EQUILIBRIUM IN HETEROGENEOUS SYSTEMS AT HIGH TEMPERATURES AND PRESSURES[1]

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Following a summary of the principles involved in chemical equilibria, there is given a brief discussion of apparatus and experimental procedure for investigations in this field. Special attention is paid to systems that include a solid phase. The effects of pressure and of temperature are considered separately and in combination. A résumé is presented of certain experimental results obtained at pressures extending to several thousand atmospheres and at temperatures exceeding 1000°C. Reference is made to the application of these results to manufacturing processes and also to volcanology and other branches of geophysics.

I. INTRODUCTION

The present objective is to review briefly the principles by which chemical equilibrium is determined, and to note some representative results and methods in the investigation of equilibrium in systems of variable composition, especially at elevated temperatures and pressures. The range of these variables for which precise measurement is feasible has been greatly extended in recent years; there now exists a vast array of significant experimental results at pressures of several thousands of atmospheres and at temperatures up to 1000°C. or more. Such results, on the one hand, are of vital importance to various manufacturing processes, and, on the other hand, give promise of solving certain fundamental problems in geology and geophysics.

The present treatment of equilibrium is limited to heterogeneous systems and also to those involving one or more solid phases. This limitation is not imposed by any lack of importance of homogeneous systems, or of liquid–vapor or liquid–liquid systems. The whole field of equilibrium is too large a subject to be treated even sketchily in the space now available. It may be noted that liquid–vapor systems form a subject of special in-

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terest and importance, and one in which there have been so many new developments that detailed treatment elsewhere is desirable.

II. THE PRINCIPLES OF EQUILIBRIUM

The fundamental principles of equilibrium are best described in the language of thermodynamics. Chemical equilibrium has a basis similar to that for mechanical equilibrium, except that the variability in chemical composition requires the introduction of new parameters expressing the properties of the variable components. This means that a quantity, the chemical potential,—or its equivalent, the activity,—must be specified for each component and these chemical potentials combined with the other more familiar thermodynamic quantities, in order to fit the laws of physical chemistry into one simple framework.

In any system, and in any combination of phases, equilibrium is determined by the basic principle of the equality of temperature, of pressure, and of the chemical potentials. For any component the appropriate chemical potential must have identical values in adjacent phases; otherwise, an equilibrium state can not exist. In homogeneous systems this rule finds expression in the well-known Law of Mass Action, which in its exact form states that at constant temperature a certain product-quotient, involving the separate activities of the various components, remains constant. For heterogeneous systems an equilibrium constant can be specified, but it does not have a similar utility. In any system, however, thermodynamics makes its best contribution by supplying a quantitative basis for the study of equilibrium and a convenient measure of the extent to which reactions or processes go in one direction or the other. The quantity most often employed for this purpose is F, the free energy of a substance, or ΔF, the change in free energy that occurs during the transition from one state to another. Either quantity is determined directly from the chemical potentials. It happens also that ΔF is simply related to the equilibrium constant. Moreover, for any reaction or process it is a convenient criterion of equilibrium because its magnitude is a precise indication of the distance from the equilibrium state. Any reaction, chemical or physical, may be characterized by an equation which represents the transition from one state to another. If the substances on one side of the equation are in equilibrium with those on the other side of the equation, ΔF for the reaction is zero. A large negative value of ΔF means that the reaction as written tends to proceed nearly to completion and that therefore the substances on the left-hand side of the equation have a strong chemical affinity for each other. For example, at 1400°K. and 1 atmosphere the value of ΔF for the reaction by which 1 mole of carbon dioxide is formed from carbon monoxide and oxygen is -8040 calories. This signifies a strong affinity of carbon monoxide for oxygen; even at 1400°K. carbon dioxide is dissociated to the extent of only 0.015 per cent. On the other hand, a large positive value of ΔF means that the reaction proceeds only slightly in the direction indicated. As an illustration, nitrogen and hydrogen, on combining to form ammonia at 1000°K. and 1 atmosphere, involve a change in F amounting to +14,800 calories per mole of ammonia. This gives quantitative expression to the reluctance, under these conditions, of nitrogen to combine with hydrogen; if the two gases are brought together in the stoichiometrical proportions, a maximum of 0.036 per cent will combine at the temperature and pressure under consideration to form ammonia.

