the time taken by a melt to reach equilibrium. The pick-up of sulphur by the iron was fairly fast at the start of Run 1, but it slowed down considerably before equilibrium was attained. It was for this reason that new techniques for reaching the equilibrium stage more quickly were evolved. These techniques have already been described in general terms in the EXPERIMENTAL METHOD. All but one of the subsequent values obtained for the equilibrium constant were arrived at by utilising these various methods. These results are presented in concise form in Table I. (Page 48).

The results are not written in the table in the order in which they were carried out. The numbers given for the runs are those of the equilibrium runs. All the melts (except Sample F) already contained sulphur prior to the start of the equilibrium run. Thus, apart from Sample F, the figures given for the percentages of sulphur in the melts represent the total sulphur pick-up, and do not represent the sulphur picked up during the equilibrium run. Samples D and E were synthetic melts. The latter was made from part of Sample A and some armco iron. Sample D was prepared by combining parts of Samples C and A. The figures given for the basic weights of Samples D and E were obtained by calculation. The sulphur percentages at the conclusion of the equilibrium runs were all calculated from the gains in weight of the melts. The values given for the gas compositions were those of the gas mixtures in the reservoir. It is now proposed to give the details of three representative determinations.

TABLE I.

Sample	Run	Temp. °C	Basic Weight of Iron (Gms.)	Weight of melt after Equilibrium Run (Gms.)	Weight of Sulphur in Melt after Equilibrium Run.	% Sulphur in Melt	Gas Composition in Equilibrium Run: ($\frac{H_2S}{H_2} \cdot 10^2$) c.c.	$= \frac{\frac{K}{H_2S}}{H_2} \cdot \frac{1}{\%S}$
A	4	1530	16.9933	17.1333	0.1400	0.817	0.293	0.00359
B	3	1530	17.2400	17.4204	0.1804	1.036	0.466	0.00450
B	4	1530	17.2400	17.3285	0.0885	0.511	0.217	0.00425
B	5	1530	17.2400	17.2877	0.0477	0.276	0.113	0.00410
C	1	1550	20.1230	20.2600	0.1370	0.676	0.277	0.00410
C	2	1550	20.1230	20.1863	0.0633	0.314	0.115	0.00366
D	1	1550	15.1861	15.2994	0.1133	0.741	0.323	0.00436
E	1	1570	15.9506	16.0145	0.0639	0.399	0.181	0.00454
E	2	1570	15.9506	15.9933	0.0427	0.267	0.100	0.00375
F	1	1570	20.2481	20.3291	0.0810	0.398	0.178	0.00447
G	2	1600	19.8255	19.9496	0.1241	0.622	0.261	0.00420
G	3	1600	19.8255	19.9601	0.1346	0.674	0.308	0.00457

Sample E was the first synthetic melt made. A gas mixture was first prepared. An analysis of this gas gave 0.181 c.c. hydrogen sulphide to 100 c.cs. hydrogen. The value of K was taken as being known at least approximately, and for purposes of calculation it was assumed to be 0.0040. These two values for the gas composition and K were substituted in the equation:

$$K = \frac{H_2S}{H_2} \times \frac{1}{S},$$

where S = % sulphur in melt. Thus -

$$.004 = \frac{.181}{100} \times \frac{1}{S}$$

$$\therefore S = \frac{.181}{100} \times \frac{1}{.004}$$

$$= 0.45\% \text{ sulphur.}$$

It was thus necessary to prepare a melt containing 0.45% sulphur, which would be nearly in equilibrium with the gas mixture. Such a melt was obtained by mixing part of Sample A with armco iron. In preparing the melt the percentage of sulphur in Sample A was taken from the analysis of it and not from the gain in weight. These two percentages differed slightly and they will be discussed later. The synthetic melt prepared in this particular example contained 0.445% sulphur, and on heating it at 1570°C in the gas mixture its weight had not changed greatly after 205 mins.

