Most geologic processes take place in the crust and upper mantle in the presence of one or more fluid phases, and the composition of the fluids may vary widely from one environment to the next. Not surprisingly, little experimental information is available on the physical and chemical properties of even the most simple of geologically relevant fluids over the complete range of temperature, pressure, and composition conditions present in these environments. This lack of data may be attributed to the extreme difficulty, time, and highly-specialized apparatus often required to obtain this information using conventional experimental techniques. Perhaps the major limitation, however, has been the inability to satisfactorily sample the fluids present in experiments at elevated temperatures and pressures (also discussed in Chapter 18). Sampling is a particularly difficult problem when the fluid of interest is saturated in one or more fluid or solid phases at experimental conditions, or if it becomes saturated during sampling or cooling to ambient conditions.

Recently, Steiner and Bodnar (1984) described a technique for sampling fluids at elevated temperatures and pressures that eliminates, or at least minimizes, many of the problems associated with other, more conventional techniques. With this technique, small amounts of the fluid, or fluids, present at experimental conditions are trapped by healing fractures in quartz.
to form synthetic fluid inclusions. Numerous tests showed that the trapped fluid in the system C-O-H-S-Na-K-Cu-Cl-Cu-Fe is identical in composition and density to the fluid present at experimental conditions. Moreover, the synthetic fluid inclusions preserve this fluid during quenching to ambient conditions, thus providing a representative sample of the fluid that was present at experimental conditions. By analyzing the fluid inclusions using standard microthermometric techniques, a variety of fluid properties representing a wide range of P-T-X trapping conditions may be easily determined. In this chapter, we describe in detail the procedures for synthesizing fluid inclusions and describe several applications of synthetic inclusions in experimental geochemistry.

EXPERIMENTAL PROCEDURE

The procedures used to produce synthetic fluid inclusions were developed mostly through trial-and-error experimentation. The discussion that follows describes these procedures in detail and was written with the newcomer to the field of hydrothermal experimentation in mind, so that others may avoid many of the problems we encountered in the development of this technique. The procedures apply specifically to the formation of synthetic fluid inclusions in quartz. However, these same procedures, perhaps with minor modifications, may be used to trap inclusions in other host phases for those applications where quartz might not be suitable.

The starting materials used in this study were large, inclusion-free Brazilian quartz crystals obtained from the Pennsylvania State University College of Earth and Mineral Sciences Mineral Museum. The crystals were cut into 2-3 cm thick slabs, and ~4 mm diameter cores were cut from the slabs using a diamond coring tool.4

During coring, the quartz must be securely attached to the stage of the drill press to avoid breaking the cores or damaging the coring tool. This was accomplished by first mounting the quartz slab on a silica firebric with Lakeside cement and then attaching the brick to the drill press with two large clamps. With the slab thus firmly attached, the quartz was cored using a cutting speed of ~700 rpm with water as the coolant. By applying a constant, smooth, up-and-down motion (rather than applying constant force to the cutting surface), an unbroken core 2-3 cm long was easily obtained in less than 5 min. After cutting the cores, each was examined to verify that it was free of Lakeside cement; any remaining cement was easily removed with a razor blade and methanol. The cores were then cleaned in distilled water in an ultrasonic bath.

4 Diamond core drill model number 14052 available from Kingsley North Inc., Norwalk, Michigan.
The cleaned cores were fractured by heating them to 350°C in an oven and, immediately upon removal from the oven, immersing them in cold, distilled water. This technique produced hundreds of closely spaced fractures radiating from the edge into the interior of the core without causing the cores to disintegrate, as discussed in detail below. After fracturing, the cores were placed into a vacuum oven at approximately 150°C overnight to remove any water that might have entered the fractures during the fracturing process. The dried, fractured cores were then stored in a vacuum desiccator until needed.

The temperature at which the cores are fractured (350°C) was not chosen arbitrarily but, rather, was found to be the optimum temperature based on several experiments. Previous tests showed that if the cores were heated to <260°C, they did not fracture when immersed in cold water. When heated to 200–300°C, only a few fractures developed, and the fracture density was insufficient to assure that each 2-mm thick disk, that would eventually be cut from the core after heating the fractures would contain at least one fracture (i.e., the fracture density was less than one fracture per millimeter). In addition, in this temperature range, the fractures did not propagate very far into the core, thus reducing the surface area of the fractures and, consequently, the number of inclusions that could potentially be formed as the fracture healed. When heated above approximately 400°C, a significant number of fractures cut completely through each core, causing them to disintegrate into several unusable pieces.

Fracture-healing experiments, to form synthetic fluid inclusions, were conducted in annealed silver-palladium (Ag80–Pd20) or platinum capsules having an outside diameter of 5 mm and a wall of thickness of 0.100 mm (0.15 mm). The choice of capsule material for individual experiments was based on the composition of the fluid phase involved. For experiments in which chloride brines were used, platinum capsules were preferred because of the tendency of silver from silver-palladium capsule to dissolve in the fluid at high temperatures. Gold capsules are unsatisfactory for chloride-bearing fluids for the same reason. Alternatively, silver-palladium is preferable to platinum for iron-bearing compositions because of the tendency of the latter to absorb iron and become brittle. When in doubt, platinum should be used because of its relative inertness in most fluid environments and because of its ductility, which minimizes the possibility of leakage during the experiment.

To seal the capsules, we used a technique similar to that described by Burnham and Davis (1971). This design resulted in a cylindrical container, rather than the capsule-shaped or pillow-shaped containers which result from other sealing techniques and which were unsuitable for this study. To produce these cylindrical capsules, disks, approximately 6 mm in diameter, were punched from sheets of silver-palladium or platinum, depending on the capsule material, using a standard paper punch. The disks were then placed into a specially designed press and formed into Petri-dish-shaped
caps. The press was designed so that the caps so produced would fit snugly inside the 5-mm tubing and could be easily welded circumferentially to seal the capsule. This technique produced a cylindrical capsule that maximized the internal volume as a function of capsule length.

After welding one end cap into place, the starting materials were loaded into the capsule. The preferred capsule-loading sequence is solid phases first, followed by fluid phases, and finally the quartz core. First, a small amount of silica gel or crushed quartz was placed into the capsule. Although we found that the fractures would heal without this additional source of silica, adding silica resulted in shorter heating times and produced "higher quality" inclusions (i.e., rounded or negative crystal-shaped inclusions) as compared to irregularly shaped inclusions. Also, when an additional source of silica was provided, no overgrowth of new quartz approximately a few tens to a few hundred micrometers thick was formed on the original quartz core. These overgrowths contain primary fluid inclusions that proved to be very useful for interpreting fluid-phase-equilibrium properties (see Bodnar et al., 1983).

After loading silica gel into the capsules, any solid phases required to achieve the desired fluid composition as experimental conditions were added, and their amounts determined by weighing. These included silver oxalate or oxalate acid (to produce CO₂), salts, metals, and so on. It should be emphasized, however, that whenever possible the starting fluid composition should be prepared in bulk beforehand and an appropriate amount loaded into the capsule using a microfilter syringe. This is, for an H₂O–NaCl bulk composition of 10 wt% NaCl, a stock solution of this composition should be prepared, and the solution added to the capsule using a microfilter syringe, rather than adding NaCl and H₂O individually to the capsule to achieve this composition. This procedure obviously simplifies the loading procedure and greatly reduces uncertainties in the composition resulting from weighing such small amounts of the individual components when loaded separately.