The advantage of having a single quantity that conveniently and precisely describes equilibrium and the tendency to react, is obvious. This quantity is applicable to so-called physical reactions as well as to purely chemical reactions. If we are dealing with the solubility of a substance in a solution, and if we symbolize the act of dissolving by the equation $S \rightarrow L$, then at saturation ΔF is zero, and a large negative value of ΔF means undersaturation, i.e., a strong tendency to dissolve, whereas a positive value of ΔF is associated with a state of supersaturation. For example, the ΔF associated with the dissolving of 1 mole of sodium chloride in water at 25°C. is -2780 calories.

III. EFFECT OF TEMPERATURE

The change of equilibrium as the temperature varies is of great importance. The simple and well-known equation for expressing the effect of temperature on ΔF, and hence the effect of temperature on equilibrium, is

$$\frac{d\left(-\frac{\Delta F}{T}\right)}{dT} = \frac{\Delta H}{T^2}$$

in which H is the heat content or enthalpy, and ΔH is therefore the negative of the ordinary heat of reaction (ΔH being positive when heat is absorbed). Qualitatively, this equation means that if ΔH is positive, an increase of temperature makes ΔF more negative,—in other words, the reaction in question goes more nearly to completion. Possibly the most important of all the qualitative laws of physical chemistry is the generalization that endothermic reactions proceed best at high temperatures. On the other hand, if ΔH is highly negative, i.e., if the reaction heat as ordinarily expressed is large, then high temperature tends to inhibit the reaction. So much for the qualitative implications. Quantitatively the equation is even more important. It allows us to determine the behavior of reacting substances over a wide range of temperatures without making a large number of measurements. Values at as few as two temperatures (although three or four are often preferable) may be used to establish the complete equilibrium–temperature curve. By a reversed application of the equation, heats of reaction and other thermal quantities may be determined by measurements of equilibrium at several temperatures.

IV. EFFECT OF PRESSURE

The equation $\mathrm{d}\Delta F/\mathrm{d}P = \Delta V$ characterizes the effect of pressure on ΔF and hence on the tendency of a given set of substances to react. In this equation ΔV is the aggregate change of volume that occurs when the reaction proceeds to completion in the direction indicated. Here, again, an interesting and important qualitative form may be given to the principle. This may be stated as follows: If ΔV is negative, an increase of pressure makes ΔF smaller, that is to say, makes the reaction as written proceed more nearly to completion. In other words, high pressure favors the existence of materials of small volume, i.e., high density. This is an interesting example of important relations that are in exact agreement with what one might conclude by intuition or common sense. It seems quite reasonable that pressure should tend, not only to produce a simple contraction of objects on which it acts, but also to squeeze them into other states of higher density. Like the corresponding equation for temperature, this relation, however, has an even more important quantitative use and is the basis, as will be shown later, of a powerful method for investigating equilibrium at extreme pressures. At the moment it is sufficient to note the interesting conclusion that, if there are two possible states of aggregation the second of which has the lower volume, then there is some pressure (possibly very high) at which the second state will predominate. We know, for example, without any measurement except of density, that diamond at a sufficiently high pressure is the stable form of carbon. It is certain also that garnets, which do not form at atmospheric pressure, must at a sufficiently high pressure be the stable form of the corresponding silicate mixtures.

V. DIRECT DETERMINATION OF EQUILIBRIUM AT HIGH TEMPERATURES

The essential requisites are a furnace for producing high temperatures and a means of measuring the temperatures with adequate precision. Owing to their convenience, electric furnaces of the wire-wound resistance type are commonly employed. For measurements that continue for a considerable period of time, an automatic temperature regulator is indispensable. A large number of types of such regulators have been devised, some depending upon the electromotive force of a thermocouple to actuate the regulating mechanism, and others using different principles. A remarkably successful regulator used for many years at the Geophysical Laboratory works on the principle of the Wheatstone bridge, the furnace winding being one arm of the bridge and variations in temperature causing an unbalanced E.M.F. which by an appropriate mechanism regulates the current through the furnace so as to maintain the temperature at a constant value.

Without going into detail concerning the various methods of measuring high temperatures, it may be noted that for temperatures beyond the range of the mercury thermometer three principal types of instruments are used. These are the thermocouple, the resistance thermometer, and the radiation pyrometer. The platinum–rhodium thermocouple finds extensive use because, first, it is capable of high precision at temperatures up to 1700°C.—which covers the range of the greater part of the experimental studies in this field—and also because the thermocouple measures temperature practically at a point and is thus adapted for working with very small samples. A combination of platinum resistance furnace, automatic temperature regulator, thermocouple, and a potentiometer to read the electromotive force is considered by many to be the most generally useful equipment for the determination of equilibria at high temperatures.

