

A chemical study of Hawaiian magmatic ga
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To Dr. Naughton
with many thanks for all
the help you've given me

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A CHEMICAL STUDY
OF
HAWAIIAN MAGMATIC GASES

A THESIS SUBMITTED TO THE GRADUATE SCHOOL OF THE
UNIVERSITY OF HAWAII IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
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By
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To

Joanie, Alison and Sassafra-Priscilla

To

Joanie, Alison and Sassafra-Priscilla

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INTRODUCTION

The spectacular sight of a volcano in eruption has fascinated mankind since prehistoric times. Early man thought volcanoes to be the work of all-powerful gods residing in the earth. The ancient Hawaiians, for instance, had the greatest respect for the legendary Volcano Goddess Pele, whom they feared would punish them with lava flows if she were displeased. This belief has survived to the present day; people on the island of Hawaii still offer gifts to Pele to win her favor.¹

A volcano is an extension of one of the huge bodies of subterranean rock material called magma, which solidifies to form the igneous rocks of the earth's crust. Lava is magma which has flowed onto the earth's surface, and volcanic gases are the volatile materials associated with the magma. Both provide a means of studying magmas, whose chemical composition must otherwise be inferred from the rocks they form.²

A magma is a hot, fluid substance, consisting generally of a silicate phase, but sometimes also containing a separate gas phase. It may solidify or crystallize over a range of temperatures, from 1200°C. down to about 500°C., to form a variety of minerals and rocks. The solidification process may be extended over a wide range of time and space by fractional crystallization. If there is a separation of some of the components producing a change in the composition of the magma, this process is called differentiation. The volatile components of the magma, often called mineralisers, are believed to be very important in determining the course of differentiation. Furthermore, the residual solutions and gases left after the bulk of the magma has solidified or crystallized play a very important role in the formation of the ore deposits which contain large concentrations of the rarer components of the earth's crust.³

It is, of course, not possible to reach down into a crystallizing

magma and sample its volatile components. It is necessary to rely upon more indirect methods, such as analysing the gases given off by igneous rocks when they are heated under vacuum, or examining the gases and condensates from fumaroles. As a result, there has been much controversy in the literature regarding the amount and composition of volatile magmatic materials. There has been much speculation (e.g., Craton, 1945) regarding their influence on volcanic phenomena, but little is actually known.⁴ As a first step in gaining this knowledge, it is essential to develop systematic methods for studying volcanic gases and condensates, and to attempt to find the relationship between them and the original magmas from which they are presumably derived.

The purpose of this investigation has been to apply the techniques of modern chemistry to the study of the volatile components of Hawaiian magmas. As an approach to this problem, it seemed desirable in the beginning to develop and extend the technique of vacuum fusion of rocks as a means of studying the oxidation state of their constituent elements. It was originally intended to study the geologically important regions of the Mg-Fe-O-Si system, and to examine the relationships between dissolved volatile material and the oxidation state of iron. Preliminary investigation, however, showed that too many uncertainties were introduced by the equipment presently available because of unavoidable reactions of the fused rock with crucible materials.

Accordingly, the problem of magmas was approached from another direction - a study of the gases of the volcano Kilauea. A number of circumstances combined to make this possible. Most important was the 1959-60 eruption of Kilauea, which provided an opportunity for the collection of gas samples by modern methods. The gas chromatography system

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developed for analyzing gases from rocks was adapted easily to the analysis of volcanic gases. Furthermore, the establishment of the University of Hawaii Computing Center made available a high-speed digital computer for use in studying the complex equilibria occurring in volcanic gases.

This thesis is therefore logically divided into two sections: First, an investigation of the applicability of the vacuum fusion technique to the determination of the oxidation state of the constituent elements of rocks, and second, a chemical study of the gases of the volcano Kilauea. It was hoped that these studies would complement each other in adding to our knowledge of the gases from volcanoes and heated rocks, thus helping to provide further understanding of the relationship of these gases to the primary volatile materials associated with magmas and volcanic rock types.

PART I. AN INVESTIGATION OF THE APPLICABILITY OF THE VACUUM FUSION TECHNIQUE TO THE DETERMINATION OF THE OXIDATION STATE OF THE CONSTITUENT ELEMENTS OF ROCKS

I. Review of the Pertinent Literature

A. The gases in rocks

The gases present in rocks and minerals have been studied since the time of R. W. Bunsen in the middle of the 19th century. Much of this early work is fragmentary and qualitative, and of little value in understanding the nature of such gas-rock systems. The results of these early studies have been reviewed by F. W. Clarke (1916).⁵

The first significant work on degassing rocks was done by Gautier between 1900 and 1910.⁶ The gases he found he attributed to reactions occurring within the rocks at high temperatures. For instance, the presence of hydrogen he explained by the reaction of ferrous oxide with water, and carbon monoxide by the reduction of carbon dioxide by hydrogen. Sulfides he showed to be hydrolyzed by steam at moderately high temperatures to hydrogen sulfide, which in turn was further oxidized to sulfur dioxide and hydrogen upon raising the temperature.

Chamberlin (1908) carried on extensive research along the same lines, reaching much the same conclusions.⁷ His work, however, suffers from the fact that he neglected water in his analyses, since he did not consider it to be a gas.

The most extensive work to date on the gases in rocks is due to E. S. Shepherd (1925, 1938),^{8,9} who devoted over 20 years to the study of volcanic gases and the gases in rocks. He found that the gases obtained from igneous rocks were principally water, carbon dioxide and nitrogen, with smaller amounts of hydrogen, carbon monoxide and sulfur dioxide. Quantitatively speaking, however, Shepherd was unable to

correlate the extreme variability in the composition of the gases with the nature of the rock studied, which led him to conclude that little information regarding the history of a particular rock sample could be gained from a study of its volatile constituents.

Using high-vacuum techniques, Terada (1954) studied the gases obtained upon vacuum fusion of Hawaiian igneous rocks.¹⁰ He attempted to correlate the oxidation state of the extracted gases, expressed by the ratio CO_2/CO , to the oxidation state of the iron contained in the silicate, expressed by the ratio $\text{Fe(III)}/\text{Fe(II)}$. Some degree of correlation was noted.

B. Systematic studies of gas-silicate systems

The difficulties encountered by Shepherd and by Terada are, at least in part, due to the extremely complicated systems they were studying. It is necessary to turn to relatively simple artificial systems in order to unravel the complex equilibria involved. Since some iron oxide slags are similar in composition to naturally occurring magmas and igneous rocks, much of the pertinent research on gas-oxide and gas-silicate systems has been carried out by metallurgists. Their results, however, may be applied equally well to geochemical problems.

One of the chief difficulties encountered in any high-temperature study involving iron is that a number of oxidation states of this element are possible. In order to systematize the study of iron-containing oxides and silicates, it is necessary to have a convenient means of controlling the oxidation state of iron. The easiest way presently known of doing this is to pass a gas stream of known oxygen partial pressure over the sample. If, for instance, gas consisting of a mixture of carbon dioxide

and carbon monoxide is used, the heterogeneous equilibrium

$$\text{CO}_2(\text{g}) + \text{Fe}^{++}(\text{silicate}) \rightleftharpoons \text{CO}(\text{g}) + \text{Fe}^{+++}(\text{silicate}) + \text{O}^{--}(\text{silicate})$$

will permit an exact knowledge of the oxidation state of iron.¹¹

This technique, first used by Darken and Gurry (1945) in studying phase relations in the system iron-oxygen, has gained widespread acceptance in recent years.¹² An excellent review of the method and of the results obtained from it has been written by Muan (1958).¹³ A critical examination of the results of these investigations gives a fairly complete understanding of heterogeneous equilibria involving iron.

The first study of heterogeneous equilibria between gases and iron oxides in igneous rocks was made by Kennedy (1948).¹⁴ He concluded that a knowledge of the Fe(III)/Fe(II) ratio in a cold, unaltered igneous rock would permit a determination of the oxygen partial pressure under which the rock was formed, providing a reasonable estimate could be made of the crystallization temperature of the rock.

Eugster (1957, 1959) has applied heterogeneous equilibria involving changes in oxidation state to metamorphic systems, using such considerations to explain the stability relations of annite, $\text{KFe}(\text{II})_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$.^{15,16}

Fujii (1958) extended the work of Terada concerning the relationships between the oxidation state of iron and the composition of the gases obtained upon vacuum fusion of silicates.¹⁷ To do this, he prepared artificial samples of fayalite (Fe_2SiO_4) and brought them to equilibrium with an atmosphere of carbon dioxide, carbon monoxide and argon at 1100°C , which is below the melting point of fayalite. He was able to extract the gases which dissolved in the silicate during the equilibration, and to

correlate the function $\log (p_{\text{CO}_2}/p_{\text{CO}})$ in the extracted gases to the ratio $\text{Fe(III)}/\text{Fe(II)}$ in the silicate. He also noted a similar straight-line relationship between $\log (p_{\text{CO}_2}/p_{\text{CO}})$ in the equilibrating atmosphere and $\text{Fe(III)}/\text{Fe(II)}$ in the fayalite, in agreement with the work of Darken and Gurry. In both cases he discovered that discontinuities in the plots corresponded to transitions between different iron-containing phases. Thus, there were three regions in his plots: the first, at low $p_{\text{CO}_2}/p_{\text{CO}}$, corresponding to the presence of metallic iron in the sample; the second, at intermediate values of $p_{\text{CO}_2}/p_{\text{CO}}$, corresponding to the presence of large amounts of fayalite and some magnetite (Fe_2O_3); and the third, at high $p_{\text{CO}_2}/p_{\text{CO}}$, corresponding to the presence of fayalite and large amounts of magnetite. The positions of the lines in the extraction plots differed from those in the equilibration plots. In other words, the composition of the gas extracted from a fayalite sample differed from that of the equilibrating gas. Fujii attempted to account for these differences in terms of the effect of water adsorbed on the fayalite upon the equilibrium between carbon dioxide and carbon monoxide.

C. Object of the research

The object of the research described in this section of the thesis is to evaluate the technique of vacuum fusion as a means of studying the oxidation state of the constituent elements in rocks and minerals. To do this, a modification of the powerful technique of gas chromatography was developed for analysis of gases extracted from artificial silicate systems similar to those used by Fujii. It was hoped that a suitable technique of gas extraction could be developed, thereby making possible a convenient method for determining the oxidation state of the constituent

elements of rocks. Using this technique, it was planned to study the relationships between gas content and the oxidation state of iron in the Mg-O-Fe-Si system.

II. Experimental Work

A. Equilibration method

A gas purification train based on that described by Rist and Chipman (1958) was constructed for the preparation of mixtures of carbon dioxide, carbon monoxide and argon, thus defining known oxygen partial pressures.¹⁸ The carbon dioxide was dried over anhydrous and purified from oxygen over copper turnings at 450°C. The carbon monoxide was prepared by passing dry carbon dioxide over graphite at 1100°C., and purified from residual carbon dioxide over concentrated potassium hydroxide and ascarite. The argon, used as a carrier to minimize thermal diffusion, was purified from water, carbon dioxide and oxygen in columns containing anhydrous, ascarite and magnesium turnings at 590°C. The relative amounts of the component gases in the mixture were controlled by adjusting their various flow rates. The final equilibrating mixture was obtained by passing the purified gases through a glass bead mixer, followed by a final dehydration in a dry ice-acetone trap.

The equilibration of an artificial iron silicate sample was carried out by bubbling the gas mixture through the molten sample. For this purpose, a long platinum tube was introduced into the heating chamber through one of the o-ring joints (see Fig. I-A), and pushed down into the melt. Samples of the equilibrating mixture were taken and analysed by gas chromatography.

A single melt of fayalite (Fe_2SiO_4) prepared by C. Fujii was

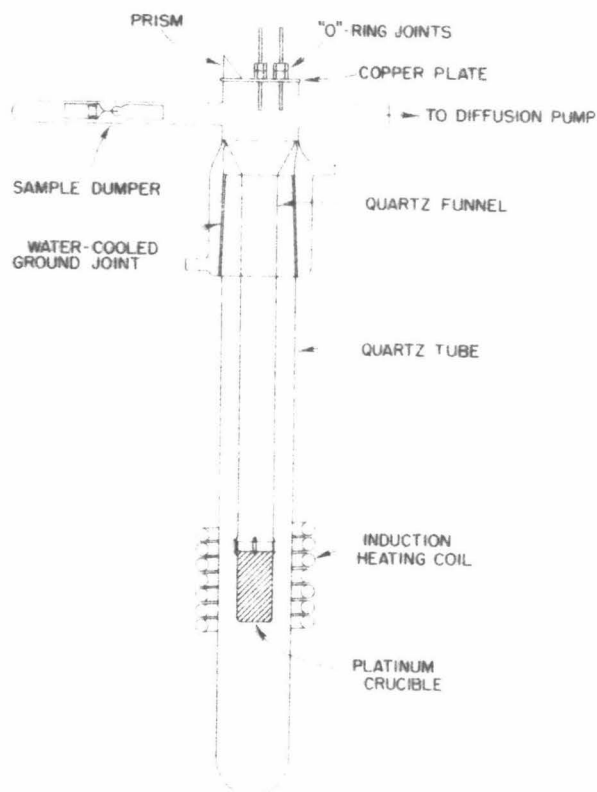
equilibrated in this manner. When cool, the melt was removed from the platinum crucible and ground in a diamond mortar to pass 20-40 U. S. Standard mesh. This sample was used in a series of vacuum fusion tests to evaluate the precision of the method.

B. Extraction of gases

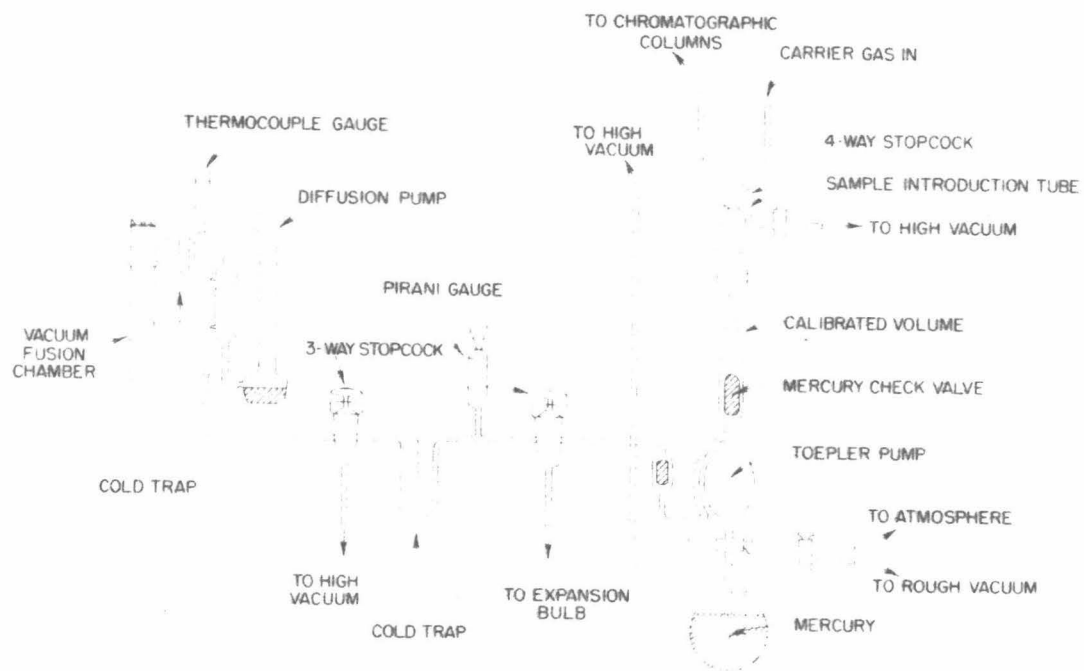
A high-vacuum system, capable of attaining pressures of 10^{-6} mm., was constructed for the extraction of gases from rocks by the vacuum fusion technique. The system is shown diagrammatically in Fig. 1. A single-stage mercury diffusion pump, backed by a Welch Duo Seal oil pump, provided the high vacuum. The apparatus consisted of three main parts: a heating chamber for extraction of gases, a system of traps and bulbs for the collection and measurement of water vapor, and a Toepler pump for collection of the remaining gases for analysis.

The heating chamber, shown in detail in Fig. 1-A, was a vertical tube two inches in diameter and approximately two feet in length. Its upper portion was made of Pyrex, and its lower, removable portion of fused quartz, connected to the former by a water-cooled ground joint. The platinum (or platinum-rhodium) crucible was suspended at the bottom of the quartz funnel inside the quartz end of the chamber. Near the top of the chamber a side arm was connected from which the sample could be dumped into the crucible. Sealed to the top of the chamber was a water-cooled copper plate, on which were mounted two o-ring joints and a pyrex prism used for viewing and optical temperature measurement. A single stage mercury diffusion pump connected near the top of the chamber provided rapid removal and "quenching" of gases after extraction. In later trials, a dry ice-acetone trap was placed in between the pump and

FIGURE 1. GAS EXTRACTION APPARATUS



A. Heating Chamber



B. Complete Apparatus

the heating chamber to keep mercury vapor away from the degassing melt.

The crucible was heated by a Lepel 4 Kw. high frequency induction furnace whose heating coil fitted neatly around the quartz end of the heating chamber. Temperature measurements were made using a Leeds and Northrup optical pyrometer sighted through the pyrex prism on the bottom of the crucible.

Water vapor extracted from the rock samples was collected by freezing in a trap cooled with dry ice-acetone slush. After the water vapor was released from the cold trap, its pressure was measured in a known volume by a Pirani gauge equipped with a sensitive galvanometer for accurate measurements in the range between 20 and 200 microns. If necessary, the water vapor could be expanded into one or more of three large bulbs of known volume to bring the pressure into the desired range.

Calibration of the Pirani gauge presented a problem because of the difficulty in introducing accurately known amounts of water into the vacuum system. The calibration was finally carried out by oxidizing quantitatively known amounts of hydrogen in a copper oxide tube at 300°C., and measuring the resultant water pressure.

A manually-operated Toepler pump was used to condense the rest of the extracted gases into a conveniently small volume. The total amount of dry gas was measured by bringing the mercury level in the pump to one of several calibrated marks, and measuring the difference in height between that level and the level of a column of mercury in a vacuum.

Known amounts of the gas could then be expanded into another small volume connected to the gas chromatography system by a four-way stopcock. Turning this stopcock 90 degrees resulted in the gas being flushed into one of the chromatographic columns for analysis.

The procedure for extracting the gas from rock was essentially the following: The sample was weighed into a small pyrex cylinder, closed at one end and wired to a piece of iron. This was placed in the side arm above the heating chamber, and the chamber sealed and evacuated. With the diffusion pump operating, the crucible was degassed at a temperature higher than that to be used in the determination. At the same time the walls of the heating chamber were degassed with the oxygen torch, and the sample flamed gently to remove adsorbed water. A blank was run, which usually turned out to be negligible.

The crucible was then heated to the temperature to be used in the trial, and the sample dumped in by moving the piece of iron with a magnet. The gases evolved were collected for a desired interval, usually four minutes. The water vapor was frozen out in a dry ice-acetone trap, and the rest of the gas pumped to the small volume above the Depler pump. The water vapor was measured with the Pirani gauge, and the other gases by gas chromatography. In general, the procedure used in analyzing volcanic gases (described in Part II) was followed, except that it was not necessary to analyze for sulfur-containing gases in the case of artificially prepared samples.

After each run, the quartz end of the heating chamber was removed and cleaned with aqua regia to remove platinum evaporated from the crucible. The sample was removed from the crucible by heating the crucible in a Meker burner flame and quenching quickly in a water bath. The platinum crucible was then cleaned with hydrofluoric acid.

III. Discussion of Results

The results of a series of duplicate trials on the artificial iron

silicate sample are presented in Table I. The ratios CO_2/CO and $\text{H}_2\text{O}/\text{H}_2$ in the gases extracted from the same sample varied widely; no correlation could be made with such variables as weight of sample, volume of gas extracted per gram of sample, type of crucible used, or time. However, a sample run with a faulty diffusion pump did show significantly higher values for CO_2/CO , as well as a complete absence of oxygen, which occurred in large quantities in the gases obtained from samples run with a properly operating pump.

The presence of oxygen in the extracted gases was unexpected, since the sample was allowed to come to equilibrium in an atmosphere of negligible oxygen partial pressure. Therefore, a series of experiments were undertaken to determine its origin. Study of the rate of evolution of gas with time showed that the initial burst of gas was largely carbon monoxide and hydrogen, and that most of the oxygen, together with water and carbon dioxide, occurred in the remainder of the gas, evolved more slowly. Experiments in which the gases were allowed time to react with the hot platinum crucible showed that there are shifts in the water gas equilibrium depending on the temperature of the crucible, but no oxygen was obtained. Keeping the mercury vapor from the diffusion pump away from the hot crucible in a further experiment had no effect; oxygen was still observed in the extracted gases.

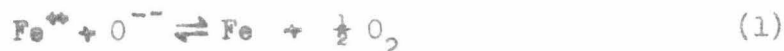
However, a fresh burst of oxygen was observed when some small pieces of platinum foil were dumped into a degassing melt, indicating that reaction of the slag with the crucible was perhaps producing the oxygen. This was confirmed by an experiment in which the fayalite was kept from coming in contact with the platinum by placing a silica crucible inside the platinum one. No oxygen was then observed in the extracted gases,

TABLE I
RESULTS OF VACUUM FUSION DETERMINATIONS

	wt sample (grams)	VOLUMES AT N. T. P.						
		ml gas	ml gas per gram	ml CO ₂	ml CO	ml H ₂ O 2	ml H ₂	ml O ₂
1	0.610	0.201	0.330	0.056	0.018	0.108	0.013	0
2	0.593	0.133	0.226	0.018	0.0018	0.109	0.0004	0.003
3	0.616	0.083	0.134	0.010	0.0021	0.012	0.0003	0.002
4	1.244	0.230	0.185	0.037	0.037	0.122	0.0010	0.035
5	0.720	0.167	0.232	0.010	0.0025	0.080	0.0021	0.075
6	1.285	0.206	0.160	0.030	0.014	0.102	0.0059	0.061
7	1.558	0.254	0.163	0.050	0.0057	0.106	0.0014	0.092
8	1.194	0.137	0.115	0.024	0.0084	0.079	0.0045	0.013
9	0.613	0.087	0.142	0.010	0.0063	0.055	0.0012	0.018

even after several hours of heating.