Sample B, Run 3 is a good example of the technique of reaching equilibrium by melting the iron first in a relatively high concentration of hydrogen sulphide and then in mixtures which are successively weaker in hydrogen sulphide. The weight of the armco iron after it had been melted to constant weight in hydrogen was 17.2400

gms. A gas mixture containing a relatively high proportion of hydrogen sulphide was prepared, and on analysis it was found to contain 1.310 c.c. hydrogen sulphide to 100 c.cs. hydrogen. The iron was melted in this atmosphere for two hours at 1530°C . After that run (Run 1), the pick-up of sulphur by the iron was 0.1275 gm. Hydrogen was then passed into the gas in the reservoir, and an analysis of the new mixture gave 0.620 c.c. hydrogen sulphide to 100 c.cs. hydrogen. The melt was heated at 1530°C for two hours in this weaker mixture. This was Run 2, and at the end of this run the melt had picked up a further 0.0600 gm., making a total gain in weight of 0.1875 gm. At this stage it was necessary to clean the sulphur deposition out of the reaction tube by passing hydrogen through it at about 1580°C . Some hydrogen was added to Run 2 mixture, and the resulting gas when analysed was found to contain 0.466 c.c. hydrogen sulphide to 100 c.cs. hydrogen. After two hours at 1530°C in this mixture (Run 3), the melt lost 0.0081 gm. and, because of this, the mixture was unaltered. The run was then stopped by quenching the melt, and the sulphur deposition was cleaned out of the reaction tube. On continuing with Run 3, the melt gained in weight by only 0.0010 gm. in 165 mins. and K was then calculated from the available data.

It has already been mentioned how the percentage of sulphur in some melts was reduced by melting in a stream of hydrogen so as to decrease the time taken to reach equilibrium in a known gas mixture. Such a method was adopted in the case of Sample E, Run 2. After Run 1, the melt contained approximately 0.064 gm. sulphur. The composition of the Run 1 gas mixture was 0.181 c.c. hydrogen

sulphide to 100 c.cs. hydrogen and, at the conclusion of the run, hydrogen was passed into the remaining gas. The new gas contained 0.100 c.c. hydrogen sulphide to 100 c.cs. hydrogen. Taking K as being 0.004, and letting S = weight of sulphur in the melt, then:

$$.004 = \frac{.1}{100} \times \frac{(15.95 + S)}{100.S} ,$$

where 15.95 (gms.) is the approximate "basic weight" of the iron. On evaluating, S = 0.04 gm. Thus the sulphur in the melt had to be reduced from about 0.064 gm. to 0.040 gm. The melt had therefore to lose 0.024 gm. sulphur to be nearly in equilibrium with the new gas mixture. The sample was accordingly melted in hydrogen in order to decrease the percentage of sulphur in it. It was heated in the hydrogen until it had lost about 0.018 gm., so that it contained somewhat more than the equilibrium amount of sulphur. On melting in the mixture, the sample lost 0.003 gm. during 180 minutes, and K was then calculated. Thus, this was also an example of approaching the equilibrium state from the high-sulphur side.

It has already been pointed out that the high-temperature balance recorded the slight pick-up of sulphur by the suspension as well as the melt. Thus, even at the equilibrium stage, the high-temperature balance was recording weight changes. These changes in weight during the latter parts of the equilibrium runs are given in Table II (page 52) under the heading H.T.B. Also given, under the heading L.T.B. (low-temperature balance), are the changes in the weights of the melts after the equilibrium runs, when the crucible and melt alone were weighed at room temperature.

T A B L E II.

Sample	Run	Temp. °C	K.10 ²	H.T.B. Sulphur Pick-up during Equilibrium Run.		L.T.B. Sulphur Pick-up from Equilibrium Run.	
				Weight (Gms.)	Time (Mins.)	Weight (Gms.)	Time (Mins.)
A	4	1530	0.359	+0.0050	110	+0.0060	200
B	3	1530	0.450	+0.0040	90	+0.0010	165
B	4	1530	0.425	-0.0026	210	-0.0077	210
B	5	1530	0.410	+0.0060	180	+0.0006	180
C	1	1550	0.410	+0.0030	30	+0.0130	180
C	2	1550	0.366	+0.0050	60	-0.0017	180
D	1	1550	0.436	+0.0050	30	+0.0104	150
E	1	1570	0.454	-0.0010	140	-0.0074	205
E	2	1570	0.375	-0.0010	40	-0.0030	180
F	1	1570	0.447	+0.0025	50	-0.0010	240
G	2	1600	0.420	-0.0030	60	+0.0380	210
G	3	1600	0.457	+0.0013	30	+0.0105	180

The plus sign denotes a gain in weight, and the negative sign a loss in weight. The times given are those during which the changes in weight occurred. It can be seen from this table that, except for four results, the changes in weight given under L.T.B. are all in the third decimal place. In the four exceptions (Sample C Run 1, Sample D Run 1, and Sample G Runs 2 and 3) the melts had changed weight more appreciably after the equilibrium run, but the changes in the weights of ~~these~~ melts, recorded by the high-temperature balance, during the latter parts of the equilibrium runs are relatively smaller, when allowances are made for time and the gain in weight of the suspension.

