and has somewhat the characteristic "eutectic structure" under the microscope. The other and lighter portion shows a complex structure of interlocked crystals, although not sharply defined. Unetched specimens did not yield photomicrographs owing to the ease with which the surface of the metal "dragged" under polishing. The darker component is the softer, the lighter crystalline material showing in relief after polishing.

VI. Summary.

1. This research was merely a preliminary study of the conditions necessary to produce "yttrium mixed metal" analogous to "cerium mixed metal."
2. The method of preparing anhydrous chlorides of the yttrium earth metals has been extended from the scale of atomic-weight determinations to that of large scale operations.
3. Yttrium mixed metal has been prepared in powder form by decomposing the anhydrous chlorides with sodium *in vacuo* and by the electrolysis of these chlorides in the fused condition.
4. Electrolysis of a solution of the oxides of the yttrium earth metals in fused cryolite has been studied; it is a less efficient method than the previous ones.
5. Loss of yttrium chloride by volatilization has been demonstrated.
6. Yttrium mixed metal has been obtained in coherent form for the first time by sintering the metal powder *in vacuo*. The resulting mass tends to disintegrate while metallographic specimens are being prepared from it, and upon exposure to the air.
7. Some of the properties of "yttrium mixed metal" have been recorded.
8. Further work in the preparation of the metal and its alloys is contemplated.

URBANA, ILLINOIS.

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY OF THE CARNEGIE INSTITUTION OF WASHINGTON.]

THE EQUILIBRIUM BETWEEN CARBON MONOXIDE, CARBON DIOXIDE, SULFUR DIOXIDE AND FREE SULFUR.

BY J. B. FERGUSON.

Received August 9, 1918.

Introduction.

The reduction of sulfur dioxide by reducing gases presents an interesting problem to the vulcanologist and to the industrial chemist as well as to the more mathematically inclined physical chemist. The role of the sulfur gases in volcanic activity and particularly the role of these gases in the activity of Kilauea in Hawaii has long been a matter of conjecture and the present investigation was undertaken to shed some light upon this question. A knowledge of the free energy of sulfur dioxide would enable one to calculate many of the equilibria which may exist between the volcanic gases under the divers conditions found during an eruption and a study of the reaction between sulfur dioxide and carbon monoxide at high temperatures was considered more direct and better suited for determining this quantity than a study of any of the other gas reactions involving sulfur dioxide. The results of this investigation are presented in detail in the following paper.[1]

With the exception of the results of a few qualitative experiments the literature is devoid of reference to this reaction. The experiments conducted by Berthelot,[2] Hännisch-Schröder,[3] Smith and Hart,[4] and Scheurer and Kestner[5] indicate that sulfur dioxide may be slowly reduced by carbon monoxide to free sulfur at temperatures as low as that of red heat, in which case some carbon oxysulfide may also form but that if the reduction takes place at temperatures as high as white heat the reaction probably follows solely the equation

$$2CO + SO_2 = 2CO_2 + S.$$

Qualitative Experiments. Stream Method.

The equilibrium constant for the reaction

$$CO + {}^1/_2SO_2 \rightleftarrows CO_2 + {}^1/_4S_2$$

for various temperatures was calculated by means of the Nernst approximate formula; the values so obtained indicate that, at temperatures below 900°, the reaction goes so far toward completion as to preclude the possibility of carrying on an investigation at these low temperatures.

Before quantitative experiments could be made at higher temperatures some knowledge of the reaction velocity was required and for this purpose some qualitative experiments were undertaken. As the calculations, just referred to, indicated the impossibility of the reaction reversing at low temperatures, in planning these experiments it was only necessary to avoid those experimental conditions which would give rise to subsidiary reactions such as that involving the formation of carbon oxysulfide which would obscure the results.

Accordingly a gas mixture containing 25% carbon monoxide, 25% sulfur dioxide, and 50% nitrogen, by volume, was made up in the belief that the carbon monoxide concentration in the final gases would be so reduced that the subsidiary reactions might be safely neglected. On September 11, 1913, this gas mixture was passed through a porcelain tube heated in an electric furnace. When the tube was heated to temperatures below 900° a mere trace of sulfur condensed in the cold end of the tube; when

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[1] A partial summary of the results was published in *J. Nat. Acad.*, **3**, 371 (1917).

[2] *Compt. rend.*, **96**, 298 (1883); *Ber.*, **16**, 566 (1883).

[3] *Polytech. J.*, **258**, 225 (1885); *Jahresb.*, **1885**, p. 2059.

[4] *J. Soc. Chem. Ind.*, **5**, 643 (1886); *Jahresb.*, **1886**, p. 2054.

[5] *Compt. rend.*, **114**, 296 (1892); *C. B.*, **1**, 473 (1892).

heated to 1000° a small quantity of sulfur was found condensed, but when heated to 1100° a much greater quantity was found indicating a rapid increase in the reaction velocity at this latter temperature. It seemed probable that above this temperature equilibrium could be reached without a special catalyzer and also, with the aid of a suitable catalyzer, at somewhat lower temperatures. In view of the analytically unfavorable situation of the equilibrium at low temperatures, as calculated, 1000° was thought to be the lowest feasible temperature at which to work.

Quantitative Experiments. Stream Method.

The experimental work about to be described was of a preliminary nature in the sense that it produced no valuable numerical results, although in the manner in which it was carried out and in the apparatus it required, it compared favorably with the more fruitful work of a later date.

