QUARTZ SOLUBILITY IN POTASSIUM HYDROXIDE SOLUTIONS UNDER ELEVATED PRESSURES AND TEMPERATURES WITH SOME GEOLOGICAL APPLICATIONS

by

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Thesis Supervisor

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Chairman, Departmental Committee on Graduate Students

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During the course of several years (1951 to 1954) many determinations of the solubility of optical grade quartz in potassium hydroxide solutions have been made. The method used was essentially the same as that employed by Kennedy in his work on the solubility of quartz in water; in many respects the present investigation can be considered as an extension of Kennedy's work. As is to be expected the results are quite similar to those obtained for the silica-water system, but the solubilities are higher. It has been found that the critical end point region is probably very limited in the ternary system, but because of experimental difficulties the extent of this region could not be determined.

To aid in the understanding of the problems involved and of the results obtained a rather lengthy section on theoretical possibilities has been included. This section is concerned mainly with critical phenomena and their effects on solubility relations in two and three component systems. To anyone familiar with the commonly used phase diagrams this discussion should present sufficient background to understand the difficulties involved in the experimental work.

Finally, after a brief discussion of the "acid" versus the "alkaline" hypothesis of ore fluids, the results are applied to a consideration of ore genesis. It is thought that the behavior of the experimental solutions may be similar to that present in natural hydrothermal solutions. This idea is expanded to show

how certain structures and textures can be explained easily. Such phenomena as colloidal replacements and successive mineralizations are to be expected and can be explained readily by a single period of activity. It is not necessary to assume many periods of activity interspersed with periods of quiescence. This is in many ways a much more appealing picture of ore deposition than some of the complicated ideas presented in the past.

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Quartz Solubility in Potassium Hydroxide Solutions under Elevated Pressures and Temperatures with some Geological Applications

Paul L. Cloke

INTRODUCTION

In order to understand better the relations which may exist in ore solutions, the writer has determined solubilities of quartz in potassium hydroxide solutions of varying concentrations and at elevated pressures and temperatures. Determinations have been carried out principally at four concentrations: 0.010 molal KOH, 0.015 molal KOH, 0.050 molal KOH, and 0.150 molal KOH. In addition the solubilities in water have been investigated by Kennedy and by Morey. Solubilities at intermediate concentrations can be approximated fairly closely from graphs plotting KOH concentration against silica content. Measurements were not made above 550°C because of the extreme corrosiveness of the solutions and the consequent difficulty of containing them in a bomb.

The results are of considerable interest to geology in that they clarify some of the reactions possible in multicomponent systems. It is thought that some of these reactions may occur in rising ore solutions.

APPARATUS:

Bombs: Four types of bombs were used in the experimental work. All of them were kindly loaned to the author by Prof. George C. Kennedy, formerly of Harvard University and now at the University of California, Los Angeles. Except for temperatures above 370°C, or for very high pressures, a cone-in-cone type bomb was used, as shown in figure 1 and plate 1. Most of the determinations were made with two such bombs. For higher temperatures two special cobalt-nickel steel bombs (figure 2 and plate 2) were used. These had a Bridgeman type unsupported area seal. One stainless steel bomb with the same type seal was also used (figure 3). The fourth type, used only for cooling curves, was of stainless steel with an internal thermocouple and Bridgeman type seal (figure 4). All of these bombs, except the last, have been previously described by Kennedy.

In the early part of the work, the furnaces were controlled by Thyratron control units. It was possible to maintain a steady temperature to within one degree. Later, temperature control was by simple on-off potentiometer units (Foxboro and Bristol's Potentiometers), cf. (plate 3). These units maintained temperature within plus or minus two to two and one-half degrees, and