As the melts had been changing slightly in weight at the conclusion of the runs, it could not be assumed that they were completely in equilibrium with the gas mixtures. However, as it was known whether a melt had been gaining or losing sulphur, it was possible to indicate whether K was smaller or larger than the calculated value. For example, the value of K for Sample B Run 3 is 0.00450, but at the end of Run 3 the melt had been picking up sulphur slowly, thus K would be really slightly less than 0.00450. On this basis the values of K have, in Table III (page 54), been grouped into two sections according to whether the melt was losing (K increasing) or gaining (K decreasing) sulphur at the conclusion of the run. The average values for K at each temperature are also given and it can be seen that they are good representations of the experimentally found values. For example, the average value at 1530°C is practically the same as that for Sample B Run 5, and during this run the melt only changed weight by 0.0006 gm. after

T A B L E I I I

Temperature °C	K increasing	K decreasing	Average of K
1530	0.00425	0.00359 0.00450 0.00410	0.00411
1550	0.00366	0.00410 0.00436	0.00404
1570	0.00454 0.00375	0.00447	0.00425
1600	0.00420	0.00457	0.00439

three hours. The same sort of thing applies to the other temperatures.

The equilibrium constant of the reaction may also be calculated by expressing the concentrations of the iron and FeS in the melt as mole fractions. Representing this constant as K_M , then:

$$\begin{aligned}
 K_M &= \frac{H_2S}{H_2} \times \frac{Fe}{FeS} \\
 &= \frac{H_2S}{H_2} \text{ (volume ratio)} \times \frac{Fe \text{ in melt . 88}}{FeS \text{ in melt . 56}}
 \end{aligned}$$

In Table IV (page 55) the data for calculating the constants in this manner are tabulated and the values of K_M are given.

T A B L E IV.

Sample	Run	Temp. °C	Basic weight of Iron (Gms.)	Weight of Melt after Equilibrium Run (Gms.)	Weight of Iron in Melt after Equilibrium Run (Gms.)	Weight of FeS in Melt after Equilibrium Run (Gms.)	Gas Composition in Equilibrium Run: ($\frac{\text{H}_2\text{S}}{\text{H}_2} \cdot 10^2$) c.c.	$K_M = \frac{\frac{\text{H}_2\text{S}}{\text{H}_2}}{\frac{\text{Fe}}{\text{FeS}}}$
A	4	1530	16.9933	17.1333	16.750	0.3850	0.293	0.2003
B	3	1530	17.2400	17.4204	16.920	0.4961	0.466	0.2498
B	4	1530	17.2400	17.3285	17.090	0.2434	0.217	0.2394
B	5	1530	17.2400	17.2877	17.160	0.1312	0.113	0.2323
C	1	1550	20.1230	20.2600	19.880	0.3768	0.277	0.2297
C	2	1550	20.1230	20.1863	20.010	0.1741	0.115	0.2077
D	1	1550	15.1861	15.2994	14.990	0.3116	0.323	0.2442
E	1	1570	15.9506	16.0145	15.840	0.1757	0.181	0.2565
E	2	1570	15.9506	15.9933	15.880	0.1174	0.100	0.2125
F	1	1570	20.2481	20.3291	20.110	0.2228	0.178	0.2524
G	2	1600	19.8255	19.9496	19.610	0.3413	0.261	0.2356
G	3	1600	19.8255	19.9601	19.590	0.3702	0.308	0.2562

