HYDROTHERMAL SYNTHESIS AND DETERMINATION OF EQUILIBRIUM BETWEEN MINERALS IN THE SUBLIQUIDUS REGION[1]

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ABSTRACT

The basis of the experimental determination of mineral stability by synthetic methods is critically discussed. It is considered that synthesis alone does not necessarily give a true picture of equilibrium relations. Some less frequently used methods of determining equilibrium conditions are briefly discussed.

INTRODUCTION

For some time, and especially since 1950, data concerned with equilibrium in hydrothermal systems have been produced in impressive quantities. In part, the objective of this work has been to define the physical conditions under which minerals and assemblages of minerals have formed in nature. But when all these data are surveyed, confusion is obvious. The student of petrology or mineralogy interested in these fundamental studies, but not familiar with their execution, finds himself in difficulties; for frequently, when a system has been studied by independent workers, the results reported as representing equilibrium differ quite extremely. His study might lead him to reject the value of all experimental work, or he might even conclude that equilibrium has several definitions. If possible, such confusion must be eliminated. There can be no question in the thermodynamic sense of what constitutes equilibrium. As will be stressed in what follows, experimental evidence is commonly unsatisfactory, and few of the published diagrams merit the connotation "stable equilibrium.'

The purpose of the present discussion is to outline, with selected examples, the basis and limitations of the synthetic method of determining equilibrium and to indicate some other methods. This discussion, while being critical, is not intended to detract from the value of experimental data which have been accumulated. When these data are surveyed it is evident that we now

[1] Manuscript received March 14, 1960.

have a broad picture of the stability relations of some metamorphic minerals—a much clearer picture than we had prior to 1950.

The study of dry melt systems will not be considered here but has recently been reviewed by Roedder (1959), who has been most careful to discuss the difficulties associated with establishing equilibrium.

Experiments designed to give information regarding the fields of stability of mineral phases or phase assemblages upon a P-T or P_{H_2O}-T diagram fall into several distinct categories:

1. Direct synthesis of mineral phases
2. Measurement of vapor pressure during reactions involving a gas phase
3. Reversible reactions between minerals and destruction of minerals
4. Measurement of relative solubilities of two alternative chemically equivalent phases over a range of P and T
5. Differential thermal analysis
6. Calorimetric measurements of heat capacities and heats of reaction

The merits and limitations of each of these methods will now be reviewed.

DIRECT SYNTHESIS OF MINERAL PHASES

THE PHYSICOCHEMICAL BASIS OF THE SYNTHETIC METHOD

Most data on fields of mineral stability have been obtained by synthesis of phases or phase assemblages. The normal procedure is to allow some arrangement of components giving the desired composition to react for sufficient time at a constant pressure and temperature until new phases have appeared

and the reactants disappeared. The time allowed for this process by most experimenters has been of the order of days and seldom more than a few weeks. In a typical reaction $A \leftrightarrows B$, it is found that A forms from the mix at some temperature (say 290° C.) lower than that at which B forms from the same mix (say 310°) and the equilibrium temperature is assumed to be near the mean temperature (300°). The rates of most reactions involving silicates are sufficiently sluggish for quenching to preserve the state of the solid phases as they existed at the elevated P and T of the experiment.

What is the basis for considering that syntheses of this kind indicate conditions of equilibrium? Consider the problem of determining the equilibrium temperature of the reaction

$$A(H_2O) \leftrightarrows B + H_2O$$
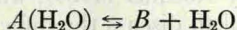
at a water pressure of 1,000 bars where $A(H_2O)$ and B are complex silicates. The starting material for the synthetic study may be, for example, a glass, or possibly a mixture of oxides chemically equivalent to B. If the oxide mix is chosen, then to facilitate reaction, the components selected are in a highly reactive state, perhaps coprecipitated gels. The free-energy relations may be as indicated in figure 1. The starting materials must be less stable than either $A(H_2O)$ or B in the region of the equilibrium temperature, and the formation of either represents a decrease in free energy of the system. The phase which forms initially depends not on the position of the equilibrium temperature but rather on the competition between two rate-controlling processes: the rates of nucleation and rates of growth.

If the metastable phase preferentially forms nuclei and grows, its transformation to the stable phase depends to some extent on differences between the lower curves of figure 1. The same factors of nucleation
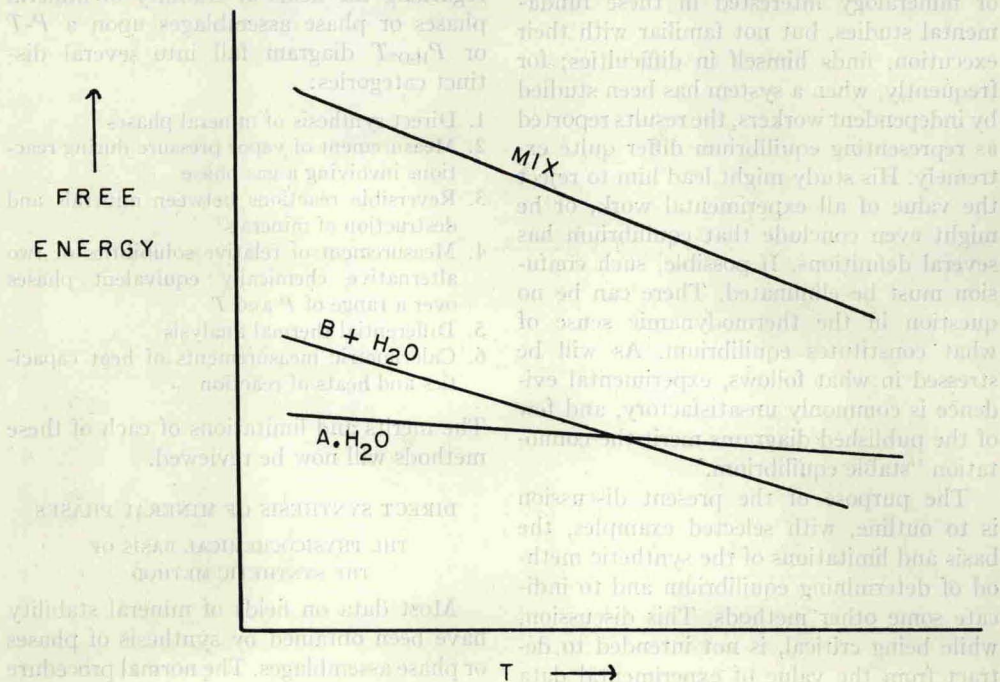