In view of these results, it is possible to account for the presence of oxygen in terms of the equilibrium between ferrous oxide and its component elements



At the temperatures of the vacuum fusion trials, the partial pressure of oxygen due to this reaction is very small, 3×10^{-13} atm. at 1200°C .¹⁹ However, it is known that metallic iron is quite soluble in platinum at high temperatures. In phase equilibrium studies on iron-containing oxides and silicates, loss of iron to the crucible must be taken into account by recalculating the composition of the sample. Usually, an attempt is made to minimize this loss by using an old crucible which has been well saturated with iron.²⁰

If iron is removed from the melt by solution, the equilibrium (1) will be shifted to the right, resulting in the evolution of oxygen. To account for the volume of oxygen obtained in the extractions, only about 10^{-6} moles of iron (approximately 0.01% of the iron in an average sample) would have had to dissolve in the crucible. Furthermore, as long as iron continues to dissolve in the platinum, more and more oxygen will be evolved.

It seems evident from these experiments that the presence of oxygen in the extracted gases was the chief source of error affecting their composition. The extent to which the oxygen reacted with reducing gases such as hydrogen and carbon monoxide depended on the time the gases remained near the hot crucible. The rate of removal (quenching) of the gases in turn depended on the variable speed and efficiency of the diffusion pump. However, the initial burst of gas, being largest in comparison to the

amount of oxygen, was least affected. The initial gas sample was therefore most representative of the original composition of the gas.

In order to use the vacuum fusion technique to determine the oxidation state of the constituent elements of rocks, the reaction producing oxygen must be eliminated. One possible method would be to use an "iron-saturated" crucible. However, the term "iron-saturated" is a rather loose one. The solubility of iron in platinum depends on a number of factors, particularly the temperature. To prevent the evolution of oxygen from interfering with the other gases, the amount of iron dissolving in the crucible would have to be kept less than 10^{-8} moles for the size of samples used. It would be necessary to use a crucible made of virtually a saturated solution of iron in platinum. These conditions seem almost impossible to attain in practice. The crucible would have to remain saturated at the temperature of the determination, after being degassed at a higher temperature at which the solubility of iron in platinum would be lower.²¹

In view of the preceding discussion, the question may be raised as to how Terada and Fujii were able to obtain correlation at all between the composition of the extracted gas and the oxidation state of iron. At least part of the answer is that vacuum fusion is as much an art as a science. They were able to minimize the effect of the oxygen by developing a routine in which every step of the procedure was done as nearly as possible the same way each time. Furthermore, they used the same crucible over and over again, so that they may have been able to minimize the effect of solution of iron in platinum noted above.

However, in order for the analyses of the extracted gases to have any real significance, the extraneous oxygen must be eliminated, for

otherwise the uncertainty remains whether or not the oxygen has caused a change in the composition of the gas. Platinum is the most inert of all the refractory materials which would be satisfactory for a crucible. Since Schumann, Powell, and Michal (1953) found that the composition of the gas in equilibrium with an iron silicate melt depends on the silica content, any silica-containing material would not be satisfactory.²² Boron nitride (BN) is a possibility, but little information is available regarding its reactions with liquid metals, slags and salts.²³

At the present time there seems to be no known crucible material which satisfies the stringent condition of neither affecting the composition of the melt nor the oxidation state of the gases. Therefore, in order to make the method workable, the sample would have to be heated in the absence of a crucible. In recent years, a number of excellent ways of doing this, such as arc-image and solar furnaces, have been developed.

Some preliminary experiments were carried out on the release of gas by dissolution of the rock in acids, and by crushing in vacuum. Provided a suitable container material can be developed, both methods show some promise. However, in view of the time necessary to perfect any of these techniques and the excellent opportunity to collect volcanic gases presented by the recent eruption, this problem was not pursued further. It was decided to approach the oxidation equilibria of magmatic gases by a study of the gases evolved during eruption.

IV. Conclusions

The following conclusions may be reached regarding the applicability of the vacuum fusion technique to the study of the oxidation state of the

constituent elements of rocks:

1. Solution of metallic iron in the platinum crucibles used in vacuum fusion determinations accounts for the presence of oxygen in the gases extracted from a silicate melt.
2. Because of the possibility of reaction of the oxygen with the extracted gases, thereby changing their oxidation state, platinum is not a suitable crucible material for such work.
3. Until a crucible material can be found which is truly inert with respect to an iron silicate slag, vacuum fusion cannot be used to determine with certainty the oxidation state of the constituent elements of a rock.
4. The correlation between oxidation state and gas content found by earlier investigators is probably due to the use of iron-saturated platinum crucibles which minimized the evolution of oxygen.
5. If side reactions could be eliminated during the extraction of rock gases, the study of such gases would be an excellent technique for the elucidation of the fundamental nature of volatile magmatic materials occurring in solution in rocks.

PART II. A CHEMICAL STUDY OF THE GASES OF KILAUEA VOLCANO

I. Review of Pertinent Research

A. Gas analyses

Volcanic gases. Volcanic gases have been sampled at various places throughout the world since the middle of the 19th century. Allen (1922) has tabulated these early results, most of which suffer from primitive techniques in sampling and in analysis.²⁴ They are of limited usefulness, and need not be considered here.

Hawaiian volcanoes, because of their non-explosive nature, have provided an excellent opportunity for the collection of volcanic gas samples. During the period between 1910 and 1920, Jaggar, Day and Shepherd collected gases from a lava lake which had formed in the Halemaunau Crater of Kilauea volcano (Jaggar, 1940).²⁵ The best of the samples were obtained by Jaggar and Shepherd during 1918 and 1919 from hissing flame cracks and from cupolas formed over lava fountains.

The analyses of the six samples Jaggar considered to be the best are tabulated in Table II. The data are presented with oxygen and the corresponding atmospheric quantities of nitrogen, carbon dioxide, and water subtracted. The assumption that oxygen is an atmospheric contaminant was justified by later studies of the ferrous ion content of volcanic rocks. The existence of the observed quantities of Fe(II) is possible only at very low oxygen partial pressures (Kennedy, 1948).²⁶ It should also be noted that no analysis was made for hydrogen sulfide, since Shepherd assumed it to be decomposed at the temperatures of sample collection.²⁷

Jaggar (1940) published a systematic survey of the samples of

TABLE II. GASES OF KILAUEA LAVA LAKE
SIX BEST SAMPLES OBTAINED BY JAGGAR AND SHEPHERD, 1919-1920

Sample No.	CO ₂	CO	H ₂	N ₂	Ar	SO ₂	S ₂	SO ₃	Cl ₂	H ₂ O	Total
S7	17.25	0.62	0.26	5.88	0.18	9.75	1.07	0.00	0.25	64.18	99.94
J18	17.55	0.74	0.83	4.50	0.12	10.81	0.22	3.22	0.13	61.88	100.00
J13	16.96	0.58	0.96	3.35	0.66	7.91	0.09	2.46	0.10	67.52	100.59
S2	17.95	0.36	1.35	37.84	UDT*	3.51	0.49	—	UDT*	38.48	99.98
S5	9.54	1.12	1.53	10.47	0.00	9.90	2.72	—	0.00	64.71	99.99
S3	33.48	1.42	1.56	12.88	0.45	29.83	1.79	—	0.17	17.97	99.55

Volume percentages at 1200°C., 760 m Pressure

(Table from Ellis, p. 426)

*UDT = Undetermined

1910-1920.²⁸ Recognizing that not all samples are equally valid representatives of volcanic gas, he graded them in terms of the conditions of sampling and the extent of atmospheric contamination. Arranging his samples in order of excellence, he found that the better the sample, the less carbon dioxide and water it contained, and the more carbon monoxide, hydrogen and sulfur dioxide. On this basis, Jaggar postulated that volcanic gases are formed from a solution of the latter three gases in the magma, and that their combustion at the surface is one of the sources of volcanic heat.

Following the steam explosion of 1924, there occurred a relatively quiet period in the history of Kilauea. Because of the inaccessibility of Mauna Loa eruptions, very little opportunity arose for the collection of gases from Hawaiian volcanoes for the next 40 years. Some collections were made by Ballard from Mauna Loa in 1940, and by Naughton from a Puna eruption of Kilauea in 1955, but the present work is the first extended study of Hawaiian volcanic gases since the time of Jaggar and Shepherd.²⁹

In recent years there has been renewed interest in volcanic gases throughout the world. The development of such powerful analytical techniques as mass spectrometry and gas chromatography has provided a chance for more meaningful work on such gases. The realization of the possible importance of these studies to the understanding of the mechanism of mineral transport in the gas phase has provided further incentive.³⁰

Research on the gases and condensates from Japanese volcanoes has been carried on by Iwasaki and Katsura (1956, 1958),^{31,32,33} Sakai and Nagasawa (1958),³⁴ and Oana (1960).³⁵ In the USSR, Surnina (1959)³⁶ has collected and analyzed gases from volcanoes in Kamchatka.

Fumarolic gases. Much more easily collected than volcanic gases are relatively low-temperature fumarolic gases. A great deal of research has been devoted to such gases, and to the alterations and deposits made at the throats of fumaroles. Studies have been made at such diverse locations as Wairakei, New Zealand; Valley of Ten Thousand Smokes, Alaska; Steamboat Springs, Nevada; and Yellowstone National Park. Water is always found to be the overwhelmingly dominant gas, present to the extent of 99% and more. Other gases which have been recognized include carbon dioxide, oxygen, carbon monoxide, methane, hydrogen sulfide, sulfur dioxide, hydrogen, nitrogen, ammonia, argon, hydrogen chloride, and hydrogen fluoride.³⁷

D. E. White (1957) has summarized our present knowledge of the different types of thermal waters of volcanic origin.³⁸ He has presented evidence based on isotopic studies which indicates that only about 5% of the water reaching the surface at volcanic springs and fumaroles came from a crystallizing magma, the rest coming from other sources. White listed four factors which are believed to control the composition of volcanic waters. These are (1) the type of magma, and its state of crystallization, (2) the temperature and pressure of the emanation during and after its departure from the magma, (3) the extent of and condition of mixing with meteoric water and water from other sources, and (4) reactions with wall rocks.

The gases emanating from the Sulphur Banks, a solfataric fumarole along the northern boundary fault of Kilauea caldera, were first studied by E. T. Allen (1922), who found the gas to be at least 96% water.³⁹ An extensive program of research on Sulphur Bank gases was carried out by S. S. Ballard and J. H. Payne (1940).^{40,41} They found varying amounts

of carbon dioxide, sulfur dioxide and air in samples collected from the drill holes. Prior to the 1940 eruption of Mauna Loa, they also noted a small amount of hydrogen sulfide in the gas. Concluding that the presence of hydrogen sulfide was due to the imminence of eruption, they suggested that frequent sampling of the gases would permit prediction of eruptions.

B. Theoretical work on magmatic gases

The conditions governing the formation of a separate gas phase in the magma have been studied by Verhoogen (1949), who presented a rigorous thermodynamic development of the heterogeneous equilibria which would prevail.⁴² He showed that variables often neglected by geologists, such as partial molar volumes, could account for the formation of a separate gas phase even though the partial pressures of volatile materials do not exceed the total pressure on the system. He also defined rigorously the conditions for transport of relatively non-volatile substances in a separate gas phase, and derived equations which would apply under the condition of non-uniform pressures arising from gravitational fields or osmotic effects. Verhoogen emphasized the need for high-temperature, high-pressure data on the solubility of volatiles in molten silicates, since the only data he had available from which to draw any specific conclusions was that of Goranson (1938) on water-feldspar systems.⁴³

The first attempt to calculate the equilibrium composition of magmatic gases was made by Ellis (1957).⁴⁴ Using model systems based upon the analyses of some typical volcanic gas samples, he calculated the equilibrium composition of a magmatic gas phase at temperatures between 500°C. and 1200°C., and at pressures between 1 atm. and 1000 atm. He

found that the calculated compositions of his model systems corresponded roughly to the analyses of volcanic gas samples collected under the conditions at which the calculation was carried out. For instance, he found that at high temperatures sulfur dioxide is the predominant sulfur-containing gas, in agreement with the high-temperature samples collected by Jaggar and Shepherd at Kilauea, and that at low temperatures hydrogen sulfide is the predominant sulfur-containing gas, in agreement with low-temperature samples collected at fumaroles throughout the world. Since he was also able to account, qualitatively at least, for the small amounts of hydrogen, carbon monoxide, methane, carbon oxysulfide and ammonia which are sometimes found in volcanic gases, he concluded that volcanic gases are in a state of approximate chemical equilibrium. At high pressures he found that water, carbon dioxide and hydrogen sulfide predominate, and concluded (in contradiction to Jaggar's hypothesis) that volcanic gases arise from high-temperature, high-pressure equilibria between these gases and the hydroxides, carbonates and sulfides in the magma.

Two very important considerations which Ellis neglected are (1) the oxidation state of the elements composing the gas, and (2) the limits set by stability relations among minerals in the magma. Krauskopf (1959) took these factors into account in a calculation of the equilibrium composition of a magmatic gas phase assumed to exist at 600°C. and 1000 atm.⁴⁵ Basing his computation upon known equilibria between minerals present in igneous rocks, he was able to set general limits on the partial pressures of some of the gases. For the rest, Krauskopf found it necessary to rely on volcanic gas analyses. Using his calculated composition, he also attempted to show the possibility of mineral transport in the gas phase.

In spite of some degree of success, enough discrepancies occurred to indicate that transport by solution must also be very important.

Although some understanding of the nature of volcanic gases can be obtained from these studies and from the collections of Jaggar and Shepherd, there is a need for a specific experimental test of the attainment of equilibrium in the gases. These experiments would then indicate the best way to study the role of gases in magmatic processes.

C. Object of the research

The object of the research described in this section of the thesis was the study of the chemical composition of the gases emitted by Kilauea volcano and by its associated solfatara, the Sulphur Banks. The technique of gas chromatography was adapted for use in collecting and analyzing the gases, in order to eliminate many of the sources of error encountered by earlier investigators. A theoretical investigation, based on the principles of chemical thermodynamics, was carried out to verify the attainment of chemical equilibrium in the gases collected at the surface, and to study the equilibrium variation of the gases with temperature, pressure and oxidation state.

II. Experimental Work

A. Gas sampling

In the past, most workers have collected volcanic gas samples in some form of pump, either by forcing the volcanic gas to displace the air in a bulb, or by allowing the volcanic gas to expand into an evacuated bulb. In Hawaii the most successful past collections were made in evacuated glass bulbs attached to a long tube. The tube, made of glass or quartz, could be thrust down into a gas vent and the tip broken off,

allowing the gas to rush in. After collection, the tube was closed temporarily with a cork or stopper until the glass could be sealed with a torch.⁴⁶ An improved version of the evacuated bulb, developed by Ballard (1938), made use of stopcocks for opening and closing the bulb.⁴⁷

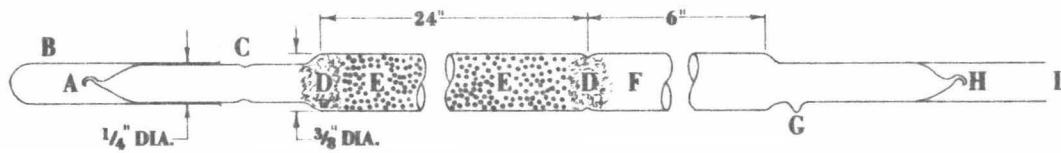
The method of sampling described here is novel, designed to prevent reactions between the gases after collection. This was accomplished by placing a column of activated silica gel in the sample tubes to adsorb and separate the more reactive gases.

The sample tubes, illustrated in Fig. 2-A, were prepared as follows: A piece of Pyrex tubing, 8 mm. in diameter and 2 ft. in length, was sealed to a bulb made from a 10 x 250 mm. Pyrex test tube, leaving a small constriction between tube and bulb. The section E of the tubing was packed with 20-60 U. S. Standard mesh silica gel, held in place by plugs of glass wool at the ends of D. A delicate break-off tip was made at the end A, and a piece of glass tubing B wired onto the end A to protect the tip during handling. A tube G was sealed to the bulb end for evacuation of the sample tube, and an inner seal break-off tip H for convenient opening of the sample at the time of analysis.

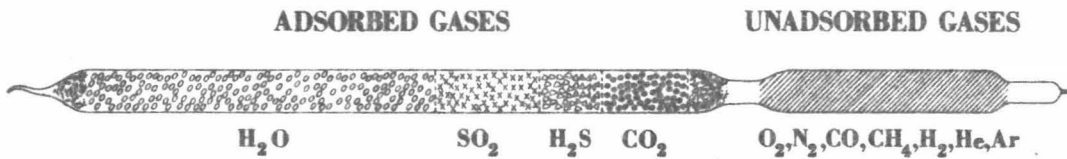
The sample tube was then attached to a high-vacuum system and evacuated at a temperature of 300°C. for two or more hours. The connection to the pumping system was sealed off under vacuum, to produce a small and compact unit which proved easy to handle in the field.

In order to collect a sample, the protective piece of tubing B was removed, and the tube thrust into a gas-emitting vent. The break-off tip was smashed, and the sample tube held in place briefly. Upon removal from the vent, the open end of the tube was covered quickly with a closed piece of Teflon tubing, prior to permanent sealing of the glass. Sometimes it

FIGURE 2. SILICA GEL SAMPLE TUBES

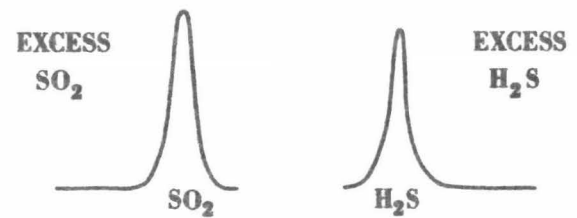


A. Construction

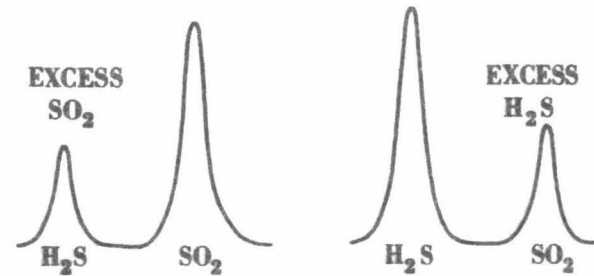


B. Probable Distribution of Gases

BULB COLLECTIONS



SILICA GEL TUBE COLLECTIONS



C. Effect on a Typical Gas Chromatographic Analysis

was found possible to seal off the tube opening by pushing the tip against the red hot lava in the vent to collapse the softened glass.

B. Gas Analysis

Possible methods of analysis. The analytical techniques used by most of the earlier investigators of volcanic gases were based on technical Orsat methods.⁴⁸ Such methods are adequate for many of the components of volcanic gas, but do not work very well for others, including hydrogen sulfide. Trace components are difficult to analyze and are often beyond the sensitivity of the apparatus.

Terada (1954) used high-vacuum techniques based on the selective "freeze-out" of the components of a gas mixture.⁴⁹ This is a laborious method, subject to large errors and also not very well adapted to the analysis of traces. Its chief disadvantage, however, is that the analysis depends upon a prior knowledge of the components of the gas. An incorrect assumption as to the components present will lead to a completely erroneous analysis.

The method of analysis used in this investigation, gas chromatography, is a powerful and versatile technique. It permits qualitative as well as quantitative analysis, thus avoiding the pitfalls of high vacuum work by showing up unexpected components. Because of its extreme sensitivity, both major and trace components of a gas mixture can be satisfactorily analyzed. It is easy to operate and requires a minimum of time for analysis. Perhaps the most satisfactory method yet applied to the analysis of volcanic gases, it should be capable of resolving much of the controversy pertaining to magmatic gases.

Principles of gas chromatography. Gas chromatography is a physical

method of separation, based on the distribution of materials between a moving gas phase and a stationary liquid or solid phase. If the stationary phase is a solid, the technique is referred to as Gas-Solid Adsorption Chromatography (GSAC), since separation depends upon the selective adsorption of a mixture on the solid phase. If the stationary phase is a liquid held on an inert supporting material, the technique is called Gas-Liquid Partition Chromatography (GLPC), with separation depending upon the selective partition of the components of a mixture between the liquid and gaseous phases. Both techniques were employed in this investigation, GSAC for the separation of permanent gases and GLPC for the separation of condensable gases.

In practice, the stationary phase is sieved and packed into lengths of tubing to make a chromatographic column. The moving gas phase, called the carrier gas, is allowed to pass through the column at a suitable flow rate. A mixture of gases or liquids is then introduced into the column for separation. In this investigation, this was done by introducing the desired pressure of gas into a loop connected to the carrier gas line by a four-way stopcock. Turning the stopcock 90 degrees resulted in the sample being flushed into the column, from which it was eluted by the carrier gas.