Brief reference should be made to the various methods for determining equilibrium. Perhaps the most familiar one is the heating-curve method. In order to measure the melting point of a material, the time–temperature curve is taken while the material is raised up to and above the temperature at which it becomes liquid. In the ideal case the temperature as measured at a point within the material remains constant for a considerable period of time when the temperature has reached the point at which liquid and solid are in equilibrium. Many materials, notably silicates and other substances that form a viscous liquid, do not yield heating curves in which there is any region of constant temperature; but for such materials the melting point is nevertheless indicated, more or less clearly, by a change in direction of the curve.

A less familiar procedure is the so-called quenching method (6). This is applicable to material in which equilibrium is attained slowly and is peculiarly advantageous for such substances, because they do not yield heating curves with sharp indications of melting points or other inversions. The method has been applied with special success to the study of silicates. A small charge wrapped in platinum foil is suspended in an electric furnace and held at a constant temperature for a time necessary for equilibrium to be obtained. The charge is then dropped from the furnace into water or mercury, and the equilibrium is thus "frozen." Subsequent examination of the charge shows whether the material at the particular temperature was above or below the equilibrium point. Further trials allow an approximation to this temperature within successively narrowed limits. Although this method might at first thought appear somewhat crude when compared to the heating-curve method, it has been applied with great success to the investigation of difficult silicate systems.

VI. DIRECT DETERMINATION OF EQUILIBRIUM AT HIGH PRESSURES

Such measurements require a means for producing, maintaining, and measuring pressure. In essence the apparatus for producing pressure is a pump. This may take the form of an ordinary pump with valves and auxiliary equipment for actuating the pistons, or in the case of very high pressures may be a simple bomb and piston capable of utilizing only a single stroke of the piston. The production of leak-proof joints and packings is a complicated and difficult technique, but it is now a relatively simple matter to produce and control satisfactorily pressures up to 20,000 atmospheres or more. Pressures of twice this amount are obtained readily by supporting the outside of the bomb by means of a tapered ring (4), but much less accuracy and flexibility of performance are possible at these high pressures. Recently a greatly increased range of pressures has become available by utilizing the increase of strength caused by hydrostatic pressure. Preliminary experiments have indicated that pressures in excess of 200,000 atmospheres are attainable.

In any experimentation at extreme pressures an outstanding difficulty is the obtaining of a suitable medium for transmitting the pressure. Even at 20,000 atmospheres there are very few liquids that at room temperature do not become frozen, either in the sense of changing to a crystalline solid, or of becoming highly viscous or even glassy. Among ordinary liquids pentane seems to be the only suitable one for pressures of this magnitude. At somewhat lower pressures other hydrocarbon liquids may be employed, but at pressures much higher than 20,000 atmospheres there is no entirely satisfactory medium. A gas such as nitrogen and argon may be used up to the pressure (probably very high) at which a crystalline solid is produced, but there are practical difficulties in handling and storing the gases. For the present at least it appears that whenever we deal with pressures that exceed a few tens of thousands of atmospheres, we must be reconciled to the imperfect transmission of pressures associated with flow in so-called solid materials. This circumstance imposes an important limitation on the accuracy of measurements at extreme pressures.

There are two principal types of method that are suitable for measuring pressures that exceed a few thousand atmospheres. One method involves the force exerted on a piston, which may be either the piston that produces the pressure or a separate piston. Friction, especially when a packing is is used, introduces a considerable uncertainty, although this can be reduced by averaging the readings taken with increasing and decreasing pressure. The second general method, which is capable of high precision, makes use of the change in resistance of a metal exposed to hydrostatic pressure. This change is large enough to permit the determination of pressure to greater accuracy than that with which the pressure scale is now known. In manganin, which is the material commonly used, the relation between pressure and change in resistance is nearly linear up to several thousand atmospheres, if the gauge is properly constructed (3). At 25,000 atmospheres a departure from linearity of 1 or 2 per cent has been observed (5). It should be noted that at these higher pressures, the installation and maintenance of the resistance–pressure gauge becomes increasingly difficult, on account of the necessity of introducing the electric leads through insulated and pressure-tight packings. The estimation of pressures much above 25,000 atmospheres is usually carried out through a calculation involving the force exerted on a piston and its area.