FIG. 1.—Possible free-energy relations between a reactive oxide mix and two crystallization products $A \cdot H_2O$ and B at constant pressure. The intersection of the lower lines occurs at the equilibrium temperature of the reaction $A \cdot H_2O \rightarrow B + H_2O$. Data in table 1 provide some indication of the separation of these curves.

and growth again are effective. But for rapid reaction there must be some significant difference between the two curves, and significant supersaturation is necessary. This implies that transformation of $A(H_2O)$ to B, or vice versa, is likely to be a slow process near the equilibrium temperature. At large distances from this equilibrium temperature there is a much better chance of the stable phase forming. It would be fortuitous if the kinetic factors should so change at the equilibrium temperature that a true boundary of equilibrium could be obtained by such a synthesis; it is much more likely that one phase will appear over too wide a range. Ostwald's step rule, so commonly illustrated in synthesis, emphasizes this point.

port the principle. Unpublished data of the writer indicate that epidote is stable relative to its high-temperature breakdown products in much of the region studied by Ehlers (1953).

It should be noted that a fundamental difference exists between most studies of dry melts and those systems considered here. In dry-melt studies the common starting material is a homogeneous glass. The free-energy relations of this system would be similar to those indicated in figure 1 if the curve for $B + H_2O$ represents glass, and the curve for $A \cdot H_2O$ represents the solid phases. The important feature is that, near the melting point, the glass does not have the large "excess free energy" that is characteristic of the mix. Crystallization of met-

TABLE 1

FREE ENERGY OF FORMATION OF STABLE AND METASTABLE EQUIVALENTS FROM TYPICAL STARTING MATERIALS AT 298° K

Reaction	$\Delta G°$ (kcal)	Ref.*
SiO_2 (glass)$\rightarrow SiO_2$ (cristobalite)	-1.2	a
SiO_2 (glass)$\rightarrow SiO_2$ (quartz)	-1.5	a
$CaO+SiO_2$ (glass)$\rightarrow CaSiO_3$ (wollastonite)	-22.9	a
$CaO+SiO_2$ (glass)$\rightarrow CaSiO_3$ (pseudowollastonite)	-22.1	a
$2MgO+2SiO_2$ (glass)$\rightarrow 2MgSiO_3$	-21.98	a
$2MgO+2SiO_2$ (glass)$\rightarrow Mg_2SiO_4+SiO_2$ (quartz)	-19.5	b
$CaO+CO_2$ (gas)$\rightarrow CaCO_3$ (calcite)	-31.12	a
$CaO+CO_2$ (gas)$\rightarrow CaCO_3$ (aragonite)	-30.87	a

* References: (a) Rossini et al. (1952); (b) Fyfe et al. (1958) p. 23.

In table 1 free energies of formation of some phases from oxide mixes are shown. It will be noted that the free-energy differences between stable or metastable phases are normally trivial compared with the free energy of formation from the oxides. It is not surprising, for example, that aragonite can be easily grown where calcite is stable.

Goldsmith (1953) has stressed the relation between structure and ease of crystallization in his simplexity principle which suggests that phases with a large entropy will crystallize with greater ease than equivalent low-entropy phases. With some of the cases discussed by Goldsmith (e.g., jadeite), it is now known that failure to crystallize in early studies was due to experimental conditions being outside the fields of stability. But many cases (e.g., epidote) sup-

astable phases from the glass near the melting point is likely to be much less common, but it is not impossible. Further, all barriers dependent on transfer must be reduced at elevated temperatures.

STARTING MATERIALS IN SYNTHESIS

The master of chemical synthesis is the organic chemist, and perhaps the geologist has learned too little from his experience. In a typical issue of *Chemical Abstracts* there will be about twenty compounds listed with formula $C_4H_8O_2$. It is probable that an organic chemist could synthesize many of these at 1 atmosphere and the boiling point of alcohol, yet many will be metastable. The remarkable array of organic compounds results in part from the shrewd choice of arrangement of carbon atoms which the

chemist looks for in his starting materials. There are differences in the two problems, but perhaps some experimental geologists have been slow to realize that they can completely change the products of a synthesis by changing the type of starting materials.