After the components of a mixture have been separated on the column, each component must be detected and measured. This was done in this investigation by taking advantage of the characteristic thermal conductivities of gases. The thermal conductivity of the pure carrier gas was compared to that of a mixture of carrier gas and each component as it emerged from the column. The result was a series of peaks, one for each component, which registered on a recording potentiometer. The area under

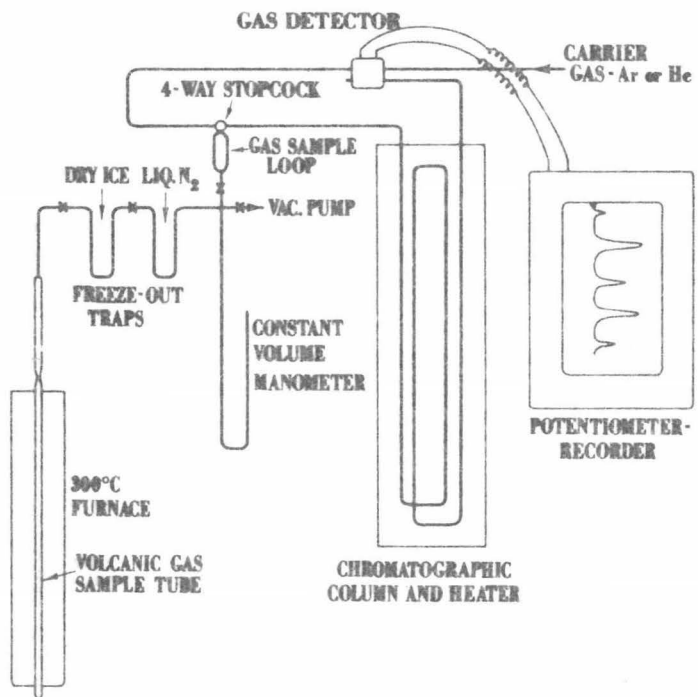
each peak was proportional to the partial pressure of the component gas it represented, providing a quantitative analysis of the mixture.⁵⁰

Description of the apparatus. A schematic diagram of the gas chromatographic apparatus used in the analysis of volcanic gas samples is presented in Fig. 3-A. The volcanic gas sample tubes, after being sealed to a ground joint, were attached to the system as shown. Two freeze-out traps of known volume were available for the separation of the sample into three major fractions: the "permanent" gases, non-condensable in liquid nitrogen; the "condensable" gases, condensable in liquid nitrogen; and water vapor, condensable in dry ice-acetone. A constant-volume manometer provided a means of measuring the pressure of sample introduced into the chromatographic columns through the gas sample loop and four-way stopcock. A Welch Duo-Seal oil pump was used to evacuate the system.

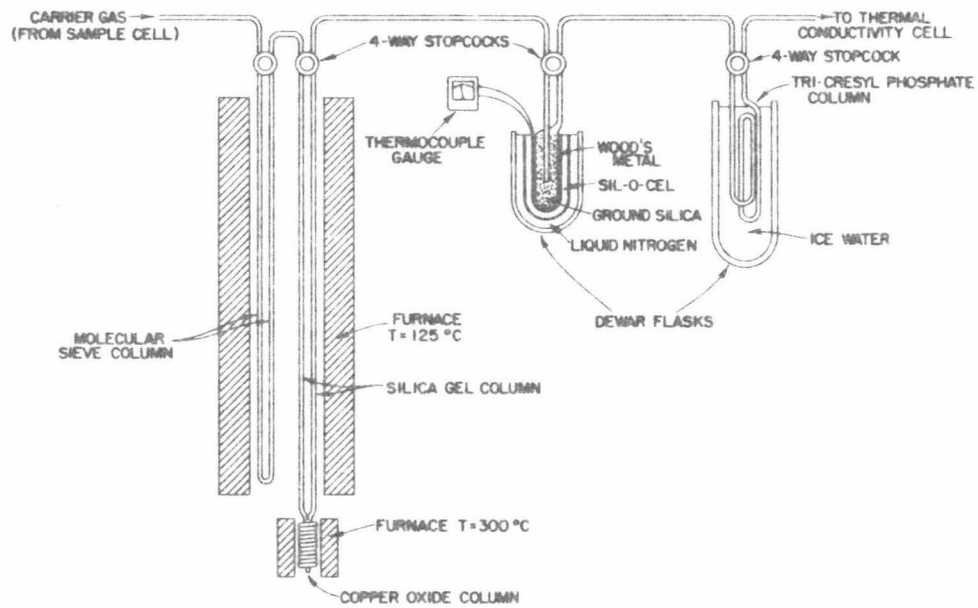
The four chromatographic columns used in the analysis, represented by "Chromatographic Column and Heater" in Fig. 2-A, are shown in detail in Fig. 2-B. Each column was connected to the carrier gas line by means of a four-way stopcock, so that any column could be used either separately or in series with one or more of the others, depending upon the positions of the stopcocks. Typical chromatograms produced by each of the columns are depicted in Fig. 4, and the operating characteristics of the columns are summarized in TABLE III.

The "molecular sieve" column was essentially the one described by Janak, Krejci and Dubsky (1959).⁵¹ It contained "Molecular Sieve 5A", an artificial zeolite produced by the Linde Air Products Company, ground to pass 40-60 U. S. Standard mesh, and packed in four foot sections of 8 mm. Pyrex tubing. Four sections were used (making a 16 ft. column) which was placed in a five-foot, nichrome-wound vertical tube furnace,

FIGURE 3. GAS CHROMATOGRAPHY APPARATUS

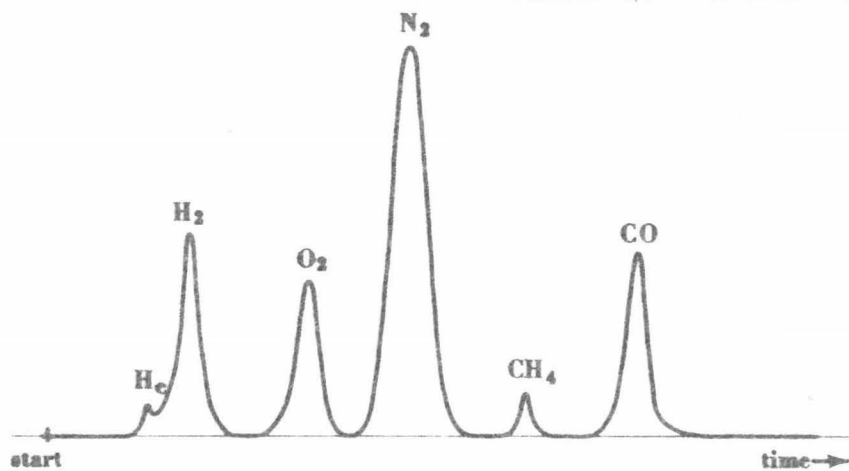


A. Schematic Representation of Entire Apparatus

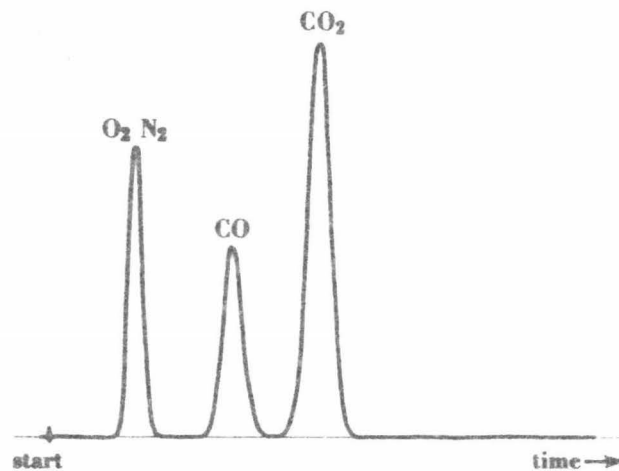


B. Gas Chromatographic Columns

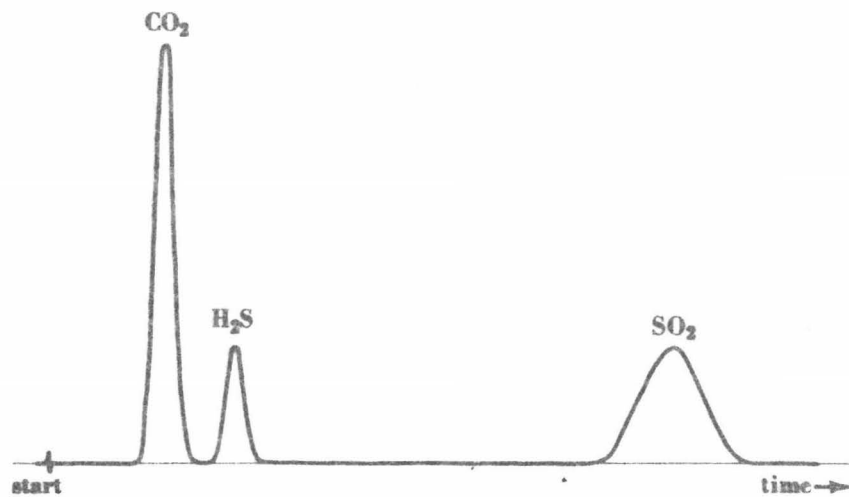
FIGURE 4. TYPICAL GAS CHROMATOGRAMS



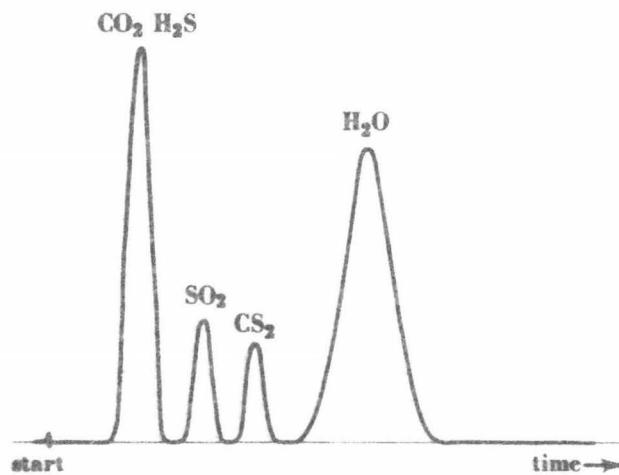
A. Molecular Sieve Column



B. Silica Gel-Copper Oxide Column



C. Tricresyl Phosphate Column



D. Differential Cold Trap

TABLE III. CHARACTERISTICS OF THE CHROMATOGRAPHIC COLUMNS

A. MOLECULAR SIEVE. T = 125°C. Argon Flow 20 ml./min.

GAS	RETENTION TIME	RETENTION VOLUME	VOLUME NTP REPRESENTED BY 1 cm ² AREA ^{1,2}
He	3.8 min.	76 ml.	0.402
H ₂	4.4	88	0.367 x 10 ⁻³ ml.
O ₂	8.1	162	2.98
N ₂	10.0	200	3.40
CH ₄	13.8	276	1.37
CO	18.7	374	5.09

B. SILICA GEL COPPER OXIDE. T = 125°C. Helium Flow 20 ml./min. (CuO T = 300°C.)

O ₂ , N ₂	4.1	82 ml.	— ³
CO	7.2	144	3.38
CO ₂	10.1	202	3.38

C. TRICRESYL PHOSPHATE. T = 0°C. Helium Flow 12 ml./min.

CO ₂	3.4	41 ml.	3.38
H ₂ S	5.8 min.	70	1.30
SO ₂	6.5	318	2.42

D. DIFFERENTIAL COLD TRAP. Helium Flow 10 ml./min.

H ₂ S	3.1	31	1.30
CO ₂	3.2	32	3.38
SO ₂	5.2	52	2.42
CS ₂	5.8	58	1.10
H ₂ O	9.6	96	— ³

¹ Chart Speed - 0.33 inch per minute.

² Recorder Sensitivity - 1 millivolt full scale.

³ Not used for quantitative analysis.

and activated by heating at 350°C. for 12 hours. Operating at a temperature of 125°C., and with an argon flow-rate of 20 ml./min., this column was capable of separating helium, hydrogen, oxygen, nitrogen, methane and carbon monoxide in 20 minutes.

The silica gel column is similar to the one described by Smith, Swinehart and Lesnini (1958).⁵² It consisted of 16 ft. of 40-60 U. S. Standard mesh silica gel packed into four-foot sections of 8 mm. Pyrex tubing. Halfway through the column (after 8 ft. of silica gel) there was connected a one-foot helical Pyrex column containing copper oxide pellets. The silica gel sections were placed in the 125°C. vertical tube furnace next to the molecular sieve column, and the copper oxide helix in a smaller furnace, operating at 300°C.

The operation of this column may be described as follows: Using helium carrier at a flow rate of 20 ml./min., a sample containing permanent gases, carbon monoxide and carbon dioxide, was passed into the column. In the first silica gel section, carbon dioxide was separated from the other gases. Upon reaching the copper oxide, the carbon monoxide was oxidized to carbon dioxide. As such, the carbon monoxide was separated from both the permanent gases and the carbon dioxide in the second silica gel section. The time required for this operation was about ten minutes, and the technique greatly simplified the determination of CO_2/CO ratios in the gases extracted from artificial silicates.

The tricresyl phosphate (TCP) column was essentially the one developed by Ryce and Bryce (1957) for their work on organic sulfur compounds.⁵³ The column packing was prepared by sieving Johns Manville C-22 firebrick to be retained by 40-60 U. S. Standard mesh, taking particular care to remove smaller particles. The firebrick was washed with hydrochloric acid,

rinsed with distilled water and dried at 145°C . A slurry was made from an ether solution of 16 g. of tricresyl phosphate and 55 g. of the firebrick. The ether was removed by evaporation with constant stirring over a hot plate, and the packing dried at 120°C . The TCP-saturated firebrick was packed into five 18-inch loops of 8 mm. Pyrex tubing, which were connected together in such a way so that the column could be inserted in a large Dewar flask.

Operating at a temperature of 0°C . (in an ice bath) and with helium carrier gas flowing at 12 ml./min., the TCP column was capable of separating carbon dioxide from hydrogen sulfide in about seven minutes. A very diffuse sulfur dioxide peak followed in about 30 minutes.

In order to provide a quicker and more sensitive way of analyzing sulfur dioxide, a differential cold trap was developed for the separation of the condensable gases according to their boiling points. Although not strictly a chromatographic column, this technique functioned in much the same way, and gave good results. Its construction may be described as follows: An inner-seal type of gas condensation trap was surrounded by a snug-fitting layer of Wood's metal, into which had been set a copper-constantin thermocouple. Around this was placed an insulating layer of Johns-Manville Sil-O-Gel, held in a Pyrex test tube. The trap itself was filled with 40-60 U. S. Standard mesh silica glass, to provide a mechanical surface for condensation of gases from the non-condensable helium carrier gas. Such a surface was necessary to prevent mechanical transport of condensed particles of gas through the trap.

Separation of a mixture of condensable gases was obtained by releasing a sample to the trap, which had been cooled by liquid nitrogen. The Dewar flask containing the liquid nitrogen was then removed, and the

trap allowed to heat up slowly in air. Separation of gases with widely varying boiling points, such as carbon dioxide, sulfur dioxide, carbon disulfide and water was obtained in about ten minutes. Hydrogen sulfide, however, could not be separated from carbon dioxide because their boiling points were too close together. Therefore, for analysis of all of the condensable gases, it was necessary to use this trap in conjunction with the TCP column.

The separated components of a gas mixture were detected by a Gow-Mac thermal conductivity cell, Model 9234 (TE-111), which consisted of a stainless steel block into which two holes had been bored. In each of the resulting cells was placed a tungsten wire, heated by an electrical current. The two wires were connected as two arms of a Wheatstone bridge, the other two arms of which were variable resistances.

The operation of the cells may be described as follows: Pure carrier gas was passed through one of the cells and the gas coming out of the column through the other. With pure carrier gas in both cells, the circuit was balanced by varying the resistances, so that there was no net potential across the bridge. When a component gas emerged from the column, the thermal conductivity of the mixture of component and carrier gas in the detector cell was different from that of the pure carrier gas in the reference cell. As long as the partial pressure of component gas was low, this change in thermal conductivity was proportional to the change in the partial pressure of the gas. The resulting change in the resistance of the tungsten wire (because of its different temperature) caused a net potential to be set up across the bridge.

This potential was measured with a Wheelco recording potentiometer to give a differential chromatogram consisting of a series of peaks, one

for each component of the mixture. The area under each peak was proportional to the amount of the corresponding component in the mixture, thereby providing a means of quantitatively analyzing the mixture. Areas were measured by multiplying the height of the peak by its width at half the height; i.e., the peak was approximated by a triangle having those dimensions.

Known mixtures of the possible components of volcanic gas were separated on the chromatographic columns, and a characteristic retention volume (flow rate multiplied by retention time) determined for each component. In practice, however, the same conditions of column temperature, carrier gas flow rate and recorder chart speed were always used, so that it was possible to use characteristic distances on the chromatograms for identification.

In general, carrier gases were chosen to provide maximum sensitivity toward the gases to be analyzed. For the permanent gases, with relatively high thermal conductivities, argon was used because of its low value for this property. This choice provided particularly great sensitivity for hydrogen and helium. Similarly, helium, a gas with high thermal conductivity, was used as a carrier for the poorly conducting condensable gases. The carrier gases were carefully dried, but otherwise used just as they came from the cylinders. Flow rates were measured by using a Predictability ball-type flowmeter, which was calibrated by displacement of water.

Carefully measured amounts of each pure gas were used to calibrate the apparatus for quantitative analysis. Plots were made of peak area vs. pressure in the sample bulb. For every gas, a linear calibration curve passing through the origin was obtained. The slopes of these curves

were used as conversion factors in finding the partial pressures of the gases in the sample.

Analytical Procedure. The sample tubes were prepared for analysis by sealing a ground joint to the inner seal break-off tip (Part I of Fig. 2-A). Inside the tube was placed a glass-enclosed iron rod, to be used in opening the sample by smashing the break-off tip. In the case of silica gel tubes, the section E containing the silica gel was wrapped with a heating tape and insulated with several layers of asbestos cloth. The sample tube was attached vertically to the system as shown in Fig. 3-A, and opened by lifting the iron rod with a magnet and dropping the rod on the break-off tip. Water vapor in the samples was collected in the first trap by means of a dry ice-acetone bath.

Analysis of vacuum bulb samples was conveniently carried out by separating the gas into two fractions on the basis of condensability in a liquid nitrogen bath. The ratio between the two fractions was determined (previous to condensation) by using the silica gel column to find the carbon dioxide content of the sample. The non-condensable portion of the gas was analysed using the molecular sieve column and the condensable portion using the TGP column and the differential cold trap. An outline summarizing the course of the analysis is given in TABLE IV.

Similarly, the silica gel tube samples were separated into two fractions according to whether the gases were adsorbed on the silica gel. Upon opening the sample, the gases not adsorbed on the silica gel were expanded into the constant volume manometer, and the pressure measured. Analysis of this portion was carried out using the molecular sieve and silica gel columns. A liquid nitrogen bath was then placed around the second trap, and a vacuum applied to the whole system including the sample

TABLE IV. OUTLINE OF ANALYTICAL PROCEDURE FOR
EVACUATED BULB SAMPLES

1. The bulb was opened and its total pressure measured.
2. The ratio of condensable gases to uncondensable gases was determined using the silica gel column.
3. The condensable gases were condensed using liquid nitrogen.
4. The uncondensable gases H_2 , O_2 , N_2 , CH_4 and CO were analyzed using the molecular sieve column.
5. The condensable gases were expanded and analyzed as follows:
 - a. H_2S using the tricresyl phosphate column.
 - b. SO_2 using the differential cold trap.
 - c. CO_2 by difference.
6. The H_2O was collected in a removable trap and weighed.

tube. The latter was then heated gradually, over a period of two hours, to 300°C. At the end of this time essentially all of the water vapor in the sample was in the dry ice-acetone trap, and the remainder of the adsorbed gases were in the liquid nitrogen trap. (It was assumed that adsorption of the permanent gases by silica gel was negligible at this temperature.) The gases were released from the trap; the pressure determined in the constant-volume manometer; and the analysis accomplished using the TCP column and differential cold trap. The free volume of the sample tube (necessary to find the ratio between adsorbed and unadsorbed gases) was determined by expansion of helium into the sample tube. (The water vapor content was determined by transferring it to another trap which could be removed from the system and weighed.) An outline summarizing the course of analysis is given in TABLE V.

III. Theoretical Work

A. Method of Equilibrium Calculations

In order to adapt the high-speed digital computer at the University of Hawaii Computing Center for use in calculating the equilibrium composition of volcanic gases, it was necessary to assemble a suitable "program" of instructions to the machine. There are a number of approximate methods available for the solution of complex equilibrium problems. Most of these, however, require certain assumptions to be made about the system to be studied; i.e., that one or more of the components of the system are present in large excess. One equation is then set up for each component of the system. The equations for the components are usually equilibrium constant expressions, together with material balance expressions for the various atomic species. Ellis, for instance, used such a method in his work.⁵⁴

TABLE V. OUTLINE OF ANALYTICAL PROCEDURE FOR
SILICA GEL TUBE SAMPLES

1. The tube was opened and the pressure of unadsorbed gases measured.
2. The unadsorbed gases were analyzed as follows:
 - a. CO and CO₂ using the silica gel column.
 - b. H₂, O₂, N₂, CH₄ and CO using the molecular sieve column.
3. The adsorbed gases were pumped out of the silica gel tube and condensed with liquid nitrogen.
4. The adsorbed gases were expanded and their pressure measured.
5. The adsorbed gases were analyzed as follows:
 - a. H₂S using the tricresyl phosphate column.
 - b. SO₂ and CS₂ using the differential cold trap.
 - c. CO₂ by difference.
6. The H₂O was collected in a removable trap and weighed.
7. The free volume of the silica gel tube was determined (for calculation of the ratio of unadsorbed to adsorbed gases in the sample).

A simple and powerful method of complex equilibrium calculation has recently been developed by White, Johnson and Dantzig (1958).⁵⁵ Completely general, it requires no distinction between the components present and is very well adapted to machine computation. Furthermore, the number of simultaneous equations required is only one more than the number of atomic species, thereby simplifying and speeding up the solution.