Once the solid phases had been placed in the capsule, the fluid phase (usually distilled H₂O) was added. If the mass of fluid loaded into the capsule must be known to calculate the fluid composition, the weight should be determined as quickly as possible to minimize evaporation. One of the advantages of preparing the fluid mixture beforehand and loading the fluid with a syringe, of course, is that it is not necessary to weigh the amount of fluid loaded into the capsule. After all other solid and fluid phases have been loaded, the fractured quartz core is placed into the capsule. To accomplish this, the capsule should be held at an angle of ~30° from the vertical so that the core will slowly slide to the bottom of the capsule. If the core is allowed to drop into an upright capsule, previously loaded material will splash out of the capsule, not only changing the fluid composition but also contaminating the capsule walls, precluding the ability to form a satisfactory weld to seal the capsule. After all of the starting materials and
the quartz core have been added, the capsules were sealed with an arc-welder, weighed, placed into an oven at -113°C overnight, and reweighed the next day to check for leaks.

For certain fluid compositions and run conditions, the total amount of material placed into the capsule must be carefully controlled; although it generally is not necessary to know the exact amount of fluid loaded. For example, if pure H₂O inclusions are being formed at 500 bars (50 MPa) and 800°C, the volume occupied by the H₂O at these conditions is ~9 times its volume at room temperature and 1 bar. Thus it is necessary to allow sufficient "empty-space" to accommodate this expansion; otherwise, the capsule will expand and possibly leak during the run. Similarly, if pure H₂O inclusions are being formed at fairly low temperatures and high pressures, placing too little H₂O in the capsule causes the capsule to deform around the core, potentially causing the capsule material to tear. The previous discussion suggests that the P-V-T properties of the fluids must be known before experimentation. While this is true to some extent, by making "educated guesses," and through trial-and-error experimentation, this problem can be eliminated.

In addition to the amount of material placed into the capsule, the P-T path followed from room temperature to final run conditions may affect the final inclusion composition. Preliminary tests have shown that, at temperatures above ~800-900°C, the fractures begin to heal almost immediately. Therefore, if the fluid does not attain its final equilibrium composition before reaching these temperatures, fluid of a different (and unknown) composition may be trapped in the fractures, resulting in inclusions having a composition different from the fluid composition at run conditions. For example, if the bulk fluid composition in the capsule is 70 wt% NaCl, the capsule will contain an NaCl-saturated liquid and halite at room temperature. All of the NaCl will not dissolve until a temperature of ~500°C is reached. However, if a fracture seals itself off from the surrounding fluid at 500°C, the fluid in the fracture will have a composition of ~35 wt% NaCl, assuming the fluid throughout the capsule is saturated in NaCl.

There are several procedures for eliminating, or at least minimizing, premature fracture healing. One way, obviously, is to reach final run conditions as quickly as possible. However, because of the characteristics of the pressure vessels, this is not always possible. Alternatively, premature fracture healing may be avoided by following a P-T path such that the specific volume of the fluid is always increasing during the heating process. In general, this will occur for any reasonable heating path, because fluid inclusions are generally much greater than most heating paths. This behavior may be enhanced, however, by heating the sample either isothermally or under decreasing pressure conditions. For fluid compositions and run conditions in which there is a distinct possibility that the fractures will begin to heal, some fluid may be trapped before reaching its final equilibrium composition, and the pressure should be increased to final run pressure or
higher and gradually bled off as temperature increases. We found that if the samples are heated to between 350 and 400°C under moderate pressures (50–100 MPa) and then increased to the run pressure, with pressure bled off either while the sample continues to heat or after reaching the run temperature, premature fracture healing is eliminated. Apparently, because the fluid in the fractures is continuously increasing in volume during this process, the fracture is continuously held open by fluid pressure, or at least is reopened often enough that the fluid in the fracture can reequilibrate with the surrounding fluid.

By following the previous suggestions, it is usually possible to ensure that fracture healing does not commence until the desired experimental pressure and temperature have been achieved. Conclusive evidence for this was found during the synthesis of pure water inclusions. When the necessary precautions were taken to avoid premature fracture healing, inclusions synthesized from pure water at a variety of pressures and temperatures all had the bulk density predicted from the data of Buruman et al. (1979b) for the P-V-T properties of water (Bodnar and Steer, 1985).

In synthesis experiments in which the fluid phase is homogenized at the outset of the experiments (i.e., undersaturated brines), inclusions always contain the expected chemical compositions. Likewise, inclusions formed from CO₂–H₂O mixtures appear to have uniform room-temperature phase ratios and identical temperatures of phase transitions, indicating that they have formed from a single chemically homogeneous fluid. Moreover, such inclusions exhibit the appearance and behavior expected for the pressure and temperature of formation and the bulk CO₂/H₂O ratio loaded into the capsule.

Inclusions prepared from H₂O–NaCl mixtures for which halite solution is reached by 400°C also contain the expected composition as evidenced by the salt dissolution temperature determined by microthermometry. However, inclusions prepared from bulk fluid compositions such that the salt solution temperature is greatly in excess of 400°C may exhibit some unexpected results during microthermometric examination. For example, an experiment conducted with an H₂O–NaCl solution with a bulk salinity of 68.7 wt% NaCl should yield inclusions containing three phases at room temperature—a vapor phase, an NaCl-saturated brine, and a halite daughter crystal. Furthermore, upon heating, the halite daughter crystals should completely dissolve at 600°C according to the solubility data of Potter et al. (1977) for H₂O–NaCl solutions. However, when this experiment is performed, taking necessary precautions to avoid crack-healing before the desired temperature is reached, inclusions are found to have halite dissolution temperatures ranging from ~400 to 540°C. Apparently, the fluid composition is changing even after the experimental pressure and temperature have been reached. Thus it would appear that fluid homogeneity is not achieved, in all instances, before run conditions are stabilized. This problem has thus far been documented only for very concentrated salt solutions but suggests that,
when appropriate, some independent check on fluid heterogeneities may be necessary.

The results of the preceding experiment may be considered in two parts. First, the incisions contained halite crystals displaying a range in dissolution temperatures—presumably indicating that the fluid composition was changing with time. Second, no incision contained a halite crystal that dissolved at the predicted temperature of 600°C (i.e., the measured range extended only up to \( \sim 500°C \)). Since it is likely that at least some incisions form very late in the experiment (some fractures had not yet healed by the conclusion of the experiment), this may indicate that equilibration of concentrated salt solutions may be a very slow process under those conditions.

To further evaluate the fracture-filling process, a capsule was prepared which contained a mixture of NaCl and H₂O with a bulk fluid composition of 68/7% NaCl. A segment of unfractured quartz core was then added, and the capsule was sealed with an arc welder as before and run at 725°C and 1.5 kbar (150 MPa) for 7 days. The bomb was then air-quenched to a temperature of 500°C (as indicated by an external thermocouple) and immediately placed back into the furnace, the experimental temperature and pressure returned to 750°C and 120 MPa within 25 min. Previous experimentation had shown that dropping the temperature of a quartz core rapidly through the \( α/β \) transition (about 600°C at that pressure) generates numerous joint-like fractures oriented in a cross-cross pattern at 45° to the long axis (c-axis) of the core. An additional 5 days at 750°C were allotted to allow these fractures to heal, then the capsule was removed and its contents were examined.

The procedure described above produced numerous fluid inclusions, each containing halite daughter crystals displaying a range in dissolution temperatures from 364 to 530°C. This range in temperature was considerably less than the 700°C range encountered previously, and this 0°C temperature variation is probably related to thermal gradients within the stage. Thus it appears that the fluid trapped within the healed fractures is very nearly homogeneous; however, there still remains a discrepancy of 30-50°C between the expected and observed dissolution temperatures of the halite crystals, which corresponds to a difference of approximately 5% NaCl according to the data of Potter et al. (1977). Whether this discrepancy indicates that after 1 week the fluid was still not homogeneous, or that some other factor is responsible, is unknown. In any case, it appears that the \( α/β \) fracturing technique may aid in achieving total equilibration where fluid inhomogeneity is suspected.