Gas mixtures containing carbon monoxide, carbon dioxide and sulfur dioxide in known proportions were passed over heated, crushed Marquardt porcelain at different rates, chilled, and collected over dry mercury for analysis. The temperature of the gas stream was obtained by means of a protected platinum-platinum rhodium thermoelement and a suitable potentiometer set-up. Fig. 1 is a diagrammatic representation of the furnace set-up. The porcelain-Corning glass joint near the U-tube was close enough to the furnace to prevent the porcelain capillary from plugging with solid sulfur and withstood a marvelous amount of heat ill-treatment. The crushed Marquardt porcelain was intended not only to serve as a contact mass but also to prevent the formation of stream lines in the furnace. The temperature measurements were in reality measure-

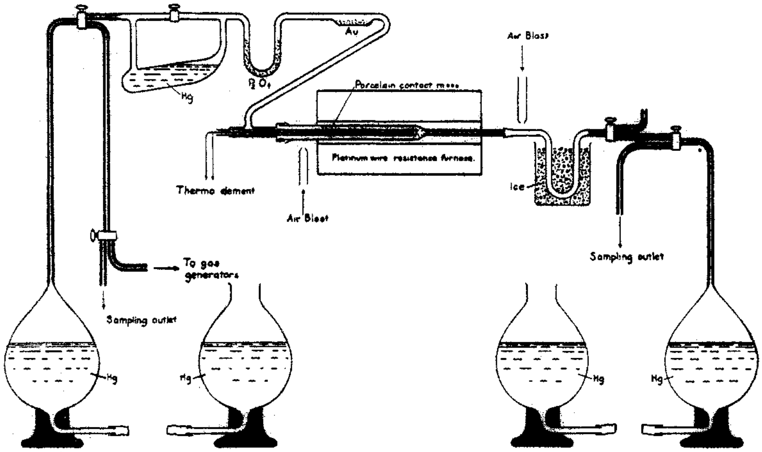

Fig. 1.—The set-up of apparatus for the early experiments by the stream method.

ments of the temperatures of the porcelain protecting tube and not of the temperature of the gas stream. It was necessary to assume that these temperatures were identical, since no better method of measuring the temperature suggested itself; but such an assumption would undoubtedly lead to some errors at high temperatures where the tube heated mainly by radiation might well have a temperature above the average temperature of the gas passing between the tube and the furnace wall at that point.

The gases used to prepare the mixtures were obtained from the following sources:

Sulfur Dioxide.—The gas from liquid sulfur dioxide, purchased in cylinders, was dried with conc. sulfuric acid and phosphorus pentoxide, and upon analysis was found to be of sufficient purity.[1]

Carbon Monoxide.—This gas was prepared by dropping conc. formic acid upon warm conc. sulfuric acid and passing the gas obtained over the following reagents: conc. sulfuric acid, potassium hydroxide, soda lime and phosphorus pentoxide.

Carbon Dioxide.—Pure sodium hydrogen carbonate and sulfuric acid were used and the gas dried with sulfuric acid and phosphorus pentoxide.

In handling the gas mixtures the greatest care was taken to exclude water vapor, since this gas would not only disturb the equilibrium in the furnace but would by the formation of moisture films render possible a selective absorption of the constituents of the final gases, and thus prevent true samples for analysis being obtained. The initial and final gases were analyzed in the following manner:

The sulfur dioxide was dissolved in an excess of an iodine solution and the excess determined by a back titration with thiosulfate. The iodine solution dissolved a part of the carbon dioxide and a trace of the carbon oxysulfide. The remaining gases were brought into contact with a solution of caustic potash which dissolved the remaining carbon dioxide and carbon oxysulfide. The carbon oxysulfide was then determined by adding this alkaline solution to an excess of an acid iodine solution and determining the excess. The residual gas, carbon monoxide, was absorbed in a cuprous chloride solution. The sulfur present in the reaction chamber was calculated by means of the equations

$$CO + {}^1/_2SO_2 = CO_2 + {}^1/_4S_2.$$

$$CO + {}^1/_2S_2 = COS.$$

The results of the first series of experiments are presented in Table I. The symbols K_1 and K_2 are thus defined:

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[1] Analyzed 99.6% SO_2 by titration. The losses of sulfur dioxide during the analysis were considerable, due to rubber connectors (used in the early form of the apparatus) and the impurities are certainly much less than the analysis indicates.

$$K_1 = \frac{P_{CO_2} - P^{1/4}_{S_2}}{P_{CO} - P^{1/2}_{SO_2}} \qquad K_2 = \frac{P_{CO} - P^{1/2}_{S}}{P_{COS}}$$

the unit of pressure being one atmosphere

TABLE I.

The Results of Experiments at 1000° by the Stream Method.

Initial gas composition.							
Direct analysis.			Calculated from the analyses of the final gases.		Rate of flow of gas.		
% CO.	% SO_2.	CO_2.	% CO.	% SO_2.	Cc. per min.	Log K_1.	Log K_2.
62.1	37.9		62.4	37.6	13.7	1.23	0.645
67.4	32.6		66.1	33.9	11.3	1.51	0.669
77.0	23.0		74.9	25.1	3.6	1.25	0.099
85.0	15.0		86.0	14.0	2.2	0.53	0.477
67.6	32.4		69.5	30.5	2.1	2.15	—0.222
72.1	27.9		71.2	28.8	2.4	2.03	—0.443
61.8	38.2		62.9	37.1	1.8	2.23	COS too small to determine
41.2	22.9	33.3	Cannot be calculated from final gases		1.2	2.20	

The agreement between the last 4 values for log K_1 is very satisfactory when one considers the magnitude of the errors in the analytical results. The values for log K_2 are not so satisfactory and since no simple explanation of them was to be found, the values of log K_1 were also viewed with suspicion.

If the value of 2.0 for log K_1 were even approximately the true value, the compositions of the final gases would be such that much more refined analytical methods than had been used would be necessary if the determinations were to be made with any accuracy whatsoever.

The agreement between the initial and calculated initial compositions was of such a character that I felt convinced the only reactions involved were

$$CO + {}^1/_2SO_2 = CO_2 + {}^1/_4\,S_2 \qquad (1)$$

$$CO + {}^1/_2S_2 = COS \qquad (2)$$

especially since this confirmed the qualitative work of the earlier investigators.

Analytical Studies.

Since the reaction $CO + {}^1/_2SO_2 \rightleftarrows CO_2 + {}^1/_4S_2$ progresses toward the $(CO + {}^1/_2SO_2)$ side as the temperature is raised many of the analytical difficulties could be avoided by working at sufficiently high temperatures, but the refractories suitable for gas work cannot be relied upon above 1200°, thus preventing the easy solution of these difficulties in this manner. It was therefore necessary to carry out a number of minor researches with the purpose of improving the analytical methods.

