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CHEMICAL EQUILIBRIUM IN MAGMATIC GASES

A. J. ELLIS*

ABSTRACT. From standard thermodynamic data the theoretical compositions of some water, sulphur, carbon dioxide, gas systems are calculated for a wide range of temperatures and pressures. The systems examined are H_2O—S_2, H_2O—S_2—H_2, H_2O—S_2—O_2, and H_2O—CO_2—S_2—H_2, with the elements present roughly in the proportions found in magmatic gases. For the last named system, the variations in the theoretical molecular gas compositions with temperature are found to correspond to those in natural gases, ranging from high temperature gases with SO_2, CO and H_2, to low temperature hot spring gases which are mainly CO_2 and H_2S.

It is emphasized that a high pressure and temperature water solution of CO_2 and H_2S existing at depth in equilibrium with carbonates and sulphides in the parent lava, could, on release of pressure, give rise to the common constituents found in magmatic gases at the surface.

The fact that the presence of other constituents such as HCl, NH_3, CH_4 and COS in natural magmatic steam can also be predicted for any temperature from theory, is used as further evidence that magmatic gases closely approach a state of chemical equilibrium. The ideas of Gautier, proposed some fifty years ago, are thus confirmed by modern chemical thermodynamics.

INTRODUCTION

There have been many discussions of the chemistry of magmatic gases, often with a view to exploiting the heat from gas reactions as energy sources in volcanism.

Numerous analyses of volcanic gases exist, but there are few that satisfy the two conditions of air-free collection of the complete gas discharge, and detailed analysis by satisfactory methods. These conditions are by no means easy to achieve, and the results of most of the early collections were almost useless because of the poor techniques used.

Clarke (1916) reviewed the work of Gautier, who between 1900 and 1910 studied the products and mechanism of degassing rocks at high temperatures. The products he obtained were ascribed to reactions occurring within the rocks at the temperature. He supposed hydrogen to form from the reaction of water with ferrous silicates, and carbon monoxide from the reduction of carbon dioxide by hydrogen. He showed that sulphides were hydrolyzed by high temperature steam to hydrogen sulphide and the oxide. Further, at still higher temperatures the hydrogen sulphide formed reacted with more water to give sulphur dioxide and hydrogen. He demonstrated how a large number of reactions were possible starting with only water, carbon dioxide, and the solid constituents of lavas. Chamberlin (1908) also made a comprehensive survey of the products from degassing rocks of all types. His results were very similar to those obtained by Gautier.

Jaggar, Day and Shepherd, have all made important contributions to the literature on magmatic gases. Their excellent collections and analyses of Hawaiian volcano gases have not been bettered, and remain as a standard of comparison for any ideas on the chemistry of these gases. Shepherd (1938) also contributed many results on the degassing of igneous rocks in vacuo. On degassing Hawaiian basalts he obtained products almost identical with those collected at the same temperature over the molten lavas at Kiluaea and Mauna Loa. In this paper Shepherd warned against the strict application of thermo-

* Member of staff N. Z. Department of Scientific and Industrial Research.

dynamics in interpreting further the results from analyses of such gases. He considered that the combination of catalysts, catalyst poisons and adsorption effects in the rock walls would influence the attainment of equilibrium in a lava and gas system.

Even if this must be kept in mind, the early success of Gautier in producing gas compositions similar to volcanic gases from simple water, carbonate, sulphide systems, should be remembered. More recently Wilson (1939) made calculations on the thermodynamic possibility of certain compounds such as sulphur dioxide, methane, carbonyl sulphide, and carbon bisulphide being present in fumaroles and hot springs of various temperatures. He showed that the lack of sulphur dioxide and carbonyl sulphide in hot spring gases was in agreement with theoretical expectations.

Jaggar (1940) has put forward the idea of a simple gas mixture, which when dissolved in the rock, would at high temperatures give rise to the typical volcanic gas products on release of pressure. With this ideal in view it was considered of interest to calculate the theoretical combination of elements in some systems with the approximate bulk composition of natural volcanic, fumarole, and hot spring gases. The theoretical assemblies of molecules could then be compared with those found in sampling the natural gases. This would give an indication of how close the natural gases come toward attainment of equilibrium.

As the gases are observed at atmospheric pressure, any calculations should first be made for this pressure. However it would be of interest to recalculate the equilibrium conditions for gas mixtures at higher pressures, of the order of thousands of atmospheres, to get an idea of the molecular form of the gases in the original deep magma if chemical equilibrium should be preserved. If a gas system could be found that had both a logical high pressure molecular form and gave equilibrium products at various temperatures that approximated those found in nature, then this would be the ideal mixture of gases sought by Jaggar.

In magmatic gases the element sulphur shows the greatest variety of compounds. Under various conditions, sulphur vapour, sulphur dioxide, sulphur trioxide, hydrogen sulphide, and carbonyl sulphide have been found by analysis. Any theoretical examination of magmatic gases would need to be centered about the chemistry of sulphur and water mixtures at high temperatures.