What factors have commonly determined the choice of starting materials in experimental studies on mineral equilibria? There is little doubt that impatience and longevity are influential. Barrer (1950), while studying silicate synthesis, was one of the first to make extensive use of coprecipitated gels, and found that phases such as orthoclase (probably disordered) could be synthesized at temperatures below 200° C. in hours. With such materials crystallization of phases is readily achieved, but the chance of these phases being metastable is maximal. Unfortunately, the second stage, transformation of the metastable to the stable form, may be a much less facile reaction and require times of a different order of magnitude. Observation that A crystallized in 5 hours and remained unchanged for 5 weeks may appear at first glance strong evidence that A is already at the bottom of the energy well; but common experience indicates that this line of reasoning may be invalid (e.g., persistence of metastable cristobalite and boehmite and disordered feldspars).

In choosing starting materials for synthesis, there is clearly an impasse. The most reactive materials, while sometimes producing stable phases, are also likely to produce metastable phases. The most desirable materials are likely to be so low in free energy that they do not react in a reasonable time. There are, however, ways of bypassing this situation, which will be mentioned below.

In recent synthetic studies, it is becoming a common practice to employ a variety of starting materials of the same bulk composition. Inspection of the products from each may indicate that one material produces phases more compatible with petrological observation than the others and hence may be producing equilibrium products. However, such selection of the "best" results is unsatisfactory and only emphasizes the fundamental limitations of the synthetic method. To quote from careful work on muscovite by Yoder and Eugster (1955): "It should be clearly stated that considerable judgment on the part of the experimenters is involved in the interpretation of the results." In the same paper the statement "although it is common for minerals to grow metastably below their stability limit, metastable growth above their stability limits has not been observed" implies judgment with which this writer does not agree. The statement accords with the common synthesis of cristobalite in the quartz stability field and the failure of quartz to appear in the cristobalite field; but it conflicts with the equally common formation of aragonite in the calcite stability field. Working irrationally on the above assumption, the writer previously identified the maximum temperature at which analcime could be synthesized as the temperature of univariant equilibrium for the reaction, analcime + quartz $\leftrightarrows$ albite + water. Subsequent work on kinetics proved this judgment invalid. The low-temperature assemblage, analcime + quartz, grows in the region where the high-temperature phase albite is stable.

PROOF OF EQUILIBRIUM IN SYNTHESIS

An equilibrium boundary between two phases A and B exists only if A can be converted to B and B to A by infinitesimal changes in P or T from the values given by the boundary curve. In practice, reaction rates become appreciable only when P or T depart widely from the equilibrium value, if reaction is anticipated in short times of days or weeks.

Yoder and Eugster (1955) showed that the reaction

muscovite $\leftrightarrows$ sanidine + corundum + water

goes from left to right at 650° C. and from right to left at 350° C. at $P_{H_2O} = 15,000$ psi. The equilibrium boundary is between

these values. In discussing the quartz-coesite boundary, MacDonald (1956) is careful to point out that "in order to demonstrate that this curve is actually the equilibrium curve, a detailed study should be made using coesite as a starting material and showing that coesite converts to quartz at pressures lower than those given by the curve." Another example, from Ervin and Osborne (1951), illustrates the point further. They state: "there is only one rigorous criterion for equilibrium . . . if while pressure and temperature remain constant, the crystals of one phase grow while crystals of a second phase disappear, then the first phase is stable with respect to the second." They continue: "therefore, this straightforward method fails, and the criterion set up for equilibrium is too rigorous for practical application in studies of this system." It is obvious that experimental workers are well aware that grave difficulties of this kind exist and in many instances have not yet been overcome. But the phase diagrams continue to be labeled erroneously as equilibrium diagrams with the added implication that the equilibrium is stable.

It is perhaps necessary to restate that an equilibrium boundary may correspond to metastable equilibrium. For example, A may be converted to B and vice versa, although there may exist a third phase C with lower free energy than either A or B. A phase or phase assemblage is in its stability field when the free energy of that phase or assemblage is lower than any equivalent phase or assemblage. Absolute proof that an assemblage is stable rather than metastable, and that a stability field is not a metastability field, is impossible (see Turner and Verhoogen [1960], p. 6–40). Excellent examples of metastable equilibria are demonstrated by Jamieson (1957) in his studies of the polymorphism of $CaCO_3$ at high pressure.

Example 1: Polymorphism of SiO_2.—Consider crystallization of amorphous silica over a temperature range of 300°–600° C. at water pressures of 100 to 3,000 bars. There is a low-temperature region within which cris-

tobalite crystallizes and a high-temperature field of quartz. The position of the quartz-cristobalite boundary (F. W. Dickson, unpublished data) depends upon the duration of the experiment (e.g., in fig. 2, curve A might be the boundary for runs of 3 days, and curve B the boundary for runs of 3 weeks). If the sample is contaminated with alkali, quartz is formed in short experiments at low temperatures. Clearly, such results have little bearing on the stability relations of the polymorphs of silica; rather, they demonstrate the overshadowing influence of nucleation in determining which phases will crystallize in a given environment.

Kinetic studies (Carr and Fyfe, 1958) show that the progress of the reaction

amorphous silica $\rightarrow$ cristobalite $\rightarrow$

silica-K $\rightarrow$ quartz

is relatively insensitive to temperature but sensitive to pressure. In the absence of catalysts, it may take months or years to convert cristobalite to quartz several hundred degrees below the upper stability limit of quartz.