Sulfur Dioxide.—Most of the details of this work have already been published.[1] The excess iodine method was found to be a very accurate method of determining sulfur dioxide in mixtures containing carbon monoxide and carbon dioxide if the proper precautions are employed such as (1), the absolute exclusion of water vapor prior to the gas sample reaching the absorbent, and (2) the use of an all-glass apparatus. In mixtures containing carbon oxysulfide the method gives high results; carbon oxysulfide partly dissolves in the iodine solution and is oxidized by it. For the analysis of such mixtures it is therefore necessary to separate the carbon oxysulfide from the sulfur dioxide prior to the determination of the latter.

Carbon Monoxide.—The errors due to manipulation alone were sufficient to cause the discarding of the method in which the carbon monoxide is absorbed by a solution of cuprous chloride.

The iodine pentoxide method was first tried out. Some evidence was obtained which indicated a slow decomposition of the iodine pentoxide at the temperature of operation, 160°, and a possibility that this decomposition begins appproximately at 100°. A careful study of the dissociation of this compound seems to be required if the method utilizing the liberated iodine is to be put on a sound basis. The method utilizing the carbon dioxide formed was more accurate, but was less convenient than the cupric oxide oxidation method, which was next tried. In it the gas is slowly pumped over hot cupric oxide (300–400°) several times until oxidized, when the resulting carbon dioxide is determined by absorption in an excess of a barium hydroxide solution, and the excess found by titration with standard acid.

Carbon Oxysulfide.—The solubility of this gas in an iodine solution and its action upon that reagent made it necessary to find some means whereby the carbon oxysulfide could be removed from the gas mixtures prior to the determination of the sulfur dioxide. Many dry and wet reagents were experimented with in vain and efforts in this direction were abandoned. The fact that carbon oxysulfide readily decomposes into carbon monoxide and sulfur when heated by a hot platinum wire was suggestive of several possibilities, one of which was found feasible. Mixtures containing carbon oxysulfide, carbon monoxide and carbon dioxide and sulfur dioxide when heated by a platinum wire, the wire being at 1000–1200°, did not change in volume, indicating that under these conditions the carbon monoxide did not react with the sulfur dioxide. The carbon oxysulfide in the mixtures was entirely decomposed into carbon monoxide and sulfur, the latter condensing on the cold walls of the container. This observation suggested at once a procedure for the analysis of such mixtures. In one sample the carbon oxysulfide and sulfur dioxide could be determined to-

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[1] J. B. Ferguson, THIS JOURNAL, 39, 364 (1917).

gether by being first absorbed in alkali and later oxidized by an iodine solution while on another the carbon oxysulfide could be destroyed by glowing and the sulfur dioxide then accurately determined by the excess iodine method.

To check the possibility of some of the sulfur dioxide being lost in this procedure a known mixture of pure carbon monoxide and sulfur dioxide was glowed and then analyzed.[1] The composition of the final mixture did not differ from that of the initial mixture by more than the errors in the sulfur dioxide determination.[2] In this connection it may be of interest to record that this same gas mixture when passing through a porcelain tube heated to 1000° reacted to such an extent that considerable sulfur was deposited in the cold end of the tube.

The porcelain tube used in the earlier experiments was then replaced by a new tube of the same general design but with a smoother capillary and the remainder of the set-up left as nearly identical with the former as was possible. The gases were analyzed by the newer methods. One experiment only was made because the result obtained differed so greatly from the older results which had indicated a value of 2.0+ for log K_1.

Table II.

Additional Result of Experiments at 1000° by the Stream Method.

Initial gas composition.							
Direct analysis.		Calc. from final analysis.					
CO.	SO_2.	CO.	SO_2.	Rate of flow.	Temp.	Log K_1.	Log K_2.
57	43	58.2	41.8	1.2 cc. per min.	1000°	1.22	COS too small to determine

Quantitative Experiments. Semi-Stream Method.

Method.

The experiment just recorded confirmed my suspicions with regard to the quenching of the gas in the earlier work. The reactions had evidently gone on after the gas had left the reaction chamber and there was no means of telling at what temperatures the reactions had stopped. Although with the new tube much less reaction must have taken place, and although with mixtures containing little carbon oxysulfide, the reaction would perhaps not have been appreciable, I was afraid to rely upon this method with mixtures containing any great excess of carbon monoxide, and so discarded this stream method for a semi-stream method in which the experimental conditions could be defined more precisely.

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[1] The wire of 0.4 mm. diameter heated by a current of 6 amperes was judged to be at a temperature between 1000° and 1100°. The whole gas sample was placed in the glower tube which was immersed in water at room temperature and glowed for 10 minutes. The gas pressure was probably about 0.1–0.2 atmospheres.

[2] Initial composition, % SO_2, 40.8. Final composition, SO_2, 40.5. Loss of SO_2 = 0.03 cc. Analytical errors usually of this order for mixtures of such concentrations.

In the new method a volume of gas could be maintained at a known temperature and pressure for a desired time, at the conclusion of which a part of the gas could be suddenly removed for analysis and then more gas introduced to replace that removed. The withdrawal of the sample was effected by connecting for a very short time (0.1–0.5 second) the reaction chamber with an evacuated vessel. Since only a part of the gas was removed from the reaction chamber in this short time, the possibility that the gases given off from the walls of the reaction chamber at the lower pressures would be able to affect the trueness of the equilibrium sample, seems too remote to merit consideration. The retention of any appreciable amount of gas by these walls might, however, render the final gases of such compositions that these would bear no simple relation to the corresponding initial gases, but this would in no way invalidate the results if complete analyses were made, although removing one of the most useful means the experimenter would have of checking up his procedure.

The new method would yield better quenched gas samples than the stream method not only because of the increased speed of sampling but also because of the great cooling effect obtained by the sudden expansion of the gas.

Apparatus.