The method is based on the principle that the free energy of a system has a minimum value at equilibrium. The only thermodynamic variables required are the chemical potentials of the various possible components. The chemical potential of the i -th gas, μ_i , will equal its standard molar free energy, F_i^0 , if we assume an ideal gas mixture. The total free energy of the system is minimized subject to the material balance constraint. This may be expressed quantitatively as follows. The free energy of a mixture of molecular species containing x_i moles of the i -th kind may be written

$$F(X) = \sum_{i=1}^n f_i \quad (1)$$

where $X = (x_1, x_2, \dots, x_n)$, a set of mole numbers.

$$f_i = x_i \left[(F^0/RT)_i + \ln P + \ln (x_i/\bar{x}) \right] \quad (2)$$

P = Total pressure in atmospheres.

$$\bar{x} = \sum_{i=1}^n x_i \quad (3)$$

In order to find the equilibrium composition, the set of positive values x_i minimizing (1) are determined. These must satisfy the condition of material balance, which may be written

$$\sum_{i=1}^n a_{ij} x_i = b_j \quad (j = 1, 2, \dots, n) \quad (4)$$

where m = The total number of atomic species.

a_{ij} = The formula number indicating the number of atoms of element j in the molecule i .

b_j = The total number of atomic weights of element j present in the mixture.

The following is a derivation of the method of steepest descent developed by White, Johnson and Dantzig for use with high-speed digital computers. We start with any set of positive values Y (y_1, y_2, \dots, y_n) which satisfy the material balance condition (4). The free energy of a mixture defined by the set of mole numbers Y is

$$F(Y) = \sum_{i=1}^n y_i \left[c_i + \ln(y_i/\bar{y}) \right] \quad (5)$$

where

$$c_i = (F^0/RT)_i + \ln P \quad (6)$$

and

$$\bar{y} = \sum_{i=1}^n y_i \quad (7)$$

Since the set of mole numbers must be positive, a Taylor's series expansion in Y is possible. The first three terms of the series are a quadratic approximation of $F(X)$. To form the expansion, we recall that the form of a Taylor's expansion in the value a is

$$f(x) = f(a) + \left. \frac{df}{dx} \right|_{x=a} (x-a) + \frac{1}{2} \left. \frac{d^2f}{dx^2} \right|_{x=a} (x-a)^2 \quad (8)$$

We define:

$$\Delta_i = x_i - y_i, \text{ and } \bar{\Delta} = \bar{x} - \bar{y} \quad (9)$$

Writing down the Taylor's expansion about each of the points y_i and collecting terms, we obtain $Q(X)$, the quadratic approximation of $F(X)$:

$$Q(X) = F(Y) + \sum_{i=1}^n \left. \frac{\partial F}{\partial x_i} \right|_{X=Y} \Delta_i + \frac{1}{2} \sum_{i=1}^n \sum_{k=1}^n \left. \frac{\partial^2 F}{\partial x_i \partial x_k} \right|_{X=Y} \Delta_i \Delta_k \quad (10)$$

This expression can be evaluated if we know the expressions for the partial derivatives evaluated at $X=Y$. To find the first derivative, we rewrite $F(X)$ as follows:

$$F(X) = \sum_{i=1}^n \left[x_i c_i + x_i \ln x_i - x_i \ln \left(\sum_{i=1}^n x_i \right) \right]. \quad (11)$$

Since $\frac{\delta x_i}{\delta x_i} = 1$, and $\frac{\delta x_k}{\delta x_i} = 0$, for $i \neq k$, the first derivative is

$$\frac{\delta F}{\delta x_i} = c_i + \ln (x_i/\bar{x}). \quad (12)$$

To find the second derivatives, we differentiate again with respect to x_i and x_k :

$$\frac{\delta^2 F}{\delta x_i^2} = \frac{1}{x_i} - \frac{1}{\bar{x}}, \quad (13)$$

and

$$\frac{\delta^2 F}{\delta x_i \delta x_k} = \frac{1}{\bar{x}}. \quad (14)$$

The Taylor's series expansion, evaluated at $X=Y$, then becomes

$$Q(X) = F(Y) + \sum_{i=1}^n \left[c_i + \ln (y_i/\bar{y}) \right] \Delta_i + \frac{1}{2} \sum_{i=1}^n \left[\frac{\Delta_i}{y_i} - \frac{\bar{\Delta}}{\bar{y}} \right]. \quad (15)$$

The procedure by which the last term in this expression is obtained is not obvious, and requires explanation. In order to substitute (13) and (14) into the last term of (10), we separate the double summation into two terms, one involving the subscript i and h , where $h \neq i$:

$$\frac{1}{2} \sum_{i=1}^n \sum_{k=1}^n \frac{\delta^2 F}{\delta x_i \delta x_k} + \frac{1}{2} \sum_{i=1}^n \frac{\delta^2 F}{\delta x_i^2} + \sum_{i=1}^n \sum_{h=1}^n \frac{\delta^2 F}{\delta x_i \delta x_h}. \quad (16)$$

The quadratic term then becomes

$$\frac{1}{2} \left[\sum_{i=1}^n \left(\frac{1}{y_i} - \frac{1}{\bar{y}} \right) \Delta_i^2 + \sum_{i=1}^n \sum_{h=1}^n \left(-\frac{1}{\bar{y}} \right) \Delta_i \Delta_h \right] \quad (i \neq h). \quad (17)$$

We rewrite the double summation in this expression in terms of the subscript i alone, by noting that it is equal to the square of

minus the terms $\sum_{i=1}^n \frac{\Delta_i^2}{\bar{y}}$. We obtain

$$\sum_{i=1}^n \frac{\Delta_i}{\bar{y}}$$

$$\frac{1}{2} \left\{ \sum_{i=1}^n \left(\frac{1}{y_i} - \frac{1}{\bar{y}} \right) \Delta_i^2 + \frac{1}{\bar{y}} \left[\left(\sum_{i=1}^n \Delta_i \right)^2 - \sum_{i=1}^n \Delta_i^2 \right] \right\}. \quad (18)$$

This expression simplifies to

$$\frac{1}{2} \left[\frac{1}{y_i} \sum_{i=1}^n \Delta_i^2 - \frac{1}{\bar{y}} \Delta^2 \right]. \quad (19)$$

Completion of the square and factoring by y_i then yields the last term of (15).

We wish to show that both $Q(X)$ and $F(X)$ are convex. To do so, we rewrite (15) as follows:

$$Q(X) = F(Y) + \sum_{i=1}^n \left[c_i + \ln(y_i/\bar{y}) \right] (x_i - y_i) + \frac{1}{2} \sum_{i=1}^n y_i \left[\frac{x_i}{y_i} - \frac{\bar{x}}{\bar{y}} \right]. \quad (20)$$

The first derivative is then

$$\frac{\partial Q}{\partial x_1} = (x_1/y_1 - \bar{x}/\bar{y}) + \left[c_1 + \ln(y_1/\bar{y}) \right] \quad (21)$$

and the second derivative

$$\frac{\partial^2 Q}{\partial x_1^2} = (1/y_1 - 1/\bar{y}). \quad (22)$$

Or referring to (13) and (22), we see that both second derivatives must not be negative, since $\bar{y} > y_i$ for $y_i > 0$. It follows that $F(X)$ and $Q(X)$ are convex and exhibit a minimum value.

To find the next approximation to the desired solution, we minimize $Q(X)$ subject to the material balance condition (4), restricting x_i to positive values. Let

$$G(X) = Q(X) + \sum_{j=1}^m \pi_j \left[- \sum_{i=1}^n a_{ij} x_i + b_j \right] \quad (23)$$

where π_j are Lagrangian multipliers. To minimize $G(X)$, its partial derivative with respect to x_i is set equal to zero. In view of (21), we obtain

$$\frac{\delta G}{\delta x_i} = \left[c_i + \ln(y_i/\bar{y}) \right] + \left[x_i/y_i - \bar{x}/\bar{y} \right] + \sum_{j=1}^m \pi_j a_{ij} = 0 \quad (24)$$

Solving this expression for x_i , there results

$$x_i = -f_i(Y) + (y_i/\bar{y})\bar{x} + \sum_{j=1}^m \left(\pi_j a_{ij} \right) y_i \quad (25)$$

where

$$f_i(Y) = y_i \left[c_i + \ln(y_i/\bar{y}) \right] \quad (26)$$

Summing (25) over i and noting that y_i must satisfy the material balance condition (4), we find

$$\sum_{i=1}^n f_i(Y) = \sum_{j=1}^m \pi_j b_j \quad (27)$$

Substitution of (25) into the material balance expression (4) for element k yields

$$\sum_{i=1}^n a_{ik} \left\{ -f_i(Y) + (\bar{x}/\bar{y}) \left[\sum_{j=1}^m a_{ij} y_i \right] + \sum_{j=1}^m \sum_{i=1}^n a_{ij} a_{ik} y_i \pi_j \right\} = b_k \quad (k = 1, 2, \dots, m) \quad (28)$$

If we denote the constants by

$$r_{jk} = r_{kj} = \sum_{i=1}^n a_{ik} f_i(Y) \quad (k = 1, 2, \dots, m) \quad (29)$$

and define the quantity u by

$$u = \bar{x}/\bar{y} - 1, \quad (30)$$

we obtain m equations of the form

$$\sum_{j=1}^m r_{jk} \pi_j + u b_k = \sum_{i=1}^n a_{ik} f_i(Y) \quad (k=1, 2, \dots, m) \quad (31)$$

Together with (27), these equations make up a symmetric set of $m+1$ linear simultaneous equations in the $m+1$ unknowns $\pi_1, \pi_2, \dots, \pi_m$ and u . This set of equations may be summarized as follows:

$$\begin{aligned} r_{11} \pi_1 + r_{12} \pi_2 + \dots + r_{1m} \pi_m + b_1 u &= \sum_{i=1}^n a_{i1} f_i(Y) \\ r_{21} \pi_1 + r_{22} \pi_2 + \dots + r_{2m} \pi_m + b_2 u &= \sum_{i=1}^n a_{i2} f_i(Y) \\ &\vdots \\ r_{m1} \pi_1 + r_{m2} \pi_2 + \dots + r_{mm} \pi_m + b_m u &= \sum_{i=1}^n a_{im} f_i(Y) \\ b_1 u + b_2 u + \dots + b_m u + 0 \cdot u &= \sum_{i=1}^n f_i(Y) \end{aligned} \quad (32)$$

B. Procedure in the Calculation of the Equilibrium Composition

The steps followed in the solution of a problem may be outlined briefly as follows:

1. A solution $Y = (y_1, y_2, \dots, y_n)$ was postulated, which satisfied the mass balance constraint, and consisted of all positive values. This guess was based on the relative abundances of the elements present, together with the relative magnitudes of the free energy functions. The guess was made as good as possible in order to cut down on the time required for solution.
2. The quantities $f_i(Y)$ and r_{jk} were calculated by equations (26) and (29).
3. The set of linear simultaneous equations (32) were solved by the

method of Crout, a numerical method involving the successive elimination of the unknowns in the equations (see App. 1).⁵⁶

Note that the number of equations required is only one more than the number of elements present, and that it is not necessary to have an equation for each individual component, as in other methods.

4. Using the values obtained for the unknown multipliers, the total possible changes in the mole numbers were calculated from the equation

$$\Delta_i = -f_i(Y) + y_i \left(u + \sum_{j=1}^m a_{ij} \pi_j \right). \quad (33)$$

This is obtained easily from equation (25), with $\Delta_i = x_i - y_i$.

5. The actual change in the mole numbers was limited to fractional amounts $\lambda \Delta_i$ using the largest value of λ satisfying the following conditions:

- a) All mole numbers are positive.
- b) The minimum point is not passed. This was ensured by calculating the directional derivative $\frac{dF(\lambda)}{d\lambda}$ from the equation

$$\frac{\delta F}{\delta \lambda} = \sum_{i=1}^n \Delta_i \left[c_i + \ln \left(\frac{y_i + \lambda \Delta_i}{\bar{y} + \lambda \bar{\Delta}} \right) \right]. \quad (34)$$

The maximum value of λ for which this expression had a negative value was found.

6. The next-improved set of mole numbers y_i' were then calculated, using
- $$y_i' = y_i + \lambda \Delta_i \quad (35)$$

Depending on the accuracy of the original guess, between 4 to 15 iterations were required to reach the minimum point.

Trace components not included in the original calculation were

determined using the unknown multipliers π_j , which represent the free energy contribution of the elements j to the mixture. A convenient equation for this purpose was derived by differentiating the expression for $G(X)$ with respect to x_i , replacing $Q(X)$ with the exact function $F(X)$, and setting the result equal to zero. There is then obtained

$$x_i = \bar{x} \exp \left[-c_i + \sum_{j=1}^m a_{ij} \pi_j \right]. \quad (36)$$

This expression also served as a check to ensure that no major components had been left out of the original calculation.

C. Computer Programming

In order to adapt this method to use on the IBM Type 650 Data Processing System, it was necessary to write a program in the FORTRAN language developed by the International Business Machines Corporation for use with their FOR TRANSIT Automatic Coding System. Especially well adapted to scientific uses, FORTRAN consists of statements similar in form to algebraic equations. The method requires no extensive knowledge of the inner mechanism of a computer.

The FOR TRANSIT System consists of three major parts: (1) a translator which converts statements which make sense to people (FORTRAN) into a self-consistent machine language (IT), (2) a compiler, which converts the IT statements into step-by-step instructions to the 650 in a symbolic (SCAP II) language and, (3) an assembler, which produces an optimized program designed to execute the symbolic program in a minimum of time. The FORTRAN program is all that the programmer is required to prepare: this consists of a "source program" written in the FORTRAN language and punched onto data processing cards. The machine then converts this program into

a final "object program" by the three steps described above. This final program, together with the necessary input data cards, makes up the final working set of instructions. The answers are punched out on output data cards. These answers may be printed out by using the output cards in an addressograph machine.

Two programs were written, one to calculate the equilibrium composition of the major components according to the general method on page 47, and the other to determine the concentrations of trace components, using equation (35) and the output from the first program. A listing of the individual steps in these programs is given in Appendix II.

III. DISCUSSION OF RESULTS

A. Evaluation of Experimental Techniques

1. The collection of volcanic gas samples

In November 1959, after a four-year lapse, the volcano Kilauea on the Island of Hawaii resumed activity. Two separate stages in the eruption were recognizable. The first occurred at the Kilauea Iki crater, separated from the Kilauea caldera to the west by Byron's Ledge. Starting on November 14, a line of lava fountains on one side of Kilauea Iki began pouring lava down into the crater. The activity soon shifted to a single fountain, which attained heights of up to 1700 feet. Eruption continued until November 21, when the fountain suddenly ceased. After five days, activity resumed, only to stop again within 24 hours. Altogether, there were sixteen phases in the eruption, with lava pouring back down the vent from the lava lake after each phase.

The lava fountain of Kilauea Iki built up a huge cinder cone on the rim of the crater, in the direction of the prevailing winds. This cinder cone was later named Puu Puai. Samples of gas were obtained from red-hot cracks and rifts at the summit of Puu Puai on the following occasions: 1) November 30, 1959, about 12 hours after the end of the third phase of the eruption; 2) January 20, 1960, one month after the end of the eruption; and 3) April 11, 1960, about four months after the eruption. It is interesting to note that temperatures of 900°C . were measured only two feet below the surface of the cone as late as August 1960, eight months after eruption ceased.

The second stage of the 1959-60 eruption of Kilauea occurred in the Puna District, on the flank of the volcano. On January 13, 1960, a line of lava fountains began along a rift near the village of Kapoho. As in

the other stage, the scene of eruption was soon transferred to a single fountain, which reached heights of more than a thousand feet. Eruption continued without pause until February 19. By this time the lava flow had completely wiped out Kapoho village and spread several miles to the sea.

Volcanic gas samples were taken from this area on two occasions. The first set was obtained during the eruption, on January 21, 1960, from a series of vents along the rift line northwest of the large cinder cone. The second set was taken on April 12, 1960, two months after the eruption, from degassing cinders at the edge of the largest crater in the cinder cone.

Closely connected to Kilauea volcano is the solfataric fumarole, the Sulphur Banks, situated along a fault at the northern edge of the Kilauea caldera. Gases escape from this fault, depositing sulfur and volatile salts, and altering the original olivine basalt to rocks composed largely of silica in the form of opal, with lesser amounts of kaolinite.⁵⁷ Magnetite and ilmenite in the rocks remain largely unchanged.

Use has been made of the gases for sulfur steam baths, and a pipe sunk at this location about 1922 provides a convenient means for obtaining air-free samples of the gases evolved. Samples were taken here on several occasions before, during, and after the 1959-60 eruption of Kilauea.

The results of analyzing gas samples from these three locations are summarized in TABLE VI. The data is presented in the form of mole percentage of the dry gas. Water vapor is also present in large amounts to the extent that the gases noted in the table (aside from air

TABLE VI. ANALYTICAL RESULTS - VOLCANIC GAS SAMPLES

MOLE PERCENTAGES IN THE DRY PORTION OF THE GAS

PART A - KILAUEA IKI CINDER CONE

SAMPLE NO.	DATE	METHOD OF COLLECTION	H ₂	O ₂	N ₂	CH ₄	CO	CO ₂	H ₂ S	SO ₂	A ¹	B ²
A	11/30/59	Vacuum Bulb	0.019	19	81	0	0	0.64	0.00087	0.00097	0.65	2
C	"	" "	0.0027	16	80	0	0	3.5	0.012	tr	3.5	5
D	"	" "	0.0059	19	79	0	0	1.4	0.00042	0.21	1.6	2
E	"	" "	0.0014	21	78	0	0	1.1	0.00016	0.00062	1.1	0
F	"	Silica Gel Tube	0.027	17	83	0	tr	0.45	0.15	0.0069	0.60	4
H	"	"	0.0032	23	77	0	tr	0.27	0.044	0.0017	0.27	-2
1	1/20/60	"	0.0014	12	87	0	tr	2.0	0.010	0.053	2.1	9
2	"	"	0.0021	12	87	0	0	1.3	0	0.14	1.4	9
4	"	"	0.0042	10	88	0	0.073	2.1	0	0.30	2.4	11
6	"	"	0.0019	17	83	0	0	1.2	0.00021	0.22	1.4	4
12	4/11/60	"	0.0016	24	76	0	0	1.2	0	0.020	1.2	-3
13	"	"	0.0043	20	80	0.0063	0.022	0.652	0.00040	0.035	0.62	1
14	"	"	0.059	17	79	0	0.089	4.0	0	0.0046	4.0	4

¹ A = Percent volcanic gas in the dry portion of the sample.² B = Percent oxygen deficiency compared to air (21 - % O₂ ^{air} dry portion of sample).

TABLE VI. ANALYTICAL RESULTS - VOLCANIC GAS SAMPLES (Continued)

PART B - KAPOHO

SAMPLE NO.	DATE	PLACE	METHOD	H ₂	O ₂	N ₂	CH ₄	CO	CO ₂	H ₂ S	SO ₂	CS ₂	A ¹	B ²
0	1/21/60	Dead Cone Rift	Silica Gel	0.0024	24	76	0	0	0.17	0.00025	0.025	0	0.17	-3
1	"	Vent-Rift	"	4.0	92	62	0.54	0.63	25	0	0.10	0	39	8
2	"	"	"	11	0.26	30	0.96	0.55	56	0	4.3	0	70	20
3	"	"	"	0.0089	17	83	0.0050	0.014	0.19	0.00048	0.0073	0.0042	0.20	4
4	"	"	"	13	0	15	0.69	2.6	67	0.93	0.029	0.79	85	21
11	4/12/60	Cinder Cone	"	0	20	80	0	0	0.15	0	0.0055	0	0.12	1
13	"	"	"	0.028	18	82	0	0	0.36	0.025	0	0	0.33	3

¹ A = Percent volcanic gas in the dry portion of the sample

² B = Percent oxygen deficiency compared to air (21 - % O₂ air portion of sample).

TABLE VI. ANALYTICAL RESULTS - VOLCANIC GAS SAMPLES (Continued)

PART C - SULPHUR BANKS

SAMPLE NO.	DATE	PLACE	METHOD	H ₂	O ₂	N ₂	CH ₄	CO	CO ₂	H ₂ S	SO ₂	CS ₂	A ¹	B ²
M	8/59	Well	Silica Gel	0.00080	8.9	32	0	0	57	0.51	0.04	0	59	0
1	1/21/60	"	Vacuum Bulb-wet	0	12	45	0	0	43	0	0.35	0	43	0
2	"	"	Silica Gel	0.0014	3.2	14	0	0	76	1.4	5.1	0	83	3
3	"	"	"	0.0013	0.077	6.6	0	0	85	3.6	5.7	0	93	20
4	"	Natural Vent	"	0	1.8	62	0	0	20	0	0.074	0	36	18
13	4/11/60	Well	"	0.00012	10 ⁻⁵	10 ⁻³	0	0	98.5	3x10 ⁻³	1.5	0	100	21

¹ A = Percent volcanic gas in the dry portion of the sample.

² B = Percent oxygen deficiency compared to air (21 - % O₂ ^{air} dry portion of sample).

contamination) form only one to two mole percent of the total.