In accounts of synthetic investigations of silicate systems, not infrequently cristobalite is listed as one of the constituent phases of so-called "equilibria," crystallized at temperatures within the stability field of quartz. Such data are immediately suspect as including assemblages known to be metastable.

Example 2: The system $MgO-H_2O$.—Although a half-dozen papers on the system $MgO-H_2O$ have been published in the past nine years, the boundary between brucite and periclase has not been fixed with the precision merited by the accuracy now possible in control and measurement of pressure and temperature.

The first synthetic study was made by Bowen and Tuttle (1949), using the now familiar hydrothermal quenching apparatus. The starting materials used were brucite and periclase, so that equilibrium was approached from two directions. Their results, based on five experiments of two to there

hours' duration, are reproduced as curve *A* in figure 3.

Roy, Roy, and Osborne (1953) used the same technique as Bowen and Tuttle, starting with a variety of natural and synthetic samples of brucite and periclase. Their equilibrium curve (*B* of fig. 3) is nearly 300° C. below that of Bowen and Tuttle. It is apparent that in the work of Bowen and Tuttle, either brucite persisted far above its stability limit, or periclase that had formed in some runs reverted to brucite during quenching. From the experience of Roy *et al.*, the latter alternative seems the more likely. As they had maintained the water pressure throughout the whole experi-

ment, including the quenching, it is further possible that the temperatures of their boundary might also be too high. Roy and Roy (1957) reinvestigated the system using both temperature and pressure quenching (i.e., the pressure was dropped simultaneously with the temperature). Their runs were as long as 168 hours, and they concluded that the work of 1953 was little in error. However, in this writer's opinion, a difficulty remains in that phases assumed present during the experiment might not be preserved during quenching, for release of pressure during quenching would allow reversion of brucite to periclase. Hence phase identification is based on textural evidence.
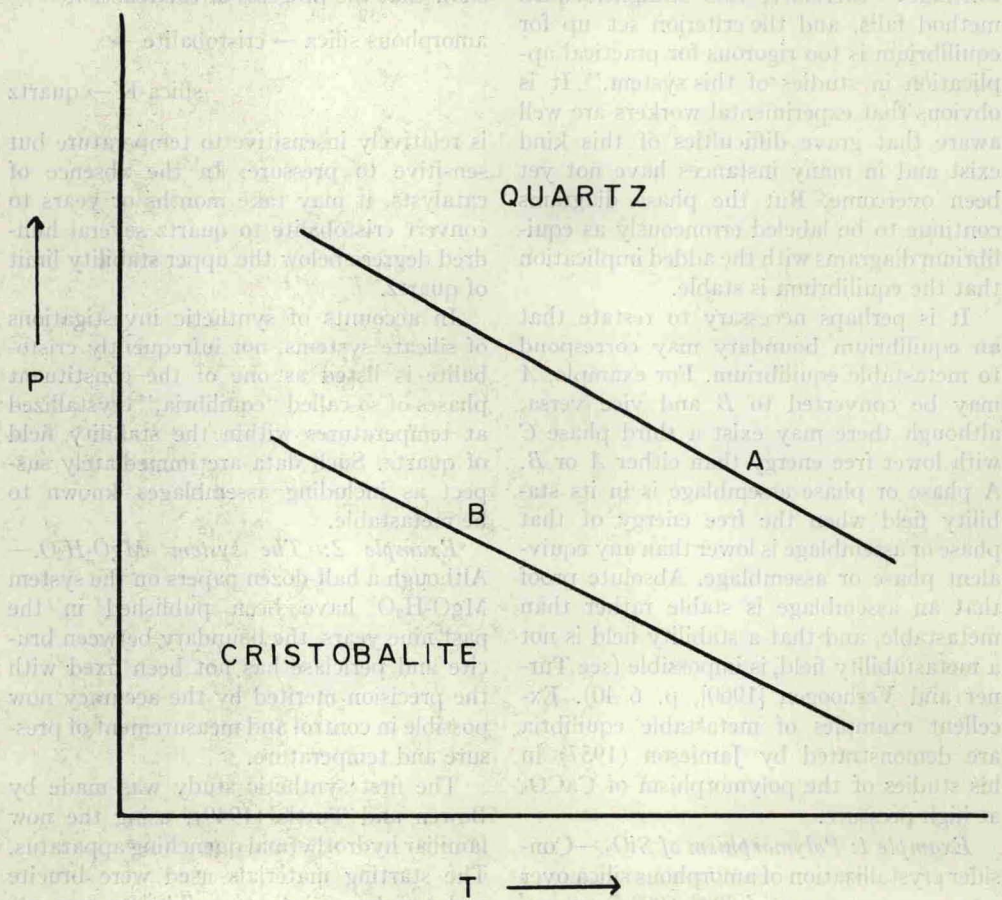
FIG. 2.—Phases synthesized from amorphous silica at low temperatures. Curve *A* might be that found when the experimental time is three days; curve *B* when this time is three weeks. Additional complexity due to regions where silica-*K* and tridymite may form are omitted.
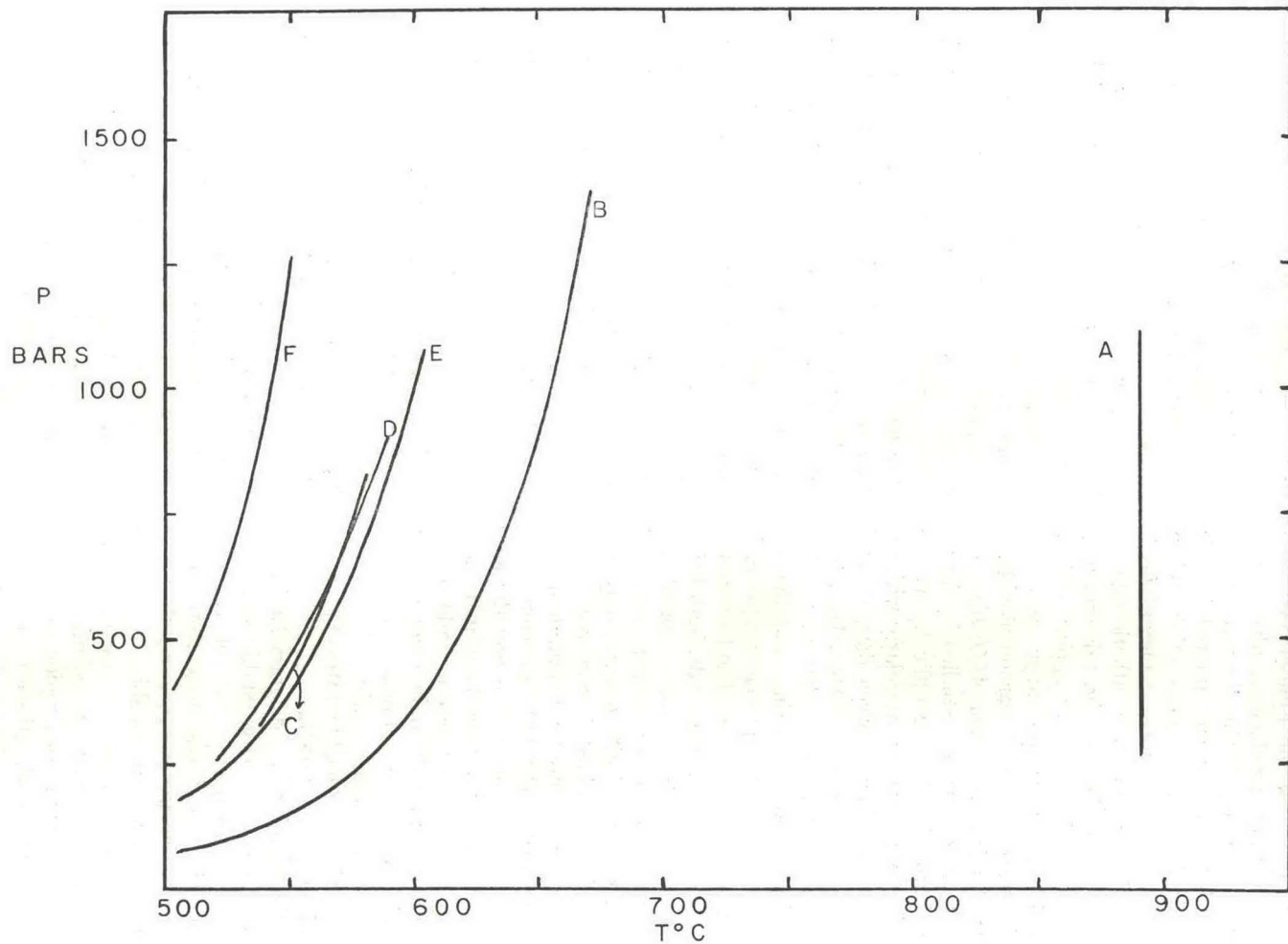
FIG. 3.—"Equilibrium" curves for the reaction brucite → periclase + water. Curve *A* from Bowen and Tuttle (1949); *B* from Roy, Roy, and Osborne (1953); *C* from Fyfe (1958); *D* from Kennedy (1956); and *E* and *F* from thermodynamic calculations of MacDonald (1955). The differences in curves *E* and *F* are attributed to effect of particle size.