The apparatus is shown in Fig. 2. The outlet to the gasometer was closed with a mercury seal after the air had been swept out and the gasometer then filled with the gas desired. The glass capillary-porcelain joint was made tight by means of a brass cap covered with de Khotinsky cement.[1] This method insured a minimum gas space in this connection, in this respect being superior to any glass-porcelain joint I could make.

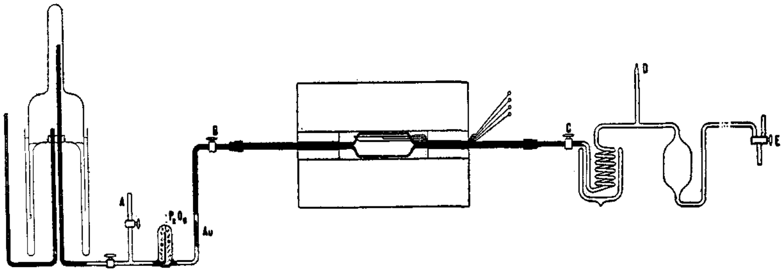

Fig. 2.—The set-up of apparatus for the final experiments by the semi-stream method.

At the beginning of a run the stopcock B was closed and that portion of the apparatus between it and the gasometer was evacuated and then filled with the gas mixture. The furnace tube and the remainder of the system was then evacuated, tested and sealed off at D. The stopcock C was closed and the stopcock B opened partially several times in such a

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[1] A well-known commercial cement manufactured for just such purposes in this country.

manner that the gas pressure gradually rose until it equalled that of the gas in the gasometer. Care was always taken lest the gas should be admitted so rapidly that when it became heated a back pressure would be set up. After the gas had been in the furnace for the required time the stopcock C was quickly opened and closed; the time consumed was from 0.1 to 0.5 second. The stopcock B was opened and the chamber refilled, in the same manner as in the initial filling. During the time this gas was reacting, the sample was pumped from coil and bulb into the analyzing apparatus and if desired for analysis stored in one of the mercury reservoirs. As a rule the first few samples were rejected in order to avoid any errors due to the selective adsorption of the gases by the walls of those portions of the apparatus with which they came into contact, including the stopcock grease. Samples of from 15 to 25 cc. were obtained, depending on the size of the reaction chamber; the latter were obtained with the silica tubes. Each sample was analyzed separately when possible. Two or three samples only could be obtained, as the stopcock C and the deposited sulfur both were apt to cause trouble if more were attempted. The carbon dioxide snow about the coil served to hasten the precipitation of the sulfur and also to cool it; when it was not used, this sulfur found its way into the analyzing apparatus where it formed mercury sulfide and rendered the apparatus unfit for accurate measurements. The stoppage of the reactions by the chilling of the reacting gases was not dependent upon the use of this cooling agent, the reactions having apparently ceased before the gases emerged from the porcelain tube. Experience showed that if the coil be left immersed in the carbon dioxide snow, much of the sulfur dioxide in the sample would remain with the sulfur in the coil despite prolonged pumping,[1] and the carbon dioxide snow was therefore removed from around the coil completely before any attempts were made to pump the sample into the analyzing apparatus.

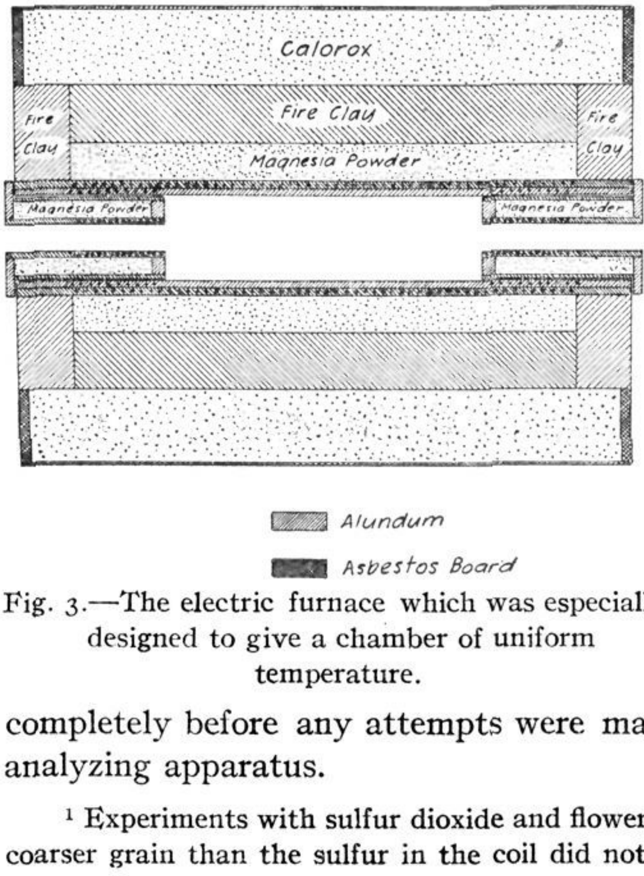

Fig. 3.—The electric furnace which was especially designed to give a chamber of uniform temperature.

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[1] Experiments with sulfur dioxide and flowers of sulfur which was perhaps of much coarser grain than the sulfur in the coil did not indicate any such retention of sulfur dioxide at the same temperature.

Temperature Uniformity in the Electric Furnace.

The supply of porcelain tubes was somewhat limited, and for this reason a furnace had to be designed for use with the tubes on hand. The furnace shown in Fig. 3 proved satisfactory, being capable of producing a temperature uniformity of ±0.5° at the required temperatures for the periods of time desired. The details of the development of this furnace have been published[1] and need not be repeated here. In Figs. 4 and 5 are curves indicative of its behavior.

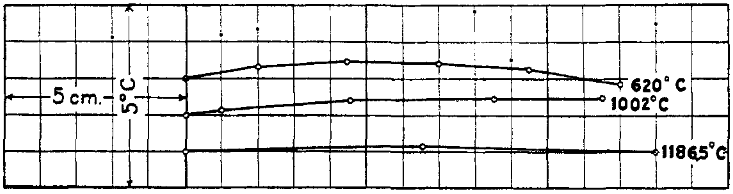

Fig. 4.—Temperature uniformity in the furnace chamber. Each curve represents the temperatures found along the chamber at a given time.