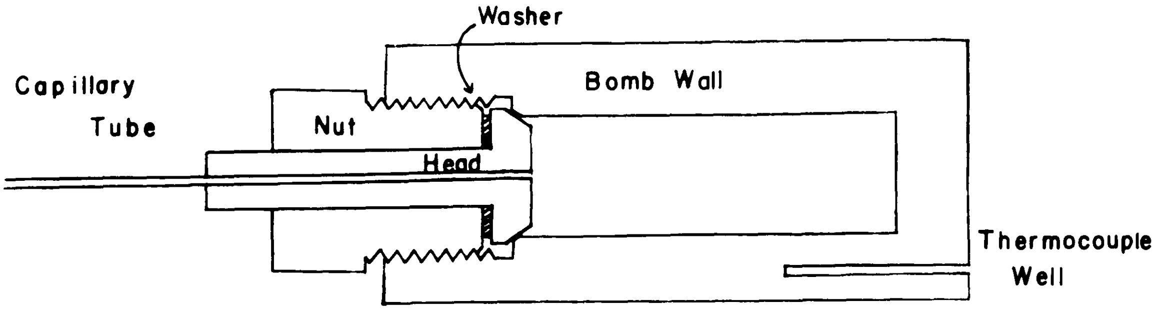


Figure 1

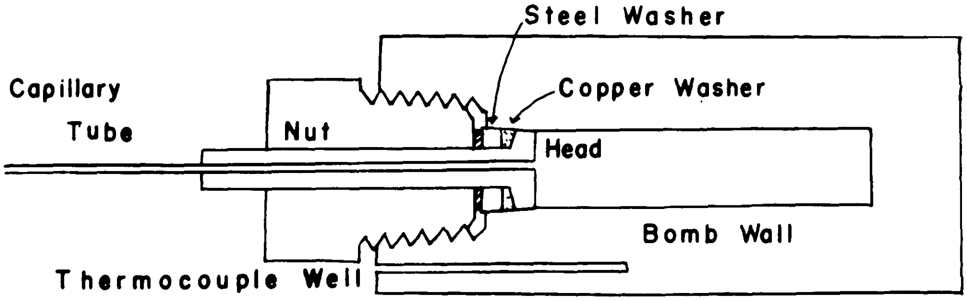


Figure 2

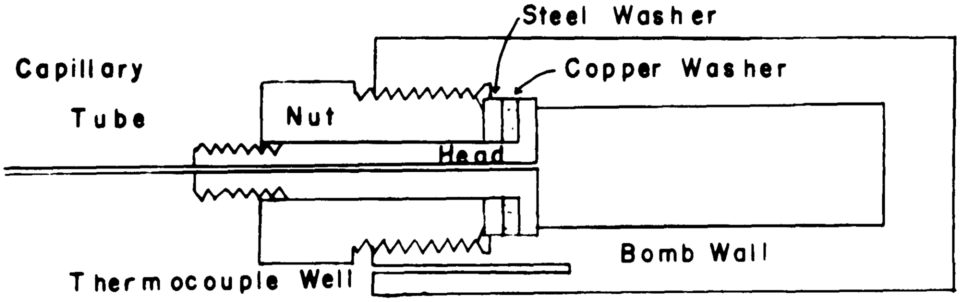
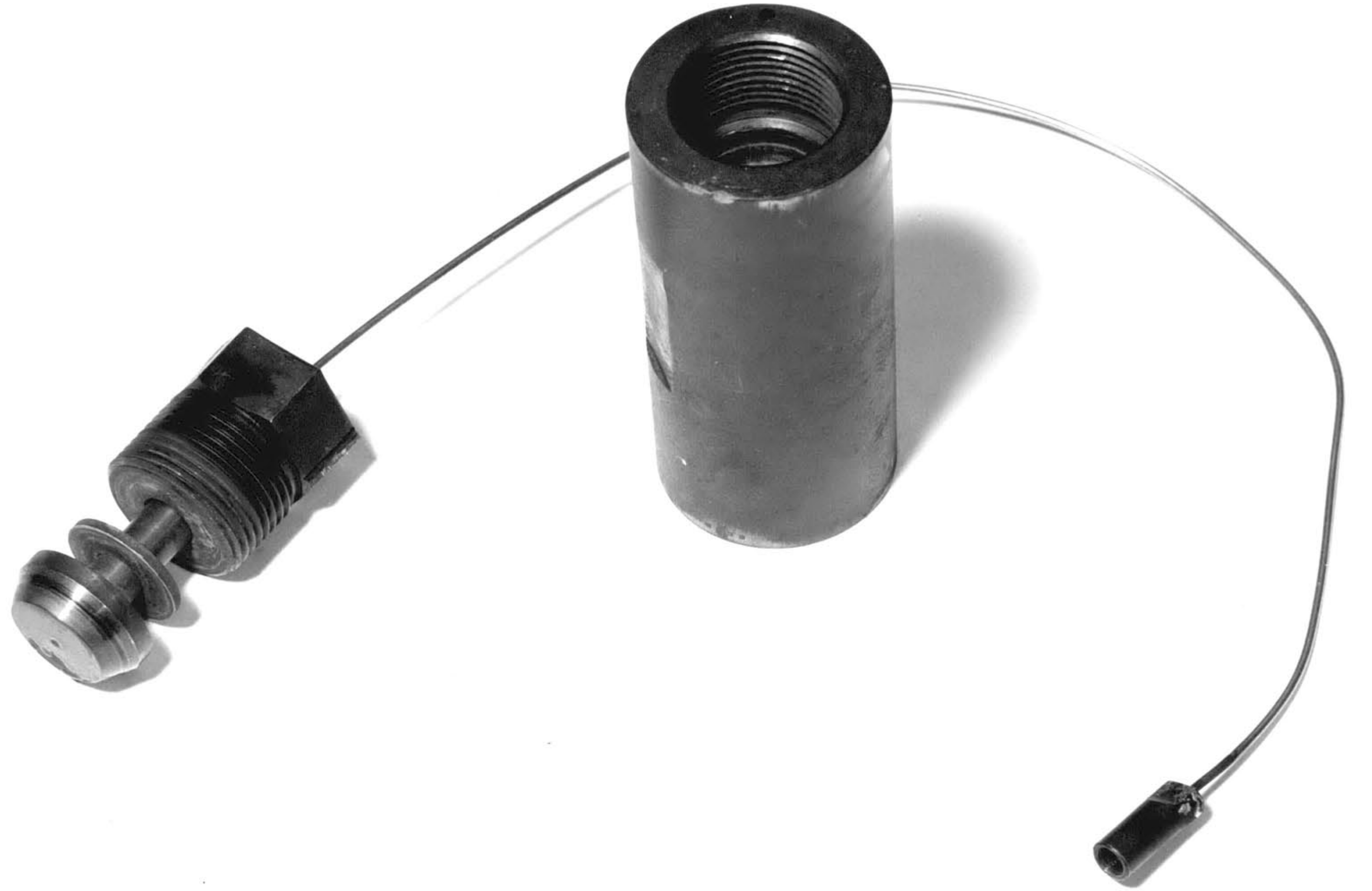