Upon completion of a run, the capsules should be cleaned and weighed to verify that they have not leakted. The capsules are then carefully opened, the goal being to recover the core in one piece. To accomplish this, the following technique has proven satisfactory. First, the end cap is removed with wire cutters. Then, a portion of the capsule lip is grasped with a small pair of needle-nosed pliers and peeled back in a spiraling downward
direction by rotating the pliers. The result is a single, long coiled strip of capsule material and, with practice, a single piece of quartz core containing the fluid inclusions. The core is then washed in distilled water and prepared for petrographic examination and heating/freezing studies.

To facilitate easier handling of the cores during sample preparation, the following steps are taken. Glass tubing having an inside diameter of 5 mm is cut into lengths of ~10 cm. One end of each tube is closed in a flame and powdered CRYSTALBOND® adhesive is loaded into the tube. Each tube is then warmed slowly over a flame while held at a 45° angle with the open end pointed away. The adhesive is melted and allowed to bubble for a few seconds (a procedure intended to remove the air bubbles from the cement), then placed in a rack to cool. Once the tubes have cooled, the quartz cores are inserted (usually one core per tube), and the tubes are placed into an oven at ~135°C. After about 15 min, the cement remolds and the cores settle to the bottom of the tube. At this point, the core is turned off and the samples are allowed to cool slowly to room temperature. (Rapid cooling at this point causes the cement to fracture, making cutting of the disks more difficult.) It is important that the core not be added directly on top of the powdered cement, because when the cement begins to melt, the bubbles will expand and force the core out of the top of the sample tube. If the inclusions have a substantial internal pressure at room temperature (i.e., high-bulk density inclusions and those containing expandable gases), it may be undesirable to heat them to 135°C. In such cases, a different adhesive, Bio-Plastic, may be substituted for the CRYSTALBOND and the heating steps omitted.

After the glass tubes containing the cores have been prepared, the cores are cut into ~0.5–1.0 mm thick disks using a low-speed saw with a fine blade. Finally, the disks are polished on both sides using fine 5- and then 0.5-μm polishing grits on a glass plate. After polishing, the glass support ring may be removed by dissolving the resin (CRYSTALBOND or Bio-Plastic) in acetone.

APPLICATIONS

Solubility Studies

Synthetic fluid inclusions provide a relatively simple and fast technique for determining solubilities of highly-soluble salts, such as NaCl and KCl. Most previous studies to determine solubilities of these salts employed the “break-in-step” technique which involves a discontinuity in pressure-

1 CRYSTALBOND is a one-component, thermoplastic polymer that is soluble in acetone. CRYSTALBOND is available from American Products, Inc., Oshawa, New York, U.S.A.

2 Bio-Plastic is a two-component, hydroxy-based plastic polymer available from Wacker Chemicals, Munich, Germany.
volume or pressure-temperature plots (cf., Kevit, 1942; Potter et al., 1977). In theory, this technique works very well, but in practice the discontinuities at the phase boundaries are often so slight that the phase boundary determination is not very accurate (see, e.g., Potter et al., 1977, their Fig. 2). In the synthetic fluid-inclusion technique, the temperature of dissolution is monitored optically, thus eliminating much of the uncertainty concerning the dissolution temperature.

In principle, the use of synthetic fluid inclusions to determine solubilities, using the system H₂O–NaCl as an example, is as follows. Synthetic fluid inclusions of known H₂O–NaCl bulk composition are formed at some temperature and pressure well above the solubility limit of the component being studied (NaCl), that is, in the one-fluid-phase field. During quenching from run conditions to ambient conditions, the original single-phase inclusion becomes saturated in NaCl and precipitates a halite daughter crystal in addition to a vapor bubble. The inclusions are then heated on a microscope stage, and the temperature at which the halite dissolves is recorded. The solubility of halite at this temperature is therefore equal to the known concentration of NaCl originally loaded into the capsule.

To verify that this technique works, synthetic inclusions containing a 43 wt% NaCl solution were produced at 600°C and 3 kb (300 MPa). This temperature and pressure was chosen because it is well above the liquidus and the liquid–vapor region for this composition, thus the fluid was trapped in the one-phase field. In addition, the density of the fluid is such that the liquid–vapor homogenization temperature is above the halite dissolution temperature, and the halite will, therefore, dissolve along the liquid–vapor–halite (L + V + NaCl) curve.

The synthetic fluid inclusions produced at these P-T-X conditions contain three phases at room temperature—a vapor bubble occupying ~24 volume%, a halite crystal occupying ~9 volume%, and an NaCl-saturated liquid (composition = 26.48 wt% NaCl) occupying 67 volume% of the inclusion (Fig. 17.1). When heated from room temperature, the inclusion follows the liquid–vapor–solid (L + V + NaCl) curve and the solubility of NaCl increases, resulting in a decrease in the size of the halite crystal (Fig. 17.1). At 34°C the halite completely dissolves (Fig. NaCl; Fig. 17.1); therefore, the solubility of halite at 34°C is 41 wt%, which agrees exactly with the value predicted by the equation of Potter et al. (1977).

Solubilities of more complex systems may also be studied with synthetic inclusions, as illustrated by the H₂O–NaCl–KCl system. Synthetic inclusions containing 22.3 wt% KCl, 30.4 wt% NaCl, and 47.2 wt% H₂O were formed at 600°C and 3 kb (300 MPa). At room temperature, inclusions with this composition contain a vapor bubble, a halite crystal, a sylvite crystal, and an NaCl- and KCl-saturated liquid (composition = 11.4 wt% KCl, 20.4 wt% NaCl) (Fig. 17.2). When heated from room temperature, the inclusions follow the four-phase equilibrium curve (liquid + vapor + halite + sylvite), which moves to higher KCl and lower NaCl concentrations for the composi-
FIGURE 17.1. Temperature-pressure properties of the H2O-NaCl system showing the path followed by an H2O-NaCl fluid inclusion with a composition of 41 wt% NaCl when heated from room temperature. At room temperature the inclusion contains a vapor bubble (black circle) and a halite crystal (square) with "11" inside in solution to liquid. When heated the halite crystal becomes smaller in NaCl solution, and completely disappears at 300°C (Tm(1NaCl)). With continued heating the vapor bubble disappears at the homogenization temperature (Th = 310°C).

ion of the liquid phase in equilibrium with sylvite and halite (Fig. 17.2). As a result, the sylvite crystal begins to dissolve and the halite crystal gets larger as NaCl comes out of solution. At ~140°C, the sylvite completely dissolves (Fig. 17.2); the halite crystal, however, has continued to increase in size because the NaCl solubility minimum in the presence of sylvite is not reached until ~150°C. With continued heating beyond 150°C, the inclusion leaves the four-phase equilibrium curve and follows a path toward the NaCl apex in the H2O-NaCl-KCl ternary as NaCl dissolves into the liquid (Fig. 17.3) and, at ~331°C, the last of the halite dissolves. This point defines the bulk composition of the inclusion. The temperatures of dissolution of sylvite (140°C) and halite (331°C) agree very well with values reported by other workers for solubility relations in the H2O-KCl-NaCl ternary (see Rouedder, 1984, his Fig. 8-25), indicating that synthetic fluid inclusions can be used to determine solubilities of highly soluble salts.

The validity of the technique described previously for determining the solubilities of salts is based on the assumption that the bulk composition of
the inclusions is the same as that of the solution or mixture loaded into the capsule. All of the inclusions in the previous examples exhibited similar phase ratios at room temperature and similar temperatures of various phase changes, indicating that this assumption is valid for these inclusions. However, for extremely high salinities, this assumption is not always valid because the fractures may begin to heal, isolating pockets of fluid from the surrounding fluid before all of the salt has dissolved. However, we have already described above several techniques for eliminating, or at least minimizing, the possibility of premature fracture healing.