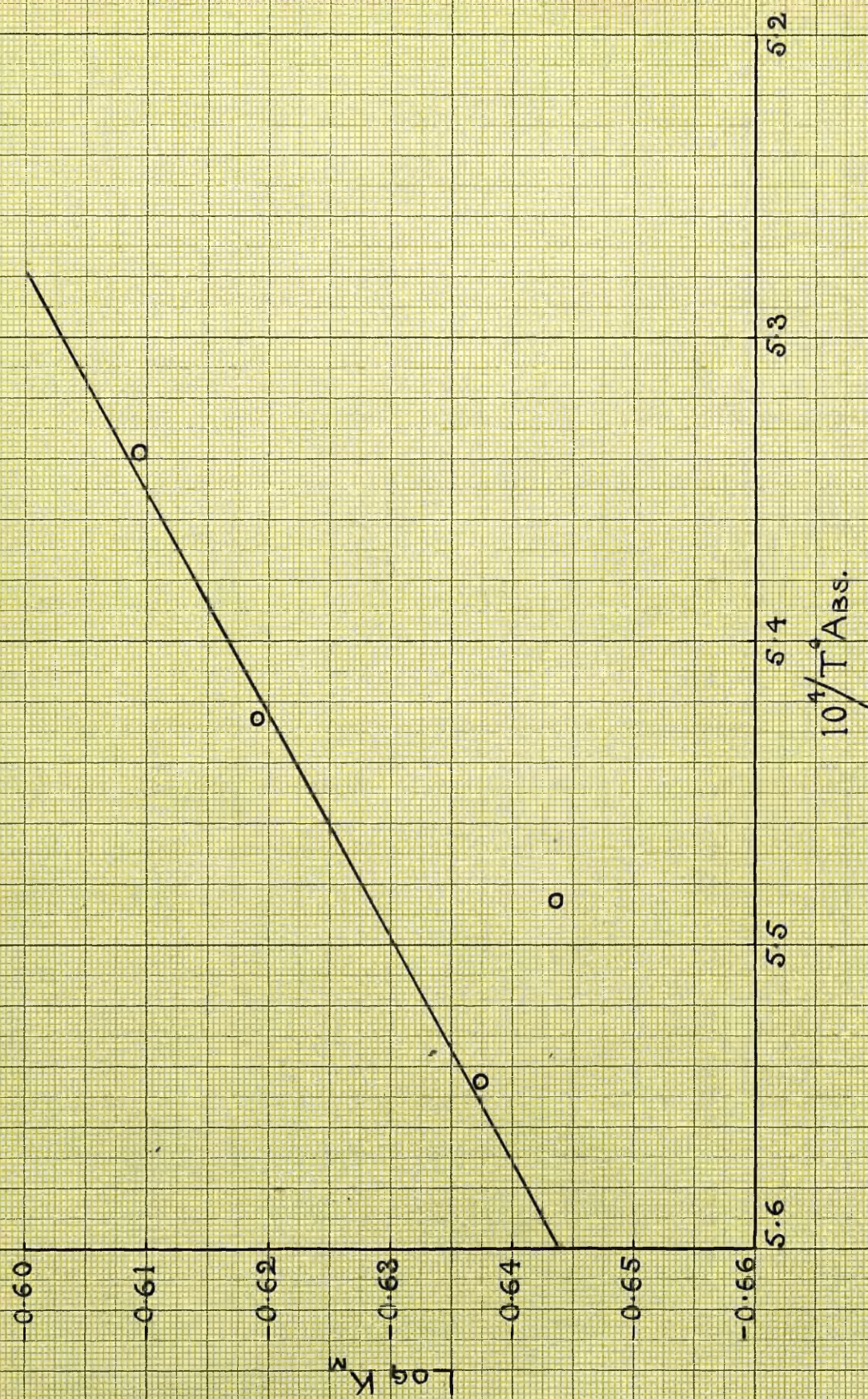


Fig. 8— VARIATION OF $\log K_M$ WITH RECIPROCAL OF TEMPERATURE.

The average values of K_M at each temperature are as follows:

Temp. °C	K_M (Average)
1530	0.2305
1550	0.2272
1570	0.2405
1600	0.2459

In fig. 8, $\log K_M$ has been plotted against the reciprocal of the absolute temperature. The graph so obtained should be theoretically a straight line, and it can be seen that the value of K_M at 1550°C is obviously on the low side. The other three values lie nearly on a straight line, and the equation of this line is:

$$\log K_M = \frac{-1341}{T} + .107 ,$$

where T = temperature (°Absolute).

All the values of K (and K_M) so far considered were obtained by using the gain in weight of the melt to calculate the sulphur percentage. Most of the melts were analysed chemically for sulphur and, as Table V (page 57) illustrates, quite good agreement was obtained between the two percentages. Samples II, III, and IV were three of the early melts which were analysed. Samples B and E fell out of the crucibles when further runs with them were being attempted; the crucibles had been rather badly cracked, due to many quenchings, and they broke during the extra runs. Sample G was not analysed. The values of K calculated from the sulphur analyses are included in Table V, together with the corresponding values

TABLE V

Sample	% S from Analysis of Melt	% S from Gain in Weight of Melt	$K \cdot 10^2$ (Analysis)	$K \cdot 10^2$ (Weight Gain)
II	0.964	1.012	---	---
III	0.765	0.808	---	---
IV	0.155	0.157	---	---
A	0.810	0.817	0.362	0.359
B	---	0.276	---	0.410
C	0.320	0.314	0.359	0.366
D	0.732	0.741	0.441	0.436
E	---	0.267	---	0.375
F	0.400	0.398	0.445	0.447
G	---	0.674	---	0.457

obtained from the increase in weight of the melts. There is little difference between these values and, as most melts were used to obtain more than one value for K, it is better that all the constants considered should be those based on the gain in the weight of the melt.