Figure 3

Plate 1

Cone-in-cone type bomb



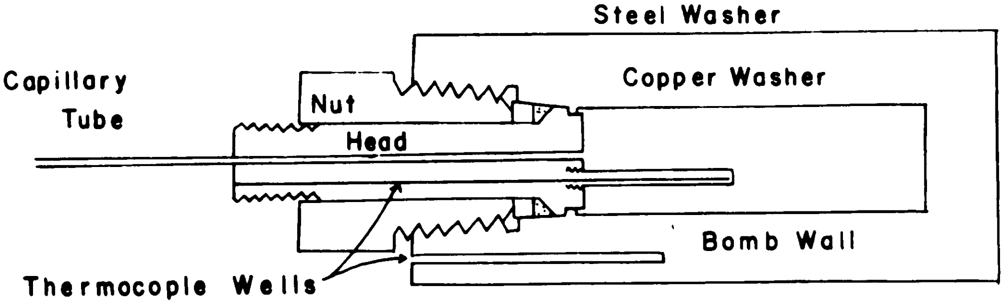


Figure 4

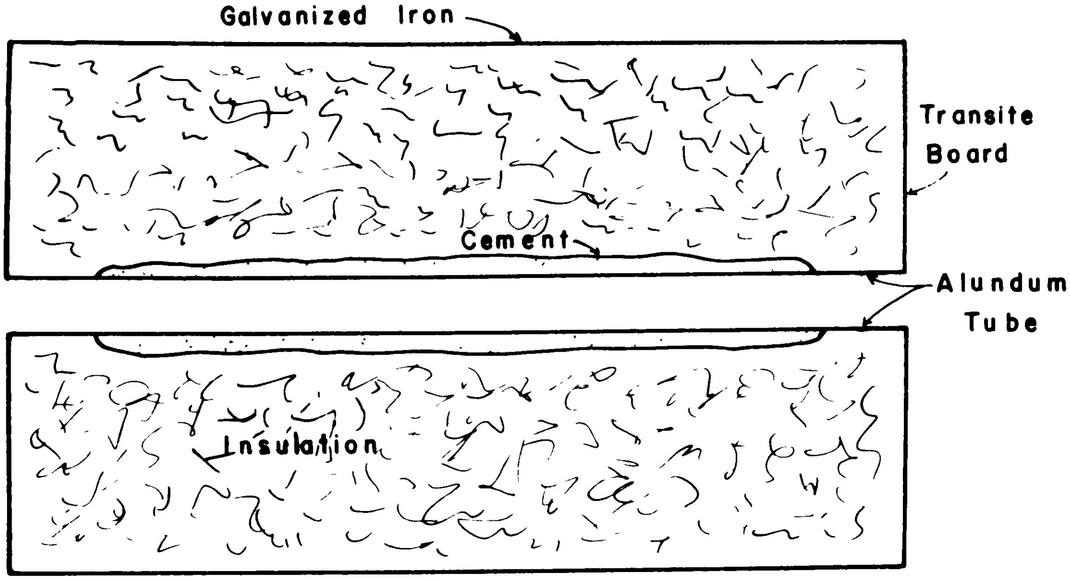


Figure 5

Plate 2

Unsupported area type bomb

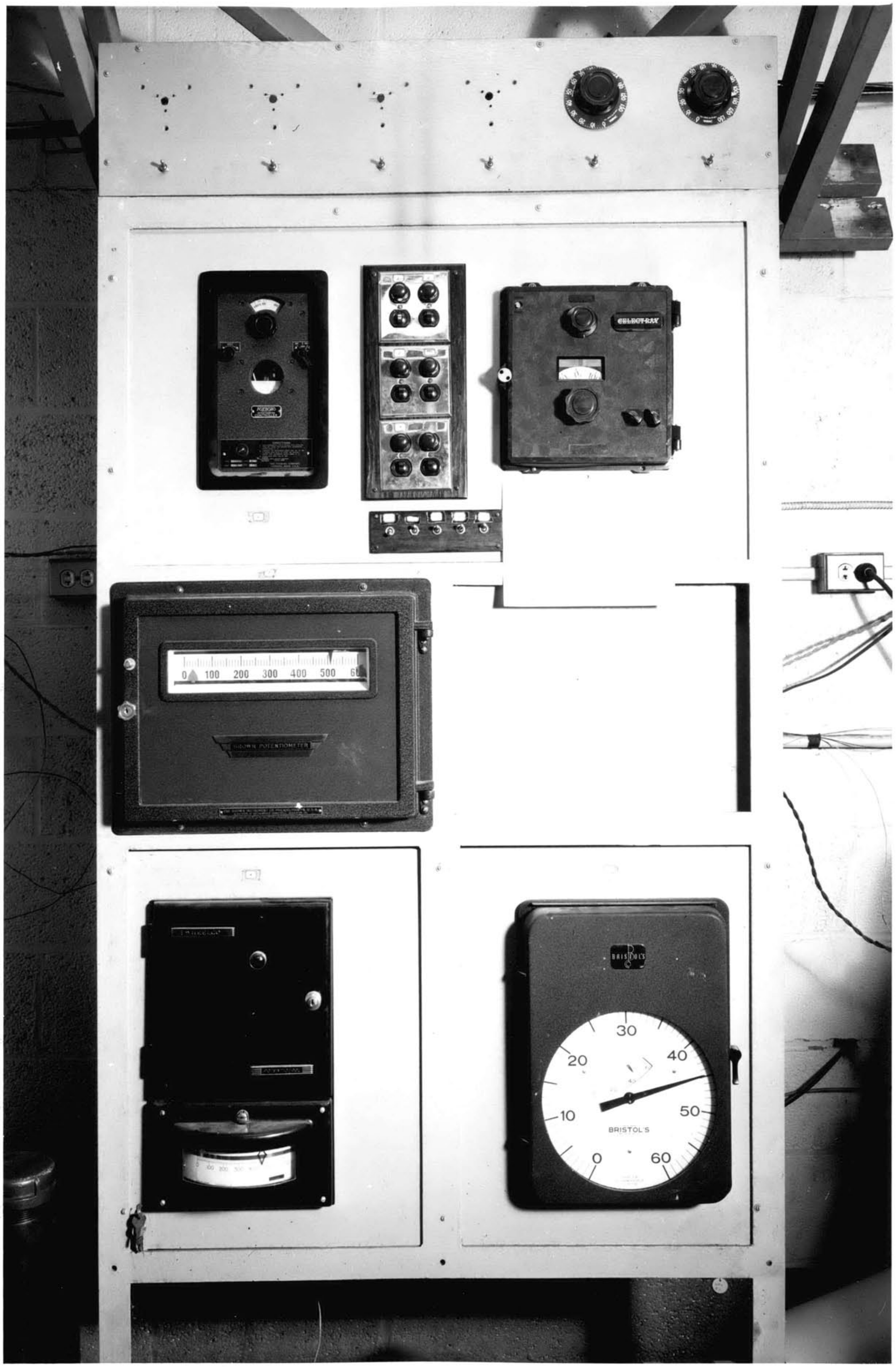
were much simpler to keep in working condition.

The furnaces themselves consisted of 24" alundum tubes of 3" inside diameter wound with Nichrome, Kanthal, or Chromel-A wire (ca. 20 gauge). The winding formula was one recommended by Professor Kennedy and is illustrated in figure 6. The wire was tightly wound on the tube without scoring the tube, since Kennedy found that he obtained better results if the tube were unscored. The wire was then cemented to the furnace with alundum cement or with "Sauereisen." These tubes were secured inside a galvanized iron cylinder of 14" diameter which was packed firmly with dry magnesium oxide cement (85% MgO, 15% asbestos) as shown in figure 5, and plate 4.

Pressures were measured through small capillary tubes leading out from the bomb to Bourdon type guages. The arrangement of pressure apparatus is shown in figure 7 and in plate 4. To measure the pressure inside a bomb, valves 3 and 4 were kept closed and valves 1 and 2 were opened. The pressure was then pumped to a value estimated to exceed slightly that inside the bomb. Then valve 1 was closed, and either valve 3 or valve 4 opened. The pressure would then drop slightly to the value inside the bomb. If there were no drop of pressure, it might mean that the capillary tube had been blocked.