Using modern thermodynamic data various gas systems are now considered. In all the calculations given, the gases are treated as ideal. Pressures are used uncorrected by fugacity coefficients. Fortunately when high pressures are involved, the temperatures of interest are usually also high, so fugacity coefficients will remain of the order of unity. As this paper deals only with broad generalizations, the numerical values given are not really important, except as a basis for comparison and discussion.

A. SYSTEM H_2O—S_2 MOLECULAR RATIO 100:1

The equilibrium constitution of an original mixture of water and sulphur molecules in the ratio of 100:1 is examined at various temperatures and pres-

sures. The ratio is of the order commonly found in natural gases. As possible final constituents S_2, H_2O, H_2S, SO_2 and H_2 are considered. Sulphur trioxide is not likely to be present. At the partial pressures of sulphur vapour involved in the following systems the only sulphur molecule of importance is diatomic sulphur S_2. (Stull, 1949).

For the calculation, the three components of the system may be chosen as S_2, SO_2 and H_2O. Equilibrium relations can then be applied to relate the other two constituents to these components.

$$K_1 = \frac{\mathbf{p}_{H_2}^4 \cdot \mathbf{p}_{SO_2}^2}{\mathbf{p}_{H_2O}^4 \cdot \mathbf{p}_{S_2}} = \frac{\mathbf{x}_{H_2}^4 \cdot \mathbf{x}_{SO_2}^2 \cdot \mathbf{P}}{\mathbf{x}_{H_2O}^4 \cdot \mathbf{x}_{S_2}} \quad (1)$$

$$K_2 = \frac{\mathbf{p}_{H_2S}^4 \cdot \mathbf{p}_{SO_2}^2}{\mathbf{p}_{H_2O}^4 \cdot \mathbf{p}_{S_2}^3} = \frac{\mathbf{x}_{H_2S}^4 \cdot \mathbf{x}_{SO_2}^2}{\mathbf{x}_{H_2O}^4 \cdot \mathbf{x}_{S_2}^3 \cdot \mathbf{P}} \quad (2)$$

These express the equilibria

$$S_2 + 4H_2O = 4H_2 + 2SO_2$$

$$3S_2 + 4H_2O = 4H_2S + 2SO_2.$$

x is the mole fraction. and **p** the partial pressure of the constituent in the final mixture.

P is the total pressure on the system. Thus $\mathbf{p}_A = \mathbf{P}.\ \mathbf{x}_A$.

Three other relationships are needed to give five simultaneous equations that can be solved for the five constituents at any temperature and pressure. Conservation of mass equations can be used, and also the fact that the sum of mole fractions is unity. Ratio of oxygen to sulphur atoms = 50 =

$$\frac{\mathbf{x}_{H_2O} + 2\mathbf{x}_{SO_2}}{\mathbf{x}_{H_2S} + \mathbf{x}_{SO_2} + 2\mathbf{x}_{S_2}} \quad (3)$$

Ratio of hydrogen to oxygen atoms = 2 =

$$\frac{2(\mathbf{x}_{H_2O} + \mathbf{x}_{H_2S} + \mathbf{x}_{H_2})}{\mathbf{x}_{H_2O} + 2\mathbf{x}_{SO_2}} \quad (4)$$

$$\mathbf{x}_{H_2O} + \mathbf{x}_{H_2} + \mathbf{x}_{SO_2} + \mathbf{x}_{H_2S} + \mathbf{x}_{S_2} = 1 \quad (5)$$

Values of K_1 and K_2 were computed from standard thermodynamic properties of the gases. Values of standard free energies and heats of formation were taken from Latimer (1952) with the exception of the free energy of formation of diatomic sulphur gas which was taken from Kelley (1937). Heat capacity data for the gases was taken from Kelley (1949) in all cases. The calculated values of K_1 and K_2 are given in table 1.

TABLE 1

T°K	K_1	K_2
600	4.10×10^{-19}	3850
800	2.14×10^{-13}	61.4
1000	6.95×10^{-10}	5.28
1200	1.72×10^{-7}	1.09
1400	9.54×10^{-6}	0.374

Some solutions of the five equations above are given in table 2. Results are given in mole fractions $\times 10^3$.

TABLE 2

Mole Fractions × 10^3

T°K	P(atmos.)	x_{H_2O}	x_{H_2S}	x_{SO_2}	x_{H_2}	x_{S_2}
600	1	980.2	13.2	6.6	0.016	0.007
800	1	979.6	13.0	6.8	0.60	0.029
1000	1	975.3	11.5	8.2	4.9	0.063
1200	1	963.5	7.5	12.1	16.8	0.079
1400	1	949.0	2.6	17.0	31.4	0.035
1200	10	970.8	10.1	9.7	9.3	0.047
1200	100	976.2	11.1	7.9	4.8	0.021
1200	1000	979.0	11.6	7.0	2.4	0.010

It is not necessary to give more than three examples at pressures other than atmospheric. The trend with increasing pressures is similar at all temperatures i.e. that of higher hydrogen sulphide and water, and lower sulphur dioxide, hydrogen and sulphur.