As will be discussed later, subsequent work by Kennedy (1956) and Fyfe (1958), using different methods, produced results indicating even lower "equilibrium" temperatures.

A major difficulty encountered in this system is due to speed of reaction. When reaction rates become comparable with feasible quenching rates, the synthetic method loses sharpness. Fortunately, this difficulty seldom arises. It probably applies mainly to reactions in two-component systems, such as oxide-water and oxide-carbon dioxide.

Example 3: The system Al_2O_3-H_2O.—In this system, extensively studied by Ervin and Osborne (1951), the difficulty is one of nucleation; it arose particularly with regard to equilibrium between diaspore and boehmite, polymorphs of $Al_2O_3 \cdot H_2O$. The writers were well aware that metastable crystallization was occurring, and the observations they made represent a reproducible phenomenon. Alumina gel and γ-alumina were used as starting materials, both being unstable species. To obtain reasonable results, it was found necessary to add seed crystals. In the majority of runs, only diaspore seeds were added, but in some, seeds of diaspore, boehmite, and corundum were used. As Ervin and Osborne emphasize: "the possibility of metastable growth under these conditions must be kept in mind." If seeds of only one phase are added, the experiment is prejudiced in favor of that phase. If seeds of several phases are added, in a short run the phase which dominantly forms will be controlled by rates of propagation of nuclei and growth.