Plate 3

Temperature control panel


CELECTRAY
0 100 200 300 400 500 60
BROWN POTENTIOMETER
BRISTOL'S
30
20
40
10
50
BRISTOL'S
0
60

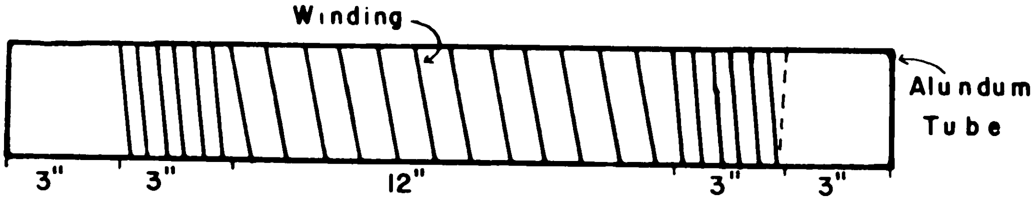


Figure 6

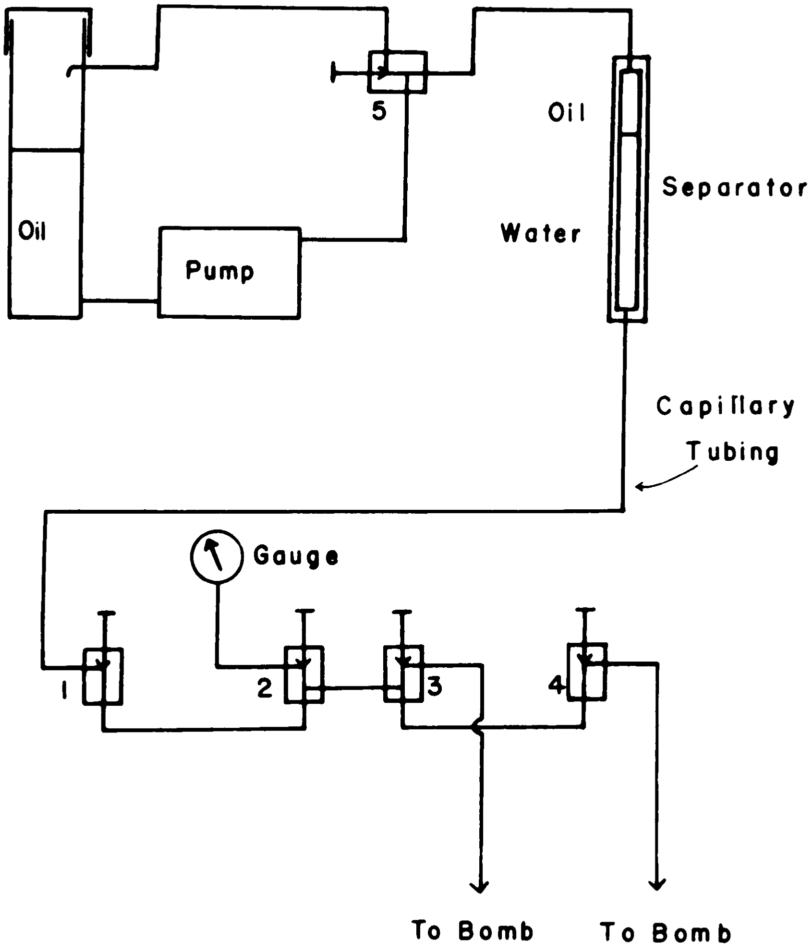
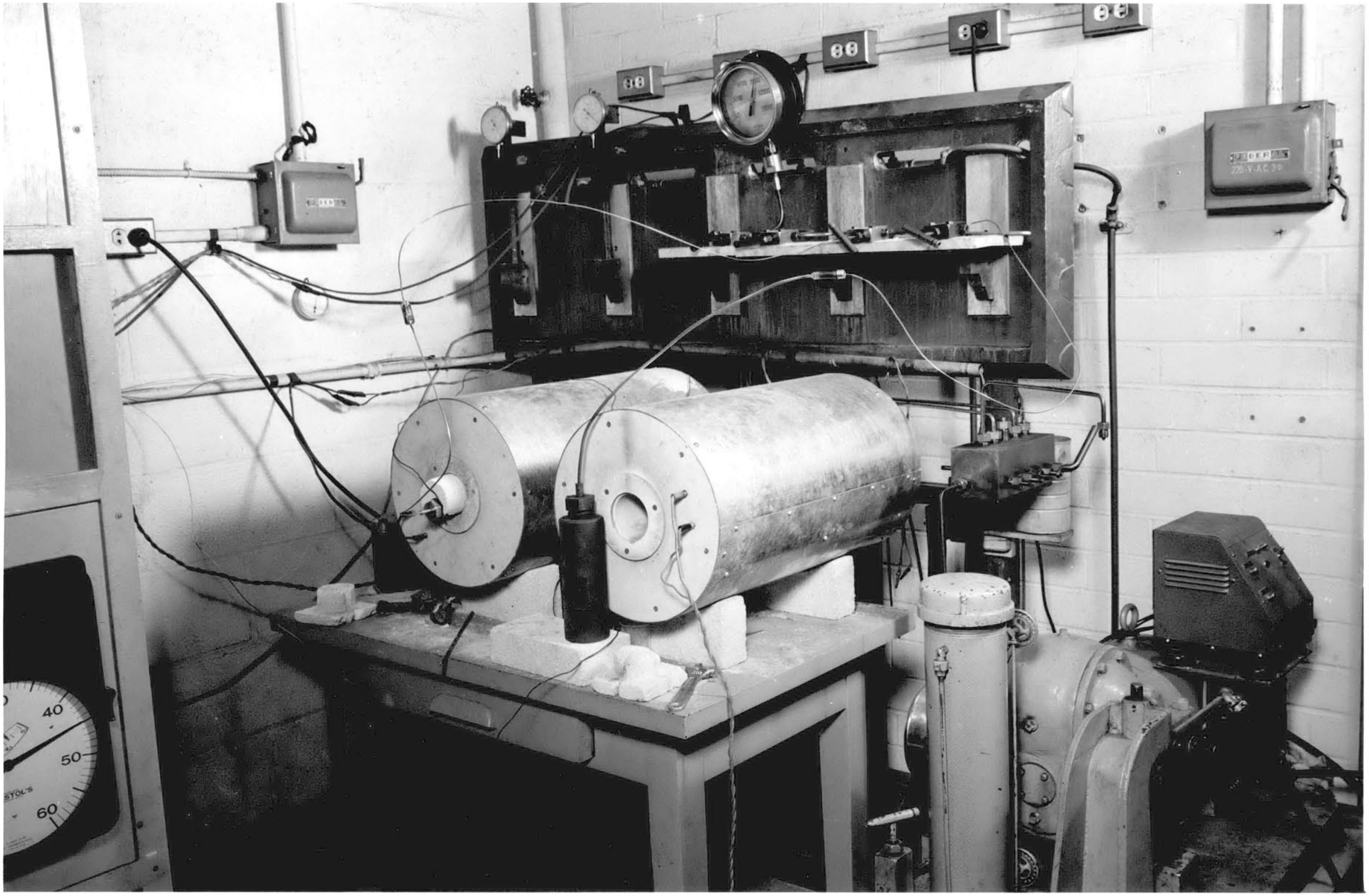


Figure 7

Plate 4

Pressure apparatus, pump,
and furnaces


40
50
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STOL'S

EXPERIMENTAL METHODS

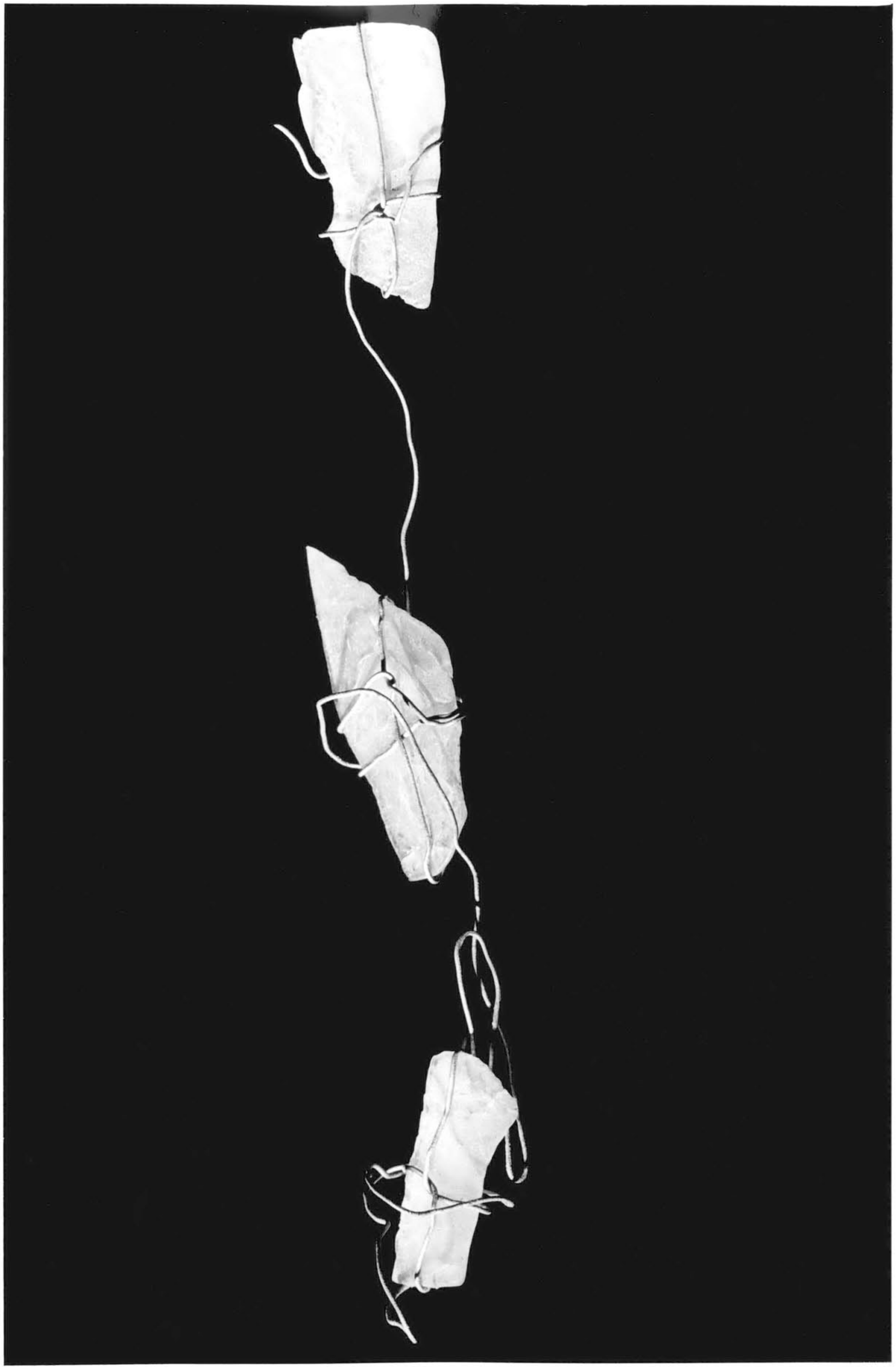
The investigations were carried out principally by measuring the loss of weight of quartz plates during the course of a run. These plates were of the same stock material as used by Professor Kennedy in his work on the solubility of silica in water and were of optical grade α quartz. Three or four plates about 2mm thick and 1 sq. cm area were tied firmly in a string by platinum wire as shown in plate 5, weighed, and lowered into the bomb. Then a measured amount of potassium hydroxide solution of known concentration was pipetted into the bomb, the bomb sealed and placed in the furnace. After remaining in the furnace for several hours to several days, the bomb was removed and quenched in water or in air. The bomb was then opened, the quartz plates removed, dried, and weighed. During the course of the run the pressure and temperature were measured several times to insure that no slow leaks were present. Knowing the weight of quartz dissolved and the weight of solution added, it was possible to calculate the solubility. Since the bomb volume was nearly constant, it was also possible to obtain pressure-volume-temperature data simultaneously.