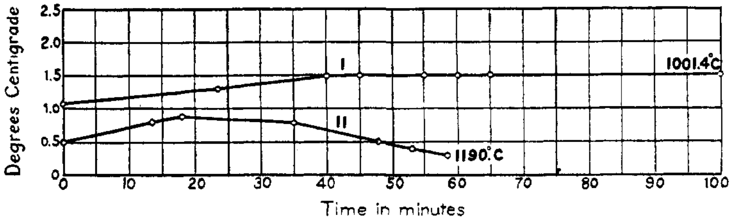

Fig. 5.—Temperature constancy in the furnace chamber. Each curve represents how the mean temperature of the chamber varied with time.

Initial Experiments without Contact Mass at 1000°.

The first experiments were carried out, using Royal Berlin porcelain "pyrometer" tubes with capillaries of one mm. bore and central chamber of 15 × 5 cm. outside dimensions. They were glazed on the outside only.

The results are given in Table III.

$$K_1 = \frac{P_{CO_2} P_{S_2}^{1/2}}{P_{CO} P_{SO_2}^{1/2}} \qquad K_2 = \frac{P_{CO} P_{S_2}^{1/2}}{P_{COS}}.$$

Unit of pressure = one atmosphere.

The agreement between the values 1.16 and 1.19 just given and that value of 1.22 obtained for log K_1 in the last experiment by the stream method, using portions of the same gas mixture was so good that in view of the great difference in the two procedures I felt sure equilibrium had been reached—until I had completed some further experiments. Attention is called to this example of a misleading good agreement to emphasize

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[1] J. B. Ferguson, *Phys. Rev.*, 12, 79 (1918).

the danger of misinterpreting results if one dares to be optimistic. Since it seemed inconceivable that the samples had not been properly chilled, the results were calculated on the basis that the carbonoxysulfide obtained had been present in like amounts in the equilibrium gases.

Table III.

Results of Experiments with Plain Porcelain Pyrometer Tubes, Semi-Stream Method, at 1000°.

Initial gas composition.						
Direct analysis.		Calc. from final analysis.				
CO.	SO_2.	CO.	SO_2.	Gas taken after. Min.	Log K_1.	Log K_2.
57	43	57.5	42.5	38	1.16	COS too small to determine
57	43	57.8	42.2	32	1.19	
73.4	26.6	73.4	26.6	33	0.75	—0.03
73.4	26.6	Partial analysis only		18	0.69	—0.12
73.4	26.6			270	0.79	—0.13

The results were all lower than my earlier calculation led me to expect, and experiments were therefore planned using contact masses, upon the assumption that in none of these latter experiments had the gases completely reacted.

Before giving the details of these experiments, a description of the analytical apparatus, which attained its final form at this time, should properly be given.

Final Analytical Apparatus.

The final apparatus as it was used to analyze mixtures of carbon monoxide, carbon dioxide and sulfur dioxide is shown in Fig. 6. The various parts will be described.

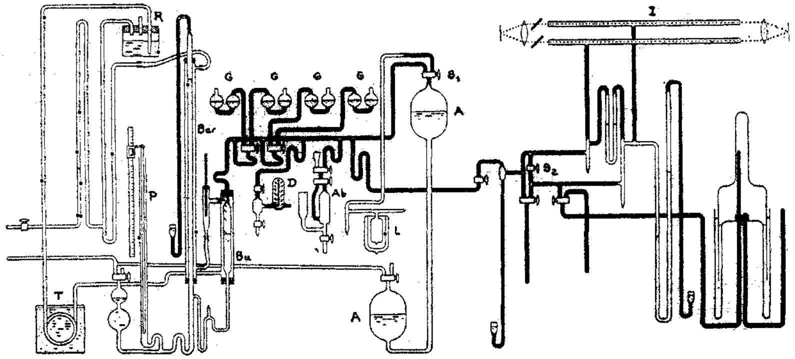

Fig. 6.—The final analytical apparatus including a buret, Bu, barometer, Bar, absorption pipet, Ab, liquid air bulb, L, mercury pump, A, and gas interferometer, I.

Water-jacket System.—The temperature of the water in the water jacket was kept constant to 0.05°. Air under a few pounds' pressure was used to circulate the water which was thus carried to the upper reservoir R, from which it siphoned down through (1) a copper tube helix immersed in a thermostat, T, (2) the water jacket on the buret Bu, (3) the thermometer tube, and (4) the water jacket on the barometer Bar. The temperature of the water in the upper reservoir was usually from 0.2 to 0.5° below that in the buret water jacket. The heat supply in the thermostat was obtained from a 3-heat simplex heater wound in a tight helix surrounding the stirrer. The current was varied from one heat to another but never shut off. This gave a very compact arrangement for obtaining the heat supply required which was somewhat larger than an ordinary thermostat would have needed. The thermo-regulator[1] was of a slightly different design from that ordinarily used, in that the adjustments were made by means of an external piston tube in respect to a fixed platinum wire.

Gas Measuring Device.—The gas was measured by compressing it to one of the known volumes available in the buret, and then reading the pressure. The coarse adjustment was made by the air pressure and the final by means of a small bore piston tube, P. In the earlier work a large bore piston tube alone was used, but owing to frequent breakages the method was abandoned.

Air Pump and Lines.—The air pump AA was operated by gravity and compressed air. The stopcock S_1 at the top of the upper bulb was of large bore and allowed a minimum of stopcock grease to be carried along by the mercury, and was the only stopcock through which any quantity of mercury had to pass and remain in the apparatus.

The sample gases were admitted through this large stopcock S_1, the liquid air bulb L being removed and the furnace system sealed in its place.