In addition to determining solubilities of highly soluble salts such as NaCl and KCl, synthetic inclusions may also be used to determine solubilities of low-soluble materials such as base-metal sulfides. Nowak and Bodnar (1984) showed that by adding a large excess of powdered chalcopyrite to capsules containing a 10 wt% NaCl solution, inclusions containing chalcopyrite daughter minerals were produced. More importantly, when these inclusions are heated, the chalcopyrite completely dissolves, and reprecipitates when the inclusions are cooled. If the volume percent chalcopyrite in individual inclusions can be determined at room temperature by measuring the daugh-
ter mineral and the inclusion sizes, these data may be used to determine the solubility of chloroapatite at various temperatures. Obviously, this method will have a poor precision and accuracy but should at least provide a "ballpark" estimate of the solubility.

**P-V-T Studies**

Volumetric P-V-T data for geologically applicable fluids are required to interpret results of laboratory and experimental studies of various geologic processes. Roeder (1984) states that "The most critical need for the interpretation of microthermometric data on fluid inclusions is a firm experimental data base on the P-V-T-X properties of the various pertinent systems..." (p. 577). Similarly, Burnham and Davis (1971) showed that, given adequate experimental P-V-T data on appropriate fluid compositions, thermodynamic relations of various fluid-melt systems may be derived.

Unfortunately, P-V-T data for geologically reasonable fluid systems over the necessary range of temperatures, pressures, and compositions are extremely limited. At the present time, the only systems that have been investigated over a wide range of P-T-X conditions are H2O, CO2, and H2O–NaCl, and data for even these best-known systems do not extend to the extreme ranges of temperature and pressure encountered in natural systems. The lack of experimental P-V-T data is due, in large part, to the tremendous amount of time and highly-specialized apparatus required to obtain such information using conventional experimental techniques. Synthetic fluid inclusions, however, provide a relatively fast and simple method of obtaining reasonably accurate P-V-T data for a variety of fluid systems over a wide range of temperatures and pressures.

The procedure for determining volumetric P-V-T properties of fluids using synthetic fluid inclusions is illustrated in Figure 17.2. Fluid inclusions of a known composition are trapped by healing fractures in a particular host mineral phase (quartz in this study) at a known formation temperature and pressure (Tf, Pf; Fig. 17.3). At room temperature the inclusions contain two or more phases, consistent with phase equilibrium and volumetric properties of the bulk fluid at those temperatures. Thus a simple low-salinity aqueous fluid results in inclusions containing a liquid having the same salinity as that of the bulk fluid and a vapor bubble that is essentially a vacuum at room temperature (Tr; Fig. 17.3). When heated, the inclusions follow the appropriate phase boundary (the liquid–vapor curve for the inclusions shown in Fig. 17.3) and, at some higher temperature, the inclusions homogenize. At the homogenization temperature (T hm; Fig. 17.3), the inclusion contains a single fluid phase, and the density (or specific volume) of this phase may be obtained from available volumetric data for a fluid of the appropriate composition at vapor-saturation conditions. For

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* Much of the information presented in this section is from Bodnar and Sisson (1985).
example, if a pure H₂O fluid inclusion homogenizes to the liquid phase at 357°C, the specific volume of the inclusion fluid is 1.7403 cm³/g (Kesman et al., 1985).

If it is assumed that fluid inclusions represent constant-volume (isochoric) systems, the specific volume of the fluid inclusion at the homogenization temperature is the same as the specific volume of the fluid at formation conditions. Fluid inclusions are, however, not strictly isochoric. In particular, the decreased solubility of the host mineral at the homogenization temperature as compared to the formation temperature results in precipitation on the inclusion walls, leading to decrease the inclusion volume. Similarly, contraction of the host mineral during cooling results in a smaller inclusion volume at homogenization than at formation conditions. Conversely, the decreased confining pressure and the high internal pressure tend to increase the inclusion volume at homogenization relative to formation conditions. These various opposing effects rarely cancel each other, resulting in an inclusion volume at homogenization that is different than the inclusion volume at formation.

For trapping pressures less than about 4 or 5 kb (400–500 MPa) and for internal pressures less than about 1 kb (100 MPa), the pressure effects only
result in an increase in the inclusion volume of a few tenths of a percent and can be ignored. However, for higher pressure conditions, the volume change can be significant and should be included in the calculations. Similarly, the effect of precipitation on the inclusion walls is probably very small, owing to lack of available P-V-T data on SO₂-fluid systems. A rigorous evaluation is not possible. The effect of temperature depends not only on the difference between the homogenization and formation temperatures, but also on their absolute values, and can be quite large. Thus a fluid inclusion with a homogenization temperature of 100°C and a trapping temperature of 550°C would have a volume at homogenization and, therefore, a specific volume of the enclosed fluid, that is approximately 5% less than that at formation, ignoring the minor increase in inclusion volume due to pressure. The net effect of these various contributions is that for most inclusions, the volume of the inclusion at the homogenization temperature is smaller than the volume at trapping. Stated differently, the measured homogenization temperatures of a fluid inclusion (7Vnb, Fig. 17.3) trapped at known P-T conditions is lower than the value predicted (7Vnb, Fig. 17.3) from the known specific volume of the fluid at formation conditions.

Using synthetic fluid inclusions, the specific volume of pure H₂O over the range 200–700°C and 1–3 kb (100–300 MPa) has been determined, and these results have been compared with previously published data on the volumetric properties of H₂O. Results of 150 pure H₂O fluid-inclusion homogenization temperature determinations from 14 samples are summarized on Table 17.1. Also shown on Table 17.1 are experimental conditions, calculated specific volumes of the inclusions, and percent deviation of these values from the data of Durham et al. (1969a). The data for one sample, run at 700°C and 1 kb (100 MPa), are not included in Table 17.1. Inclusions in this sample all homogenized at 374 ± 1°C, some to the vapor phase and some by critical behavior. This resulted in a wide range of calculated specific volumes, from ~3.2 to ~4.0 cm³/g (Koeman et al., 1978). These inclusions were, therefore, not suitable for determining P-V-T properties.

The specific volume of H₂O in the inclusions at homogenization was obtained from the measured homogenization temperature and data for the specific volume of H₂O along the liquid–vapor curve (Koeman et al., 1978). These values are listed in column 5 of Table 17.1. The uncorrected specific volumes have been corrected for the thermal expansion of quartz to obtain a better approximation of the specific volume of H₂O at trapping conditions (Table 17.1, column 6). The corrected specific volumes were obtained by determining the percent volume increase of quartz as a result of heating from the homogenization temperature to the formation temperature using the data of Skinner (1969). In these calculations, the coefficient of thermal expansion of quartz was assumed to be independent of pressure. The uncorrected specific volumes obtained from the measured homogenization temperatures were then increased by an amount equal to the percent increase in the volume of quartz upon heating from the homogenization.
<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Specific Volume of H₂O Obtained from Synthetic Inclusions</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>224.6 - 226.9</td>
</tr>
<tr>
<td>400</td>
<td>300.6 - 308.8</td>
</tr>
<tr>
<td>500</td>
<td>353.3 - 355.5</td>
</tr>
<tr>
<td>600</td>
<td>372.2 - 373.4</td>
</tr>
<tr>
<td>700</td>
<td>174.2 - 175.9</td>
</tr>
<tr>
<td>800</td>
<td>248.4 - 251.8</td>
</tr>
<tr>
<td>900</td>
<td>302.2 - 305.0</td>
</tr>
<tr>
<td>1000</td>
<td>338.8 - 339.9</td>
</tr>
<tr>
<td>1100</td>
<td>361.8 - 361.9</td>
</tr>
<tr>
<td>1200</td>
<td>335.6 - 337.1</td>
</tr>
<tr>
<td>1300</td>
<td>300.2 - 313.9</td>
</tr>
<tr>
<td>1400</td>
<td>262.2 - 263.7</td>
</tr>
<tr>
<td>1500</td>
<td>304.0 - 314.8</td>
</tr>
<tr>
<td>1600</td>
<td>330.9 - 332.4</td>
</tr>
</tbody>
</table>