In their equilibrium diagram Ervin and Osborne indicate a large stability field of boehmite. Subsequent work of Kennedy (1959), who had access to entropy data, presents convincing evidence that the phase boehmite is always metastable although this might be impossible to prove by direct synthesis. The conversion of boehmite to diaspore in the low-pressure region would take excessive time in the absence of diaspore seeds, but with long runs Kennedy was able to form diaspore from boehmite-diaspore mixtures in the region of boehmite synthesis.

Example 4: The system $NaAlSi_3O_8 + SiO_2 + H_2O$.—In this system, neglecting the high-pressure field of jadeite + quartz, only three phases are known to occur with free quartz, namely, albite, analcime, and sodium-mordenite. Reasoning purely from the respective water contents, we might expect that at low temperatures mordenite would be stable, followed by analcime and albite at high temperatures. What relations have been found experimentally?

Barrer and White (1952) studied the crystallization of highly reactive gels, which in some cases had been dried or thickened by evaporation so that in all probability they would contain nuclei. From the most siliceous composition Barrer found that at low temperatures analcime dominated; at 210° C. mordenite was the major phase, and this in turn passed to albite at 360° C. Some analcime was erratically scattered through reaction products dominated by mordenite. Fyfe (1955), using an oxide mix, found a low-temperature field of mordenite, which at 220° C. was succeeded by analcime which in turn passed to albite at 300° C. The analcime-albite boundary was diffuse; but for no good reason the upper limit of analcime was selected as the defining criterion. Barrer and Fyfe used short-run times.

Subsequently, more detailed work was reported in Coombs, Ellis, Fyfe, and Taylor (1959). A study of kinetics indicated that analcime was the phase tending to grow metastably in the albite field, and accordingly, the analcime-albite boundary was reduced to 280° C. in agreement with findings of Sand, Roy, and Osborne (1957). Coombs *et al.* found that with oxide mixes containing amorphous silica, mordenite again appeared as the stable phase up to 230° C. But when quartz was substituted for the more reactive amorphous silica, mordenite was not found at temperatures as low as 115° C., and analcime was synthesized. In mixes where sodium bicarbonate was used as the source of soda, mordenite was synthesized up to 275° C., above which albite became stable. Although one may attempt to explain these observations (cf. Coombs *et al.*), it is clear from this array of data that our understanding of

the equilibrium relations between mordenite, analcime, and albite remains confused. The nature of the starting material profoundly influences the product synthesized. Clearly, some other approach would be desirable.

Example 5: The system $CaAl_2Si_2O_8 + SiO_2 + H_2O$.—Coombs *et al.* (1959) used some dozen starting materials in runs of around 30 days' duration. A high-temperature dehydration reaction

wairakite $\rightarrow$ anorthite $+$ SiO_2 $+$ water

was consistently found, but the reaction temperature varied by as much as 150° C., and the width of the wairakite field varied by as much as 80° C. Epistilbite, or calcium mordenite, depending on the reactivity of the initial mix, appeared in the low-temperature field. The common natural lime zeolites, laumontite and heulandite, failed to appear at all. It was found that in runs of a week's duration wairakite would form and persist at temperatures where anorthite and quartz would be produced if the runs were of a month's duration. Moreover, even in runs of a month's duration, cristobalite was present among some of the reaction products.

SYNTHESIS AT HIGHER TEMPERATURES

The situation is only partly improved at higher temperatures, even though reactions might be expected to proceed faster. In work involving synthesis of aluminum silicates and hydrates from the composition Al_2O_3-$4SiO_2$, Carr and Fyfe (in press) have found that three different starting materials produce three different fields of synthesis. The upper limit of pyrophyllite at 15,000 psi varies from 440 to 530° C., and the higher-temperature phase produced is either mullite, corundum, or an andalusite-like phase (all with quartz). From some starting materials pyrophyllite could be synthesized at temperatures where, with longer runs, synthetic pyrophyllite produced the andalusite-like phase. Other workers have also reported different products. In the low-pressure region Roy and Osborne (1954) report mullite as the decomposition product

of pyrophyllite; Kennedy (1955) reports a mullite-sillimanite solid solution; and Roy (1954) has synthesized andalusite.

Yoder and Eugster (1955) used seven starting materials for work on the reaction

muscovite $\leftrightarrows$ sanidine $+$

corundum $+$ water .

At 15,000 psi water pressure, the upper limit of muscovite was found to vary from below 600° C. to above 650° C. This range of 50°$+$ may not appear large, but it is perhaps of the same order as the span of some facies or subfacies. The same writers' work on phlogopite (1954), where the stability limit of phlogopite is above 1,000° C., is not free from evidence of disequilibrium in synthetic results. Yoder and Eugster state that "great care had to be exercised in evaluating the data." In some runs, mixtures of phlogopite and its breakdown products were synthesized more than 300° C. below the evaluated upper stability limit.

SYNTHESIS AT HIGH PRESSURES

A number of synthetic studies have recently been carried out at pressures of more than 10,000 bars. In some (Robertson, Birch, and MacDonald, 1957) the experimental apparatus is basically similar to that used at lower pressures. Many other results have been obtained from the squeezer apparatus (Griggs and Kennedy, 1956). From experience with the alumina-water and silica systems, it might be expected that high pressures would facilitate attainment of equilibrium. However, in most systems considered, the desired transformation involves conversion of metastable low-density phases to stable high-density phases. It would seem likely that the nucleus of a dense phase would be smaller than that of a less-dense phase and that the ΔV^* of nucleation would be such as to favor metastable nucleation of dense phases at high pressures. As yet, there have been too few experiments described to come to any conclusions. The writer's limited experience with the squeezer-type apparatus has, however, indicated that the problem of starting materials may

be just as critical at 15,000 bars as at lower pressures.