The Interferometer.—The Zeiss interferometer I as received from the manufacturer contained too large tubes to be of any use and new tubes had to be constructed. Attempts to make such tubes of glass were not successful and the tubes used were of brass 4 mm. inside diameter with an inside coat of enamel which was given an especially dull finish to prevent reflections. This enamel seemed to adsorb sulfur dioxide out of a mixture of carbon dioxide and sulfur dioxide so that the instrument could only be used for the confirmation of the purity of the carbon monoxide. To do this both sides of the interferometer were evacuated by a good mechanical pump (capable of 0.001 mm. at least) and then shut off from the pump and from each other by the necessary stopcocks. The unknown carbon monoxide was then admitted to the one side and pure carbon monoxide to the other until its pressure was as near that of the unknown carbon monoxide as it could readily be made. As this pressure adjustment using a mercury manometer was too insensitive, the stopcock S_2

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[1] J. B. Ferguson, This Journal, 40, 6, 929 (1918).

connecting the two sides was then opened and the assumption was made that the pressure adjustment took place before the gases could contaminate each other through the process of diffusion.

Procedure.—A gas sample of about 20 cc. was withdrawn from one of the small reservoirs G into the pump AA and the capillary leading to the reservoir filled with mercury from the buret. The reservoir stopcock being closed, the gas sample was then forced into the buret and measured, after which it was taken via the pump to the liquid air bulb L where the carbon monoxide was separated from the carbon dioxide and sulfur dioxide. The carbon monoxide was then pumped from this bulb, forced into the buret, measured, and then allowed to expand into the interferometer where its purity could be tested. The liquid air being removed from around the bulb, the carbon dioxide and sulfur dioxide were pumped from the bulb and forced into the buret and measured. The measurement completed, the gas was then forced into the absorption pipet Ab containing the iodine solution. As the T tube prevented all the samples being forced into the pipet, dry air from the drier D was used to wash the trace in the T into the pipet. The iodine solution was then removed from the pipet and titrated with thiosulfate.

For mixtures containing carbonoxysulfide, the apparatus was slightly more complex, but was not used in the final measurements, as it was found that this gas was not present in mixtures obtained in a proper manner. The additions consisted of another stopcock and a glower. The gas was measured and the carbon monoxide separated from the carbonoxysulfide, carbon monoxide and sulfur dioxide by means of the liquid air. The remaining mixture was glowed, yielding a mixture of carbon monoxide, carbon dioxide and sulfur dioxide, and the liquid air was again used to separate this carbon monoxide from the carbon dioxide and sulfur dioxide. The carbon dioxide and sulfur dioxide were then treated with the iodine solution in the usual way. The examination of the carbon monoxide obtained from the glowing showed that it was pure carbon monoxide.

Experiments with Broken Porcelain at 1000°.

Broken Marquardt porcelain was first used as a contact mass and was contained in a silica glass tube of the shape of the porcelain "pyrometer" tubes previously used. The silica glass has several advantages over porcelain in that the capillaries are smoother and the central chamber may be opened and resealed again.

In Table IV are the results of one series of experiments.

For comparison the results of an experiment with a part of the same mixture but without a catalyzer will be cited. The carbon oxysulfide and sulfur dioxide values were 10.4 and 5.0%, respectively.

TABLE IV.

Results of Experiments at 1000° Using a Porcelain Contact Mass.

Initial gas.					
CO.	SO_2.	Temp.	Gas taken after. Min.	% COS.	% SO_2.
73.4	26.6	1000°	24	2.4	1.7
73.4	26.6	1000°	21	...	0.96
73.4	26.6	1000°	18	...	0.72

The second contact mass was platinized Marquardt porcelain. The former contact mass was immersed in a solution of platinic chloride and then ignited at 1200°. A silica tube was used as in the case of the broken porcelain.

With this contact mass, after the initial run it was very difficult to obtain initial and final mixtures that would agree. After the initial run, air was forced through the tube in order to burn out the sulfur and in subsequent runs the final mixtures always contained too much sulfur dioxide. Had pure sulfur dioxide only remained behind it would have caused no trouble, but the evidence pointed not to sulfur dioxide but sulfur trioxide,[1] and if it were the latter a change in the mode of calculating the sulfur pressure would be necessary. For this reason every effort was made to avoid this difficulty.

The results are given in Table V.

Experiments at 1190° with and without a Contact Mass.

There was a possibility that one might obtain an equilibrium without a contact mass at this temperature, and as this was most desirable since silica glass tubes could not be used and the porcelain tube suitable for use with a contact mass would have to be improvised, experiments were made first with the porcelain pyrometer tubes and later with one of these tubes in which platinum had been deposited by igniting in it some platinic chloride. Finally, platinized broken porcelain was used in a porcelain tube, the open end of which was closed by means of a sealed-in tightly fitting porcelain capillary tube which was of such a length that there was no appreciable gas space in the portions of the tube not at the desired temperature.

The results are given in Table VI.

Discussion of Results.

General.

In every research requiring the manipulation of much apparatus, many results are obtained which, though inconclusive, have greatly aided the experimenter in the final solution of his problem. The character of the present problem and the fact that the work was done by one man alone, insured that this should be no exception. Most of these results

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[1] SO_3 is known to be adsorbed by platinum. Bodenstein and Fink, *Z. physik. Chem.*, 60, 1 (1907).

TABLE V.

Results of Experiments at 1000° Using a Platinized Contact Mass.