*Formation temperature (°C).*

*Formation pressure (kb or MPa/100).*

*Range of measured homogenization temperatures (°C).*

*Average homogenization temperature (°C) and number of measurements (in parentheses).*

*Uncorrected specific volume of H₂O (cm³/g) obtained from average homogenization temperature and data of Kelemen et al. (1983).*

*Specific volume of H₂O corrected for thermal expansion of quartz (data from Skemer, 1965).*

*Slightly deviated from corrected specific volume and data of Burnham et al. (1966b).*

To compare the results obtained here with previously published data, specific volumes of H₂O as a function of temperature along the 1, 2, and 3 kb (100, 200, 300 MPa) isotherms reported by Burnham et al. (1966) are also plotted on Figure 17.4. Although there is some scatter, the agreement between the two data sets appears to be good. A more rigorous comparison of the data is presented in Figure 17.5, in which the percent deviation between the two data sets is shown in histogram form; the data are also listed in Table 17.1 (column 8). As shown on Figure 17.5, 10 of the 14 corrected specific-volume determinations obtained from synthetic inclusions agree with the data of Burnham et al. (1966a) within ±1%. These results suggest that the synthetic inclusion technique does provide a reasonable approximation of the P-V-T properties of H₂O.

Having verified that synthetic fluid inclusions may be used to determine P-V-T properties of H₂O and assuming that this technique is valid for fluid
of other compositions, we have used synthetic inclusions to determine the density of a 20-wt% KCl solution over the range 300-700°C and 1-3 kbar (100-300 MPa). Experimental conditions, measured homogenization temperatures, and calculated specific volumes obtained from 14 samples are listed in Table 17.2. One sample, run at 700°C and 1 kbar (100 MPa), contained coexisting vapor-rich and sylvite-bearing inclusions, indicating that the inclusions were formed in the solid-fluid-phase field. Thus this sample could not be used to determine P-V-T properties. However, these inclusion types may be used to determine phase-equilibrium properties, as described previously (Johanson et al., 1985).

Uncorrected densities (Table 17.2, column 5) were obtained from measured homogenization temperatures and data for densities of vapor-satu-
FIGURE 17.5. Percent deviation between specific volumes of L and obtained from synthetic fluid solutions and values reported by Beranek et al. (1969a). Data are also listed in Table 17.1 (column 3).

rated 20 wt% KCl solutions (Khishinullin and Borovsk, 1966). These values were then corrected for the volume increase produced by the thermal expansion of quartz, as described above to obtain corrected densities at the temperature and pressure of formation (Table 17.2, column 6). The corrected densities are plotted on Figure 17.6 and "best-fit" curves drawn through the data points to show the change in density as a function of temperature along the 1, 2, and 3 kb (100, 200, 300 MPa) isobars. Also shown on Figure 17.6 are vapor-saturated densities from Khishinullin and Borovsk (1966) and four data points from Egorov et al. (1976) for a 20 wt% KCl solution at 100 kg/cm² (~981 bars or ~98.1 MPa). Although the pressures are slightly different, there is good agreement between our results and those of Egorov et al. (1976). Unfortunately, owing to lack of other data for 20 wt% KCl solutions in this temperature and pressure range, a rigorous evaluation of the accuracy of our results is not possible.

The data shown on Figure 17.6 were utilized to construct the more commonly used isothermal P-T projection showing various isotherms for a 20 wt% KCl solution (Fig. 17.7). Densities and vapor pressures along the liquid-vapor curve are from Khishinullin and Borovsk (1966), and the liquid-vapor curve has been extrapolated to 700°C based on our earlier observation that the sample ran at 700°C and 1 kb (100 MPa) was below the liq-uid-vapor curve (i.e., in the two-phase field). The isotherms shown on Figure 17.7 represent best-fit straight lines through four data points. In actuality,
the isochores should be very slightly concave upward in this temperature and pressure regime based on a comparison with P-V-T properties of H$_2$O–NaCl solutions (Pottet and Brown, 1977; Hibbert, 1959). As a result, the pressure one would determine at the highest pressures shown in Figure 17.7 (3 kb or 300 MPa) would be too low for a given temperature by approximately 50–100 bars (5–10 MPa).

To obtain actual densities or specific volumes of the fluids as we have done here, volumetric data along the liquid–vapor curve are required for the fluid of interest. Fortunately, these data are available for many fluids of geologic interest, and for those fluid compositions for which data are not available, adequate theoretical models exist which closely approximate P-V-T properties along the vapor-saturation curve (e.g., Pottet and Mass, 1987; Connolly and Bodnar, 1993). Even if experimental or theoretical data are unavailable for a particular fluid composition the P-T trend of the isochore (of unknown values) may still be obtained from synthetic inclusions. For many applications, particularly for interpreting fluid inclusion microthermometric data, it is the path of the isochore in P-T space that is important, and not necessarily the value of the isochore. (For more on the reliability of these types of data, see Chapter 18.)
Critical Properties

Many natural fluid inclusions contain fluids having the critical density or degree of fill, as evidenced by their homogenization behavior. Unfortunately, a rigorous interpretation of microthermometric data obtained from these inclusions is often not possible, owing to lack of experimental data on the critical properties of solutions of geologic interest. However, a reasonable approximation of these values may be obtained from synthetic fluid inclusion studies.

The technique for determining the critical properties of fluids is shown schematically on Figure 17.8. This figure was constructed for the H₂O system, although the same basic principles apply to fluids of other compositions. If synthetic fluid inclusions are trapped at various temperatures and pressures, three different types of inclusions may result. If the P/T condi-
tions are such that the trapped fluid has a density greater than the critical density (open circles on Fig. 17.8), the inclusions homogenize to the liquid phase by shrinkage and disappearance of the vapor bubble \( \sqrt{T/L \cdot V} \rightarrow 1 \). Conversely, if the fluid in the inclusion has a density less than the critical density (solid circles on Fig. 17.8), the inclusions homogenize to the vapor phase by expansion of the vapor bubble to fill the inclusion at the liquid phase evaporation \( \sqrt{T/L \cdot X} \rightarrow V \). Finally, if the inclusion homogenizes neither by shrinkage nor expansion of the vapor bubble but rather by fading of the meniscus between the liquid and vapor phases, the inclusion contains a fluid with the critical density and must have been trapped at the critical point (C.P. on Fig. 17.8) or along the P-T projection of the critical isochore (Fig. 17.8).

Thus, by monitoring the homogenization behavior of inclusions trapped at various known P-T conditions, the position of the critical isochore in P-T space may be bracketed. This approximate position of the critical isochore may be refined by decreasing the temperature and/or pressure increments in subsequent runs, depending upon the quality of the data required.