There are several methods for determining the behavior of materials under pressure and thus obtaining information as to equilibria. One of the most important is the volume-change method, which is commonly used to detect a transition under pressure from one state to another. The procedure is merely to make simultaneous pairs of readings of the pressure and of the piston position; measurements can be made with high precision. The volume-change method, therefore, gives a delicate indication of transformations, such as the melting of a solid, the dissolving of one phase in another, and other changes such as polymorphic transformation. This method is analogous to the heating-curve method for investigations at elevated temperatures. In using the heating-curve method we are in effect measuring temperature and entropy, whereas in the volume-change method for pressure experimentations we are utilizing the thermodynamically comparable pair of factors, pressure and volume.

VII. EQUILIBRIUM AT HIGH TEMPERATURES COMBINED WITH HIGH PRESSURES

When the difficulties incident to high-pressure experimentation are superimposed upon those incident to high temperatures, the necessary technique has appeared to be quite formidable. Much care in the design of the apparatus was necessary, and one must expect to spend a considerable amount of time in keeping the apparatus in running order. There are two principal varieties of apparatus for combined high temperature and high pressure. The first uses external heating, and the second is arranged for internal heating by means of an electric heating coil.

An example of a bomb with external heating is that used by Morey (9) in the investigation of the behavior of silicates in the presence of water under pressure. The bomb is a simple cylinder closed at the bottom and provided with a packing nut at the top. A sample of material to be studied, contained in a gold or platinum crucible, is placed within the bomb, together with the appropriate amount of water, so that at the chosen temperature the desired pressure will be developed by the expansion of the water. This apparatus is especially well suited for experiments with materials which quench readily. In its simplest form no means are provided for measuring directly either the temperature or the pressure within the bomb. The pressure is calculated from the amount and temperature of the fluid used, and the temperature is measured by means of a thermocouple inserted in a small hole in the wall of the bomb. Pressure and temperature are limited by the characteristics of the metal used. In the newer types of stainless steels the practicable limit is of the order of a few hundred atmospheres pressure at a temperature of 600 to 800°C.

An example of interesting work carried out by the simple bomb with external heating is found in the ternary system water–potassium silicate–silica, investigated by Morey and Fenner (10). Equilibrium with various mixtures was determined by what has been called a hydrothermal quenching method. The essence of this method is to use a rate of cooling, neither too great nor too small, such that the cooled sample preserves the equilibrium conditions existing at the chosen temperature and pressure. It was found possible to delineate the stability fields in the ternary system and to determine the variation of vapor pressure with the change in ratio of silica to potash. With a more elaborate type of apparatus measurements have been obtained in the system soda–silica–water. Of especial interest are the results on the lowering of the melting point of $Na_2O \cdot SiO_2$ by the action of water at various pressures (11).

An example of high-pressure apparatus with internal heating is that used by Smyth and Adams (12). The novel features of this bomb were, first, the use of a hydraulic press to hold the lid on the bomb, and second, the cooling of the walls by circulating water through spiral grooves which were turned on the outside of the inner shell before the assembling of the inner and outer shells. Heating was attained by means of a small resistance furnace made by winding platinum or platinum–rhodium wire on a refractory tube and surrounding the tube by a suitable insulating material. For such apparatus the choice of this insulating material is very important. It must be a poor conductor of heat and at the same time not be so fluffy that it will be displaced or blown away by the violent currents due to addition or removal of the pressure fluid. Magnesium oxide, which is an excellent substance for ordinary electric furnaces, is not usable, because it is too light. Granular aluminum oxide (alundum) is a fair thermal insulator and fulfills the requirements of resisting satisfactorily the disturbances accompanying the increase or release of pressure.

The medium originally used to transmit pressure was carbon dioxide. More recently nitrogen has been substituted for the carbon dioxide and has been found to have the advantage of a comparatively small (effective) thermal conductivity. This is an important feature, because it is always difficult to attain high temperature in a region surrounded by a gas under pressure. At pressures of several thousand atmospheres all gases have a density comparable with ordinary liquids, and the problem of maintaining elevated temperatures in a gas at high pressure may be compared to using a resistance coil to obtain a red heat in the middle of a beaker of water. Both conduction and convection enter into the loss of heat, and in both these respects nitrogen is a great improvement over carbon dioxide.

