

HYDROTHERMAL SYNTHESIS AND DETERMINATION OF EQUILIBRIUM BETWEEN MINERALS IN THE SUBLIQUIDUS REGION¹

W. S. FYFE

University of California, Berkeley

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

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.

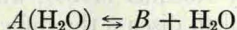
DIRECT SYNTHESIS OF MINERAL PHASES THE PHYSICOCHEMICAL BASIS OF THE SYNTHETIC METHOD

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

¹ Manuscript received March 14, 1960.

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 $A \rightleftharpoons B$, 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



at a water pressure of 1,000 bars where $A(\text{H}_2\text{O})$ and B are complex silicates. The

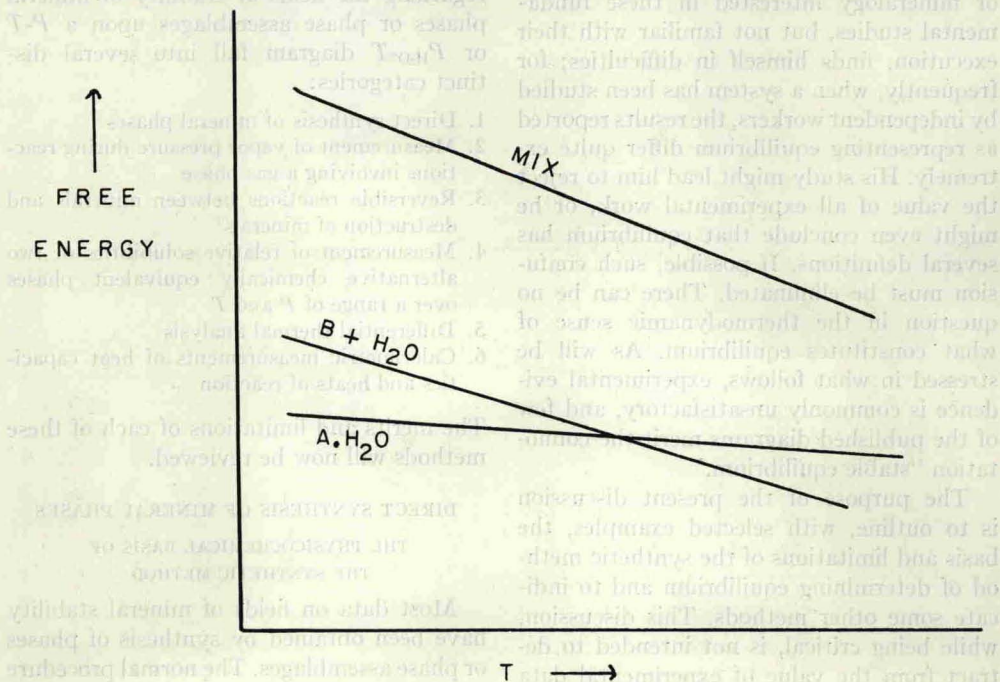


FIG. 1.—Possible free-energy relations between a reactive oxide mix and two crystallization products $A \cdot \text{H}_2\text{O}$ and B at constant pressure. The intersection of the lower lines occurs at the equilibrium temperature of the reaction $A \cdot \text{H}_2\text{O} \rightarrow B + \text{H}_2\text{O}$. Data in table 1 provide some indication of the separation of these curves.

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 $A(\text{H}_2\text{O})$ 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