2. Sampling Techniques

Evaluation of samples. Reference to TABLE VI, in which are presented the analyses of a number of volcanic gas samples collected during the recent Kilauea eruption, shows that there was a wide divergence in the results, even between samples collected at the same time and place. In order to understand this poor precision, it is necessary to consider some of the difficulties entailed in getting the samples. It is almost impossible to obtain a sample without some mixing with air at the time of collection, unless the investigator is fortunate enough to be able to seal the sample bulb in the vent. There is a very sharp temperature gradient at the mouth of a vent, amounting to a change of several hundred degrees per foot. The sample tube must be broken off as far into the vent as possible beyond this region of temperature flux and atmospheric oxidation. The blue flame, reported by Jaggar, indicating combustion of gases at the mouth of a vent, was not observed in this investigation, and could not be used as an aid in determining where to break off the tip.⁵⁸

These difficulties show why a wide range in the quality of samples is likely. It is not valid to take a series of samples at the same time and place, then average them to get meaningful results. Some of the samples will be excellent, others, very poor. It is preferable to find some means of evaluating the samples and to use only the better ones in forming conclusions about the nature of volcanic gases. Jaggar realized this, and used two criteria, based on conditions of collection and composition, to evaluate his samples. Both gave some indication of the amount of atmospheric contamination of the gases.⁵⁹

In the light of present knowledge, one possible criterion is the percentage of dry volcanic gas in the bulb. The less extraneous air that gets into the sample, the better it is. Another criterion could be based upon the fact that oxygen reacts quantitatively with the volcanic gases at high temperatures, and that nitrogen reacts only slightly. If we make the assumption that all the nitrogen is ultimately atmospheric in origin, the amount by which the oxygen-nitrogen ratio departs from the value for air will indicate the amount of atmospheric contamination of the gas before it was collected. This assumption regarding nitrogen is reasonable as a first approximation since nitrates and other nitrogen compounds are only very minor constituents of volcanic rocks.⁶⁰ Furthermore, Hoering has studied the isotopic ratios in nitrogen and argon of samples collected at the Sulphur Banks, and found them to be the same as for air.⁶¹

The following two criteria have been included in TABLE VI:

A = Percent volcanic gas in dry portion of sample.

B = Percent oxygen deficiency compared to air,

= $21 - \%$ oxygen found in air portion of sample.

If we consider only silica gel samples, it is seen that the analyses of the relatively air-free samples collected at Kapoho are more interesting (i.e., contain a greater variety of gases) than those of Kilauea Iki, which were much contaminated by air.

Among the Kilauea Iki samples, those collected in January had a larger nitrogen excess than those of November, and were correspondingly more oxidized. They were therefore poorer representatives of the primary magmatic gas.

Advantages of silica gel tubes. White colloidal sulfur had previously been observed on the walls of evacuated bulb samples collected during

the 1955 eruption of Kilauea. Presumably this was due to reactions such as



which removed sulfur from the gas phase. A gas-chromatographic analysis of the samples then showed only one sulfur-containing gas, in excess either hydrogen sulfide or sulfur dioxide.

To ascertain whether or not a column of activated silica gel placed in the sample tube would prevent this reaction, varying amounts of water vapor, carbon dioxide, sulfur dioxide and hydrogen sulfide were heated to 100°C. and sampled at the time of mixing by (1) evacuated bulbs and (2) silica gel tubes of the type depicted in Fig. 2. Analysis of the evacuated bulb samples showed only hydrogen sulfide or sulfur dioxide, depending on which was present in excess; analysis of the silica gel tube samples showed both hydrogen sulfide and sulfur dioxide in approximately the same proportions in which they were mixed.

A probable explanation of the above is that the silica gel selectively adsorbed the various gases, thereby separating them and preventing reaction. The likely distribution of gases in the sample tube, based on the order in which they emerge from a gas chromatographic column of silica gel, is shown in Fig 2, together with a representation of the effect of the column on a gas chromatographic analysis. Tests have shown that samples collected in this way may be left for several months at room temperature with no danger of further reaction, since the rate of diffusion of the gases adsorbed on the column is slow enough for the gases to remain essentially separated.

An examination of the samples collected at Kilauea Iki on November 30, 1959, shows that the method of sampling did make a difference in the

results obtained. Thus the samples collected in silica gel tubes contained more sulfur-containing gases (predominantly in the reduced form, hydrogen sulfide) than those samples collected in vacuum bulbs, where much of the sulfur-containing gas had reacted to form solid sulfur. The largest component of the sulfur gases remaining in the simple vacuum bulbs was sulfur dioxide, presumably from reaction with air. Since these samples were collected at a much higher temperature, 700°C ., than the laboratory mixtures, oxidation by atmospheric oxygen would readily occur in the evacuated bulb samples taken at Kilauea Iki. In the silica gel tubes, the adsorbent prevented this reaction as well as the autoxidation of sulfur-containing gases in the presence of condensed moisture.

3. Sources of Errors in Analysis

A number of errors inherent in the gas chromatographic technique also contributed to the observed lack of precision in the volcanic gas samples. One of the most important sources of error was inaccuracy in measuring peak areas. Janak (1960) has made a statistical survey of a large number of methods of integration.⁶³ He found that approximation to a triangle by multiplying the height by the width at half the height, (the method used in this investigation) was comparable with most other manual methods. He found the mean relative error for peaks smaller than 0.5 cm^2 to be 19.2%, for peaks between 0.5 and 1.0 cm^2 , 12.5%, and for peaks between 1.0 cm^2 and 3.0 cm^2 , 4.3%.

This source of error was particularly important in samples contaminated by large amounts of air. The volcanic gases were then present in trace amounts, often near the limits of sensitivity of the apparatus. Upon recalculating the composition of these samples after elimination of atmospheric contaminants, the magnitude of the error became quite large.

Also contributing to the uncertainties in the gas chromatographic results were such factors as non-linearity of the detector response and variations in flow rate and column temperature. Compared to errors in measuring peak areas, these factors were relatively small, especially since calibration was carried out using pure compounds at pressures over the whole range of partial pressures found in the unknowns.

When the pressure of gas in the apparatus was low, errors in measuring pressures were quite large. As often as possible, these errors were minimized by measuring the pressure at a relatively high value and then expanding the gas into the sample introduction tube as many times as necessary to obtain measurable peaks. The pressure of the sample was calculated using the ideal gas law and the known volumes of the constant volume manometer. Under the experimental conditions of low pressures and moderate temperatures, any error introduced by non-ideality of the gases was far outweighed by uncertainty in reading the manometer. This uncertainty was, nevertheless, no larger than errors in measuring the areas of peaks.

The sources of error in the water determinations were principally those in weighing small amounts of any material. Some uncertainty was always introduced by the necessity of having to put stopcock grease on the removable traps. This was always wiped off as carefully as possible. The chances of any water escaping through the dry ice-actone trap were very small due to the low vapor pressure of water at the temperature of the bath and the plug of glass wool in the trap, which prevented mechanical transport of ice crystals through the trap.

B. Calculated Equilibrium Composition of Volcanic Gases

1. Introduction

In order to gain further insight into the observed variations in composition of volcanic gases, and to explore possible pathways toward determining the nature of the primary magmatic gas, a thermodynamic study was made of a typical volcanic gas phase. The approach of Ellis was followed, in that a typical volcanic gas sample, Kilauea Iki F, was used as a starting point.⁶⁴ It was selected because it was collected under conditions indicating that it was a good representative sample of volcanic gas, relatively uncontaminated by previous contact with the atmosphere. A preliminary check had shown the Kilauea Iki samples to be in equilibrium, whereas the Kapoho samples were not. Therefore a Kilauea Iki sample was chosen for the model system.

Using the general method of minimizing the free energy, the equilibrium composition of the gaseous portions of the system S-C-O-H represented by "Kilauea Iki F" was determined at a number of temperatures, pressures, and oxidation states. The following relative atomic ratios, based on the analysis of the sample, were used in the calculations:

S	1.000	O	142.2
C	2.680	H	275.5

The results were summarized in a series of plots, which are reproduced in Figures 5 through 8. Part A of each diagram shows the variations in the major components of the system (except water, which is essentially constant), in plots of the partial pressures of these components. In plots of the logarithms of the various partial pressures, Part B illustrates the variations in the composition of the following possible components: water, hydrogen, carbon dioxide, carbon monoxide, hydrogen sulfide, sulfur dioxide, sulfur vapor, sulfur monoxide, sulfur trioxide, carbon oxysulfide, carbon disulfide, methane, hydroxy, free radicals, etc.

oxygen.

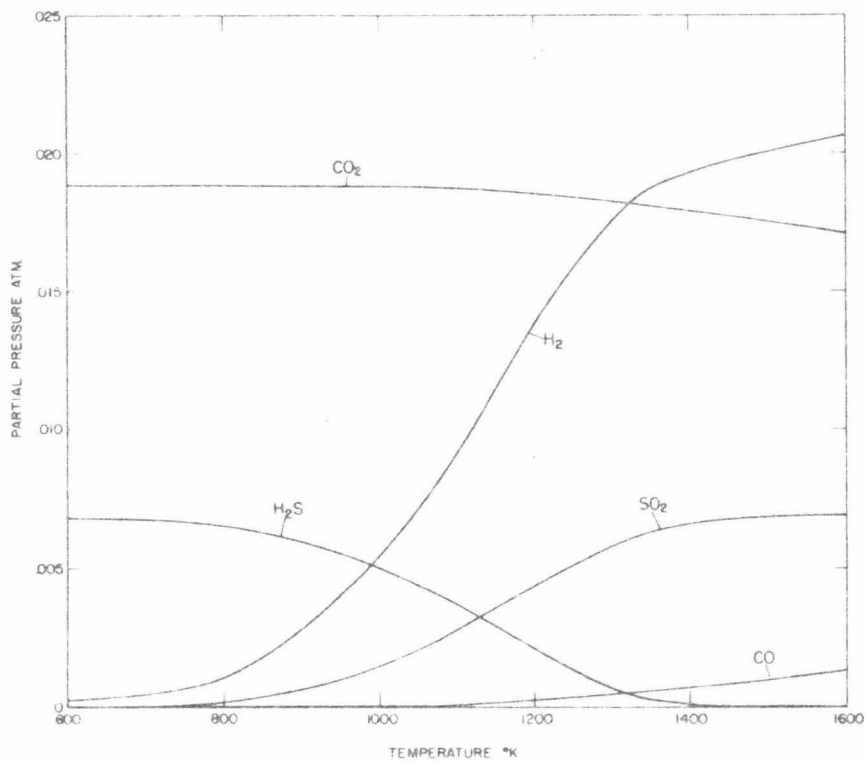
2. Variation with Temperature

The calculated equilibrium composition of the volcanic gas system S-C-O-H at atmospheric pressure and temperatures between 400°K. and 1600°K. is shown in Fig. 5. Water is the dominant constituent throughout, decreasing very slightly as the temperature is raised. Carbon dioxide is the major carbon-containing gas, and also decreases with temperature. At lower temperatures, hydrogen sulfide is the principal sulfur-containing gas, being replaced by sulfur dioxide above 1150°K. Hydrogen and carbon monoxide increase with temperature, with hydrogen rising very rapidly in the region of transition between the sulfur gases. Figure 5-A agrees very well in its form with the results of Ellis.⁶⁵ There are, however, shifts in the positions of the curves because a slightly different gas composition was used in this investigation.

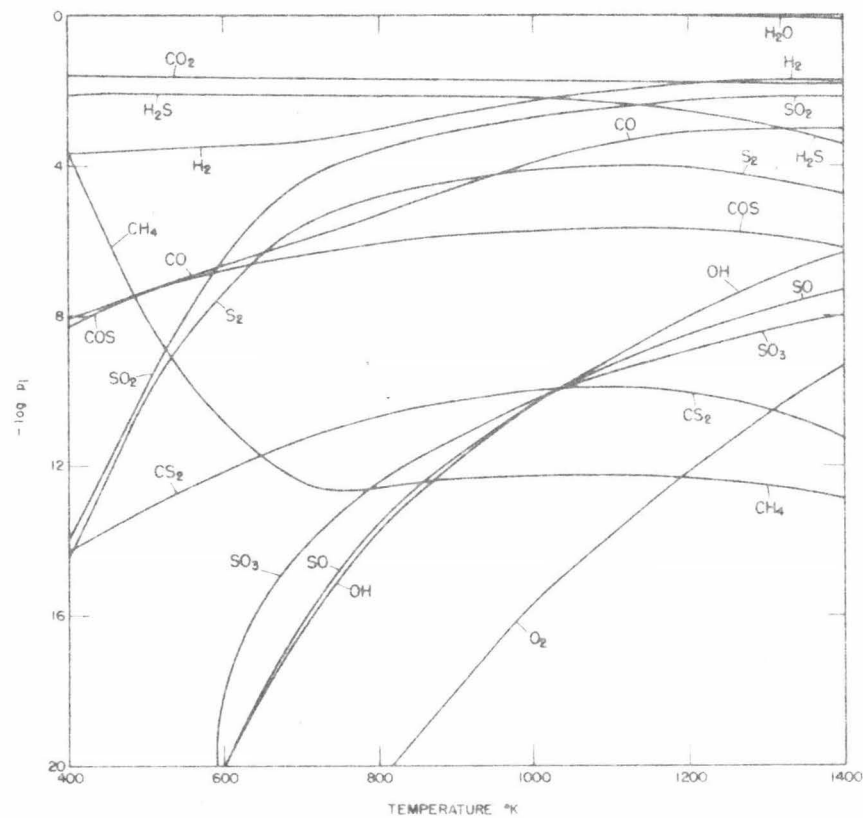
Comparison of the calculated composition at 800°K. with the experimental data on the sample Kilauea Iki F (TABLE VII) showed that there was excellent agreement at this lower temperature. Evidence was thus provided that volcanic gases are in equilibrium at the time of collection, lending justification to further thermodynamic treatment. Further discussion of the attainment of equilibrium and the temperature discrepancy is presented in Part C of this section, with reference to the effect of meteoric water on the apparent temperature of equilibrium.

The minor components of the gas, present in such small amounts as to be undetectable, with the present analytical apparatus, are represented in Fig. 5-B. It is seen that many of them, including sulfur trioxide, sulfur monoxide, hydroxyl free radical, and oxygen, increase rapidly with temperature. Others, such as carbon disulfide, carbon oxysulfide, methane,

FIGURE 5. EQUILIBRIUM VARIATION WITH TEMPERATURE OF
THE GASEOUS PORTION OF THE SYSTEM S-C-O-H



A. Major Components (Except H₂O)



B. Major and Minor Components

TABLE VII. COMPARISON OF CALCULATED EQUILIBRIUM
COMPOSITION WITH EXPERIMENTALLY DETERMINED
COMPOSITION OF THE VOLCANIC GAS SAMPLE
KILAUEA IKI "F"

	<u>Mole Percentages</u>	
	Experimental	Calculated
H ₂ O	97.2	97.2
H ₂	0.12	0.13
CO ₂	1.90	1.90
CO	trace	0.0055
CH ₄	0	10 ⁻¹⁰
H ₂ S	0.67	0.66
SO ₂	0.030	0.030
COS	0	10 ⁻⁴
CS ₂	0	10 ⁻⁹
	T _{OBS} - 750°C.	T _{CALC} - 525°C.

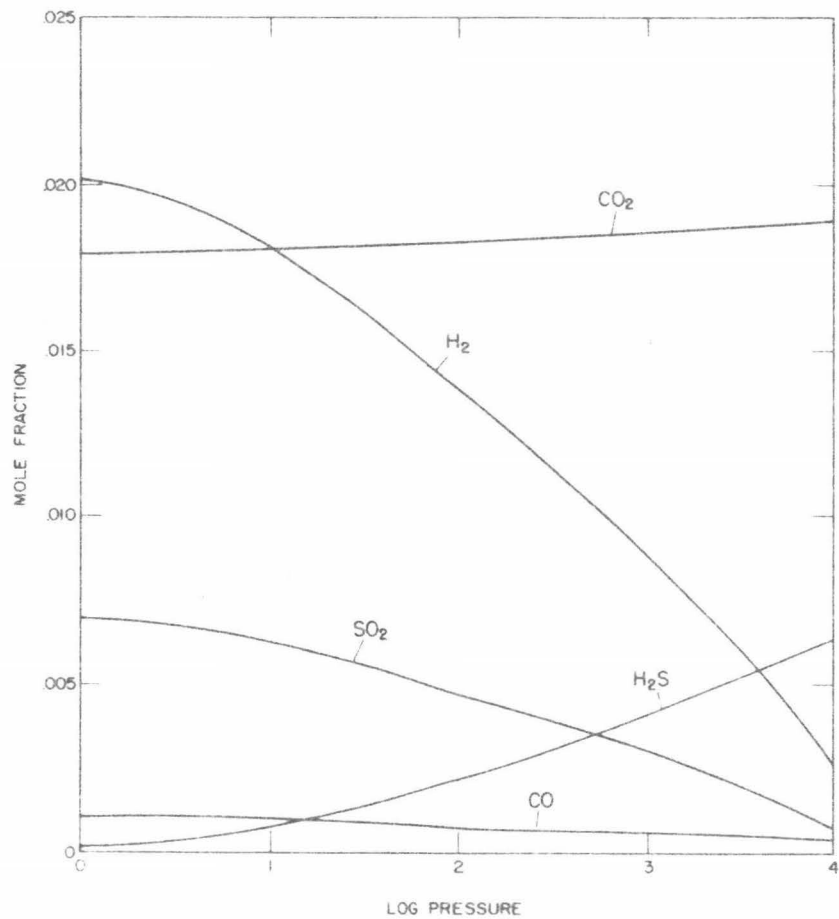
and sulfur vapor reach a broad maximum in the region of equivalence between hydron sulfide and sulfur dioxide. One gas, methane, also increases very rapidly at low temperatures. Verification that the sample chosen was truly representative of volcanic gas is apparent from the very small partial pressure of oxygen in equilibrium with the gas at the temperatures of interest. The p_{O_2} is well within the limits necessary for the stability of the various minerals occurring in the magma and solidified lava, indicating further that there had been very little atmospheric contamination of this particular sample.

3. Variation with Pressure

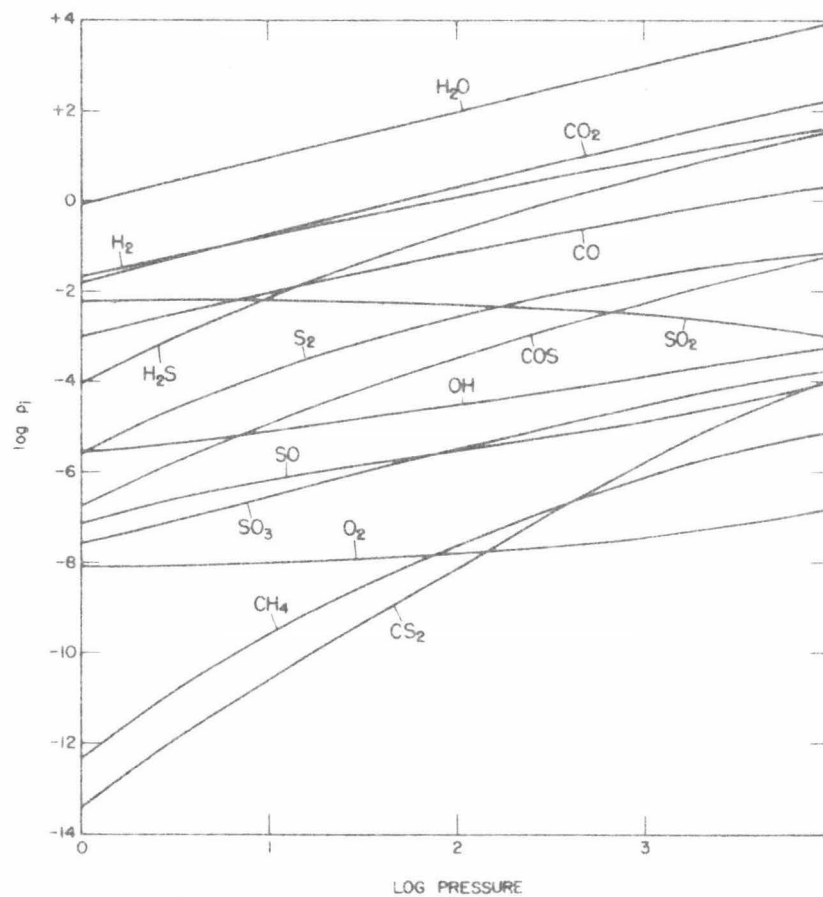
Shown in Fig. 6 are changes in the model volcanic gas system at a temperature of 1500°K ., and pressures ranging from 1 atm. to 10,000 atm. In Fig. 6-A, the mole fraction is plotted instead of the partial pressure, in order to keep the plots all on the same graph. To obtain the partial pressure of any component at a given total pressure of the system, it is necessary only to multiply the mole fraction of the component by the total pressure.

It must be pointed out here that errors due to the assumption of an ideal gas system, while negligible at atmospheric pressure, increase rapidly with increasing pressure. Nevertheless, the temperature considered is high enough (1500°K .) that the fugacity coefficients remain of the order of unity. For instance, the fugacity coefficient of water at 1500°K . and 1000 atm. is about 0.95; and that of carbon dioxide is about 1.2.⁶⁶ In very accurate work, an additional iteration cycle would have to be added to the computation program to take into account the fugacities of the gases. The plots presented here, however, are designed

FIGURE 6. EQUILIBRIUM VARIATION WITH PRESSURE OF THE GASEOUS PORTION OF THE SYSTEM S-C-O-H



A. Major Components (Except H₂O)



B. Major and Minor Components

to show the general trends in the composition of the system with increasing pressure, and are not intended to be used quantitatively.