Constant specific volume curves (isochors) were by far the easiest to determine. This is, of course, a direct consequence of the fact that the bomb volume

Plate 5

String of quartz plates

tied by platinum wire



was essentially constant. To determine the proper amount of solution to add, a certain isochor was chosen. Then the bomb volume less the volume of quartz and platinum was divided by the chosen specific volume. This gave the grams of solution to be added. Since the density of the solution was very nearly 1.0, this was also the number of milliliters. To simplify the experimental procedure and speed the operation, the volume of solution just determined was rounded to the nearest whole milliliter.

In some cases it proved advantageous to construct pressure-temperature cooling curves so as to locate points at which phase changes occurred. These curves were of course run at constant volume. The bomb with the internal thermocouple was most useful for these determinations.

Crystalline phases, when they occurred, were identified by the aid of the petrographic microscope. For some runs X-ray powder photographs or the optical spectrograph was used.

CRITICISM OF TECHNIQUES

Several factors which are implicit in the method were considered of small importance during the course of the work. Their effects were therefore not rigorously determined. The most important of these are: 1) The effect of the dissolved air on the solubility, 2) the effect on the solubility of the iron and iron oxides dissolved in the solution, and 3) the solubility of the platinum wire. Other errors arise from inaccuracies of pressure and volume measurements, fluctuations of temperature, and weighing. These are discussed in a separate section.

No attempt was made to evaluate the effect of dissolved air on the equilibrium. Because the air included in the bomb when sealing is quite small in amount, and because of the high pressures, it is presumed that most or all of the air is dissolved in the liquid. Presumably nitrogen does not enter into the reaction in any way. Oxygen would react with the bomb to increase the amount of iron oxides. Therefore, air should not affect equilibrium. To support this contention it is worth noting that Kennedy and Morey obtained nearly identical results when they independently measured the solubility of quartz in water. Kennedy's method was the same as used here; Morey's technique was a continuous flow process and excluded air from the process. For pure water then, it is apparent that the presence of air is of no significance.

In the case of potassium hydroxide solutions, there will be a reaction between the carbon dioxide of the air and the potash to form potassium carbonate. Morey's and Friedman's work indicates that in general the effect of CO_2 is to decrease solubilities in silicate systems. It is to be presumed then that the measured solubilities will be slightly low. However, calculation of the effect shows it to be quantitatively negligible.

For a specific volume of 2.5, the largest that could profitably be used, the bomb will be slightly less than half filled with liquid when sealed. For a bomb of 100 cc. capacity, using 0.01 m KOH, this means that 40 cc. of solution have been added or 0.0004 moles of KOH. Sixty cc. of air contains about 0.00268 moles of gas, or about 8.1×10^{-7} moles of CO_2. Assuming no solubility of quartz in K_2CO_3 this gives an error of 0.20% as compared to the best precision of 1%. Since the example computed is an extreme case, this effect can be ignored.

The effect of iron and other oxides dissolved from the bomb walls is believed to be small. It was found that one of the bombs almost always gave rise to rather high iron content in the solution. Other bombs and especially cobalt alloy bombs gave lower iron contents. In all cases, however, the solubilities determined at the same temperatures and specific volumes were the same. No runs with gold* or platiuum liners were attempted.

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*A few runs were tried with a gold liner, but the lining was old and had scaled off in many places.

In spite of the apparent duplication of results, however, there was reaction between the iron and the silicate solution. Along the sides of the bomb cavity, on the quartz plates, and on the platinum wire there were often formed tiny monoclinic crystals. Analysis by means of the optical spectrograph showed potassium, iron, and silica, Optical data confirmed the substance as iron orthoclase, $KFeSi_3O_8$. This was never in large amount, generally being less than 0.0005 gram. from a run containing about 50 cc. of solution. This amount of iron orthoclase would contain 0.0003 grams of silica corresponding to 1/2 to 1 per cent of the quartz dissolved. In some runs much greater amounts of iron orthoclase were formed, and in these cases, mostly at large values of the specific volume, the results were not used. It should be noted that precipitation of $KFeSi_3O_8$ decreases the potash content of the solution and therefore the quartz solubility. The error is therefore less than that determined by the computation above.

In one run at about 550°C the bomb reacted so strongly with the silica that the entire inside surface of the bomb was coated with fayalite.

There is undoubtedly some solution of the platinum wire during each run. Over a period of 10 runs, the loss in weight of platinum was so slight as to be undetectable. It is obvious that this error is entirely negligible. According to Dr. Morey solution of platinum wire in many of his experiments imparts a reddish color to the wire. This red color or a black color was observed quite regularly in the present experiments.

Early in the work it was thought that the use of copper wire, which is easily bent, would reduce the chances of accidentally chipping the quartz with stiff platinum wire. Accordingly a run was tried with copper wire; after the run the sides of the bomb were liberally spotted with copper crystals and the solution had assumed a dirty reddish brown color.

One further difficulty is that of locating the boundary between the liquid-quartz region and the liquid-vapor-quartz region. The problems involved are explained in considerable detail in the section on theoretical background. At relatively low temperatures (below about 340°C) it is possible to locate this transition by observing the sharp break of slope of the isochors on a pressure temperature graph. At temperatures near and above the critical point of water (374°C) this break can no longer be observed. As explained later, however, the solubility now shows a sharp increase at the beginning of the phase change liquid→liquid-vapor boundary as the pressure is dropped at constant temperature, (Cf fig. 65). Location of the phase boundaries by the latter method is somewhat less precise but both methods give results within about 3% in terms of solubility values.

ERRORS IN MEASUREMENTS

Errors of measurement include temperature, pressure, volume, and weight. Compared to the scatter of points, probably caused mainly by the factors just discussed, the measuring error can be practically ignored.

Temperatures were measured by means of chromelalumel or iron-constantan thermocouples. The former were used with the Thyratron units. A few of the chromel-alumel thermocouples were checked against the boiling point of water and found to give an error of less than a quarter of a degree. It was not thought necessary to calibrate the iron-constantan elements since the temperature fluctuation during the course of a run undoubtedly exceeded the error in the readings. On the basis of Kennedy's results the greatest error probably arises from temperature inhomogeneity in the bomb. Since the apparatus was in part borrowed from Professor Kennedy, and is otherwise entirely similar to his, it seems probable that the temperature variation in a bomb did not exceed 1°C. Figure 8 shows the temperature variation along a furnace with the bomb not in place. The high conductivity of a bomb will flatten the curve still more. Considering all effects the values recorded in the tables of data are believed to be accurate to within 3 degrees.