	Gas composition.							
	Initial.	Initial calc.	Final.	Furnace.	Heat treatment.	Log K.	No. expt.	Remarks.
CO	70.3	..	...	...	1000° first sample taken after 23 min.	..	...	SO_2 determined only.
SO_2	29.7	..	0.59	0.48		1.66	1	
CO	70.3	..	...	...	1000° second sample taken after 23 min.	..	...	SO_2 determined only.
SO_2	29.7	..	0.43	0.35		1.73	2	
CO	70.3	70.5	16.8	13.92	1000° third sample after 26 min. and fourth sample after 21 min.			Two samples combined for analysis.
SO_2	29.7	29.5	0.34	0.28		..	...	
CO	..	..	82.86	68.66		..	...	
S_2	..	..	...	17.14		..	...	
COS	..	Too small to determine				1.78	3	
CO	70.3	..	...	...	1000° fifth sample after 22 min.	..	...	Slight loss of SO_2 during analysis.
SO_2	29.7	..	0.26	0.21		1.84	(4)	
CO	66.9	66.4	5.6	4.56	998° first sample after 30 min., second sample after 30 min.			Two samples combined for analysis.
SO_2	33.1	33.6	3.4	2.77		..	...	
CO_2	..	..	91.0	74.16		..	...	
S_2	..	..	...	18.5		..	...	
COS	..	Too small to determine				1.80	(5)	
CO	66.9	..	1.9	1.66	990° for 60 min.	..	...	Excess SO_2 assumed to have been obtained from SO_3.
SO_2	33.1	..	20.9	18.3	1004° for 22 min.	1.75	...	
CO_2	..	..	77.2	67.54		..	...	
S_2	..	..	...	12.51		..	6	
						1.79	6*a*	Excess SO_2 assumed to have been obtained as SO_2.

TABLE VI.
Results of Experiments at 1180–1190°.

	Gas composition.								
	Initial.	Initial calc.	Final.	Furnace.	Heat treatment.	Contact mass.	Log K_1.	Remarks.	No.
CO	66.9	66.7	18.3	15.50	1185°. 40 min. first gas out.	Plain Berlin porcelain pyrometer outside glazed only.	0.97	Equilibrium approached from (CO + $^1/_2$ SO_2) side.	1
SO_2	33.1	33.3	9.15	7.74					
CO_2	..	..	72.55	61.42					
S_2	..	..	...	15.34					
CO	66.9	..	14.68	12.28	1185°, 55 min. second gas out.	Plain Berlin porcelain pyrometer outside glazed only.	1.13	Equilibrium approached from (CO + $^1/_2$ SO_2) side.	2
SO_2	33.1	..	7.36	6.16					
CO_2	..	..	77.96	65.25					
S_2	..	..	...	16.37					
CO	66.9	..	12.3	10.22	Gas in 1185°, lowered to 1100°, held 20 min., raised to 1185° in 30 min. and held 25 min.	Plain Berlin porcelain pyrometer outside glazed only.	1.27	Equilibrium approached from (CO_2 + $^1/_4$ S_2) side.	3
SO_2	33.1	..	6.14	5.10					
CO_2	..	..	81.56	67.74					
S_2	..	..	...	16.94					
CO	66.9	66.7	16.9	14.24	1181°, 56 min., first out.	Platinized porcelain pyrometer tube.	1.02	Equilibrium approached from (CO + $^1/_2$ SO_2) side.	4
SO_2	33.1	33.3	8.46	7.13					
CO_2	..	..	74.64	62.90					
S_2	..	..	...	15.73					
CO	66.9	66.7	15.2	12.75	1181°, 54 min., second out.	Platinized porcelain pyrometer tube.	1.11	Equilibrium approached from (CO + $^1/_2$ SO_2) side.	5
SO_2	33.1	33.3	7.57	6.35					
CO_2	..	..	77.23	64.72					
S_2	..	..	...	16.18					
CO	66.9	66.8	15.15	12.69	1181°, 55 min., third gas out.	Platinized porcelain pyrometer tube.	1.12	Equilibrium approached from (CO + $^1/_2$ SO_2) side.	6
SO_2	33.1	33.2	7.35	6.16					
CO_2	..	..	77.50	64.92					
S_2	..	..	...	16.23					
CO	51.6	50.7	4.6	3.99	Gas in at 1165° and heated to 1190° in 80 min. and held 20 min.	Platinized Marquardt porcelain.	1.18	Equilibrium approached from (CO_2 + S_2) side.	7
SO_2	48.4	49.3	33.6	29.12					
CO_2	..	..	61.80	53.51					
S_2	..	..	...	13.38					
CO	51.6	51.0	4.6	3.99	1190°, 75 min.	Platinized Marquardt porcelain.	1.185	Equilibrium approached from (CO + $^1/_2$ SO_2) side	8
SO_2	48.4	49.0	33.1	28.63					
CO_2	..	..	62.3	53.89					
S_2	..	..	...	13.49					

have been omitted from the paper as I felt that they, with the inevitable accompanying explanations, would tend to bore if not confuse the reader. If in so doing I have created in the minds of those readers who have had no actual experience in such work an erroneous impression as to its difficulties, this will no doubt be corrected by the knowledge that this research though commenced in September, 1913, was not completed until March, 1917.

Thermodynamical Calculations.

Two interesting calculations may be made from the values of the equilibrium constants—the heat of reaction and the thermodynamical constant I. The former may best be obtained by means of the equations[1]

$$-RT \ln K = \Delta H_0 - \Delta\Gamma_0 T \ln T - {}^1/_2\Delta\Gamma_1 T^2 - {}^1/_6\Delta\Gamma_2 T^3 - IT.$$

$$\Delta H = \Delta H_0 + \Delta\Gamma_0 T + {}^1/_2\Delta\Gamma_1 T^2 + {}^1/_3\Delta\Gamma_2 T^3.$$

If the specific heat of sulfur vapor be assumed to be equal to that of oxygen and the specific heats of the permanent gases as given by Lewis[2] be used, the equation for $\Delta\Gamma$ for the reaction

$$CO + {}^1/_2SO_2 = CO_2 + {}^1/_4S_2$$

becomes

$$\Delta\Gamma = -1.375 - (0.0028T + 0.000{,}00093T^2).$$

For purposes of comparison it is perhaps better to consider not the heat of this reaction but rather the heat of formation of sulfur dioxide from rhombic sulfur (S_R) and oxygen at room temperature as calculated from these results. For this calculation, in addition, we require the following data:[3]

$$2S_R = S_{2g} : \Delta\Gamma = 1.74 - 0.0084T$$

$$\Delta H_0 = 29600$$

$$CO + {}^1/_2O_2 = CO_2 : \Delta\Gamma = -(2.75 - 0.0056T + 0.000{,}000186T^2)$$

$$\Delta H_0 = -67510$$

The calculation leads to a probable value of 68500 calories, which is in as good an agreement with Berthelot's[4] best value of 69400 as could be expected in view of the effect on log K_1 at the lower temperature of slight analytical errors.[5] These errors would scarcely warrant a value

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[1] G. N. Lewis, THIS JOURNAL, **35**, 1 (1913).