The critical temperature may be obtained from the homogenization temperature of inclusions that homogenize by fading of the meniscus between the liquid and vapor phases. If the approximate location of the critical isochore is not known before the initial experiments are run or if large temperature and/or pressure increments are used, several experiments
may be required to finally produce inclusions with the critical density. However, once the critical temperature ($T_c$ on Fig. 15.8) and the $P-T$ trajectory of the critical isochore have been determined, the point of intersection of the critical isochore (which may be assumed to be a straight line over small ranges of temperature and pressure) with the critical temperature defines the critical pressure ($P_c$ on Fig. 15.8). Thus both the critical temperature and pressure, as well as the $P-T$ projection of the critical isochore, may be obtained from synthetic fluid inclusions. In addition, the critical density may be obtained by estimating the liquid-to-vapor ratio at room temperature, provided the compositions and densities of the phases at room temperature are known or can be approximated. The accuracy of such critical density determinations is obviously poor and depends upon the shape of the inclusion and its contained phases, that is, sizes of irregularly-shaped inclusions and phases may be estimated more accurately than sizes of irregularly-shaped objects.

**Phase Equilibrium Properties**

Results of numerous experimental and laboratory fluid inclusion studies suggest that many geologic processes occurring at shallow levels in the crust are associated with two or more immiscible fluids. To interpret data
obtained from fluid inclusion studies and better understand the physical and chemical conditions at which these processes occur. Phase equilibrium data on the appropriate fluid systems are required. Unfortunately, such data are scarce, particularly for geologically relevant fluid compositions and at elevated temperatures and pressures. However, synthetic fluid inclusions provide a first, simple method of obtaining this information.

In principle, the procedure used to determine phase equilibrium properties with synthetic fluid inclusions is as follows. A fractured quartz core and a fluid of known bulk composition are loaded into a capsule, and the fractures are heated at a known temperature and pressure to form synthetic inclusions. Following the run, the inclusions are examined on a petrographic microscope equipped with a heating/cooling stage. If the inclusions all have identical phase ratios at room temperature and if the composition of the inclusions as determined by microthermometric analysis is the same as the bulk composition loaded into the capsule, the temperature and pressure at which the inclusions were trapped is in the one-fluid-phase field for the bulk composition. However, if the inclusions exhibit widely variable phase ratios at room temperature, the inclusions were probably trapped in the two-fluid-phase field. Furthermore, the compositions of the phases in equilibrium at experimental conditions may be obtained by microthermometric analysis of those inclusions that trapped one or the other, but not mixtures, of the two fluids present at run conditions.

To illustrate the use of synthetic fluid inclusions to determine phase equilibrium properties, we determined the compositions of the coexisting liquid and vapor phases in the system H₂O-NaCl to 1000°C and 1500 bars (150 MPa). The topology of the H₂O-NaCl system (modified from Morey, 1977) is shown schematically in Figure 17.9. The H₂O-NaCl system is a classic example of a binary system in which the solubility curve does not intercept the critical curve (Morey, 1977). The general geometry of this system can be attributed to the fact that NaCl has a much higher melting temperature [Tf(NaCl); Fig. 17.9] and a much lower vapor pressure than H₂O.

The NaCl solubility curve (L + V + NaCl, Fig. 17.9) extends from the H₂O-NaCl eutectic (E; T = 250°C, P = 0.001 bar or 1 x 10⁻³ MPa) to the triple point of NaCl [Tf(NaCl); T = 800°C, P = 1 bar or 0.1 MPa]. Phenomenologically, the shape of the solubility curve is explained by the tendency of the addition of H₂O to increase the vapor pressure upon moving into the binary field away from the triple point of NaCl [Tf(NaCl)]. The addition of H₂O, however, tends to lower the temperature along the solubility curve, thus lowering the vapor pressure. These opposing effects become equal at a maximum pressure on the solubility curve (P = 352 bars or 39.2 MPa, T = 600°C), and additional H₂O lowers the temperature and vapor pressure to the H₂O-NaCl eutectic (E; Fig. 17.9). These same

* See Bodnar et al. (1985) for a more detailed discussion of this study.
competing effects explain the variation in pressure along the critical curve, which increases upon moving into the binary away from both the critical point of NaCl (C(NaCl)): \( T = 360^\circ\text{C}, P = 258 \text{ bars or 25.8 MPa} \) (Pitzer, 1984) to the critical point of \( \text{H}_2\text{O} \) (C(H_2O)): \( T = 374^\circ\text{C}, P = 220 \text{ bars or 22 MPa} \), reaching a maximum pressure of \( \approx 2500 \text{ bars (250 MPa)} \) at \( \approx 120^\circ\text{C} \) (Pitzer, 1984).

The most important feature of the \( \text{H}_2\text{O} + \text{NaCl} \) system with respect to this study is the large immiscibility field in which two fluid phases, commonly referred to as liquid and vapor, may coexist. This large two-phase field, which spans the entire composition range from pure \( \text{H}_2\text{O} \) to pure \( \text{NaCl} \), may be subdivided into small two-phase fields for specific \( \text{H}_2\text{O} + \text{NaCl} \) compositions. Thus, as shown on Figure 17.9, an \( \text{H}_2\text{O} + \text{NaCl} \) solution with composition \( 1 \) splits into a higher salinity liquid and a lower salinity vapor at temperatures and pressures within the field labeled L + V(1). Similarly, fluids with a composition \( 2 \) split into liquid and vapor in the field labeled L + V(2). The point at which each of these isoplethal loops becomes
FIGURE 17.10 Examples of typical fluid inclusions trapped in the two-phase (liquid + vapor) field in the system H₂O–NaCl at various temperatures and pressures. Scale bar (shown in b) equals 10 μm and applies to photomicrographs a–j. (a) Halite-bearing inclusions representing trapping of the hypersaline liquid phase at 77°C and 550 bars (5.5 MPa). (b) Vapour-rich inclusions representing trapping of the low-salinity vapor phase at 77°C and 1000 bars (100 MPa). (c) Vapour-rich inclusion containing a halite-bearing inclusion. Inclusions were trapped in the two-phase field at 80°C and 1000 bars (100 MPa). (d) Vapour-rich inclusion containing with halite-bearing inclusion. Inclusions were trapped in the two-phase field at 90°C and 500 bars (50 MPa). (e) Vapour-rich inclusion containing a halite-bearing inclusion. Inclusions were trapped in the two-phase field at 90°C and 1000 bars (100 MPa). (f) Vapour-rich inclusions containing with halite-bearing inclusions. Inclusions were trapped in the
tangential to the critical curve \((C_1)\) and \((C_2)\) represents the critical temperature and pressure for that particular composition. Additionally, the point of intersection of any two isopleths (and they may intersect only at a single point) defines the compositions of the two coexisting phases at that temperature and pressure. Thus, at the intersection of the \((L + V)\) loop with the \((L + V)\) loop \((1 = 2, \text{Fig. }17.9)\), a liquid of composition \((2)\) is in equilibrium with a vapor of composition \((1)\). At temperatures and pressures outside each isopleth loop, that particular composition exists as a single, homogeneous fluid. For compositions in excess of room temperature saturation, such as composition \((2)\), this one-phase-field field is bounded at lower temperatures by the liquidus \((L + H)(2)\); at temperatures below the liquidus temperature, an NaCl-saturated liquid is in equilibrium with solid halite. The points of intersection of various isopleth loops \((i.e.,\) the compositions of the coexisting liquid and vapor phases) have been determined by trapping synthetic fluid inclusions at various \(P-T\) conditions in the two-phase field.