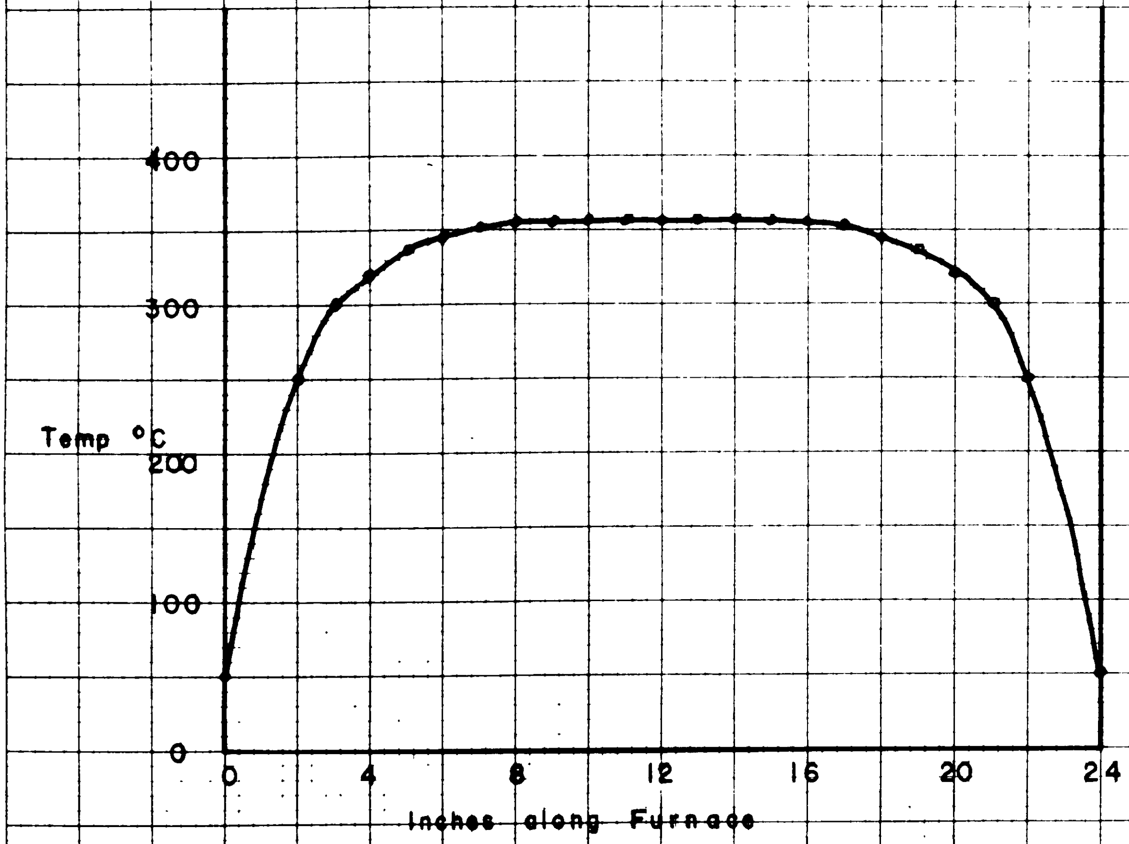


Figure 8

Pressure measurements present a somewhat greater problem. In this case the pressure in the gauge must be brought to very nearly the same value as that on the inside of the bomb before the valve connecting the two is opened. If this condition is not met a considerable amount of fluid may be lost from the bomb in filling the pressure gauge. Conversely a rather large amount of water may be added. In either case the pressure is changed on the inside, and the true pressure has not been measured. This error can be largely eliminated by the following procedure. (As an example) let us assume that the pressure dropped from 300 bars to 250 bars on opening valve 3 of figure 7. Valve 3 is then closed again, valve 1 opened and the pressure in the gauge dropped to 200 bars. Valve 1 is then closed, and valve 3 reopened. The pressure in the gauge will then rise to some such value as 245 bars. In this way the amount of fluid gained when valve 3 was first opened is approximately balanced by the amount lost when opened the second time.

It was found impossible to measure the pressure when the valve 1 was left open. In this case the very large volume of the oil-water separator predominated over the small volume of the bomb. The bomb pressure was thus brought to very nearly the original pressure in the separator.

Furthermore, if the pressure in the separator were initially high, the large amount of cold water entering the bomb cooled the "head" more than the walls, and caused the pressure seal to be broken through contraction of the head.

Pressure measurements at high temperature with the cobalt bombs proved to be considerably in error. This was discovered by trying a few runs with distilled water, plus the quartz, for which the P-V-T relations are known. The explanation of this result apparently lies in the measurement of the bomb volume. In determining this volume, it was assumed that the volume of the connecting capillary tube was negligible. However, at the high pressures attained a considerable amount of fluid could be forced into this space and drop the pressure. This effect is magnified by the fact that the capillary tube for the cobalt bomb is larger than for the steel bombs. The amounts of solution removed from the bomb by this means is fortunately not sufficient to seriously affect the solubility. The pressures measured with water were identical to the corresponding runs with KOH solutions and therefore the P-V-T relations for water can be used for this range, of conditions. Due to the uncertainty of the pressures obtained no points were plotted on the P-T diagrams for KOH solutions at high temperature. The specific volume solubility curves for this range were constructed by reading the correct volume from a P-V-T plot for water.

One run with copper oxide added to the bomb was tried to test for the measure of hydrogen. This might arise as follows:

$$2Fe + 3H_2O = Fe_2O_3 + 3H_2$$

Since the water is quite dense, evolution of hydrogen should raise the pressure. Copper oxide would reform water and drop the pressure:

$$CuO + H_2 = Cu + H_2O$$

No such drop was observed and therefore hydrogen is not evolved in appreciable amount.

The pressure gauges used were believed either to be essentially accurate, or were calibrated against "accurate" gauges. Errors on this account are thus probably relatively small. Errors in pressure due to the causes outlined above are believed not to exceed 2% to 3% at temperature below 400°C.

The volume of the bombs was measured in either of two ways. In the first method the bomb was sealed, and water was injected from a calibrated compressor until the bomb was full. Corrections were then made for the compressibility of water. Alternatively careful measurements were taken of all the inside dimensions and the volume calculated. The first method is probably more accurate, but the difference was very slight. In the computations of the specific volumes listed with the data the slight thermal expansion of the steel was taken into account. A value of 30×10^{-6} was assumed for the volume coefficient of expansion. The effect of the high pressure was not computed. Errors in the volume are probably under 1%, except as noted above.

If the quartz plates and platinum wire were free of siliceous glass and oxide particles, weighings could easily be reproduced to within one tenth of a milligram. Fortunately the iron orthoclase did not generally adhere to the quartz, and in those cases when it was present, it was easily rubbed off. Potassium hydrogen disilicate did adhere strongly to the plates in some cases (plate 6) and gave rise to erroneous readings. A highly siliceous glass formed under some conditions and also interfered. In the last two cases, however, the result could not be used in any case, since the amount of crystalline or glassy phase could not be recovered completely. This being the case the potash content of the solution was not known. These runs were valueless except for indicating stability fields of phases.

