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 .
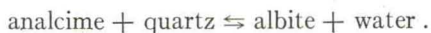
Gain or loss of weight of each phase in a fixed time is plotted against temperature, and the resulting curves show inflections at a point fixing the temperature of equilibrium.

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 $\leftrightarrows$ anorthite + gehlinite +

wollastonite + water
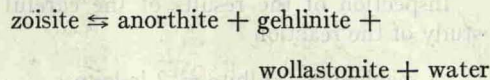
is required, rather than attempt to find pure samples of each phase, the heat of solution of some natural specimen of zoisite might first be measured; then the zoisite could be thermally decomposed to anorthite, etc., and the heat of solution of this aggregate of identical (non-volatile) composition 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.