Samples run in the two-phase-field field contained fluid inclusions exhibiting a wide range in phase ratios at room temperature with a fairly consistent bimodal distribution in individual samples. One end-member type of inclusion contained a vapor bubble, a halite crystal, and liquid. Within a group of such inclusions, the phase ratios appeared to be similar \((\text{Fig. }17.10a)\). This type inclusion trapped the high-salinity liquid phase present at run conditions. The other end-member type of inclusion contained only liquid and vapor at room temperature, and the vapor bubble appeared to fill \(>50\%\) of the inclusion \((\text{Fig. }17.10b)\). This type of inclusion trapped the low-salinity vapor phase in equilibrium with high-salinity liquid at run conditions. The presence of these two end-member types of inclusions, of greatly different composition and density in a single fracture, is evidence that the inclusions were trapped in the two-phase-field field. Examples of coexisting halite-bearing and vapor-rich inclusions, representing trapping of the end-member compositions present at run conditions, are shown in Figures 17.10c–f. Between these two were inclusions with widely varying phase ratios; most of two-phase field at 827°C and 100 bars (100 MPa). Vapour-rich inclusions containing small halite crystals (bottom right), indicating homogeneous fluid entrainment at 827°C and 1000 bars (100 MPa). (i) Vapour-rich inclusion containing small halite crystals (top right), indicating homogeneous fluid entrainment, consisting with vapour-rich inclusions that trapped only the low-salinity vapor phase at 827°C and 100 bars (100 MPa). (j) Vapor-rich inclusion containing a small halite crystal (center), indicating homogeneous fluid entrainment at 800°C and 1000 bars (100 MPa). The halite consists of vapour-rich inclusions that trapped only the low-salinity vapor phase, and with halite-bearing inclusions that trapped only the high-salinity liquid phase. (k) Vapour-rich inclusion (bottom right, top center) containing three small halite crystals, indicating homogeneous fluid entrainment at 750°C and 1000 bars (100 MPa). The halite consists of vapour-rich inclusions that trapped only the low-salinity vapor phase, and with halite-bearing inclusions that trapped only the high-salinity liquid phase.
these appear to represent original vapor-rich inclusions that trapped mostly vapor with various amounts of high-salinity liquid (Fig. 17.10g–j).

Within a given plane of inclusions, an area containing mostly halite-bearing inclusions can be seen grading into an area containing mostly vapor-rich inclusions (Fig. 17.11). It is in this mixing area between the two end-member types that inclusions with widely varying phase ratios are most often observed. This distribution of inclusion types suggests that, following initial splitting of the original homogeneous fluid into a high-salinity liquid and low-salinity vapor in the partially healed fracture, separation, probably as a result of density differences, occurred prior to final healing of the fracture to form inclusions.

In addition to the secondary fluid inclusions formed by healing fractures in the quartz core, rare primary inclusions were observed in quartz overgrowths precipitated on the core during the run (Fig. 17.12a–d). Unlike the fractures that contain both end-member types of inclusions as well as mixtures of the two, the overgrowths in a given sample contain only one type of inclusion, either the vapor-rich type or the halite-bearing variety. Most often, inclusions in the overgrowths are the vapor-rich type; very

FIGURE 17.11. Mosaic constructed from numerous photomicrographs of a plane of inclusions formed at 72°C and 1970 bars (196 Mpa) showing the distribution of inclusion types along the fracture. Note that the halite-bearing inclusions are concentrated in the upper right of the photograph, and vapor-rich inclusions are restricted to the lower left portion. This distribution presumably indicates physical separation of the liquid and vapor phases prior to final healing of the fracture. Bar scale equals 50 μm.
FIGURE 17.12. Examples of primary fluid inclusions trapped in overgrowths on the original quartz core. The scale (shown on d) equals 50 μm and applies to a–d. (a) Primary, vapor-rich fluid inclusion in quartz overgrowth trapped at 40°C and 1300 bars (130 MPa). The entire edge of the original quartz core is shown by the dark zone across the bottom of the photograph. The core itself extends out of the picture to the lower left. (b) Primary, vapor-rich fluid inclusion in quartz overgrowth trapped at 40°C and 3000 bars (300 MPa). The edge of the original quartz core is again represented by the dark zone across the bottom of the photograph. (c) Primary, halite-bearing fluid inclusion in quartz overgrowth trapped at 80°C and 1300 bars (130 MPa). The grey zone crossing the photograph diagonally represents the edge of the original quartz core. (d) Two primary, halite-bearing fluid inclusions in quartz overgrowth trapped at 80°C and 1000 bars (100 MPa). The grey area along the left side of the photographs represents the edge of the original quartz core.
rarely are the halite-bearing type seen as primary inclusions. Inclusions in the overgrowths are also generally much larger than those in fractures. Inclusions in excess of 1 mm in maximum dimension have been observed in the overgrowth quartz. Also, vapor-rich inclusions in the overgrowths appear to have more consistent phase ratios than those in fractures, and freezing temperatures of these inclusions exhibit a much smaller range as compared to similar inclusions in fractures.

The compositions of the coexisting liquid and vapor phases at experimental conditions were obtained by measuring the temperatures of halite dissolution and ice melting of the halite-bearing and vapor-rich inclusions, respectively. These values were converted to salinities in weight percent NaCl using the equations of Potter et al. (1977, 1978). Because the inclusions were sufficiently large and the quartz clear, determination of temperatures of halite dissolution was easy. Determining ice-melting temperatures was more difficult and less accurate, because many of the vapor-rich inclusions contained so little liquid that the exact point at which the ice disappeared could not be observed clearly.

The results of 550 fluid inclusion measurements from 25 samples are summarized in Table 17.5, which lists the experimental run temperatures and pressures and the range in salinities of the halite-bearing and vapor-rich inclusions in each sample, calculated from the equations of Potter et al. (1977, 1978). Included are the number of fluid inclusions of each type that were measured in each sample.

The 1000-bar (100-MPa) biobar was studied in detail, and the results, including all the measured data points, are shown on Figure 17.13. The results from the halite-bearing inclusions (light line) generally fall within a narrow range of salinities, and the data project smoothly to the minimum on this loop (critical point), determined by Sourirajan and Kennedy (1962). The range in calculated salinities of the halite-bearing inclusions is probably a result of thermal gradients in the fluid-inclusion heating/freezing stage. Salinities of the vapor-rich inclusions (left line) exhibit a much wider range in calculated salinities as compared to the halite-bearing inclusions. The vapor-rich inclusions also appear to have much less consistent phase ratios at room temperature, suggesting that some (or all) of the vapor-rich inclusions trapped a small amount of liquid along with the vapor. If this is the case, and several pieces of evidence suggest that it is (Bodnar, 1985), the minimum salinity obtained from vapor-rich inclusions in a given sample would most closely approximate the equilibrium composition of the vapor phase at experimental conditions.

Assuming that the minimum salinity obtained from vapor-rich inclusions and the average salinity obtained from halite-bearing inclusions most closely approximate the equilibrium vapor and liquid compositions at a given temperature and pressure, data from all 25 samples have been combined with data from Kuehl (1942), Sourirajan and Kennedy (1962), and Urrutia (1975) and smoothed graphically to obtain the phase equilibrium properties.
TABLE 17.3. Compositions of the coexisting liquid and vapor phases in the system H$_2$O-NaCl determined from synthetic inclusions