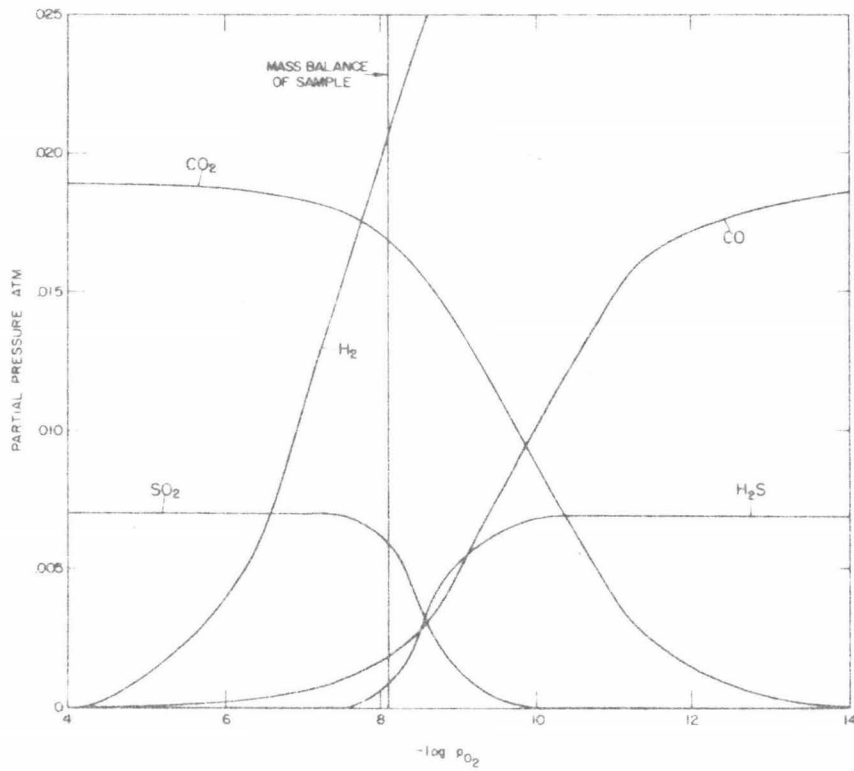
Referring to Fig. 6-A, it is seen that there is a slight increase in the CO_2/CO ratio with increasing pressure, a decrease in the relative amount of hydrogen, and the replacement of sulfur dioxide by hydrogen sulfide as the dominant sulfur gas. The effect of increasing the pressure is thus roughly the same as decreasing the temperature. The gases dominant at low temperature and low pressure become dominant again at high temperature and high pressure.

Fig. 6-B shows, as expected, that there is an increase in the partial pressures of most of the gases with increasing total pressure. There are, however, two notable exceptions. The partial pressure of sulfur dioxide decreases with increasing pressure, and the partial pressure of oxygen stays nearly constant. Thus, at high pressures, although the composition of the gas is changed (particularly with reference to the sulfur-containing gases) the oxidation state of the gases remains essentially the same. The gas phase in equilibrium with a certain mineral assemblage in the same oxidation state would be different, depending on the total pressure on the system. Thus, the gases present when a rock is formed are not necessarily those in equilibrium with it at atmospheric pressure.

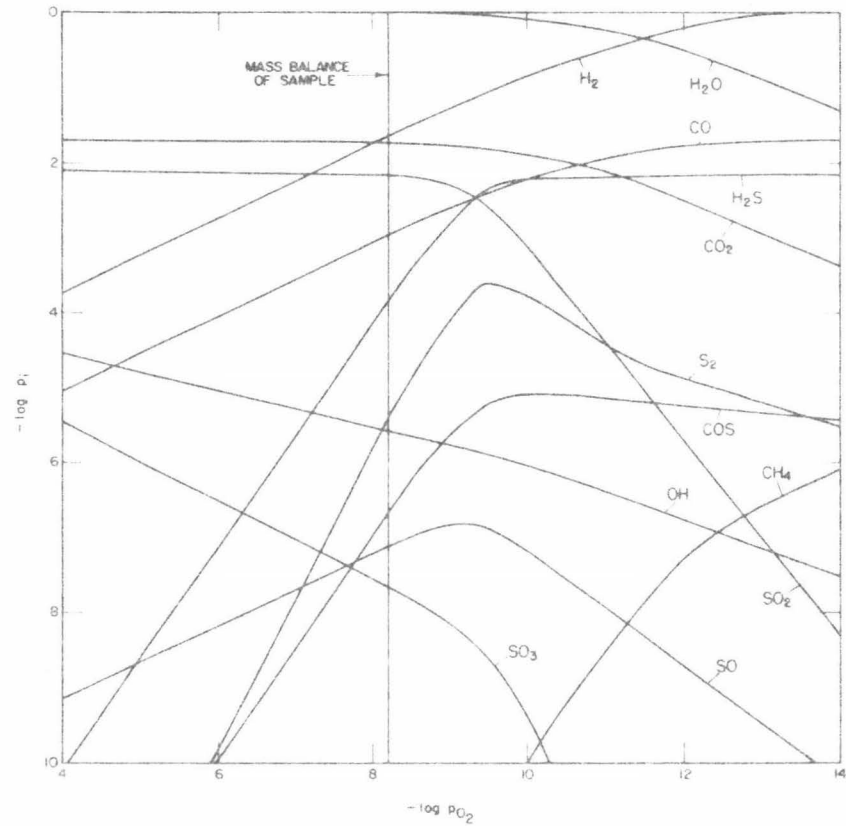
4. Variation with Partial Pressure of Oxygen

Discussion of the curves. The variation in the composition of the gases with the partial pressure of oxygen present in the system is shown in Figs. 7 and 8. Fig. 7 represents the changes at 1500°K . and 1 atm., essentially the conditions under which lava is erupted; and Fig. 8, the changes at 900°K . and 1 atm., the conditions under which most of the

FIGURE 7. EQUILIBRIUM VARIATION WITH PARTIAL PRESSURE
OF OXYGEN AT 1500°K. OF THE GASEOUS PORTION OF
THE SYSTEM S-C-O-H

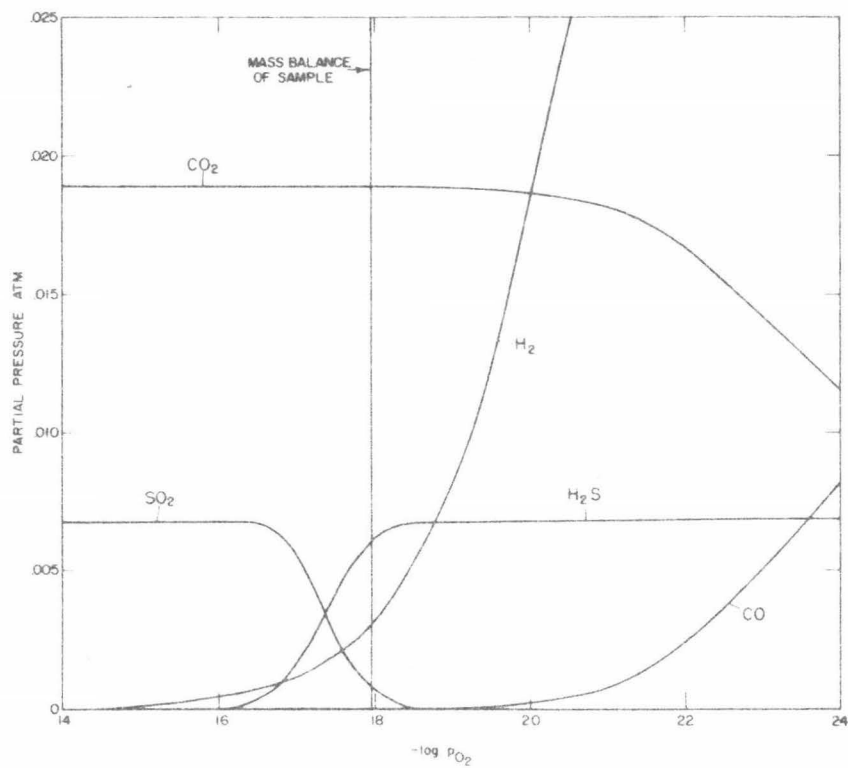


A. Major Components (Except H₂O)

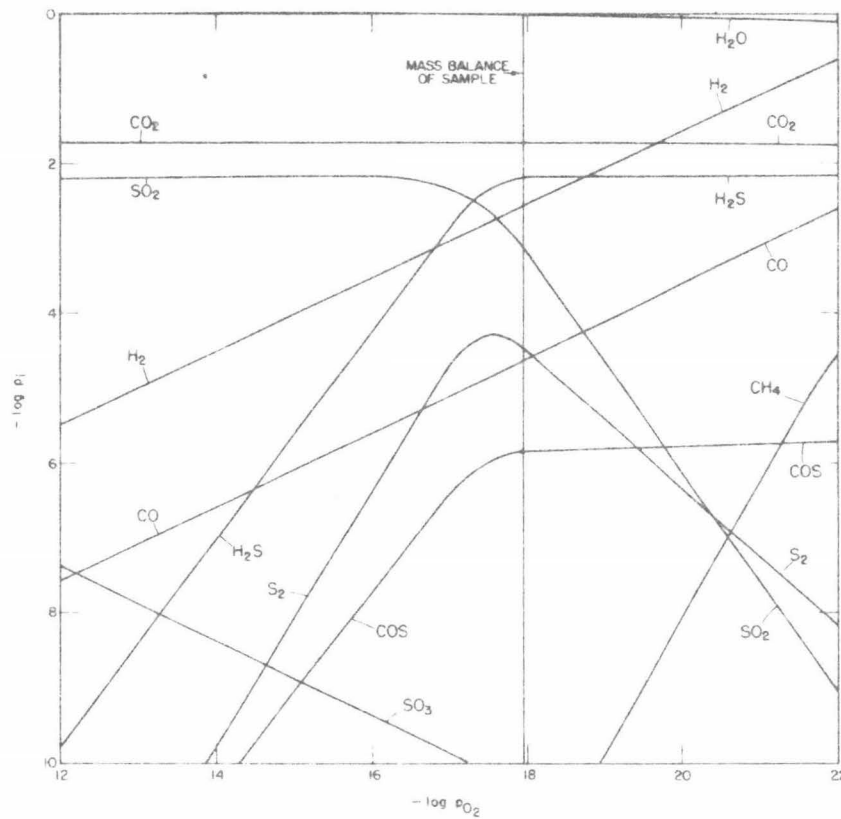


B. Major and Minor Components

FIGURE 8. EQUILIBRIUM VARIATION WITH PARTIAL PRESSURE OF OXYGEN AT 900°K. OF THE GASEOUS PORTION OF THE SYSTEM S-C-O-H



A. Major Components (Except H₂O)



B. Major and Minor Components

volcanic gas samples were collected. The calculations necessary to construct these diagrams were carried out using the minimization of free energy method. Holding the atomic ratios of sulfur, carbon and hydrogen constant, the relative amount of atomic oxygen was varied, and the equilibrium composition determined for different oxygen contents. Plots were then made of partial pressure and $-\log p_1$ as a function of $-\log p_{O_2}$.

It will be noted that there is a great deal of similarity between plots made at different temperatures. The slopes of the curves for the principal components remain the same, but their relative positions on the $-\log p_{O_2}$ axis are shifted. This shows the effect of temperature on the various equilibria. In particular, the amount of oxygen in equilibrium with a gas of a certain composition is different at different temperatures; therefore, the positions of the curves are displaced along the $-\log p_{O_2}$ axis. The equilibrium amounts of trace components other than oxygen, such as hydroxyl free radical and sulfur trioxide, also vary with the temperature; transition points in their curves are displaced vertically as well as horizontally.

Since the horizontal portion of the curve for a dominant molecular species occurs when virtually all of its significant component element is in that particular form, the position of the line relative to the vertical axis will be determined only by the amount of the element in the atomic ratios. For instance, the more sulfur there is present relative to the amounts of hydrogen and carbon, the higher the horizontal portion of the sulfur dioxide curve will be relative to the horizontal portions of the curves for carbon dioxide and water.

For each atomic species, one molecular species dominates over a given range of oxygen partial pressure, this molecule containing nearly

all of the element in that region. There is then a region of transition, followed by a range in which a different molecular species dominates. For the hydrogen-containing gases, the dominant gas is water, shifting to hydrogen at low oxygen partial pressures. Carbon dioxide is the dominant carbon-containing gas, shifting to carbon monoxide at a value of p_{O_2} greater than that of the water-hydrogen shift. At very high p_{O_2} , (not occurring in volcanic gases), the dominant sulfur-containing gas is sulfur trioxide; it is replaced by sulfur dioxide at moderate oxygen partial pressures, and by hydrogen sulfide at low oxygen partial pressures. The sulfur dioxide-hydrogen sulfide transition occurs at a value of p_{O_2} greater than that for the carbon dioxide-carbon monoxide transition.

All volcanic gas samples collected to date had values of p_{O_2} such that water and carbon dioxide are dominant. There is, however, extreme variability in the nature of the sulfur-containing gases, because most of the samples were collected in the neighborhood of the hydrogen sulfide-sulfur dioxide transition point. This is because of the stability relations among minerals occurring in the magma and in volcanic rocks, which set definite limits on the oxidation state of the associated gas. These limits are such that hydrogen and carbon monoxide cannot be the dominant gases at the temperatures of collection.

In the regions of transition between dominant species, changes occur in the slopes of the curves for minor components (Figs. 7-B and 8-B). For some of the sulfur gases, such as sulfur vapor and sulfur monoxide, this amounts to a maximum at the hydrogen sulfide-sulfur dioxide transition, since they are intermediate in oxidation state between the latter two gases. In general, however, hydroxyl free radical

and sulfur trioxide increase with increasing p_{O_2} , and methane, carbon oxysulfide and carbon disulfide decrease with increasing p_{O_2} .

Significance of the function $-\log p_{O_2}$. It will be noted that the curves in Figs. 7-A and 8-A are identical in form to typical aqueous titration curves. The partial pressure of one gas in an oxidation-reduction couple will remain essentially constant over a range of oxygen partial pressures, and then decrease rapidly to an essentially zero value, while the other gas exhibits the reverse behavior.

Similarly, in Figs. 7-B and 8-B, the curves for these species are identical in form to curves in the logarithmic pH diagrams developed by Bjerrum, Sillen and others to systematize complex equilibria in acid-base titrations.⁶⁷ For one gas in a particular oxidation reduction couple, there is a range of $-\log p_{O_2}$ over which the gas is constant, being represented by a horizontal line. After a period of transition, another region follows in which the gas decreases in proportion to $-\log p_{O_2}$, this region being represented by a diagonal line. For the other gas in the couple, the reverse behavior is observed.

It is evident that the function $-\log p_{O_2}$ is an index of the oxidation state of the magmatic gas phase, in the same way that pH ($-\log c_{H^+}$) is an index of the acidity of an aqueous solution. The function $-\log p_{O_2}$ is a convenient way of expressing the state of oxidation of the gas, and will be given the symbol mO , an easily written abbreviation.

Construction of mO diagrams. If the dominant species in the gas phase are known, it is possible to construct logarithmic partial pressure diagrams without resorting to the general method of calculation. The following discussion, based on that of Sillen, Lange, and

Gabrielson for logarithmic pH diagrams, will show how this can be done, and at the same time provide a more quantitative understanding of the mO diagrams.⁶⁸

Consider the general oxidation-reduction reaction for the i -th couple of gases,



where OX represents the oxidized form, and RED the reduced form. The equilibrium constant for this reaction may be written

$$\frac{(P_{\text{RED}_i})^n P_{\text{O}_2}}{(P_{\text{OX}_i})^n} = K_i, \quad (2)$$

where the P's represent partial pressures. (The gases are here considered to be ideal for convenience in discussion.) In logarithmic form, this equation becomes

$$mO = mK_i + n \log \frac{(P_{\text{OX}_i})}{(P_{\text{RED}_i})} \quad (3)$$

where $mO = -\log P_{\text{O}_2}$ and $mK_i = -\log K_i$, in analogy to the definitions of pH and pK_i used in aqueous solutions. The total partial pressure, P_i , of the two gases is

$$P_i = P_{\text{OX}_i} + P_{\text{RED}_i} \quad (4)$$

Simplifying assumptions can be made when the value of mO is very much different from its value at the equivalence point. When $mO < pK_i - 1$, the gas is essentially all in the oxidized form, and $P_i = P_{\text{OX}_i}$. The expression for mO then becomes

$$mO = mK_i + n \log \frac{P_{\text{RED}_i}}{P_i} \quad (5)$$

The partial pressure expressions used in making plots are then

$$\log P_{\text{OX}_i} = \log P_i \quad \text{and} \quad (6)$$

$$\log P_{\text{RED}_i} = \log P_i + \frac{1}{n} (m\text{O} - mK_i) \quad (7)$$

It is seen that the oxidized form is represented by a line of slope zero, and the reduced form by a line of slope $1/n$, where $1/n$ is the number of moles of oxygen exchanged in the reaction of one mole of the i -th oxidation couple.

On the other hand, when $m\text{O} > mK_i + 1$, $P_i = P_{\text{RED}_i}$, so that

$$m\text{O} = mK_i + n \log \frac{P_i}{P_{\text{OX}_i}} \quad (8)$$

The equations used for making plots in this region become

$$\log P_{\text{RED}_i} = \log P_i \quad \text{and} \quad (9)$$

$$\log P_{\text{OX}_i} = \log P_i - \frac{1}{n} (m\text{O} - mK_i) \quad (10)$$

The reduced form is now represented by a horizontal line, and the oxidized form by a diagonal line of slope $-1/n$. The horizontal and diagonal portions of the curves can be connected by a smooth curve extending over two $m\text{O}$ units.

As a first approximation, each oxidation-reduction equilibrium may be considered separately. For each atomic constituent, equations involving the transfer of oxygen from the dominant species to a minor species must be written, one for each minor species in each region of a dominant gas. In the case where a minor gas contains two atomic species besides oxygen; i.e., methane or carbon oxysulfide, the controlling equilibrium is the one which allows the smallest concentration of the minor gas.

Equilibrium constants for these reactions can most easily be derived from tabulated relative free energy data.⁶⁹ The standard molar

(Gibbs) free energy may be calculated from the equation

$$-\frac{F^O}{RT} = \frac{1}{R} \left[-\frac{(F^O - H^O)}{T} \right] + \frac{1}{RT} \left[H_F^O - (H^O - H_O^O) \right] 298.16 \quad (11)$$

where $-\frac{(F^O - H^O)}{T}$ is the relative free energy, $(H - H_O^O) 298.16$ is the relative heat content at 298.16°K., and H_F^O is the standard heat of formation of the gas at 298.16°K. The equilibrium constant for the redox equilibrium (1) is then given by

$$\ln K_1 = \frac{F^O}{RT} = n \left(\frac{F^O}{RT} \right)_{OX_1} - n \left(\frac{F^O}{RT} \right)_{RED_1} - \left(\frac{F^O}{RT} \right)_{O_2} \quad (12)$$

5. Variation with Partial Pressure of Water

In Fig. 9 there is presented a set of plots showing the variation of the composition of the model system with the partial pressure of water. The direction of increasing water is toward the ordinate axis, as in the oxygen plots. It is seen that the chief effect of water is that of dilution. In the system studied, there is also an oxidizing effect, as indicated by the increasing partial pressure of oxygen and of sulfur dioxide. The gases approach the oxidation state of a water-hydrogen system, which, in this case, controls a higher partial pressure of water than the entire system. The actual sample, "Kilauea Iki F", had $-\log P_{H_2O} = 0.02$, and therefore lies quite close to the ordinate axis.

It is sometimes stated that ground water is one of the chief oxidizing agents acting on magmatic systems. This study appears to support this statement. It may be true generally, because most magmatic gases are probably even more reduced than the system studied, at least until they get near the surface. It may be remarked here that it is quite

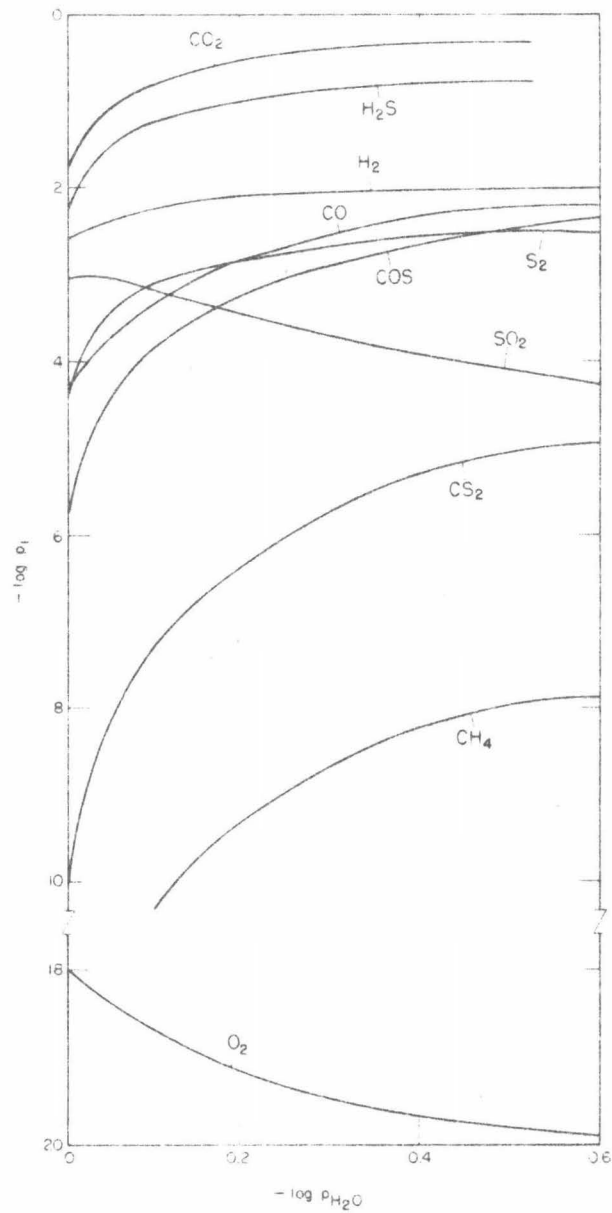


FIGURE 9. EQUILIBRIUM VARIATION WITH PARTIAL PRESSURE OF WATER AT 900°K. OF THE GASEOUS PORTION OF THE SYSTEM S-C-O-H

reasonable also to consider oxygen as a magmatic oxidizing agent in Hawaiian volcanoes because of the very porous nature of the rocks, which will allow air as well as water to diffuse down from the surface.