Most workers in the very high P-T region have been able to demonstrate reversibility under the extreme conditions used. Often the region of reversibility is tied into a region at lower temperatures where normal synthesis is used. It should be stressed that the two sets of data should converge if the time factor is comparable, but this convergence does not necessarily prove that equilibrium was established in the synthesis at lower temperatures.

DIRECT MEASUREMENT OF VAPOR PRESSURE

There are few mineral systems where direct measurements of vapor pressure are possible, and these will be systems where rather limited chemical rearrangement is involved. More complex reactions tend to be sluggish, and there are difficulties associated with such measurements over prolonged times. This method is likely to prove superior to synthetic methods, at least for simple systems, when quenching becomes difficult. A system such as MgO-H_2O is typical.

Direct measurements of the vapor pressures of brucite-periclase mixtures have been made by Giauque and Archibald (1937), Kennedy (1957), and Fyfe (1958). All were impressed by the sluggish attainment of equilibrium, attributed to either adsorption or aging of the crystalline products. This work has done much to indicate the importance of grain size on the position of an equilibrium boundary. Giauque (1949) has discussed this problem in detail. Curves C and D of figure 3 represent the findings of Kennedy and Fyfe. It will be noticed that, as expected, the equilibrium curves from direct measurements are at lower temperatures than all obtained by synthesis.

REVERSIBLE CONVERSION OF MINERAL
PHASES AND DISAPPEARANCE OF
PHASES FROM MIXTURES

If the equilibrium temperature of a reaction $A \rightleftharpoons B$ is to be determined at pressure P, a simple method, in principle, is to take a mixture of A and B and find at what temperatures only A or B remains. The method is beset by formidable difficulties associated mainly with extreme slowness of reactions. This writer is convinced, however, that valuable and reliable results can be obtained if the experimenter is willing to make experiments of months and not days. Bowen and Tuttle (1949), who used minerals extensively as starting materials, illustrate the method in their study of the reaction

$$talc \rightleftharpoons enstatite + quartz + vapor \ .$$

They succeeded in producing talc from the right-hand assemblage at 750° C. and 15,000 psi and produced enstatite + cristobalite from talc at 800° C. and 15,000 psi. The equilibrium temperature for the reaction must be above 750° C. and below 800° C.

Kennedy (1959) was able to show that, if sufficient time is allowed, a mixture of diaspore and boehmite produces diaspore in the region where boehmite tends to appear metastably. The writer has found that at 300° C. a mixture of albite + quartz + analcime produces only albite, while the same mixture at 250° C. is unchanged in runs of 3 months. The latter result provides no information, but the former provides as much useful information as scores of synthesis runs. If a mixture of A and B is used, results may be obtained in a reasonable time, which would not be obtained if A or B were left to recrystallize by themselves. An excellent example of the use of this method is provided by Tuttle and Bowen (1958) in their study of the quartz-tridymite equilibrium. If the mixture is used, the nucleation barrier is removed, and the course of crystallization depends on the different solubilities of the two phases, the stable phase having the lower solubility. The only barrier to reaction involves the transfer of material.

Much less complete, but at times useful, data relate to destruction of a mineral phase. This approach sets a maximum limit to the stability. Yoder and Eugster (1954) made extensive use of data on the decomposition

of phlogopite in their study of this system.

Finally, it must be stressed that, while work on mixtures of phases A and B may show which phase is realtively more stable at various points in the P-T field, it must always be remembered that some other phase, or phases, may actually be more stable.

SOLUBILITY MEASUREMENTS

The solubility of a stable phase or assemblage at any give T and P is less than that of a chemically equivalent metastable phase or assemblage in the same solvent. What is necessary for the use of this criterion of relative stability is some sensitive method of measuring solubilities. If complete conversion of mixtures is possible, there is no doubt that the results are convincing. Where reactions are extremely sluggish, relative solubilities indicate the directions in which a reaction is proceeding at a given temperature, even though complete conversion of mixtures is not possible in a reasonable time. Jamieson (1953) studied the calcite-aragonite equilibria, using conductance of the solutions of each as an index of solubility. Dickson and Tunell (1958) also indicate how the method could be used to obtain stability relations of the mercury sulfides. The writer is currently investigating the relative solubilities of quartz and albite in water in the presence of analcime, with a view to defining the equilibrium:

analcime $+$ quartz $\leftrightarrows$ albite $+$ water .
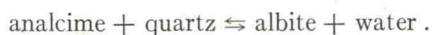
Gain or loss of weight of each phase in a fixed time is plotted against temperature, and the resulting curves show inflections at a point fixing the temperature of equilibrium.

DIFFERENTIAL THERMAL ANALYSIS

The study of D-T-A curves has been used to a very limited extent in defining stability limits. From much of the preceding discussion it is obvious that D-T-A methods can be useful only for very fast reactions, such as the α-β quartz transition. and not

for reconstructive reactions. With more sluggish reactions difficulties mentioned above are intensified, and in such cases D-T-A can provide only extreme limits usually far removed from equilibrium. Harker and Tuttle (1955) found that the results of Smyth and Adams (1923) on the dissociation of calcite, based on D-T-A data, are possibly in error by as much as 100° C. for these reasons. In this system direct measurement of vapor pressure might be desirable.