Some analyses were carried out on the gas mixtures after they had passed through the reaction tube but the compositions of the inlet and outlet gases always differed slightly. In the equilibrium runs, which were all carried out after the sulphur deposition had been removed from the reaction tube, the percentage of hydrogen



FIG. 9 — MELT WITH BLOWHOLES.



FIG. 10 — BLOWHOLE IN MELT.

sulphide in the outlet gas was lower than in the inlet gas. This difference was probably caused by the formation of fresh sulphur deposition. Examination of the reaction tube showed that the sulphur deposition occurred mainly a few inches above the hot zone in the reaction tube - that is, after the gas had passed over the melt. As the molybdenum suspension wires also absorbed some sulphur, it was probable that the inlet gas was more representative of the gas which was in equilibrium with the melt. For this reason all the values for the constants were calculated using the inlet gas composition.

Melts which had been quenched usually contained blow-holes, and often the surface of the melt rose considerably. Figs. 9 and 10 are examples of two melts containing blow-holes. When the melts were cooled slowly in the furnace they solidified to a solid mass. Fig. 11 (overleaf) illustrates the normal appearance of the melts. Pieces of alundum from the crucibles can be seen sticking to these latter melts but, as has been mentioned in the PRELIMINARY INVESTIGATIONS (page 28), this was merely a physical action. The blow-holes in the quenched melts were probably due to the very sudden decrease in the solubility of the hydrogen (and the hydrogen sulphide) when the temperature fell quickly below the freezing-point of the melt. The gases would be much less soluble in solid than in liquid iron, and so at the freezing-point there would be a sudden evolution of gas, with the consequent formation of blow-holes.



Fig. 11 — NORMAL APPEARANCE OF MELTS.