6. Importance of Complex Gas Equilibrium Calculations

The chief reason for applying complex gas equilibria to magmatic systems is that discussion is permitted of any situation, however complex it may be. Laboratory studies of complex equilibria occurring between gases and silicates at high temperatures have been carried out using simple gas systems. The results of these studies may very easily be extended to natural systems, using the methods of approach outlined in this investigation. It may be noted that the approach used is not limited to homogeneous gas systems. A recent paper by Boynton (1960) has generalized the minimization of free energy method of White, Johnson and Dantzig to polyphase, multicomponent systems.⁷⁰ Any naturally occurring mineral-gas or mineral-liquid system, regardless of its complexity, can be studied, provided the necessary free energy and activity coefficient data are available. Even in cases where data are not at hand, they can sometimes be estimated with a reasonable degree of accuracy by using the rule of "additivity of entropies".⁷¹

Oxidation-reduction reactions occurring in the gas phase are particularly easily studied. By using the method of logarithmic diagrams, the necessity for using a high-speed digital computer is eliminated. However, in cases where a computer is available, the general method is recommended, because it is quicker and not subject to possible erroneous assumptions. As more and better computers become available, the complexities of geochemical systems will become more susceptible to attack by these methods.

C. Interpretation of the Analyses of the Gas Samples

1. Introduction

The following is a discussion of the specific results obtained on analysis of gases from a low temperature solfataric source, the Sulphur Banks, and from higher-temperature volcanic sources, the Kilauea Iki cinder cone (Puu Pua'i) and the Kapoho rift. There is presented an interpretation of the results in terms of the effects of secondary atmospheric influences on the primary magmatic gases which are released from the erupting lava and from hot pumice. The attainment of chemical equilibrium in the gases will be discussed, together with the factors controlling it.

In order to provide a basis of comparison for the samples, the experimental data have been recalculated by subtracting all of the oxygen and nitrogen, as well as the carbon dioxide content of air. The gaseous portions of the system S-C-O-H, whose theoretical equilibrium composition has been discussed in Part B of this section, represent the of volcanic gases. Consideration of other possible components of the gas, such as compounds of chlorine, fluorine, nitrogen, silicon, and the heavy metals, can be made as minor corrections on the results for the principal constituents. Such a discussion will not be attempted here because of a lack of experimental data.

Analyses of gases taken from the Sulphur Banks over a two-year period are summarized in TABLE VIII. A presentation of the results of the analysis of samples from Kilauea Iki and Kapoho is made in TABLE IX. Included is the temperature observed at the time of collection of each sample together with the calculated equilibrium temperature for the composition of that sample when such a calculation was possible.

TABLE VIII. RECALCULATED SULFATARIC GAS ANALYSES OF SAMPLES COLLECTED BY SILICA GEL METHOD - O₂, N₂, CO₂ OF AIR SUBTRACTED

A. SULPHUR BANKS

SAMPLE DATE	MOLE PER- CENT OF TOTAL H ₂ O	MOLE PERCENT OF DRY PORTION								T _{OBS}	T _{CALC}
		H ₂	CH ₄	CO	CO ₂	H ₂ S	SO ₂	CS ₂			
58-1 Sept. 1958	--	0	0	0	100	0	trace	0	96.5°C.	100°C.	
59-1 Aug. 1959	99.2	0.0014	0	0	99	0.89	0.07	0	96.5°C.	100°C.	
60-1 Jan. 1960	99.1	0.0017	0	0	92	1.7	6.2	0	96.5°C.	100°C.	
60-2 Jan. 1960	99.2	0.0014	0	0	90	3.8	6.1	0	96.5°C.	100°C.	
60-3 Apr. 1960	99.3	0.0012	0	0	98.5	0.0013	1.5	0	96.5°C.	100°C.	

TABLE IX. RECALCULATED VOLCANIC GAS ANALYSES OF SAMPLES COLLECTED
BY THE SILICA GEL METHOD - O₂, N₂, CO₂ OF AIR SUBTRACTED

A. KILAUEA IKI

SAMPLE DATE	MOLE PER- CENT OF TOTAL H ₂ O	MOLE PERCENT OF DRY PORTION							T _{OBS}	T _{CALC}
		H ₂	CH ₄	CO	CO ₂	H ₂ S	SO ₂	CS ₂		
59-1*F* Nov. 1959	97.2	4.5	0	trace	70	25	1.1	0	750°C.	500°C.
59-2*11*Nov. 1959	98.1	1.1	0	trace	83	15	0.59	0	750°C.	400°C.
60-1*4* Jan. 1960	97.2	0.17	0	3.0	85	0	12	0	700°C.	--
60-2*6* Jan. 1960	77.2	0.14	0	0	84	0.015	16	0	700°C.	500°C.
60-3*12*Apr. 1960	--	0.13	0	0	98.2	0	1.7	0	600°C.	500°C.
60-4*13*Apr. 1960	93	0.62	0.91	3.1	90	0.058	5.1	0	600°C.	--
60-5*14*Apr. 1960	63	1.4	0	2.2	96.5	0	0.11	0	600°C.	--

TABLE IX. RECALCULATED VOLCANIC GAS ANALYSES OF SAMPLES COLLECTED
 BY THE SILICA GEL METHOD - O₂, N₂, CO₂ OF AIR SUBTRACTED
 (Continued)

B. KAPOHO

SAMPLE	DATE	MOLE PER- CENT OF TOTAL H ₂ O								T _{OBS}	T _{CALC}
			H ₂	CH ₄	CO	CO ₂	H ₂ S	SO ₂	CS ₂		
60-1"0"	Jan. 1960		1.4	0	0	83	0.15	15	0	500°C.	1000°C.
60-2"1"	Jan. 1960	97.2	13	1.8	2.1	82	0	0.34	?	300°C.	—
60-3"2"	Jan. 1960	97.4	15	1.3	0.76	77	0	5.9	?	300°C.	—
60-4"3"	Jan. 1960	97.2	4.5	2.5	7.0	80	0.24	3.7	?	500°C.	—
60-5"4"	Jan. 1960	97.2	15	0.81	3.1	79	1.1	0.034	0.93	500°C.	(500°C.)
60-6"11"	Apr. 1960	99.7	0	0	0	95.6	0	4.4	0	600°C.	—
60-7"13"	Apr. 1960	92.4	7.4	0	0	87	6.5	0	0	600°C.	—

2. Solfataric Cases

The analytical results of silica gel tube samples taken from the drill hole at the Sulphur Banks are summarized in TABLE VIII. It is seen that the composition of the gas changes with time. In September 1958, during an inactive period of both Mauna Loa and Kilauea, the gas consisted almost entirely of carbon dioxide and water vapor, with only a trace of sulfur dioxide. By August 1959, three months prior to the Kilauea Iki eruption, hydrogen sulfide had become a major component of the gas, and smaller amounts of sulfur dioxide and hydrogen had appeared. During the Kapoho eruption, in January 1960, the sulfur content had increased still further, with sulfur dioxide slightly more prominent than hydrogen sulfide. However, by April 1960, two months after the eruption, the sulfur content had decreased again, and reverted almost entirely to the form of sulfur dioxide.

It is evident that the increased percentage of sulfur-containing gases (predominantly in the more reduced form of hydrogen sulfide) in the Sulphur Banks gases was closely associated with the imminence of the 1959-60 Kilauea eruption. This fact is in agreement with Ballard and Payne (1940), who had observed similar behavior of Sulphur Banks prior to the 1940 eruption of Mauna Loa, and had attributed the presence of hydrogen sulfide in the gases to the eruption.⁷² They suggested that regular sampling and analysis of Sulphur Banks gases would enable prediction of an eruption by noting the presence of hydrogen sulfide.

The validity of this conclusion regarding Mauna Loa should be checked by further observations. Since analyses of fresh lava from Mauna Loa and Kilauea indicate that the two volcanoes are fed by separate shallow magma reservoirs, the mechanism by which Mauna Loa would affect

the Sulphur Banks is not at all clear.⁷³ However, observation of hydrogen sulfide in silica gel tube samples collected from the Sulphur Banks prior to an eruption of Mauna Loa might indicate a connection between the latter and Kilauea.

A mechanism capable of explaining these phenomena may be postulated by considering the relationship of a persistent fumarole such as the Sulphur Banks to the magma chamber below. A schematic representation is shown in Fig. 10-A. Gases percolate upward from the magmatic source, filtering through cracks and fissures in the rock. On their upward journey, they are subjected to the following possible changes: 1) a gradual decrease in pressure and temperature, the gases reaching the surface at approximately 95.5°C. , the boiling temperature of water at that altitude; 2) mixing with ground water, occurring at conditions approaching the critical point of water; 3) reaction with air which filters down through the porous rocks of the shield of the volcano; and 4) reaction with the surrounding rock, altering its composition.

The composition of the gas reaching the surface will depend on the rate of evolution of gas from the magma relative to the rates of these disrupting processes. Obviously, the more gas which reaches the surface per unit of time, the less changed the gas will be.

An eruption occurs when forces acting on the magma force it to move upward through the earth's crust. Powers (1954),⁷⁴ Mogi (1959)⁷⁵ and Eaton and Murata⁷⁶ have shown that the deep level source of magma is at a depth of about 30-55 km., whereas the immediate reservoir of lava during an eruption is about 4 km. On reaching this latter level prior to eruption, the magma may accumulate for a while before it finds a weak point in the rocks above and breaks through. The resulting

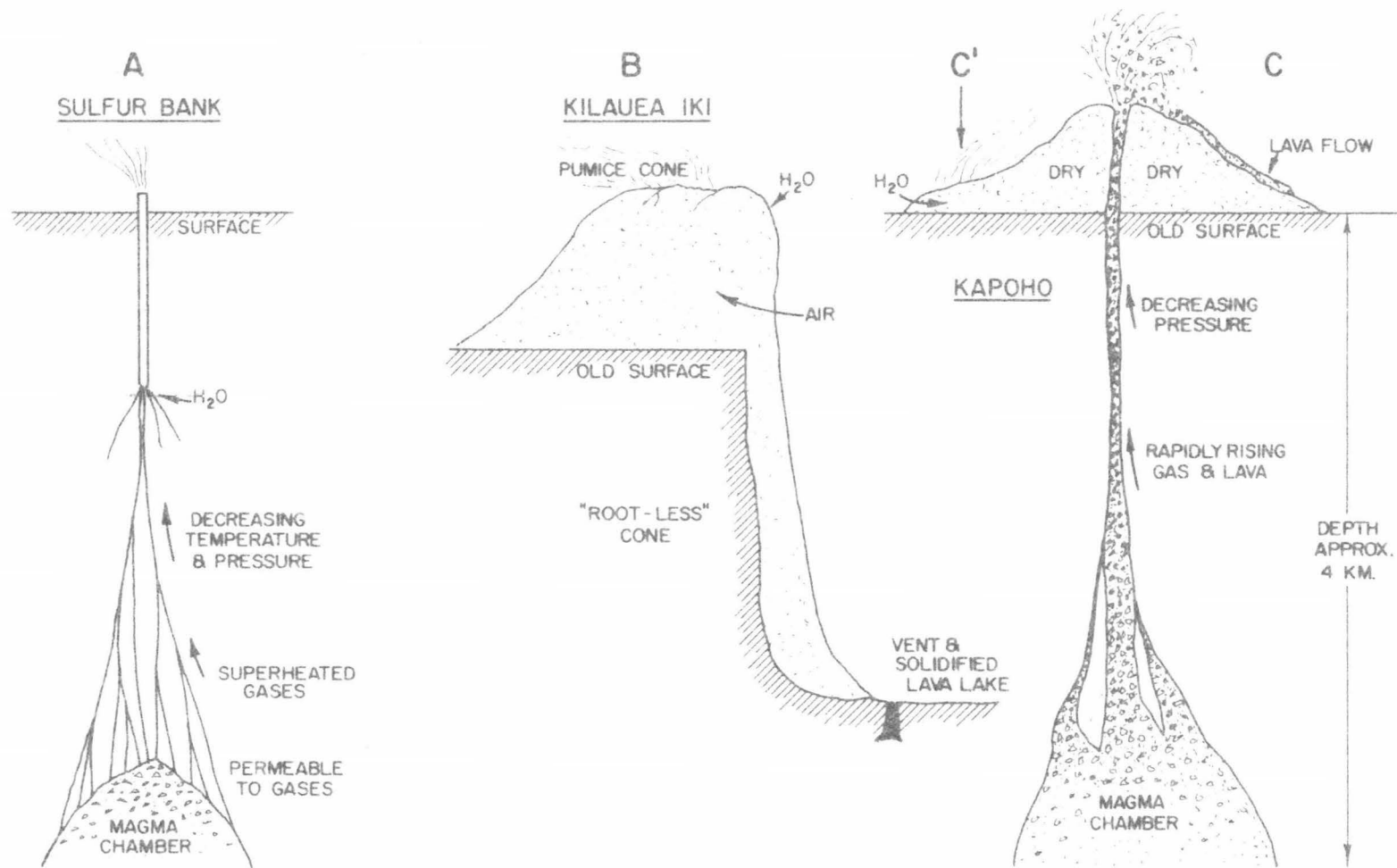


FIGURE 10. SCHEMATIC REPRESENTATION OF THE CONDITIONS OF GAS EVOLUTION

decrease in pressure on the magma will permit the separation of dissolved volatile material into a separate gas phase which permeates upward, reaching the surface at persistent fumaroles such as the Sulphur Banks.

There is undoubtedly some release of gas at all times, although more slowly and possibly from a deeper level than before and during an eruption. However, the release of gas increases tremendously in a period of volcanic activity. The various side effects noted above, which tend to both oxidize the gas and remove sulfur from it, then become less important. At these times the gas reaching the surface at Sulphur Banks will therefore be much closer in composition to the gas which originally separated from the magma; i.e., the hydrogen sulfide content will be high.

It is interesting to note these gases are in equilibrium at the conditions of collection. The reasons for this equilibrium could be: first, that mixing with water occurred at conditions where complete reaction could occur, and second, the temperature and pressure gradients are low enough for the gas to remain at equilibrium, even on reaching the surface. It will be seen that this is not the case with some of the volcanic gas samples.

3. Volcanic Gases

The results of the analyses of volcanic gases collected at Kilauea Iki and Kapoho by the silica gel method are summarized in TABLE VIII. A number of trends may be observed in the samples. In the Kilauea Iki cinder cone samples there was increased oxidation of the sulfur-containing gases after the eruption, hydrogen sulfide being largely replaced by sulfur dioxide. This was accompanied by a decrease in the total sulfur content of the samples. Relatively low-temperature samples (500°C.) obtained

from Kilauea Iki in April 1960, several months after eruption, agreed qualitatively with low temperature samples obtained from the Kapoho rift in January 1960, during eruption. Both were low in sulfur and contained large amounts of such reduced gases as methane, carbon monoxide and hydrogen.

An explanation of these trends may be given in terms of a simple picture of the conditions under which the gases were evolved. The situation at the Kilauea Iki cinder cone is represented schematically in Fig. 10-B. It consists of an extremely porous mass of loosely packed pumice, which was piled up on the edge of the crater wall by the action of the prevailing winds on the lava fountain. Since the cone was probably never connected directly to the lava vent, it can be called a "rootless cone".

The pumice cone at Kapoho, however, was much more intimately connected with the lava vents about which it was formed, as shown schematically in Fig. 10-C. Unfortunately, it was not possible to obtain samples from the Kapoho cinder cone during the eruption, as at Kilauea Iki. The samples that were obtained came from relatively low-temperature vents on the rift nearby. Here the conditions were quite different, as indicated at C' in Fig. 10.

At least two substances, atmospheric oxygen and ground water, will interact with the gases released from the lava and pumice, changing the gas composition. Both substances are oxidizing agents (See Sec. B-5 for a treatment of the oxidizing effect of water on the gas phase). The oxygen, however, cannot diffuse into hot, degassing regions; it reacts immediately with the combustible volcanic gases. Its effect over a long period of time would be to increase the amount of oxygen

in the atomic ratios defining the composition of the gas collected at the surface. Accordingly, there will be a shift toward higher oxygen partial pressures, indicated by a shift to the left in Fig. 7-E. As observed at Kilauea Iki, there will be a decrease in hydrogen sulfide and hydrogen, and an increase in sulfur dioxide. Accompanying this will be an increase in the amount of nitrogen in the samples, since nitrogen reacts only slightly with the volcanic gases. This, too, was observed at Kilauea Iki. (See TABLE II.)

The effect of water is somewhat more varied, depending on the extent to which it reacts with the volcanic gases. Referring to TABLE IV, it is seen that the calculated equilibrium temperature for higher temperature samples is almost invariably lower than the observed one. For lower temperature collections, it is not possible to calculate any equilibrium temperature. The samples do not appear to be at equilibrium, in contrast to the Sulphur Banks gases.

It is possible to explain both of these effects by postulating that the overwhelming water content of volcanic gases is largely ground water, and that this ground water is not in equilibrium with the rest of the sample. Obviously, the extent to which equilibrium is attained will depend on the temperature of the gas when it is mixed with the water. This is borne out by the gases collected at the Sulphur Banks; they are in equilibrium even at the low temperature of collection, since mixing and reaction with ground water seems to have occurred at high temperatures and pressures. If the low temperature gases collected at Karonc and Kilauea Iki were in equilibrium, they would have had much the same composition as Sulphur Banks gases.

In TABLE X is presented evidence for the assertion that the

TABLE X. EVIDENCE FOR NON-ATTAINMENT OF EQUILIBRIUM OF
VOLCANIC GASES WITH GROUND WATER

A. KILAUEA IKI F - MOLE PERCENTAGES (EXCLUDING WATER)

	Observed	Calculated T = 750°C.	
		(1) 97.2% H ₂ O	(2) 50% H ₂ O
H ₂	4.5	27.8	2.8
CO ₂	70	69.5	70
CO	trace	0.45	1.3
CH ₄	0	10.9	10 ⁻⁷
H ₂ S	25	16.5	23.9
SO ₂	1.1	8.85	0.2
CS ₂	0	10 ⁻⁷	10 ⁻⁴
COS	0	10 ⁻⁴	0.3
S ₂	--	0.02	1.2

B. KAPOHO 4

H ₂	15	20.9	14.5
CO ₂	79	84	79.5
CO	3.1	0.1	3.4
CH ₄	0.81	10 ⁻⁷	0.82
H ₂ S	1.1	3.0	3.0
SO ₂	0.034	10 ⁻³	10 ⁻¹⁵
CS ₂	0.93	10 ⁻¹⁴	10 ⁻⁸

volcanic gas samples are not in equilibrium with all of the water present. For two samples, Kilauea Iki F and Kapoho 4, the experimentally determined composition is compared with (1) the calculated equilibrium composition at the temperature of collection, and (2) the calculated equilibrium composition at that temperature assuming the sample to be only about fifty percent water (about 1/30 the amount actually present). It is seen that although the observed composition is quite different from (1), there is excellent agreement with (2).

This effect cannot be explained by ascribing it to the non-ideality of the gases, since the fugacity coefficients of water vapor are essentially unity at atmospheric pressure and the temperatures considered.⁷⁷

It was not possible during the recent eruption to collect samples of gas in intimate contact with molten lava. Such samples would presumably not be contaminated by ground water, and would provide a direct check of the above hypothesis. Nevertheless, the excellent series of samples of Kilauea gas collected by Jaggar and Shepherd during 1918-1920 were obtained under these conditions. These samples were probably collected under the most favorable conditions possible.⁷⁸ Although the gases were collected in vacuum bulbs with no attempt made to "freeze", the composition at the time of collection, the relative amounts of carbon, hydrogen and sulfur-containing gases are nevertheless significant, since these are not changed by later atmospheric oxidation of the samples. Upon examining the content of these gases, it is seen that water makes up only an average of 73 percent of the gas (excluding nitrogen) instead of the 97-99 percent observed here and in samples collected in Japan by Oana.⁷⁹ Furthermore, those samples which Jaggar considered to be collected under the best possible conditions (TABLE II) contained even less

water, 20-70 percent, corresponding roughly to the percentage which must be postulated to enable calculation of an equilibrium temperature in this investigation.⁸⁰

There remains just one more trend in the sample analyses to be accounted for. This is the decrease with time in the sulfur content of the Kilauea Iki gases. Since the cinder cone is most probably a "rootless cone", the source of volcanic gas is not molten lava in the vent, but rather the hot (perhaps even molten) pumice in the center of the cone which is degassing. The cinder cone is thus an isolated system; no more gas can be evolved than is dissolved in the pumice. Two effects combine to decrease the sulfur to carbon ratio in this gas. The first is mixing with atmospheric gases, which will increase the amount of carbon dioxide in the volcanic gases, since carbon dioxide, like nitrogen, reacts only slightly. The second is loss of sulfur-containing gases through reaction with the iron oxides in the pumice. Ferric oxide has long been used as an industrial absorber for hydrogen sulfide. Preliminary calculations, based on the method of treating heterogeneous equilibria outlined by Boynton, have shown that volcanic gases cannot be in equilibrium with iron oxides in pumice. If they were, virtually all the sulfur gases would react to form iron sulfides at temperatures lower than about 600°C. (These calculations, however, cannot be considered definitive. Not all of the possible phases which could be present; i.e., the carbonate minerals, were considered. Further work on this is in progress at the present time.)

These two effects, mixing with carbon dioxide from the air, and approach toward low-temperature equilibrium with iron oxides, will tend to decrease the percentage of sulfur in the volcanic gas. Referring

again to the samples collected by Jaggar and Shepherd under optimum conditions, it is seen that the average sulfur to carbon ratio is greater than in even the best Kilauea Iki samples. The amount of sulfur originally present may thus be greater than the sulfur content of any of the samples collected in this investigation.