B. SYSTEM H_2O—H_2—S_2 MOLECULAR RATIO 100:2:1

The effect of adding hydrogen in equivalent amount to the sulphur in System A. will now be examined. Again there are five constituents as variables, and the equilibrium equations (1) and (2) can be applied. The mass balance equation (4) must be modified. but equations (3) and (5) are used again.

$$\text{Ratio of hydrogen to oxygen atoms} = \frac{204}{100} = \frac{2(x_{H_2O} + x_{H_2S} + x_{H_2})}{x_{H_2O} + 2x_{SO_2}} \qquad (4a)$$

Some solutions to the above equations for the new conditions are given in table 3.

TABLE 3

Mole Fractions × 10^3

T°K	P(atmos.)	x_{H_2O}	x_{H_2S}	x_{SO_2}	x_{H_2}	x_{S_2}
600	1	980.3	19.6	0.04	0.099	0.000
800	1	978.8	19.1	0.52	1.6	0.009
1000	1	972.4	16.8	2.7	8.1	0.049
1200	1	957.9	11.7	7.5	22.8	0.105
1400	1	938.8	5.3	13.9	41.9	0.080
1200	10	966.8	15.0	4.5	13.7	0.048
1200	100	973.5	17.2	2.3	6.9	0.008
1200	1000	975.8	18.1	1.5	4.6	0.006

The effect of the extra hydrogen is to prevent the formation of sulphur dioxide at lower temperatures. The system at one atmosphere approaches a binary mixture of water and hydrogen sulphide at low temperatures, and a ternary mixture of water, sulphur dioxide, and hydrogen at high temperatures. The effect of high pressures is to favor the system with the fewest molecules, and hydrogen sulphide increases in concentration as in the first system.

C. SYSTEM H_2O—S_2—O_2 MOLECULAR RATIO 100:1:2

The constituents H_2O, SO_2, SO_3, H_2S, O_2, H_2, are considered as possible products from this system. The key reactions are

$$S_2 + 2O_2 = 2SO_2$$
$$2SO_2 + O_2 = 2SO_3$$
$$SO_2 + H_2O = SO_3 + H_2$$
$$2SO_2 + 2H_2O = 2H_2S + 3O_2$$

This system may be summarized without giving the evidence of detailed calculations. Sulphur dioxide will be formed completely before any SO_3 is formed. Sulphur dioxide will not react with water to give hydrogen sulphide and oxygen at any temperature in the range of interest, nor will water be decomposed by sulphur dioxide to give the trioxide and hydrogen. Over the whole temperature range of geological interest the same mixture of sulphur dioxide and water should be stable. Addition of more oxygen to the system would form sulphur trioxide but no other products.

D. SYSTEM H_2O—CO_2—H_2—S_2 MOLECULAR RATIO 100:10:2:1

By the addition of carbon dioxide to System B, the bulk composition of the gas approaches that often found in magmatic gases. Carbon dioxide is often present in natural steam at about 10 times the concentration of the sulphur compounds. With the addition of carbon compounds it is necessary to choose an extra component to define the system. The components may now be chosen as H_2O, CO_2, S_2, and SO_2. The constituents considered in the following calculations are H_2O, H_2S, SO_2, H_2, S_2, CO_2, CO, and COS. Four equilibrium constant equations are required to relate the constituents H_2, H_2S, CO, and COS and the chosen components. As before, equations (1) and (2) can be used, a third is equation (6) for the water gas reaction, and the fourth that for COS formation from H_2S, and CO_2 (equation (7)).

$$K_3 = \frac{x_{CO} \cdot x_{H_2O}}{x_{CO_2} \cdot x_{H_2}} \qquad (6)$$

$$K_4 = \frac{x_{COS} \cdot x_{H_2O}}{x_{CO_2} \cdot x_{H_2S}} \qquad (7)$$

Values K_3 and K_4 for various temperatures are given in Table 4.

TABLE 4

T°K	K_3	K_4
600	0.0366	7.96×10^{-3}
800	0.249	4.70×10^{-2}
1000	0.733	0.137
1200	1.45	0.278
1400	2.31	0.460

Four other equations are now required to be able to solve for the eight variables.