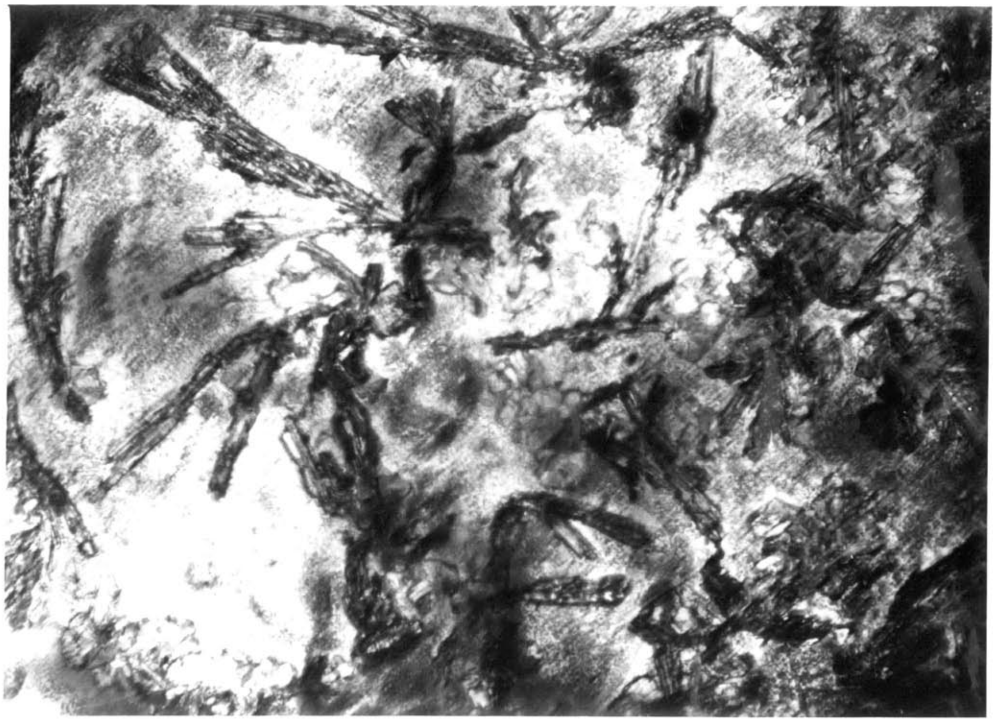
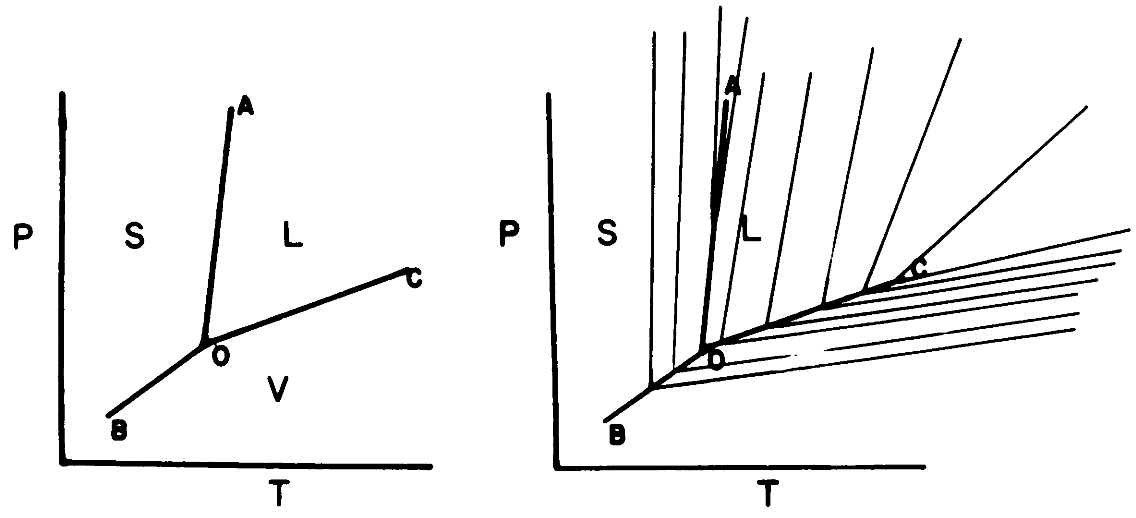


Plate 6. $KHSi_2O_5$ crystals adhering to quartz plate.

THEORETICAL CONSIDERATIONS

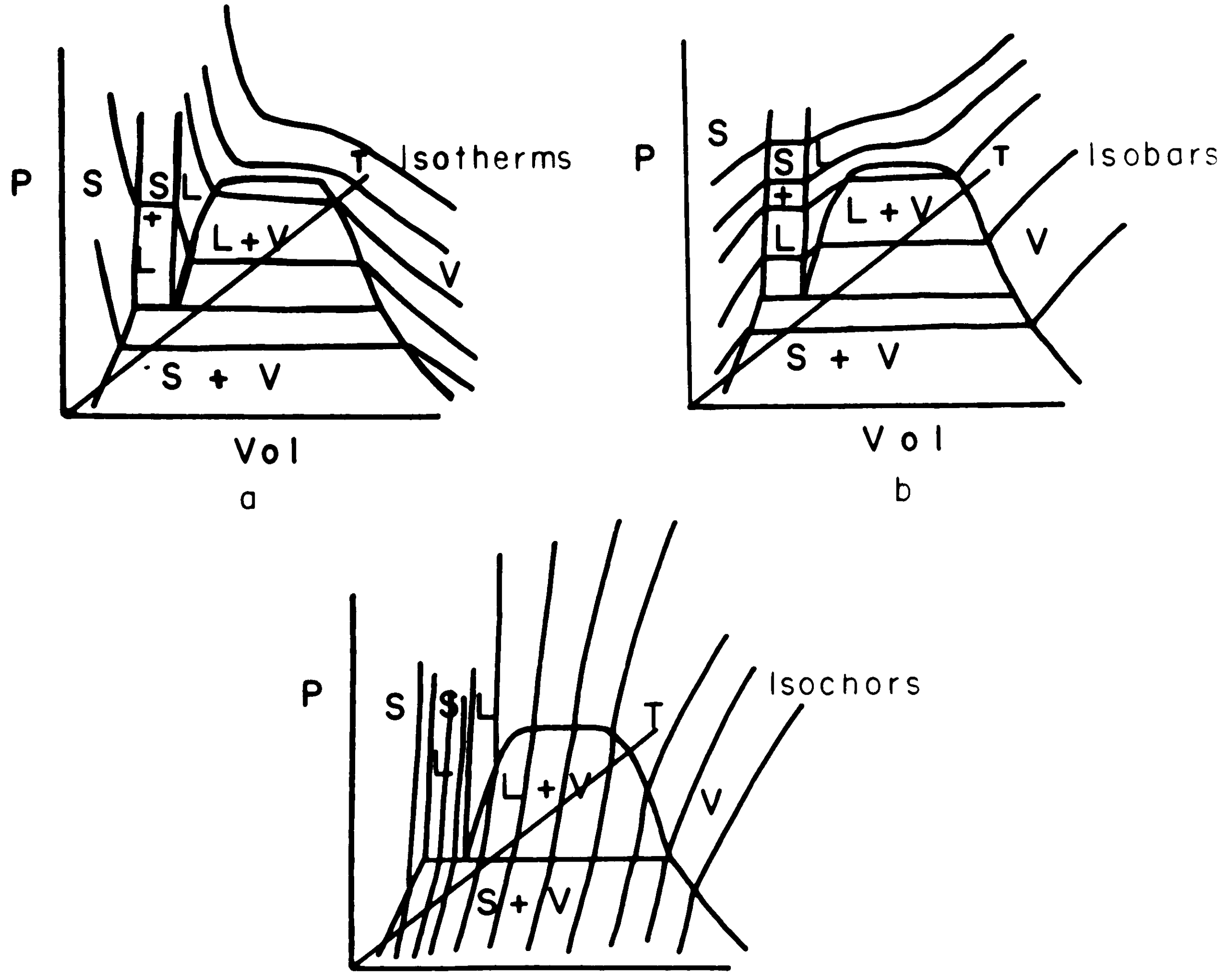
In order to understand the significance of the experimental results, it is necessary to deal in considerable detail with the theoretical possibilities in a three component chemical system. In particular the peculiar complexities of critical phenomena must be discussed. Critical phenomena in two component systems have been treated quite adequately in the literature, but for the sake of clarity this subject will be discussed again here. The more complex situations in three components will then be presented. Niggli and Smits have given in German adequate treatments of the ternary system, but very little has been written in English.