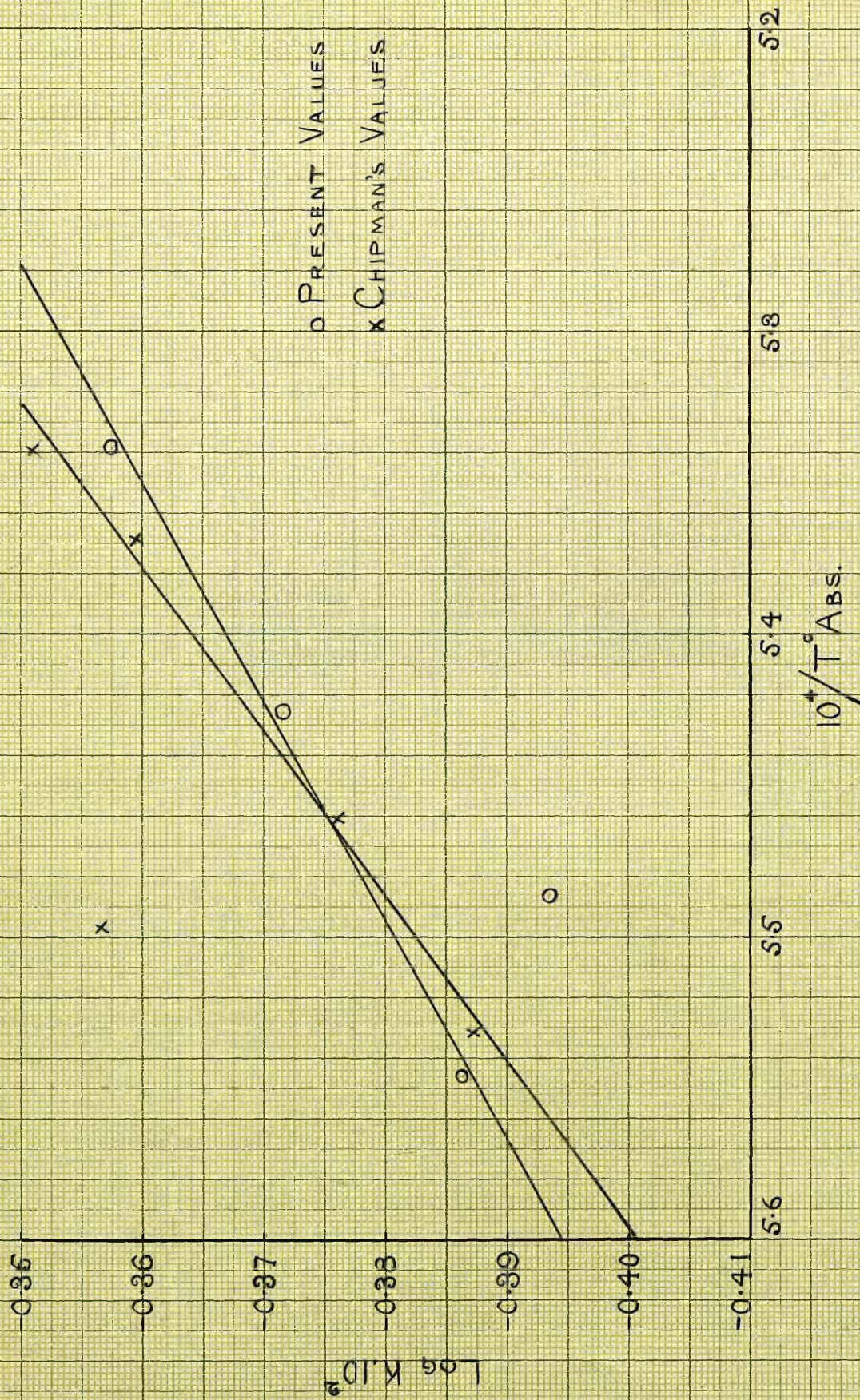


Fig. 12—COMPARISON OF PRESENT VALUES OF K WITH CHIPMAN'S.

DISCUSSION OF RESULTS.

Comparison with other Investigators.

The equilibrium constant of the reaction between hydrogen sulphide and iron at temperatures of liquid iron has been studied previously by Maurer and Bischof⁽⁹⁾, and Chipman and Li⁽¹⁰⁾. The formers' values for K are about one hundred times as large as the present values. In fig. 12, the logs of the average values of K obtained in the present investigation are plotted against the reciprocals of the corresponding absolute temperatures, and the same procedure is adopted with Chipman's results. It can be seen that there is fairly good agreement between these two sets of results. It is obvious from the graph that Chipman's value for K at 1546°C is too high, and the value at 1550°C in the present work is too low. Although Maurer and Bischof's constants differ greatly from Chipman's and the present results, all three agree in one respect - namely, that the equilibrium constant increases in value as the temperature rises. This agrees also with the findings of investigators of the reaction in the solid state.

Maurer and Bischof carried out their investigation in a Tammann furnace. In it a charge of steel was melted, and a gas of known composition was circulated in the space above the charge. After a definite time had elapsed, the gas was analysed for sulphur after passing over the charge. They knew from the analysis whether the gas had lost or gained sulphur and on this information they

deduced the direction in which the movement toward equilibrium was taking place. The initial composition was compared with the final composition of the residual gas and by this means they finally ascertained the direction of the reaction. They found that at the high temperatures of the investigation the crucibles and reaction tubes were unable to resist for more than 60 mins. at a time the chemical attack of the reactants, apart from the physical stresses to which the vessels were subjected. Because of this, it was impossible for them to prolong the operation sufficiently to attain the point of complete equilibrium. It can thus be seen that Maurer and Bischof's values are based on data which are far from conclusive as regards indicating the true equilibrium point. Their high results were possibly due in part to the relatively short time which they were forced to allow for the melt to attain equilibrium with the circulating gas mixture. This would result in the percentage of sulphur in the melt being too low, and thus K would be too high. They also used beryllia crucibles, and according to Chipman these crucibles absorbed sulphur; part of the sulphur in the gas would therefore be taken up by the crucible instead of the melt, and this would also tend to make the value of K too high.