The O_2/H_2 atomic ratio gives $\frac{120}{204} = \frac{x_{CO} + 2x_{CO_2} + x_{H_2S} + 2x_{SO_2} + x_{COS}}{2(x_{H_2O} + x_{H_2} + x_{H_2S})}$ (8)

The S_2/H_2 atomic ratio gives $\frac{2}{204} = \frac{2x_{S_2} + x_{H_2S} + x_{SO_2} + x_{COS}}{2(x_{H_2O} + x_{H_2} + x_{H_2S})}$ (9)

The C/H_2 atomic ratio gives $\frac{10}{204} = \frac{x_{CO_2} + x_{CO} + x_{COS}}{2(x_{H_2O} + x_{H_2} + x_{H_2S})}$ (10)

Also $x_{H_2O} + x_{H_2S} + x_{SO_2} + x_{H_2} + x_{S_2} + x_{CO_2} + x_{CO} + x_{COS} = 1$ (11)

The eight equations have been solved for temperatures from 600 to 1400°K at one atmosphere pressure. In outline, the method used was successive approximation. A value for the mole fraction of water can usually be guessed with reasonable accuracy and used as a starting point. Only seven equations are then left to solve. Preliminary calculations based on System B indicate that the concentrations of S_2 and COS are relatively low compared with the other constituents. If S_2 and COS are neglected in equation (9), where the hydrogen term is small and can be given an approximate value, various ratios of x_{SO_2} to x_{H_2S} may be taken to satisfy the equation. For each of these ratios, values of x_{CO} and x_{CO_2} are easily found by trial and error to agree with equations (6) and (10). (The values of x_{H_2} corresponding to the ratios taken are calculated by means of equations (1) and (2)). The various trial results are then tested in equation (8). If an agreement is not obtained between the two sides of this equation, the numerical difference is recorded. The process is continued with various ratios of x_{H_2S} to x_{SO_2}, and a graph constructed showing the change in the numerical difference from equation (8) with changing ratio. The ratio for exact agreement can be picked from the graph. By gradually improving on the initial assumptions, results are finally obtained for all eight constituents that agree with the conditions given.

The results for the system are shown in figures 1 and 2. Figure 2 is constructed so that the difference between any two adjacent lines at constant temperature corresponds to the mole fraction of the named constituent. Results are not given for higher pressures, but the trend will be the same as in System

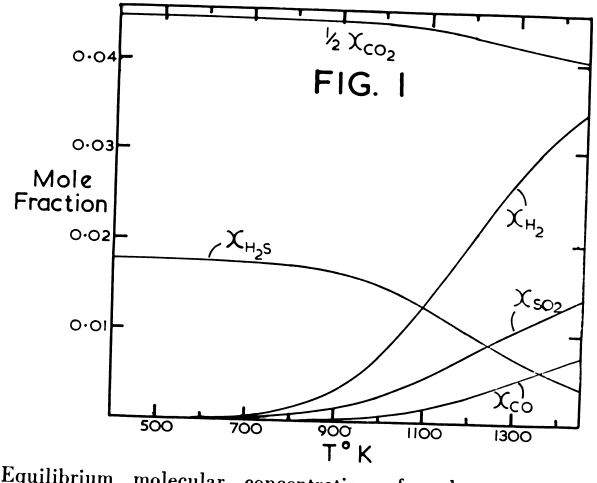

Fig. 1. Equilibrium molecular concentrations for the system H_2O—CO_2—H_2—S_2 in molecular ratio 100:10:2:1. Pressure = 1 atmosphere.

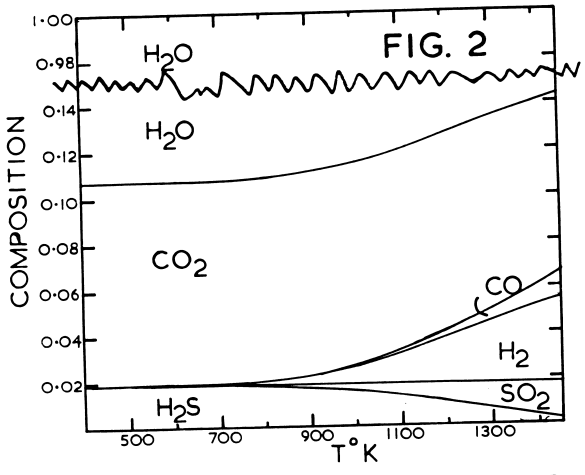

Fig. 2. Total molecular composition of the system H_2O—CO_2—H_2—S_2 in molecular ratio 100:10:2:1. Pressure = 1 atmosphere.

B. Increasing the pressure will decrease SO_2, H_2, CO and S_2, while H_2O, H_2S, CO_2, and COS will increase. Values of x_{S_2} and x_{COS} are not appreciable on the scale of the graphs, and table 5 gives their approximate values for various temperatures at one atmosphere pressure.

TABLE 5

Mole Fractions

T°K	$x_{S_2} \times 10^5$	$x_{COS} \times 10^4$
600	0.05	0.14
800	0.91	0.81
1000	4.8	2.1
1200	9.6	2.7
1400	5.3	1.5

E. EQUILIBRIA FOR ADDITIONAL CONSTITUENTS

Of the constituents of magmatic gases not considered the nitrogen and chlorine gases are the most important.

Ammonia will be involved in the equilibrium.

$$3H_2 + N_2 = 2NH_3$$

This is an exothermic reaction and ammonia will be favored at lower temperatures. The approximate mole fraction of ammonia at equilibrium for various pressures and temperatures is given in table 6. The values x_{NH_3} are for a gas containing nitrogen of constant mole fraction 0.05 and hydrogen of constant mole fraction 0.01.