<table>
<thead>
<tr>
<th>Run Conditions</th>
<th>Liquid</th>
<th>Vapor</th>
</tr>
</thead>
<tbody>
<tr>
<td>T(°C)</td>
<td>P(1.1 MPa)</td>
<td>Composition (wt% NaCl)</td>
</tr>
<tr>
<td>700</td>
<td>500</td>
<td>68.7-49.2</td>
</tr>
<tr>
<td>600</td>
<td>500</td>
<td>57.8-50.8</td>
</tr>
<tr>
<td>650</td>
<td>500</td>
<td>69.9-67.1</td>
</tr>
<tr>
<td>700</td>
<td>500</td>
<td>60.6-76.2</td>
</tr>
<tr>
<td>750</td>
<td>500</td>
<td>60.9-71.7</td>
</tr>
<tr>
<td>775</td>
<td>500</td>
<td>72.5-73.2</td>
</tr>
<tr>
<td>800</td>
<td>500</td>
<td>75.3-76.7</td>
</tr>
<tr>
<td>825</td>
<td>500</td>
<td>75.3-77.6</td>
</tr>
<tr>
<td>625</td>
<td>750</td>
<td>48.3-40.6</td>
</tr>
<tr>
<td>700</td>
<td>750</td>
<td>59.5-59.7</td>
</tr>
<tr>
<td>725</td>
<td>750</td>
<td>63.0-67.6</td>
</tr>
<tr>
<td>800</td>
<td>750</td>
<td>66.8-67.7</td>
</tr>
<tr>
<td>600</td>
<td>1000</td>
<td>34.5-36.8</td>
</tr>
<tr>
<td>700</td>
<td>1000</td>
<td>48.5-49.2</td>
</tr>
<tr>
<td>750</td>
<td>1000</td>
<td>55.5-56.5</td>
</tr>
<tr>
<td>800</td>
<td>1000</td>
<td>59.6-61.9</td>
</tr>
<tr>
<td>825</td>
<td>1000</td>
<td>62.0-64.5</td>
</tr>
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<td>850</td>
<td>1000</td>
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</tr>
<tr>
<td>900</td>
<td>1000</td>
<td>67.2-68.8</td>
</tr>
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<td>1000</td>
<td>71.2-72.9</td>
</tr>
<tr>
<td>700</td>
<td>1100</td>
<td>43.2-44.7</td>
</tr>
<tr>
<td>800</td>
<td>1100</td>
<td>57.8-59.4</td>
</tr>
<tr>
<td>800</td>
<td>1200</td>
<td>55.3-55.8</td>
</tr>
<tr>
<td>800</td>
<td>1300</td>
<td>50.0-51.2</td>
</tr>
<tr>
<td>150</td>
<td>1300</td>
<td>56.3-57.7</td>
</tr>
</tbody>
</table>

of H$_2$O-NaCl up to 1500 bars (150 MPa) and 1000°C. The results obtained from synthetic fluid inclusions are compared with data from Sokirin and Kennedy (1962) and Urrutia (1973) in Figure 17.14. Although the F-T-X region in which these two previous studies overlap with data from the present study is limited, these studies appear to be fairly good agreement between the three data sets, and the higher temperature data from this study are consistent with extrapolation of the lower temperature results of these earlier studies.

The H$_2$O-NaCl-CO$_2$ System

Using procedures similar to those described previously for H$_2$O-NaCl, phase-equilibrium properties in the H$_2$O-NaCl-CO$_2$ system have been...
determined using synthetic fluid inclusions (Stemmer et al., 1984). However, unlike the $\text{H}_2\text{O}$–$\text{NaCl}$ system for which accurate freezing-point depression and solubility data are available, permitting compositions of coexisting phases to be determined, there is no direct method for determining the compositions of the coexisting phases in the $\text{H}_2\text{O}$–$\text{NaCl}$–$\text{CO}_2$ system.

To delineate the one-phase/two-phase boundary in the $\text{H}_2\text{O}$–$\text{NaCl}$–$\text{CO}_2$ system, a bracketing technique was employed. First, experiments were conducted at a given pressure and temperature using a series of capsules, each of which contained a fluid of known composition. The samples were then examined visually and a determination was made as to whether the inclusions were formed in the presence of a one or two-phase fluid. Inclusions trapped in the presence of a one-phase fluid all have uniform room-temperature phase ratios. Where it is possible to perform heating studies (i.e., where the density is not so high as to cause rupture during heating), all inclusions trapped from a one-phase fluid undergo the same phase transformations and at the same temperatures. Alternatively, those trapped in the presence of immiscible fluids exhibit a range of phase ratios and temperatures of various phase transitions (see example, the dissolution of halite), indicating that they contain a range of compositions.
FIGURE 17.14. Comparison of the results of this present study (squares) with the data of Sorensen and Kennedy (1963) (circles) and Ungava (1979) (triangles). The critical curve is from Sorensen and Kennedy (1963) and Pliber (1964), and the solubility curve (L + V + NaCl) is from Sorensen and Kennedy (1963). Note the change from a logarithmic to a linear scale for compositions greater than 30 wt% NaCl.
Data from freezing experiments are evaluated in the same manner. In the presence of liquid water (or brine), liquid carbon dioxide, and carbon dioxide vapor, the freezing-point depression of the carbon dioxide clathrate (CO₂·5H₂O) varies as a function of the sodium-chloride content of the brine. Thus an observed range in the final melting point of the diathetite is taken as an indication of heterogeneous trapping of fluid, suggesting immiscibility.

Preliminary results in the determination of the solubility in the H₂O–CO₂–NaCl system using synthetic fluid inclusions are shown in Figure 17.15. A section through the ternary at 5 kbar (500 MPa) and 500°C. While the diagram is characterized by large experimental brackets, an important conclusion can nevertheless be drawn from these sparse data. Extensive immiscibility is indicated for the ternary at low pressures and temperatures by the theoretical predictions of Bowers and Holmogson (1985) and the experimental data of Gehrig (1980). Phase equilibria data obtained by the present method suggest that even at a pressure of 5 kbar (500 MPa), the two-phase field still covers a significant portion of the ternary. Although no data are available for direct comparison of these P-T conditions, numerous fluid inclusion studies of regionally metamorphosed terrains strongly suggest that fluid immiscibility has occurred at similar conditions in natural systems.

CONCLUDING REMARKS

The use of synthetic fluid inclusions in experimental geochemistry is, obviously, not limited to the applications described above. We described only those applications that we previously tested and know to be valid.

One of the most important applications that we foresee is the use of
synthetic inclusions to study the mechanisms of formation of natural inclusions and changes that occur in fluid inclusions following entrapment, as described by Steinr and Bodnar (1985). These and numerous other aspects of fluid-inclusion geothermometry are poorly understood, and Roedder (1984) suggests that many of the questions related to fluid-inclusion research might be resolved through careful studies of synthetic fluid inclusions formed under known physical and chemical conditions.

A second area in which synthetic fluid inclusions may prove useful is in the calibration of various microanalytical techniques. We have previously shown (Steinr and Bodnar, 1984) that the temperatures of various phase changes in synthetic inclusions can be very accurately and precisely controlled. As a result, these inclusions may be used to calibrate fluid inclusion heating/freezing stages and other temperature-measuring instruments. Moreover, because the compositions of the inclusions can be accurately controlled, they may be used as calibration standards for microanalysis. In particular, recent studies have shown that micro-Raman spectroscopy may be used to quantitatively determine sulfate concentrations (Dubbey et al., 1985) and carbon dioxide-methane ratios (Pastoor et al., 1985) of individual fluid inclusions and synthetic inclusions of known composition provide a means of calibrating these techniques. Similarly, micro-Raman analysis of synthetic inclusions of known bulk composition may be used to determine the speciation in the fluid under various conditions.

These are only a few of the many potential uses of synthetic fluid inclusions. As the technique becomes more widely used, certainly numerous other applications will be discovered.

ACKNOWLEDGMENTS

The techniques described in this chapter were developed while both authors were graduate students at The Pennsylvania State University, using the laboratory facilities of D. M. Kerrick and C. W. Burnham. Discussions with many of our colleagues, including H. L. Barnes, P. M. Bethke, J. G. Birnoe, W. L. Bourne, C. W. Burnham, C. S. Elbridge, D. Joyce, D. M. Kerrick, C. A. Kuehn, J. D. Pastoor, T. J. Reynolds, and E. Roedder, during the course of this research contributed significantly to its success. Editorial comments by the editors of this volume, H. L. Barnes and G. C. Ulmer, greatly improved the clarity and quality of the text. Partial funding for this work was provided by grants from ARCO Oil and Gas Company and the U.S. Geological Survey to R.B.

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