Although Chipman's values for K do not differ greatly from the present values, he makes some statements which are not in accordance with what was found in the present investigation. Chipman preheated the gas mixture before it entered the reaction tube, which was made of silica. This preheating was carried out by means of molybdenum filaments which were placed inside the upper

part of the silica tube. According to Chipman, these filaments were not corroded by the gaseous mixture, and no hydrogen sulphide was decomposed or absorbed by the molybdenum. In the present investigation it was found that the molybdenum wires, which were used in the suspension, gained slightly in weight after each run. This increase in weight must have been caused by the action of the gas mixture on the wires. It is probable that the molybdenum reacted slightly with the hydrogen sulphide to form small amounts of molybdenum sulphide. Also, it was found usually that after a run a thin deposit of elementary sulphur coated the molybdenum suspensions for a short distance above the hot zone. Although this deposit was readily rubbed off, it is probable that some sulphur was absorbed by the molybdenum. H. Moissan (see Mellor's "Inorganic and Theoretical Chemistry", Longmans, Green and Co., 1931, vol. XI p. 513) has found that sulphur has no action on molybdenum at 440°C , but that hydrogen sulphide at 1200°C converts the metal into a sulphide closely resembling molybdenite (MoS_2). Chipman does not state to what temperature the filaments were heated, but it seems reasonable to assume that they would be heated to about 1200°C in order to give effective preheating of the gas. His gas compositions were of the same order as those used in the present investigation. It was found in the present investigation that the action of the gas mixture on the molybdenum wires was not a corroding one, and these wires lasted for many runs and could be used even when brittle. This agrees with what Chipman found.

According to Chipman, the preheating of the gas mixture had a decided effect on the amount of sulphur absorbed by the iron in

such a manner that the lower the temperature to which the gas was preheated, the less was the amount of sulphur absorbed by the iron. This preheating of the gas is probably of use in hastening the attainment of equilibrium, but it is doubtful if it has any effect on the final equilibrium state. It was found in the present experiments that when pure iron was used it reacted rapidly at the start, despite the fact that the gas was not preheated.

Chipman also states that there was no evidence of any kind as to the deposition of liquid or solid sulphur in the cold part of the furnace, and that this confirmed preliminary calculation that the gas mixture passing through the furnace should not be decomposed. One of the chief difficulties of the present work has been the sulphur deposition on the cooler parts of the reaction tube, and the presence of such a deposition has been shown experimentally. It is interesting to note that Dahlström and Ahren⁽¹²⁾ state that any hydrogen sulphide present in producer gas is to a large extent dissociated when the gas is preheated; they found that an average of 35% of the sulphur in the producer gas was retained in the regenerator chamber.

Chipman had difficulty in finding a suitable type of crucible in which the reaction could occur without the crucible reacting with the melt or the gas atmosphere. One of the types he tried was porcelain crucibles, but they reacted with the melt. As an explanation for the reaction, Chipman says that it is probable that the alumina in the crucibles reacted with the hydrogen sulphide. Alundum crucibles, which also contain alumina, were used in the present investigation and these crucibles were found to be stable

and they did not react with the melt or hydrogen sulphide, nor did they absorb sulphur. Furthermore, these alundum crucibles were quite capable of enduring many hours heating with the melts in hydrogen sulphide/hydrogen atmospheres. Chipman's best results were obtained when using silica crucibles, which softened at temperatures above 1530°C and sometimes yielded so much that the melt flowed out.

Variation of the Equilibrium Constant with Temperature.

It has already been seen that the constant increased with temperature. Thus, writing:

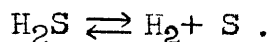
$$K_M = \frac{\text{H}_2\text{S}}{\text{H}_2} \times \frac{\text{Fe}}{\text{FeS}},$$

increase of temperature favours the formation of H_2S and Fe. According to the theorem of Le Chatelier, when heat is added to a system in equilibrium a change takes place, if possible, which is accompanied by the absorption of heat. Now, as a rise in temperature favours the formation of H_2S and Fe then, from Le Chatelier's theorem, it is probable that the production of H_2S and Fe is accompanied by the absorption of heat. Conversely, when H_2S acts on molten iron heat is evolved. Therefore there will be a smaller percentage of sulphur in a melt which has been quenched from a high temperature, than in one which has been quenched from a lower temperature, when both melts have been heated in the same gas mixture for the same period of time.

The Effect of High Temperatures on Hydrogen Sulphide.