Through the lower lid of the bomb are brought electrically insulated leads for supplying the furnace with current, and a number of leads are also supplied for connecting one or more thermocouples to the interior of the electric furnace. Nitrogen under pressure may be pumped into the bomb by means of a three-stage motor-driven compressor. The apparatus is suitable for experimentation at pressures up to 4000 atmospheres and at temperatures up to 1500°C.

An example of equilibrium measurements obtained with the externally heated bomb is given by the work on the system calcium oxide–carbon dioxide, for which Smyth and Adams (12) determined the melting relations and vapor pressures. At carbon dioxide pressures of 40 atmospheres or more, calcium carbonate will melt if the temperature is raised sufficiently. Under 40 atmospheres pressure melting begins at 1240°C. The melting point, however, is an incongruent one, the composition of the liquid not being that of pure calcium carbonate but containing an excess of calcium oxide. To attain a nearly congruent melting would require a very much higher pressure than 40 atmospheres, but the fusion temperature would probably not be much above 1340°C.

Transformation in the solid state may be investigated by the heating-curve method in an apparatus of this kind. Precise determinations on the effect of pressure on the α–β inversion in quartz have been made by Gibson (7). Another type of measurement made with a similar apparatus is illustrated by the work carried out by Goranson (8) on the solubility of water in granite magma. A bomb with the same general design was used, but the device for cooling the walls of the bomb consisted of a thin space between the inner and outer walls, rather than a spiral groove as in the original apparatus. Experiments were conducted by sealing small charges of granite with the requisite amount of water in small platinum tubes and exposing these for a sufficient length of time to the desired temperature and to a pressure sufficiently high to counteract the tendency of the water within the sealed tube to expand. The walls of the tube being thin (of the order of 0.1 mm.), there was no important difference of pressure between the inside and the outside of the tube. This investigation extended to pressures of about 4000 atmospheres and temperatures of about 1000°C. The solubility of water first rises rapidly with pressure, and then more slowly. It is interesting to observe that at a moderate pressure it is possible to have water to the extent of nearly 10 per cent by weight dissolved in the silicate mixture having the chemical composition of a typical granite.

VIII. INDIRECT, OR THERMODYNAMIC, DETERMINATION OF EQUILIBRIUM

This method depends on the circumstance that equilibrium is determined by free energy and that the free energy in turn becomes known at all pressures if the volumes and entropies of the individual phases can be determined at the corresponding pressures. The thermodynamic method is especially advantageous when pressure and composition are the variables. For such systems the method, although an indirect one, is capable of extraordinary precision and, in general, represents perhaps the most satisfactory procedure for studying equilibria at very high pressures. In this instance the experimentation reduces itself mainly to the measurement of specific volumes or densities. The method presupposes a knowledge of the state of the system at one pressure, say atmospheric, and it involves merely a measurement of the compressibilities of all the separate phases that occur in the system.

A striking example of the application of the thermodynamic method to equilibrium studies is found in the phase diagram for the system sodium chloride–water at 25°C. This diagram was worked out (1) from measurements of the compressibilities of the solid phases involved (ice, sodium chloride, and sodium chloride dihydrate) and of a series of aqueous sodium chloride solutions of varying concentrations. Another system investigated by a similar technique is the system ammonium nitrate–water at 25°C. Here a striking decrease in solubility occurs (2), reducing the solubility of the salt from 67 per cent by weight at atmospheric pressure to 26 per cent at 12,100 bars, which is the pressure at which the solubility curve for ammonium nitrate intersects that for ice $_{\mathrm{VI}}$.

In a strictly analogous manner, the solubility curves for cases in which temperature and concentration are the variables can be determined thermodynamically. Here entropy and temperature take the places of volume and pressure, and for the measurement of compressibilities we substitute the measurement of specific heats of the various phases, including a number of solutions of various concentrations. As before, we start with a known thermodynamic state at some arbitrary temperature and at the chosen constant pressure. A knowledge of the temperature at which each phase makes its appearance is also required. This information does not necessarily come from direct observation, but, as is well known, can in some instances be determined by application of the Third Law of Thermodynamics through the utilization of thermal data. It should be noted that, although the bases for the indirect determination of equilibrium curves at either high temperatures or high pressures are essentially the same, in actual practice the indirect method seems to be of more value for high-pressure equilibria. One reason for this is that volume lends itself to precise measurement in stationary systems, whereas entropy and other thermal quantities are commonly measured in a moving system.