TABLE 6

T°K.	P.(atmos.)	x_{NH_3}
400	1	1.3×10^{-3}
600	1	9.3×10^{-6}
800	1	6.6×10^{-7}
1200	1	4.1×10^{-5}
600	1000	9.3×10^{-3}
800	1000	6.6×10^{-4}
1200	1000	4.1×10^{-5}

At one atmosphere pressure ammonia should exist in the gases only below temperatures of about 400°C. Increased pressure can cause ammonia to become a stable constituent at higher temperatures. and it would possibly be present in the original magma at depth. That is. assuming that nitrogen is a primary magmatic gas; a fact that seems likely but has never been satisfactorily proved. The values of the equilibrium constants for the above reaction were taken from International Critical Tables (1930).

Hydrogen chloride is the most important chlorine compound found in magmatic gases. Its presence or absence in the steam will be decided by reactions involving metal chlorides. of type

$$H_2O + 2NaCl + SiO_2 = Na_2SiO_3 + 2HCl$$

High temperatures favor the right hand side of these reactions. The partial pressure of hydrogen chloride at equilibrium with a pressure of water vapor equal to one atmosphere is given in figure 3, together with the result for the equivalent calcium system. These results were calculated from the standard thermodynamic properties of the substances involved; in the case of the calcium system by Briner and Gagnaux (1948). The presence of hydrogen chloride in a magmatic gas will be dependent not only on the temperature, but on the type of chloride system present. Iron chlorides, calcium chloride,

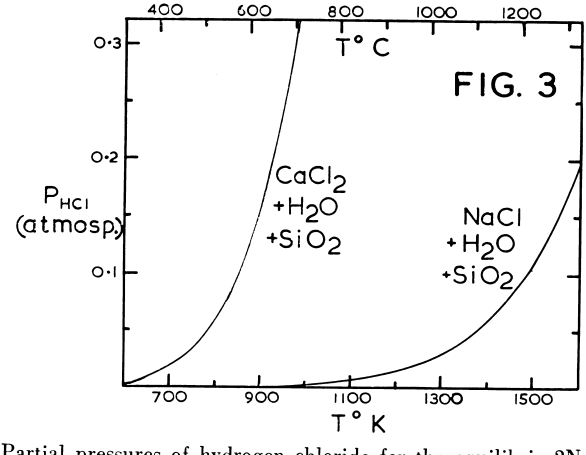

Fig. 3. Partial pressures of hydrogen chloride for the equilibria $2NaCl + SiO_2 + H_2O \rightleftarrows 2HCl + Na_2SiO_3$, and $CaCl_2 + SiO_2 + H_2O \rightleftarrows 2HCl + CaSiO_3$ at constant partial pressure of water vapour, $P_{H_2O} = 1$ atmosphere.

sodium chloride, require increasingly higher temperatures for hydrolysis to hydrogen chloride. Thus this gas may be found at relatively low temperatures of 400°C and under in an andesite fumarole area such as White Island. N. Z., but could not be expected at such low temperatures in a soda-potash rhyolitic area. Hydrogen fluoride is found in high temperature magmatic steam and results from a similar hydrolysis mechanism.

Dissociation of hydrogen chloride to chlorine and hydrogen need not be considered. Hydrogen chloride is dissociated to the extent of only 0.27 percent at 1800°K (International Critical Tables, 1930). As an approximation hydrogen chloride and nitrogen can be treated as inactive gases diluting those considered in System D, and having only a secondary effect on the equilibria.

If oxygen should be added to the system at any stage the equilibrium

$$2HCl + \tfrac{1}{2}O_2 = Cl_2 + H_2O.$$

would have to be considered. The chlorine in the Hawaiian volcano gas analyses has already been attributed by Jaggar (1940) to aerial oxidation. It may be noted also that adding a low proportion of oxygen to a system containing hydrogen sulphide could oxidise this compound only as far as sulphur and not to sulphur dioxide. This reaction is favored at low to medium temperatures.

$$H_2S + O_2 = H_2O + S_2$$

This could be the source of much of the elemental sulphur found in fumarole fields. Often in the porous ground common to such areas the fumaroles act as blowpipes, drawing in air at their bases and expelling the oxidised products in their discharges. It is a common liquid phase oxidation reaction in hot springs, producing crystalline sulphur.