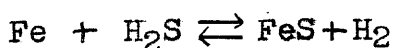
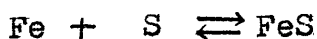
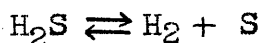
From the observations made during this investigation, it seems

probable that hydrogen sulphide is decomposed into hydrogen and sulphur at temperatures between 1530°C and 1600°C. The action would probably be better described as one of dissociation rather than of simple decomposition, and may be written:



The dissociation was probably greatest in the hot zone of the reaction tube. The temperature in this zone would be too high to allow any sulphur to deposit. This view is supported by the fact that an alundum crucible, which had been used for many runs, was analysed and found to contain no sulphur. Also, the surface of the reaction tube in the hot zone was clean. There was, of course, an upward flow of gas through the reaction tube, and this current would carry up with it some of the elementary sulphur, which would then condense on the cooler parts of the tube. The errors in the early runs were probably caused by the sulphur depositions, and by the hydrogen sulphide which was absorbed by the alundum baffle system and the reaction tube itself. That there was a sulphur deposition of some sort in the reaction tube was proved conclusively when hydrogen from a cylinder was passed through the empty tube at 1550°C. The escaping hydrogen was found to contain as much sulphur as some of the gas mixtures used in the investigation.

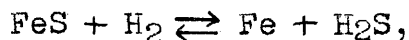
It is thus probable that the following reactions occurred simultaneously in the hot zone of the reaction tube:



All the gas mixtures contained a large excess of hydrogen, and this would tend to decrease the dissociation of the hydrogen sulphide. As the sulphur would be present in the form of vapour, the reaction between it and the iron would be reversible.

CONCLUSION

An experimental investigation has been made of the equilibrium constant of the reaction:



when it occurs at 1530°C, 1550°C, 1570°C, and 1600°C, respectively. This experimental study was undertaken in order to enlarge the present knowledge of the thermodynamics of metallurgical reactions and to facilitate the study of such other balanced reactions. An investigation was also thought desirable because of the large discrepancies between the results obtained by previous investigators (Maurer and Bischof,⁽⁹⁾ and Chipman and Li⁽¹⁰⁾) of this reaction.

The results obtained may be summarised by the equation:

$$\log K_M = \frac{-1341}{T} + .107,$$

where $K_M = \frac{\text{H}_2\text{S}}{\text{H}_2}$ (volume ratio) $\times \frac{\text{Fe}}{\text{FeS}}$ (mole fractions)

and T = temperature (°Absolute).

It has thus been shown that the constant increases slightly with rise in temperature. The results obtained agree reasonably well with those of Chipman, and they differ greatly from Maurer and Bischof's. Of these two, the former's data are based on the more definite information concerning the state of the reaction as regards equilibrium.

In previous investigations of this reaction, the sole factor used as an indication of the proximity of the reaction to the equilibrium state was a chemical analysis of the hydrogen sulphide/

hydrogen gas mixture, before and after it had passed over the melt. In the present investigation use has been made of the "high-temperature balance". By means of the high-temperature balance it has been possible to take weighings of the melt during the course of the reaction, and this has been a useful indication of the nearness of the reaction to the equilibrium state. The accuracy of the high-temperature balance has been confirmed by the agreement between it and weighings taken at ordinary temperatures after the melt had been quenched. The values obtained for the equilibrium constant have been based on the gain in weight of the melt and crucible when weighed at room temperature. The high-temperature balance has been used chiefly as a pointer to the state of the melt as regards equilibrium. That the gain in weight of the melt and crucible was due to the sulphur in the former was shown by the sulphur-analyses which were carried out on the melts. The equilibrium state was approached from both sides of the equation.

Other investigators experienced difficulty in obtaining a crucible of suitable composition for containing the melts, and they did not solve the problem satisfactorily. This difficulty was solved in the present research by using alundum crucibles which were made from a mixture of coarse and fine alundum powders. The main source of trouble in the present work was the sulphur deposition in the reaction tube, but this difficulty was surmounted by passing a rapid stream of hydrogen through the tube at 1580°C , and so driving out the sulphur. The problem of a suspension for the crucible and melt was solved by the use of molybdenum and platinum wires.

There is no doubt that the method of the high-temperature balance is a very useful one for investigating metallurgical (and other reactions. By its use one might almost say that it is possible to witness the progress of the reaction. Reference has already been made to its fruitful use by White⁽¹¹⁾, and there are many other similar avenues of research with it. For example, the effect of various metallic oxides (Al_2O_3 , MgO , Cr_2O_3 , etc.) on the dissociation of ferric oxide can be studied to good effect and, in fact, some preliminary work on this was carried out during the course of the present investigation. It should also be possible to make useful investigations of many important metallurgical reactions, such as that between manganese and iron sulphide, in the presence of various gas compositions.

ACKNOWLEDGMENTS.

The author wishes to record his indebtedness to Professor Hay and Dr. White, (both of the Metallurgy Dept. of the Royal Technical College, Glasgow), for the advice and assistance which they gave during the course of this investigation.

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