It is interesting to compare the type of diagram which represents the change of a system at varying pressure and constant temperature with the more familiar freezing point–solubility diagram, in which temperature and concentration are the variables and which refers to some constant pressure, usually atmospheric. Both kinds of diagrams contain curves which represent the equilibrium between solid and liquid and are called solubility curves, and in both types of diagrams the full area is divided into various fields representing the existence of different phases. The principal difference in appearance is that the pressure diagram appears to be upside down, the freezing-point curves *rising* until they meet in eutectics or other invariant points. This illustrates an interesting conclusion,—namely, that in general increasing pressure produces the same kind of effect as decreasing temperature. The volume of a substance, for instance, becomes greater at increased temperatures and decreased pressures. Solubility increases, as a rule, with increasing temperature, but in general is diminished by high pressure.

These newer methods furnish a striking example of the approach to heterogeneous equilibrium by the study of homogeneous equilibrium. By this powerful technique, measurements of volume and entropy at various pressures, temperatures, and concentrations form the experimental framework from which a complete knowledge of a system is derived by straightforward computation. Interrelations between the four quantities P, V, T, and X thus become of paramount importance. In the practical application of the thermodynamic method great difficulties appear to arise, principally because the quantities used in the study of solutions are the fictive or *partial* quantities. These, being determined in general from rates or slopes, entail a loss of accuracy in comparison with the primary measurements. The solution of the difficulty, of course, is high precision in the measurements, and fortunately this can readily be secured for measurements of volume even at very high pressures. It is significant that modern thermodynamics from the practical side, as applied to physical chemistry, consists mainly in the devices for the representation of data so as to utilize the basic thermodynamic relations.

IX. CONCLUDING REMARKS

From what has been said here concerning the determination of equilibrium at high temperatures and high pressures in systems containing a solid phase, it is evident that great experimental difficulties are involved and that these difficulties are gradually being nullified by new experimental and calculational methods in which volume plays an important rôle.

One of the interesting practical applications of studies of equilibria at high temperatures is in the field of refractories. The essential constituents of refractories overlap those which are of interest in petrology and include, besides silica, a number of oxides such as lime, magnesia, soda, potash, alumina, and the oxides of iron. Various combinations of these oxides have been studied, and numerous binary and ternary systems have been methodically investigated. Such measurements are immediately applicable, not only to problems of petrology, but also to the production of refractories. The important property of a refractory is, of course, its melting behavior, not only alone but in contact with other materials. It is the beginning of melting, rather than the temperature of complete melting, that is of most interest. This beginning of melting is described in terms of the eutectic temperatures of the system involved. Now that quantitative data are on hand for many of the essential mixtures, it is easy to understand a number of phenomena that formerly were quite puzzling. In materials used for spark plugs or for furnace linings and for other purposes, we can tell exactly the temperature at which softening begins and can follow the subsequent extent of the softening through study of the course of the melting curves. The practical value of such studies has been, first, the ability to make quantitative comparisons between refractories of various compositions, and second, the aid in making new and more valuable combinations.

A quite different application of indirect rather than immediate value has been to petrology and especially to volcanology. Volcanoes have attracted the attention of students of geophysics, because they give us direct evidence of a hot and active interior of the earth and because their behavior gives us a clue to the nature of the interior and of those processes by which we believe the earth itself was formed. The most striking feature of volcanic emanations, aside from the tremendous flows of molten magma, is the vast amount of volatile material discharged from volcanic vents. In these gaseous emanations, as also in those from fumaroles, water is the dominant constituent. We believe that water is an important and essential ingredient of the original or primeval magma whose consolidation has given rise to the visible crust of the earth. Since water is associated with silicate mixtures even at considerable depths, it is natural that an understanding of the primeval magma can be obtained only through a careful study of silicate mixtures in which water is present as a major constituent. Such studies involve apparatus for combined high temperatures and pressures such as have been described above. Hardly more than a beginning has been made in this line of experimentation. Much more needs to be done, but already we know something of the behavior of aqueous silicate mixtures upon cooling, and we can understand something of the way in which the cooling can act to build up great pressures sufficient for volcanic outbursts and the way in which the varied assortment of minerals present in geologic formations can be found. It is evident that an understanding of the fundamental problems of geology, such as volcanism and related phenomena, depends upon further complete and systematic investigation of the equilibrium of silicate mixtures at temperatures and pressures comparable with those prevailing at depths of several hundred miles below the surface of the earth.

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