Methane commonly occurs in magmatic steam. As Gautier showed as long ago as 1906 this product can be formed by the reaction of carbon monoxide with hydrogen.

$$CO + 3H_2 = CH_4 + H_2O \qquad (a)$$

The equilibrium concentration of methane can be calculated from the standard properties of the gases. For the purposes of calculation it was more convenient to consider the equation

$$CO_2 + 4H_2 = CH_4 + 2H_2O \qquad (b)$$

As carbon monoxide is formed by reduction of carbon dioxide with hydrogen, this equation for the direct formation of methane from carbon dioxide can be used. For a gas of original composition

$$x_{H_2O} = 0.89,\ x_{CO_2} = 0.10,\ x_{H_2} = 0.01.$$

the results at equilibrium at one atmosphere pressure for x_{CH_4} and x_{H_2} are given in table 7. Values of the equilibrium constant for the equation (b) are tabulated for various temperatures.

$$K_P = \frac{p_{CH_4} \cdot p_{H_2O}^2}{p_{H_2}^4 \cdot p_{CO_2}}$$

TABLE 7

T°K	K_P	$x_{H_2} \times 10^2$	x_{CH_4}
1000	2.78×10^{-2}	1.00	negligible
700	4.21×10^{2}	1.00	negligible
600	7.40×10^{4}	0.97	7.4×10^{-5}
500	8.73×10^{7}	0.36	1.6×10^{-3}
400	2.75×10^{12}	0.03	2.4×10^{-3}

SOME ANALYTICAL RESULTS

Some results from analyses of magmatic gases may be reviewed. There are few reasonably complete analyses available. Probably the best collections and analyses of high temperature volcanic gases are the series of Shepherd and Jaggar taken from molten basalt at Hawaii in the years 1917-19. Jaggar (1940) has reveiwed these analyses and graded them according to the conditions of collection of the sample.

Six of the samples, with highest hydrogen content, and graded excellent by Jaggar may be taken as typical of the samples with least contamination.

Fumaroles in the andesite cone of White Island in the Bay of Plenty, off the North Island of New Zealand, provide a good example of the medium temperature type of gas discharge. The hottest fumaroles have temperatures of the order of 600°C. Wilson (1953) has published analytical data for this source.

White Island

Condensate from Fumaroles (Parts by Weight)

H_2O (100). Total sulphur as H_2S(0.16) HCl(0.91). HF(0.01). H_3BO_3(0.01). NH_3(0.002). A weighted average from 4 fumarole areas.

Analysis of Uncondensed Gas (% by volume)

H_2S(2.0). CO_2(86.3). H_2(9.8). N_2(1.9). CH_4(0.00).

Unfortunately these results do not emphasize an important characteristic of this fumarole area. The total sulphur compounds in the condensate were calculated as hydrogen sulphide, but to anyone visiting the island it is obvious that both hydrogen sulphide and sulphur dioxide are being expelled in the fumarole gases. It is interesting to note that the hydrogen chloride content of the steam is of the order predicted from theory for the system $CaCl_2$—H_2O—SiO_2 at the expected partial pressure of water vapor of about 10 atmospheres.

Wilson (1941, 1953) has previously shown how the presence of polythionates in hot springs can be used as an indication of the presence of both hydrogen sulphide and sulphur dioxide in the magmatic steam heating the water. He gave examples where the presence of sulphur dioxide shown in this manner could be correlated with the higher temperature conditions of the more recently active volcanic areas in New Zealand.

The presence of both sulphur dioxide and hydrogen sulphide was shown by analyses of gas samples from Lassen Peak fumaroles during years of active volcanic activity. This was reported by Day and Allen (1925). The tempera-

TABLE 8

Sample No.	CO_2	CO	H_2	N_2	A	SO_2	S_2	SO_3	Cl_2	H_2O	Total
S7	17.25	0.62	0.76	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
S_3	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, 760mm pressure.

tures of the fumaroles were not reported, but from the description it seems that the conditions were very similar to those in the present White Island fumarole area. Their results are reproduced in table 9.

TABLE 9

Gases soluble in $Ba(OH)_2$. Percent by volume

	CO_2	SO_2	H_2S	HCl	HF
Fumarole, Lassen Peak, east side of crater of 1914; collected June 1916.	0.096	0.054	0.005	none	none
Fumarole, south side of old crater; collected by E. S. Shepherd, June 1915.	0.040	0.005	0.004	—	—

Clark (1916) summarized many examples of early analyses of gases from Vulcano and Vesuvius. The results show the change from hydrogen chloride, sulphur dioxide gases of high temperature sources to hydrogen sulphide, carbon dioxide compositions at lower temperatures.

Many analyses exist for low temperature gases from hydrothermal areas such as Yellowstone National Park (Allen and Day, 1935); Iceland (Barth, 1950); The Geysers, California (Allen and Day, 1927); and Wairakei, New Zealand. They are of similar general type, and a few examples are given in table 10. The bores for geothermal power at Wairakei, ranging in depth from 600 to 3000 ft. have provided the best samples of the complete hydrothermal fluid yet taken. At the bottom of these bores the temperatures are about 250°C, but the gases sampled from this deep hot water are very similar to those found in the steam from the natural fumaroles and boiling surface pools of this area. The bores discharge a mixture of steam and water in the ratio expected from the adiabatic expansion of a liquid water phase at about 250°C to lower pressures at the surface (Ellis and Wilson, 1955). The two analyses kindly supplied by Mr. S. H. Wilson, Dominion Laboratory, as illustrative examples, are for steam separated from the water/steam mixtures at 99°C and local atmospheric pressure. Karapiti fumarole discharges dry steam into the atmosphere at about 130°C.