D. The "Primary" Magmatic Gas

One of the problems which most interested the early investigators of volcanic gas was its relationship to a "primary" magmatic gas; i.e., the gas originally present in the magma, unchanged by surface contaminants. In view of the powerful methods of studying volcanic gases outlined in this investigation, it should be possible to attack this problem and obtain more meaningful results than have been obtained in the past. The following is a discussion of our present knowledge of magmatic gases and of suggested means for adding to this knowledge.

First, the situation is not at all as difficult as Shepherd assumed in 1938.⁸¹ We can now evaluate the various secondary influences that change the composition of the magmatic gas, such as ground water and air. Furthermore, our increasing knowledge of heterogeneous reaction kinetics, gained chiefly through research in the metallurgical industry, should in time permit evaluation of the catalytic effects of the pumice and lava rock on the gaseous reactions.

We know that the gas is in a state of homogeneous equilibrium when it reaches the surface, but it seems that only at solfataric sources does it reach equilibrium with ground water. Excellent methods for collecting and analyzing the gas as it occurs in the volcanic vents have been developed. The theoretical means are now available for extrapolating the results of analyses of these surface collections to conditions

of higher temperature and pressure. Examples of some of these calculations were presented in this thesis.

The relationship of volcanic gases to magmatic volatile material may be clarified by using some of the concepts of Ramberg (1955).⁸² It is reasonable to suppose that a magma existing at some depth in the earth's crust will tend toward a state of both mechanical and chemical equilibrium. If, however, some large-scale change occurs in the crust so that the magma is forced into a completely new environment (in terms of temperature and pressure), magmatic equilibrium will no longer exist. The time required to re-establish equilibrium will depend upon the system, and upon how different the new situation is from the previous one.

If a magma is suddenly transported from a depth of several miles to the surface, with the resulting great changes in temperature and pressure, this magma will certainly not be in equilibrium when it reaches the surface. Certain changes in its composition, however, will take place more quickly than others. Among the more rapid will be the release of dissolved gas and the establishment of homogeneous equilibrium in this gas. Among the less rapid will be diffusion-controlled processes, such as equilibrium crystallization and the establishment of heterogeneous equilibrium between the gaseous and condensed phases. This effect of rapid equilibrium attainment in the gas will permit the use of homogeneous equilibria, such as described in this thesis, to follow the composition of the gas back to the point where it is released from solution. As more data becomes available through geophysical and geochemical studies, it should be possible to make an "educated" estimate of the temperature and pressure at the point of gas release. The use of equilibrium data will then permit the surface gas composition to be extrapolated to

this point. The resulting knowledge of the sulfur vapor and oxygen partial pressures should in turn permit an evaluation of the form and type of mineral separation prevalent at the point of gas release, thus providing information on the degree of magmatic differentiation. In effect, the volcanic and fumarolic gas composition values, together with the homogeneous equilibrium which seems to prevail, provide a means by which the nature of the magma might be probed to some depth.

To learn more about the magma, a greater knowledge of the behavior of gases dissolved in silicates is needed. (This is a subject about which remarkably little is known.) It is hoped that the complementary study of silicate-gas equilibria described in Part I of this thesis would add some information on this matter. This did not turn out to be the case. However, reasonable limits on the amount and composition of the volatile constituents of the magma can be set by means of volcanic gas studies.

V. CONCLUSIONS

The following conclusions may be reached as a result of the research on volcanic gases described in Part II of this thesis:

A. Regarding the experimental techniques used for collection and analysis of volcanic gas samples:

1. An excellent means for the collection of volcanic gas samples is the use of silica gel tubes, since reaction with atmospheric gases is minimized, and the composition of the sample is "frozen" until the time of analysis.

2. The average composition of a series of volcanic gas samples is meaningless, because of wide variations in the conditions of sampling.

3. Conclusions regarding volcanic gases should be drawn from the results of samples collected and analyzed under the most favorable conditions.

4. Gas chromatography, because of its adaptability and sensitivity, is an excellent technique for the analysis of volcanic gas samples.

5. The largest errors in the gas chromatographic analysis of a volcanic gas sample result from the occasional necessity of measuring small peak areas and small pressures.

B. Regarding the use of high-speed digital computers to make complex homogeneous equilibrium calculations on volcanic gases:

1. A quick and easy check is available to ascertain whether a volcanic gas sample represents an equilibrium composition at the conditions under which it was collected.

2. It is possible to study the equilibrium variation of a typical volcanic gas phase with temperature, pressure, oxidation state of the gas and extent of ground water contamination.

These studies may in turn permit a tentative extrapolation of the analyses of volcanic gas samples back to the conditions of the primary magmatic environment.

3. Logarithmic composition diagrams showing the oxidation of a volcanic gas phase may be constructed from tabulated free energy values without making complex equilibrium calculations.

4. Provided the necessary thermodynamic data become available, the possibility of mineral transport in the gas phase may be explored using this type of calculation.

5. It is possible to estimate the degree of non-equilibrium contamination of volcanic gas samples by the environment. This is illustrated here for the case of the introduction of ground water.

C. Regarding the gas samples collected during the 1959-60 eruption of Kilauea:

1. Prior to and during the eruption, increased amounts of sulfur-containing gases, chiefly in the form of hydrogen sulfide, occurred in the samples collected at the Sulphur Banks, a solfataric fumarole at the edge of Kilauea caldera. This may be attributed to degassing of the magma as it approaches the surface. The large volume of gas then evolved minimizes the oxidizing and sulfur-removing effects of ground water, oxygen and wall rocks on the gas collected at the surface.

2. Frequent sampling of the Sulphur Banks gases may permit the prediction of eruption of Kilauea, and possibly also of Mauna Loa, by noting such effects.

3. Although gases collected at Sulphur Banks are in equilibrium at the temperature and pressure of sampling, volcanic gas samples collected at Kilauea Iki and Kapoho are not. If some of the water present

is subtracted from the volcanic gas samples, it is possible to show that the samples then represent equilibrium compositions. This is taken as evidence that the samples are contaminated with ground water, with which they are not in equilibrium if mixing occurs at or near the surface.

4. The "primary" magmatic gas is probably more reduced, and contains more sulfur and less water than any of the samples collected during the past eruption.

5. From the composition of these gases and an extrapolation of their composition through thermodynamic equilibrium data, it should be possible to evaluate magmatic conditions at least to the point of the release of gas as a separate phase. Potentially, then, there is at hand a method for examining the magma at some depth.

SUMMARY

Part I. An Investigation of the Applicability of the Vacuum Fusion
Technique to the Determination of the Oxidation State of the
Constituent Elements of Rocks

It is known that the partial pressure of oxygen in a gas mixture equilibrated with a molten iron silicate, such as occurs in a magma, controls the oxidation state of iron in the melt. In an attempt to relate the composition of gases dissolved in the melt to the oxidation state of iron, the technique of vacuum fusion was applied. A series of vacuum fusion determinations were made on a sample of fayalite, Fe_2SiO_4 , which had been equilibrated with a mixture of carbon dioxide, carbon monoxide and argon, fixing the partial pressure of oxygen at a very small value. The composition of the extracted gases turned out to be extremely variable, containing large amounts of oxygen. The presence of oxygen was attributed to the dissolving of metallic iron in the platinum crucibles used, shifting the equilibrium $\text{Fe}^{++} + \text{O}^{--} \rightleftharpoons \text{Fe} + \frac{1}{2}\text{O}_2$ in the direction of more oxygen. The varying extent of reaction of oxygen with the other gases then accounts for the poor precision. It was concluded that in order to make vacuum fusion a workable method for determining the oxidation state of the constituents of a rock, it is necessary to eliminate side reactions with crucible materials. Lacking this, the problem was set aside. The more fruitful approach to the study of volcanic volatile oxidation equilibria through analysis of volcanic gases was undertaken.

Part II. A Chemical Study of the Gases of Kilauea Volcano

A study was made of volcanic gases collected during the 1959-60 eruption of Kilauea volcano on the island of Hawaii. A new technique, based on adsorption of gases by silica gel, was used in the collection of samples. The samples were analyzed by gas chromatography and were found to be principally water and carbon dioxide, with lesser amounts of sulfur dioxide, hydrogen sulfide, hydrogen, nitrogen, carbon monoxide and methane. Complex equilibrium calculations were carried out on the IBM 650, using a general method of minimizing the free energy. A study was made of the equilibrium variation of a typical volcanic gas phase with temperature, pressure, oxidation state and water content. A graphical method, similar to logarithmic pH diagrams, was developed to systematize the variation of volcanic gas with its oxidation state. Comparison of the analyses of samples collected at Kilauea Iki and Kapoho with the calculated equilibrium composition at the temperature of collection indicated that although the volcanic gases may be in equilibrium with themselves, they do not reach equilibrium with surface contaminants such as ground water. A similar comparison on samples collected at the solfataric fumarole Sulphur Banks showed the latter to be in equilibrium with their ground water content, presumably because mixing occurred deep inside the earth. The presence of increased amounts of sulfur in the form of hydrogen sulfide was noted in the Sulphur Banks gases prior to and during the eruption. This was attributed to increased degassing of the magma, which would minimize contamination of the gases. A consideration of the various substances contaminating volcanic gases led to the conclusion that the "primary" magmatic gas is more reduced, and contains less water and more sulfur-containing gases than any of the samples collected

APPENDIX I. SOLUTION OF SIMULTANEOUS EQUATIONS

The method of successive eliminations used in solving the set of simultaneous equations may be summarized as follows. Consider the set of m linear simultaneous equations

$$\begin{aligned} A_{11}X_1 + A_{12}X_2 + \dots + A_{1m}X_m &= A_{1,m+1} \\ A_{21}X_1 + A_{22}X_2 + \dots + A_{2m}X_m &= A_{2,m+1} \\ \vdots & \\ A_{m1}X_1 + A_{m2}X_2 + \dots + A_{mm}X_m &= A_{m,m+1} \end{aligned} \quad (1)$$

The coefficients of the unknowns form a matrix (A) of order as:

$$A = \begin{pmatrix} A_{11} & A_{12} & \dots & A_{1m} & A_{1,m+1} \\ A_{21} & A_{22} & \dots & A_{2m} & A_{2,m+1} \\ \vdots & & & & \\ \vdots & & & & \\ A_{m1} & \dots & \dots & A_{mm} & A_{m,m+1} \end{pmatrix} \quad (2)$$

In order to solve the set of equations, it is necessary only to construct two more matrices, according to certain rules of operation.

The second (B) matrix is derived column by column from the first according to the following rules: the first column of (B) is identical to the first column of (A):

$$B_{ji} = A_{ji} \quad (j = 1, 2, 3 \dots m) \quad (3)$$

The first element in each of the other columns is the corresponding element of (A) divided by B_{11} :

$$B_{1k} = A_{1k}/B_{11} \quad (k = 2, 3, 4 \dots m+1) \quad (4)$$

Elements on and below the diagonal are given by the relation

$$B_{jk} = A_{jk} - \sum_{h=1}^{k-1} B_{jh}B_{hk} \quad (j \geq k, k = 2, 3 \dots m) \quad (5)$$

and elements above the diagonal by the relation

$$B_{jk} = (A_{jk} - \sum_{h=1}^{k-1} B_{jh}B_{hk})/B_{jj} \quad (j < k, k = 3, 4, \dots, m+1) \quad (6)$$

The third (C) matrix is linear and the answer is derived in reverse order, the last element first. The last element of (C) is identical with the last element of (B):

$$C_m = B_{m, m+1} \quad (7)$$

The other elements are given by the relation

$$C_k = B_{k, m+1} - \sum_{p=k+1}^{m+1} B_{kp}C_p \quad (k = m-1, m-2, \dots, 2, 1) \quad (8)$$

For a full description of the method and a derivation of the steps, the reader is referred to Milne, Numerical Calculus.⁸³

APPENDIX II. FORTRAN PROGRAMS

Since the method of computation used is of general application and not restricted to volcanic gases (or even to gases in general), it was decided that the specific FORTRAN programs used should be included in the thesis for the reference of any one interested in complex equilibrium calculations. The programs, which are presented in TABLES XI and XII, follow the outline given in the text, except that in order to conserve on time and computer "memory" there has been considerable juggling of the indices of the "DO loops" and of the specific order of the steps. Some difficulty was encountered in obtaining a completely self-consistent set of indices, and most of the time spent perfecting the programs was devoted to this problem.

For the meaning of the FORTRAN instructions in the program, the reader is referred to the IBM reference manual for the FOR TRANSIT Auto-

TABLE XI. A FORTRAN PROGRAM FOR THE COMPUTATION OF
EQUILIBRIUM COMPOSITION

```

1. DIMENSION A(14,7), FORT(14), Y(14), R(7,8), FY(14),
   PI(7), PLJ(14), BA(7,8), B(7), DEL(14), E(14), C(14)
2. READ, A, IMAX, SMAX, JMAX, KMAX
4  READ, E
3  READ, T, P, S, NMAX, QD, QT
87 READ, FORT, Y, B
5  N = 0
6  YBAR = 0.
8  DO 15 I = 1, IMAX
81 C(I) = (FORT(I) + E(I)/T)/1.98646 + NLOGF(P)
15 YBAR = YBAR + Y(I)
9  DO 35 K = 1, KMAX
10 DO 35 J = 1, JMAX
11 IF (K-J) 94, 94, 21
94 IF (J-JMAX) 7, 19, 19
7  R(J,K) = 0.
12 DO 17 I = 1, IMAX
14 IF (J-1) 16, 16, 17
16 FY(I) = Y(I)* (C(I) + NLOGF(Y(I)/YBAR))
17 R(J,K) = R(J,K) + A(I,J)*A(I,K)*Y(I)
18 GO TO 20
19 R(J,K) = B(K)
20 R(K,J) = R(J,K)
24 BUCK = 0.
25 GO TO (28, 71), K

```

TABLE XI. A FORTRAN PROGRAM FOR THE COMPUTATION OF
EQUILIBRIUM COMPOSITION (Continued)

```

71  KACK = K - 1
26  DO 27 L = 1, KACK
27  BUCK = BUCK + BA(J,L)*BA(L,K)
28  BA(J,K) = R(J,K) - BUCK
29  GO TO 35
21  IF (K - KMAX) 30, 95, 95
95  R(J,K) = 0.
23  DO 22 I = 1, IMAX
22  R(J,K) = R(J,K) + A(I,J)*FY(I)
30  BILL = 0.
31  GO TO (34, 72), J
72  JACK = J - 1
32  DO 33 M = 1, JACK
33  BILL = BILL + BA(J,M)*BA(M,K)
34  BA(J,K) = (R(J,K) - BILL)/BA(J,J)
35  CONTINUE
    PUNCH, FY, R, BA
36  PI(JMAX) = BA(JMAX, KMAX)
93  JMAY = JMAX - 1
37  DO 41 IN = 2, JMAX
38  BUS = 0.
98  ILL = KMAX - IN
39  DO 40 IT = ILL, JMAY
88  IG = IT + 1
40  BUS = BUS + BA(ILL, IG)*PI(IG)

```

TABLE XI. A FORTRAN PROGRAM FOR THE COMPUTATION OF
EQUILIBRIUM COMPOSITION (Continued)

```

41  PI(ILL) = BA(ILL, KMAX) - BUS
    PUNCH, PI
42  Q = QT
43  DO 52 I = 1, IMAX
44  PIJ(I) = 0.
45  DO 46 J = 1, JMAX
46  PIJ(I) = PIJ(I) + PI(J)*A(I,J)
47  DEL(I) = - FY(I) + Y(I)*(PIJ(I) + PI(JMAX))
48  IF (Y(I) + Q*DEL(I)) 51, 51, 52
51  Q = Q - QD
52  IF (Q) 101, 101, 50
53  CONTINUE
    PUNCH, PIJ, DEL, Q
48  DEBAR = PI(JMAX)*YBAR
53  DERFQ = 0.
54  DO 55 I = 1, IMAX
55  DERFQ = DERFQ + DEL(I)*(C(I) + NLOGF((Y(I) + Q*DEL(I))
    / (YBAR + Q*DEBAR)))
56  IF (DERFQ) 59, 57, 57
57  Q = Q - QD
58  IF (Q) 101, 101, 53
101 STOP
102 GO TO 3
59  DO 60 I = 1, IMAX
60  Y(I) = Y(I) + Q*DEL(I)

```


TABLE XI. A FORTRAN PROGRAM FOR THE COMPUTATION OF
EQUILIBRIUM COMPOSITION (Continued)

```
13  YBAR = YBAR + Q*DEBAR
61  N = N + 1
62  PUNCH, T, P, N, Q
63  PUNCH, Y, YBAR
64  PUNCH, PI, FY, R(JMAX, KMAX)
67  IF (N - NMAX) 9, 65, 65
65  IF (S - SMAX) 3, 66, 66
66  END
```

TABLE XII. FORTRAN PROGRAM FOR DETERMINING AMOUNTS OF
TRACE COMPONENTS

```
11 DIMENSION A(21, 7), E(21), FORT(21), PI(7), C(21),  
    PIJ(21), X(21), Y(21)  
12 READ, A, E, IMAX, JMAX, SMAX  
13 READ, FORT, T, P, S  
14 READ, PI  
15 READ, YBAR  
16 DO 22 I = 1, IMAX  
17 C(I) = (FORT(I) + E(I)/T)/1.92646 + NLOGF(P)  
18 PIJ(I) = 0.  
19 DO 20 J = 1, JMAX  
20 PIJ(I) = PIJ(I) + A(I,J)*PI(J)  
21 X(I) = (PIJ(I) - C(I))/2.3025851  
22 Y(I) = YBAR*EXPF(X(I))  
23 PUNCH, T, P, S  
    PUNCH, C  
24 PUNCH, X, Y, YBAR  
25 IF (S - SMAX) 13, 26, 26  
26 END
```

matic Coding System.⁸⁴ The symbols used for the various quantities used in the text are summarized in TABLE XIII.

TABLE XIII. THE MEANINGS OF SYMBOLS USED IN THE FORTRAN PROGRAMS

- $FORT(I) = \left(\frac{F^{\circ} - E^{\circ}}{T} \right)_i$, the relative free energy function of molecule i .
- $E(I) = (E^{\circ})_i$, the ground state energy at $^{\circ}K$. of molecule i .
- $T = T$, the temperature in $^{\circ}K$.
- $P = P$, the total pressure in atmospheres.
- $Y(I) = y_i$, the number of moles of molecule i .
- $YBAR = \bar{y}$, the sum of the mole numbers y_i
- $C(I) = C_i$, defined by eq. (6), p. 43.
- $FY(I) = f_i(y)$, defined by eq. (2), p. 42; the contribution to the free energy by molecule i .
- $A(I,J) = a_{ij}$, the formula number indicating the number of atoms of element j in molecule i .
- $B(J)$ or $B(K)$, = b_j or b_k , the total number of atomic weights of element j or k .
- $IMAX = n$, the maximum number of molecules present.
- $JMAX = m$, the maximum number of atomic species.
- $KMAX = m + 1$.
- $R(J,K) = r_{jk}$, the coefficients in the set of linear simultaneous equations (32), p. 47; together with $B(K)$ and $B(J)$ the elements in the first matrix in the solution of the equations.
- $BA(J,K) = B_{jk}$, the elements of the second matrix formed in the solution of a set of linear simultaneous equations.
- $PI(J) = \pi_j$, the unknowns in eq. (32); also the elements in the third (answer) matrix. This is furthermore the free energy contribution of element j to the mixture.

TABLE XIII. THE MEANINGS OF SYMBOLS USED IN THE FORTRAN
PROGRAMS (Continued)

DEL(I) = Δ_i , the change in mole number of i as a result of one iteration.

DEBAR = $\bar{\Delta}$, the sum of Δ_i , the total change in the number of moles during one iteration.

Q = λ , the parameter limiting the magnitude of the change in mole numbers.

QT = the maximum value of λ used in a particular calculation.

QD = the decrease in λ during each iteration necessary to satisfy the conditions a and b, p. 48.

DERFQ = $\frac{\partial F}{\partial \lambda}$, the directional derivative of F with respect to λ .

NMAX = the total number of iterations to be carried out to find the equilibrium composition.

N = the number of a certain iteration.

SMAX = the total number of calculations to be carried out at a given time.

S = the number of a certain calculation.

All other symbols are defined by their use in the program.

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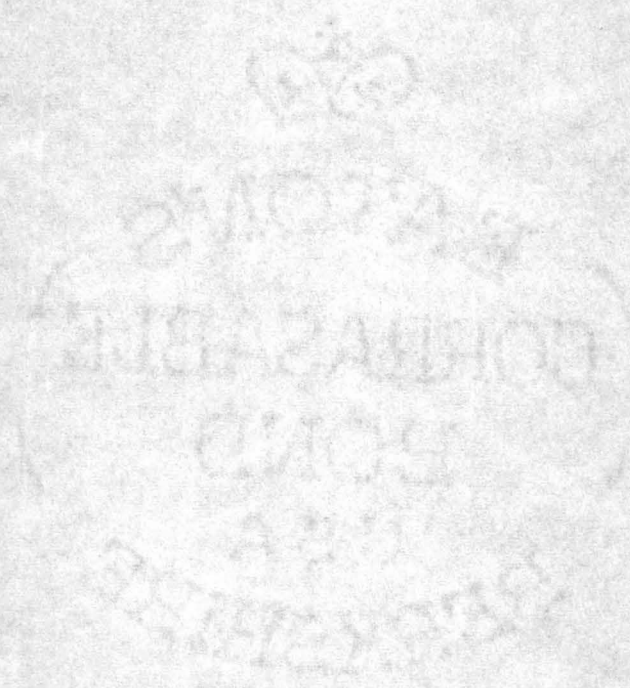
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