CALORIMETRIC METHODS

To construct a complete P-T equilibrium curve for a given reaction, $A \leftrightarrows B$ from thermal data, we require:

a) the heat of reaction at a given temperature;
b) heat capacities of A and B from 0° K to the range of temperature under consideration (these data provide the entropy of reaction);
c) molar volumes of A and B (if precise data are needed, thermal expansion and compressibility data as well);
d) P-V-T data for the gas, if a gas phase is involved.

Inspection of the results of the careful study of the reaction

nepheline $+$ albite $\leftrightarrows$ 2 jadeite

by Kracek, Neuvonen, and Burley (1951) indicates that the source of the large uncertainty in the final results is related in large part to possible errors in determination of the heat of reaction. This in turn is related to the difficulty of obtaining suitable samples of the materials for study. The importance of grain size of samples is apparent in MacDonald's (1955) calculations of the brucite-periclase equilibrium.

In favorable cases the precision with which heats of reaction of pure phases can be measured (e.g., by measuring heats of solution of reactants and products in some solvent) is very high. With quartz a heat of solution in hydrofluoric acid of some 33,000 calories has an uncertainty of only 20 cal., and (from personal communication with K. K. Kelley) this can be reduced to 10 cal. But in the case of albite two

samples measured by Kracek *et al.* differed by 1670 cal., a difference which is most serious in the resulting free energies of reaction. The uncertainty contributed by error in calculation of entropy is much less serious.

There is no doubt, however, that the final results obtained by Kracek *et al.* have been invaluable in guiding experimental studies on the jadeite problem. Direct experiments have confirmed that the calculated curves are reliable within the limits of error stated. MacDonald's (1955) calculations of the brucite-periclase equilibrium have also shown that thermal data (which in this case could certainly be improved) provide results comparable with experimental studies. These curves, *E* and *F*, are shown in figure 3, along with those from other methods of study.

Clearly, if the calorimeter is to provide more useful data, the sample problem must be resolved. One approach might be to carry all impurities through the set of measurements. If the heat of a complex reaction such as

zoisite ⇋ anorthite + gehlinite +

wollastonite + water
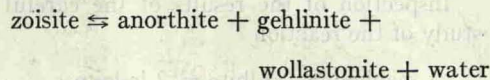
is required, rather than attempt to find pure samples of each phase, the heat of solution of some natural specimen of zoisite might first be measured; then the zoisite could be thermally decomposed to anorthite, etc., and the heat of solution of this aggregate of identical (non-volatile) composition could be measured. This approach would provide data applicable only to the given sample of unique composition. In the study of petrological problems this limitation may prove advantageous, for we are concerned with the stability of minerals rather than pure phases of ideal composition.

In reactions involving a volatile phase, errors in thermal data are least significant at low pressures, where the entropy of the gas is large. Thus in regions where direct synthesis or measurement of vapor pressure is most difficult, the thermodynamic data are most precise. In this low-pressure region

there is little doubt that in reactions involving CO_2, H_2O, etc., the calorimeter can produce results superior to those obtained by synthesis.

CONCLUSIONS

Some general conclusions which emerge from this discussion are as follows:

1. Conditions of experimental synthesis need not necessarily reflect conditions of stability. Unless revesibility of reactions is rigorously established, synthetic results should not be considered as equilibrium results.
2. In synthetic studies different starting materials of the same bulk composition commonly give significantly different results, and the equilibrium relations cannot be deduced with certainty.
3. Starting materials with a very large free-energy relative to products are undesirable if the object of the experiment is to establish equilibrium. Even excessively fine-grained materials may be undesirable because of large surface energies. (It should be noted that, as liquid and solid phases are similar in free energy in regions near the melting point, a glass will be a desirable starting material for high-temperature synthesis.)
4. Synthesis results in systems where experimentally formed phases cannot be preserved by quenching are subject to the uncertainties of interpretation of textures.
5. The study of reversible conversion of mixtures of minerals involved in a reaction may provide reliable, even if broad, limits of stability. The "normal" length of experiments needs to be increased in many cases.
6. Determinations of relative solubility of alternative phases over a range of *P* and *T* may provide a sensitive method of finding conditions of stability of the phases in question.
7. Use of the calorimeter to determine heats of reaction and of solution should be extended to provide critical thermodynamic data bearing on mineral equilibria.
8. Every equilibrium curve should be tested through consideration of available thermodynamic data and by thermodynamic arguments. Entropy changes can be estimated with reasonable precision (Fyfe *et al.*, 1958), and with volume data allow a check on values and signs of slopes in differen *P-T* regions.

In the development of any field there is a time of reconnaissance followed by a period in which more precise data are sought. In experimental petrology, this time has arrived. If we are to progress to the assignment of more exact conditions of stability in more complex systems, then we must look critically and intelligently at experimental results and methods. The term "equilibrium diagram" should not be used unless it is reasonably justified by both experimental and geological criteria. Where, as has commonly happened, experimental results conflict with inferences based on geological observations, the experimentalist has a special responsibility to scrutinize and state clearly the limitations of his laboratory procedure.

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