TABLE 10

Parts per thousand, by volume at atmosphere pressure

Source	H_2O	H_2S	CO_2	H_2	CH_4	N_2+A	NH_3	Temp. °C
Bore No. 4/1, Wairakei	999.600	0.033	0.329	0.009	0.003	0.005	0.021	250
Bore No. 9 Wairakei	999.310	0.050	0.608	0.014	0.006	—	0.012	250
Karapiti Fumarole Wairakei	999.530	0.033	0.429	0.002	Trace	0.002	0.004	130
Black Growler, Norris Basin, Yellowstone.	996.00	0.10	3.86	0.02	0.01	0.02	—	130 (about)
Well No. 2, The Geysers, California.	986.86	0.42	7.77	2.16	2.08	0.48	0.23	160
Spring at Reykir in Olfus, Iceland*	990.00	0.82	8.22	0.53	0.03	0.40	—	99

* assumed 1% gases other than water.

DISCUSSION

The results from both the theoretical calculations for certain systems, and from analysis of collected magmatic gases have been presented. Any connection between the two may now be examined.

The discussion will be centered about the idea put forward by Jaggar (1940) and mentioned earlier, of a simple gas mixture which could be dissolved in the igneous rock, and could give on release of pressure the typical magmatic gas products that are found by analysis for particular temperature conditions.

If there should be such a gas mixture the predominant sulphur equilibrium within it could be one of three main types.

A. Insufficient hydrogen, other than in water molecules to reduce all the sulphur dioxide to hydrogen sulphide at low temperatures.

B. Hydrogen, other than in water, present in at least equivalent amount to sulphur.

C. Sulphur dioxide present not dependent on the decomposition of water.

The calculations given are for the extreme type of each system. The CO_2—CO—COS equilibria may be superimposed on these simpler systems without seriously altering the conclusions which can be drawn. The nitrogen and chlorine equilibria can also be considered separately as a first approximation.

Let us for the present assume that magmatic gases approach a state of chemical equilibrium. The analytical results show that sulphur dioxide gradually disappears from the gases as the temperature becomes lower. For systems of type C sulphur dioxide is the stable product at all temperatures of interest. As this type of system does not produce the other sulphur products common to magmatic gases it need not be considered further.

Systems of type A have sulphur dioxide stable at all temperatures, but in equilibrium with hydrogen sulphide at low temperatures. It is possible that the sulphur dioxide could be lost preferentially from a magmatic gas of this type as cooler conditions were approached at the surface, so that only hydrogen sulphide was expelled in the low temperature surface gases. The effect of increasing the pressure, however, is similar to lowering the temperature, and causes the composition to approach a two to one mixture of hydrogen sulphide and sulphur dioxide in the ideal case examined. This should be the original type of composition of the deep high pressure gases for this system. Sulphates or sulphites therefore could be expected in a cooled magma that has retained its gases, but they are not common constituents of plutonic rocks. It does not seem likely that a system of Type A predominates in magmatic gases.

Systems of type B and D account for the general differences found between high and low temperature magmatic gases without any further assumptions than the initial one of chemical equilibrium between constituents. The effect of pressure on these systems is to favor water, carbon dioxide, and hydrogen sulphide which are the most likely constituents in the magma from which the gases originate. The hydrogen sulphide and carbon dioxide would exist in equilibrium with sulphides, carbonates, and high temperature water fluid, all dissolved in the hot magma. Should a high pressure gas phase con-

sisting mainly of water, carbon dioxide, and hydrogen sulphide be formed, it would subsequently have the chemical flexibility to form the common constituents found in surface magmatic gases. Thus the earlier ideas of Gautier on this type of system are confirmed by the application of modern thermodynamic data.

There is no doubt of the similarity between the theoretical results given for system D and the analytical results for the same temperatures. Only the general character of the gases can be compared, as there are wide variations in the concentrations of constituents in the various collections of gases from different sources. However, the high temperature CO, H_2, SO_2, COS constituents are predicted by calculations, as are the low temperature CO_2, H_2S compositions. It is likely that the total sulphur contents of gases from volcanic craters are much higher than in the average gas liberated from a magma, because of recycling of sulphur within the craters.

Comparison of the Hawaiian analyses with the theoretical composition of system D shows that the hydrogen content found by analysis is lower than predicted. A paper by Kennedy (1948) is interesting in this respect. From the average ferric/ferrous ratio in fresh Hawaiian basalts be deduced that there should be approximately 0.16 percent hydrogen in the volcanic gases, and providing equilibrium was maintained between lava and gas phases, a greater proportion of hydrogen should not be expected. The best of the analyses reported by Jaggar however have a higher hydrogen content than this. Also, from experimental work Kennedy showed that at 1200°C at least 20 hours were required for iron oxides to come to equilibrium with the gas phase. It appears that the hydrogen content of volcanic gases is lowered by reaction with ferric iron, but the low equilibrium content is not always obtained. The output of ferric iron in lava would have to be much in excess of the gas output of the volcano for the hydrogen concentration to be controlled in this way.