[2] G. N. Lewis and M. Randall, *Ibid.*, **34**, 1128 (1912).

[3] Lewis and Randall, *Ibid.*, **36**, 2468 (1914); **37**, 465 (1915).

[4] *Ann. chim. phys.*, [5] 22, 428 (1881). Berthelot's average value of 69260 includes results obtained from experiments in which the sulfur dioxide was determined by means of an alkaline solution. This procedure probably led to too low results in these cases. See "The Iodometric Determination of Sulfur Dioxide and the Sulfites," J. B. Ferguson, THIS JOURNAL, **39**, 364 (1917).

[5] An error of approximately 1000 cal. would be caused by an error in the CO determination of 1% of its own value, or, in the SO_2 determination, of 2% of its own value. In the most favorable case, *i. e.*, the one in which the ratio of the CO to the SO_2 in the initial mixture was 2 : 1, such errors would mean in actual percentages 0.05% CO and 0.06% SO_2, and that on samples varying from 20 to 35 cc.

as high as that given by Thomsen,[1] and the value of Berthelot will therefore be assumed in the remaining calculations.

For the calculation of I the equation becomes

$$-RT \ln K = -25915 + 1.375T \ln T - 0.0014T^2 + 0.000,000,155T^3 + IT.$$

In Table VII are the calculated values of this constant.

TABLE VII.

Calculated Value of the Thermodynamical Constant I.

Expt. No.	Expt. Table.	Log K.	Temp. Abs.	Temp. C.	I.
3	V	1.78	1273	1000	3.94
5	V	1.80	1271	998	3.87
6	V	1.75	1277	1004	4.02
6*a*	V	1.79	1277	1004	3.84
3	VI	1.13	1458	1185	Av., 3.99
4	VI	1.27	1458	1185	
7	VI	1.18	1463	1190	4.01
8	VI	1.185	1463	1190	3.99
Weighted mean value					3.99

Since $\Delta F = -RT \ln K$ we may substitute for it in the equation and then calculate the change in the free energy[2] ΔF_0 for several reactions. For the reaction $CO + {}^1/_2SO_2 = CO_2 + {}^1/_4S_2$

$$\Delta F = -25915 + 1.375T \ln T - 0.0014T^2 + 0.000,000,155T^3 + 3.99T$$

and $F_{298} = -22510$ cal.

For the reaction $S_R + O_2 = SO_2$

$$\Delta F = -68391 + 3.62\, T \ln T - 0.0007T^2 + 0.000,000,31T^3 - 25.04T$$

and ΔF_{298}[3] $= -69761$ cal.

The equation involving $\ln K$ may be reduced to the following form:

$$\log K = 5659/T - 0.6915 \log T + 0.000,30T - 0.000,000,034T^2 - 0.872$$

The values calculated by means of this equation for temperatures from 1000° to 1500° are given in Table VIII. Values are not given for either higher or lower temperatures since the assumption that the sulfur is present as S_2 would lead to results which, while of theoretical interest, could not be considered as representing the facts when carbon monoxide and sulfur dioxide react at these higher or lower temperatures.

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[1] 71080 cal. Thomsen, *Thermische Untersuchungen*, 2, 251 (1882–86).

[2] This is the thermodynamical potential at constant temperature and pressure, the ζ function of Gibbs.

[3] The value for this quantity given by Bichowsky in a paper at the Boston meeting of the Society in September, 1917, is very close to my value. The results upon which his value was based have been published (see G. N. Lewis, M. Randall and F. R. v. Bichowsky, THIS JOURNAL, 40, 362, 368 (1918), but the details of the calculations have not yet appeared.

TABLE VIII.
Calculated Values of Log K.

Temp. Abs.	Temp. C.	Log K.
1273	1000	1.75
1373	1100	1.43
1473	1200	1.15
1573	1300	0.90
1673	1400	0.69
1773	1500	0.50

The Dissociation of Carbon Oxysulfide.

A study of the dissociation of carbon oxysulfide was made by Lewis and Lacey[1] at the time when the earlier work herein presented was being completed. Since under equilibrium conditions for the reaction $CO + {}^1/_2SO_2 \rightleftarrows CO_2 + {}^1/_4S_2$ at 1000° I found no carbon oxysulfide it may be of interest to see how well this observation fits in with their results. Using the equations given by them, the heat of formation as given by Thomsen and assuming the specific heat of carbon oxysulfide identical with that of carbon dioxide, it is possible to calculate the probable carbon oxysulfide pressure in any of the equilibrium mixtures obtained. The composition obtained in Expt. 3, Table V, is probably the most favorable for the formation of this gas, and in this case the calculated carbon oxysulfide would be less than 1.5%. The assumption of Berthelot's value for the heat of formation of carbon oxysulfide would yield a much smaller percentage. Considering the nature of the calculation, my observations cannot be taken as in any way disagreeing with those of Lewis and Lacey.

Summary.

Carbon monoxide and sulfur dioxide react at temperatures between 1000° and 1200° to form carbon dioxide and sulfur vapor, with possibly traces of carbon oxysulfide in mixtures rich in carbon monoxide. The equilibrium constants for these temperatures have been determined.

Calculations have been made, based upon the determined values for these constants and the free-energy equations for this reaction and also for the reaction in which sulfur dioxide is formed from its elements have resulted.

These free-energy equations afford a means of calculating many equilibria such as the equilibrium between sulfur dioxide, oxygen and sulfur, or the equilibrium resulting from the reduction of sulfur dioxide at high temperatures by hydrogen.

WASHINGTON, D. C.

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[1] Lewis and Lacey, THIS JOURNAL, 37, 1975 (1915); 40, 359 (1918).