Gases with a hydrogen content of the order of 10 percent have been collected by Day and Shepherd in 1912 (Jaggar, 1940) by pumping gases from flame cracks in Hawaiian basalt. It seems that the removal of hydrogen from a magmatic gas stream by ferric iron is a variable effect depending on the velocity of gas discharge, and the kinetics of the various reactions. It is undoubtedly important, but because of its variable nature is difficult to allow for in a theory as general as the present one. The presence of nitrogen in most analyses adds the possibility of aerial oxidation of hydrogen, and makes the problem still more difficult to assess.

It is of course impossible that a gas system of the exact bulk composition corresponding to an original water, carbon dioxide, hydrogen sulphide mixture will remain intact at all temperatures in all volcanic areas. Under suitable conditions there will be deposition of sulphides, or of sulphates; perhaps oxidation by rocks containing ferric iron, or by entry of air to the system. It is believed that each individual case could be treated as a variation of this original mixture with due allowance for local conditions, such as mineral formation or oxidation. By adding to the products of this basic system the concentrations of hydrogen chloride, ammonia and methane predicted in

figure 3 and tables 6 and 7, a very fair approximation of the various magmatic gases found in the field is obtained.

It is not expected that exact chemical equilibrium will always be established in magmatic gases. Indeed the opposite would be more correct. It is likely however, that in the majority of cases the systems approach the equilibrium conditions quite closely, especially within the gas phase. With extremely rapid processes such as explosive volcanic eruptions the constitution of the gases liberated would resemble more closely those predicted for deeper high pressure conditions than for atmospheric pressure. Thus hydrogen sulphide and ammonia might be expected in high temperature gases under such circumstances.

Some consequences may be considered of assuming the basic character of magmatic gases is due to equilibrium changes within a simple gas system.

It is not necessary for hydrogen to be an original component in the magma. It can be produced by the reaction of hydrogen sulphide with water at high temperatures. If a certain amount of sulphur dioxide should be lost from high temperature steam by neutralisation reactions, three times its molecular concentration of hydrogen would be left permanently in the gas to exist along with hydrogen sulphide at low temperatures.

$$H_2S + 2H_2O = SO_2 + 3H_2$$

As the concentration of hydrogen is usually low in cooler hydrothermal gases, only a small proportion of sulphur as sulphur dioxide would need to be lost in this way.

Carbon monoxide would not be a constituent at high pressures in the original magma. Hydrogen and carbon monoxide were considered by Jaggar to be fundamental exudations from the inner earth. This does not seem to be a necessary assumption in the light of the present work.

It is often considered that elemental sulphur is the original sulphur compound in the deep magma. From the systems investigated it appears that hydrogen sulphide is more likely to be that compound. Sulphur could be deposited either from the equilibrium proportion of sulphur vapor present in the gases or from partial oxidation of hydrogen sulphide.

Carbonyl sulphide would be an equilibrium constituent of medium temperature magmatic steam, reaching a maximum concentration at about 1200°K. The instability of hydrogen sulphide in high temperature steam reduces the concentration of carbonyl sulphide at temperatures above this. The concentration would never become very high.

Equilibrium relations for both methane and ammonia were calculated separately from system D. This was done partly for simplicity, but mainly because misleading results would be obtained by their direct addition to the constituents of this system. As hydrogen disappears almost entirely at low temperatures in the ideal closed system, ammonia and methane would not appear. However, free hydrogen is found in almost all magmatic gas samples not contaminated by oxygen, even at lowest temperatures. A possible mechanism for the existence of this hydrogen has been given. By taking reasonable and appreciable values for the mole fraction of hydrogen at low temperatures the possibility of ammonia and methane formation is more correctly shown.

There is no heat liberated by the change from high pressure to low pressure constituents at high temperatures. The processes in a rising volcanic gas would be adiabatic and not isothermal but values of ΔH in cals/mole for certain key reactions can be given for a temperature of 1200°K.

$$H_2S + 2H_2O = 3H_2 + SO_2. \quad \Delta H^\circ_{1200} = 54400$$
$$CO_2 + H_2 = CO + H_2O. \quad \Delta H^\circ_{1200} = 7900.$$

There would be no spontaneous rise in temperature because of internal chemical reaction in the gases on releasing the pressure as was visualized by Jaggar for a basic magmatic gas mixture.

In conclusion it may be said that the agreement between field results and those calculated is an indication that magmatic gases approach a state of chemical equilibrium, and that the usual thermodynamics of gas reactions can be usefully applied to such problems. It appears that Shepherd was unduly pessimistic about the effects of contamination and adsorption ruling out further interpretation of the constituents found by sampling volcanic gases.

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UNIVERSITY OF OTAGO
DUNEDIN, NEW ZEALAND