The one-component case is, for present purposes, adequately represented by figures 9 and 10. Figure 9 shows the pressure-temperature equilibrium relations of a pure substance. In the region designated by S in figure 9a only solid may exist at equilibrium, in the region L only liquid, and in the region V only vapor. Along the line OA liquid and solid are in equilibrium, along OB solid and vapor, and along OC liquid and vapor. OA continues, so far as is known, indefinitely upward, and OB continues downward until it either intersects the zero pressure isobar or reaches absolute zero temperature. OC terminates at C,



a b

Figure 9



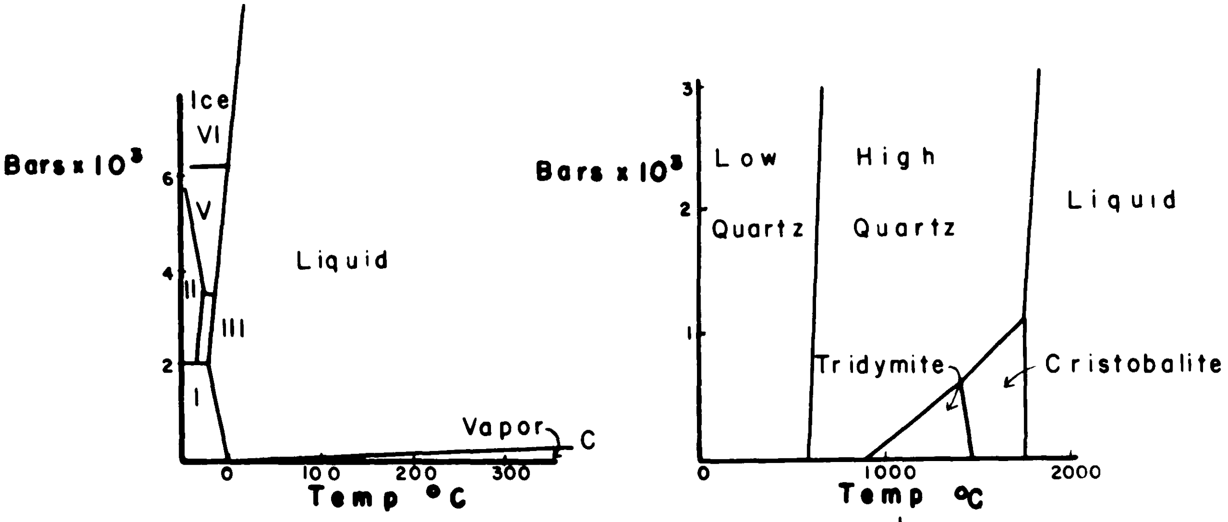
a b c

Figure 10

the critical point of the system. O itself is the triple point where solid, liquid, and vapor are in equilibrium. Figure 9b shows lines of constant volume (isochors) in addition to the PT relations.

Figure 10 includes volume relationships in addition to pressure and temperature. Here the regions L, S, and V have the same significance as before. The areas L + V, L + S, and S + V represent conditions where two phases are present; two phase tie lines are shown. Figure 10a shows the isotherms of the system, figure 10b the isobars, and figure 10c the isochors. A projection of these relations onto the P-T plane gives rise to figure 9. Other complications may arise in one-component systems, for example those shown in figure 11a,b, but the present work is sufficiently restricted so that we need not consider the inversions of quartz and ice. Likewise we are not concerned with allotropy and incongruent melting.

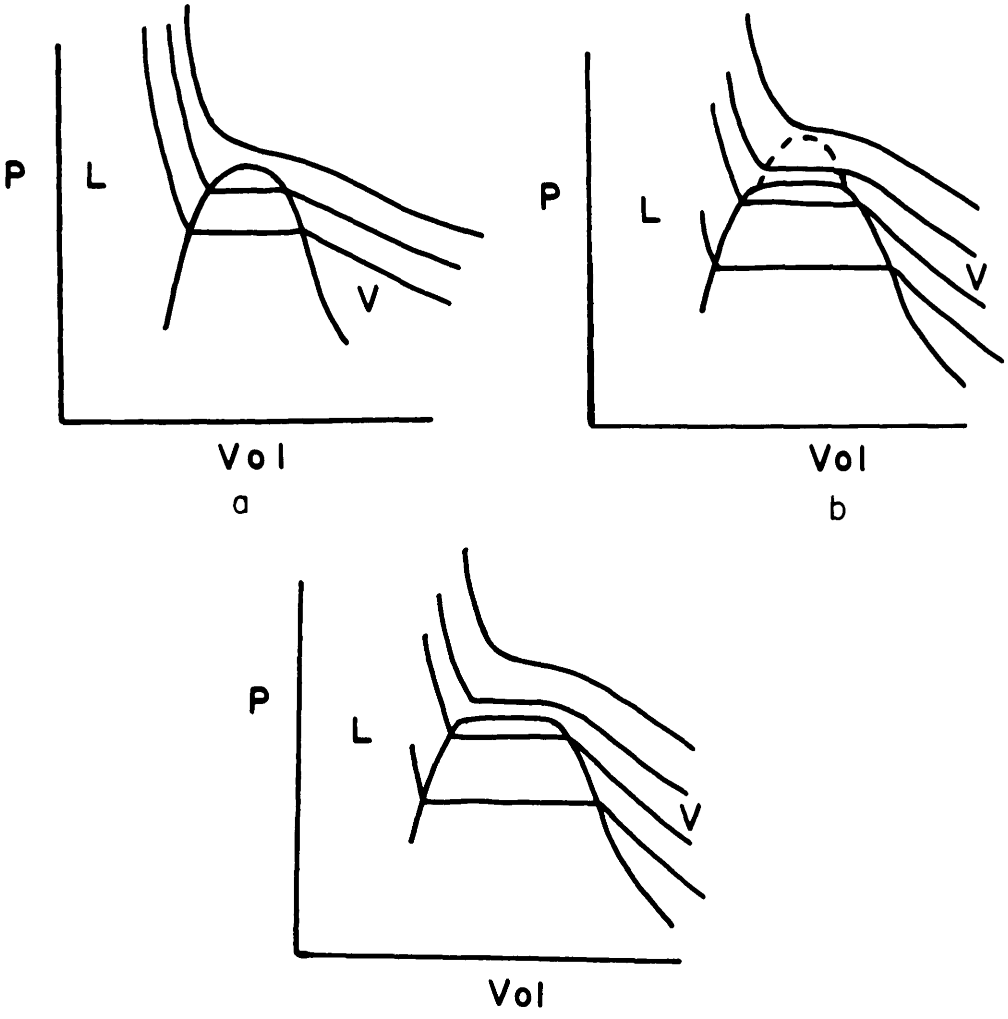
In the classical case it has been assumed, largely on the basis of Van der Waal's equation of state, that the liquid vapor loop in a P-V projection will be roughly parabolic as shown in figure 2a. However, Harrison and Mayer on the basis of statistical mechanics conclude that above the pressure and temperature at which the meniscus disappears there exists a region where the isotherms are



a

b

Figure 11



a

b

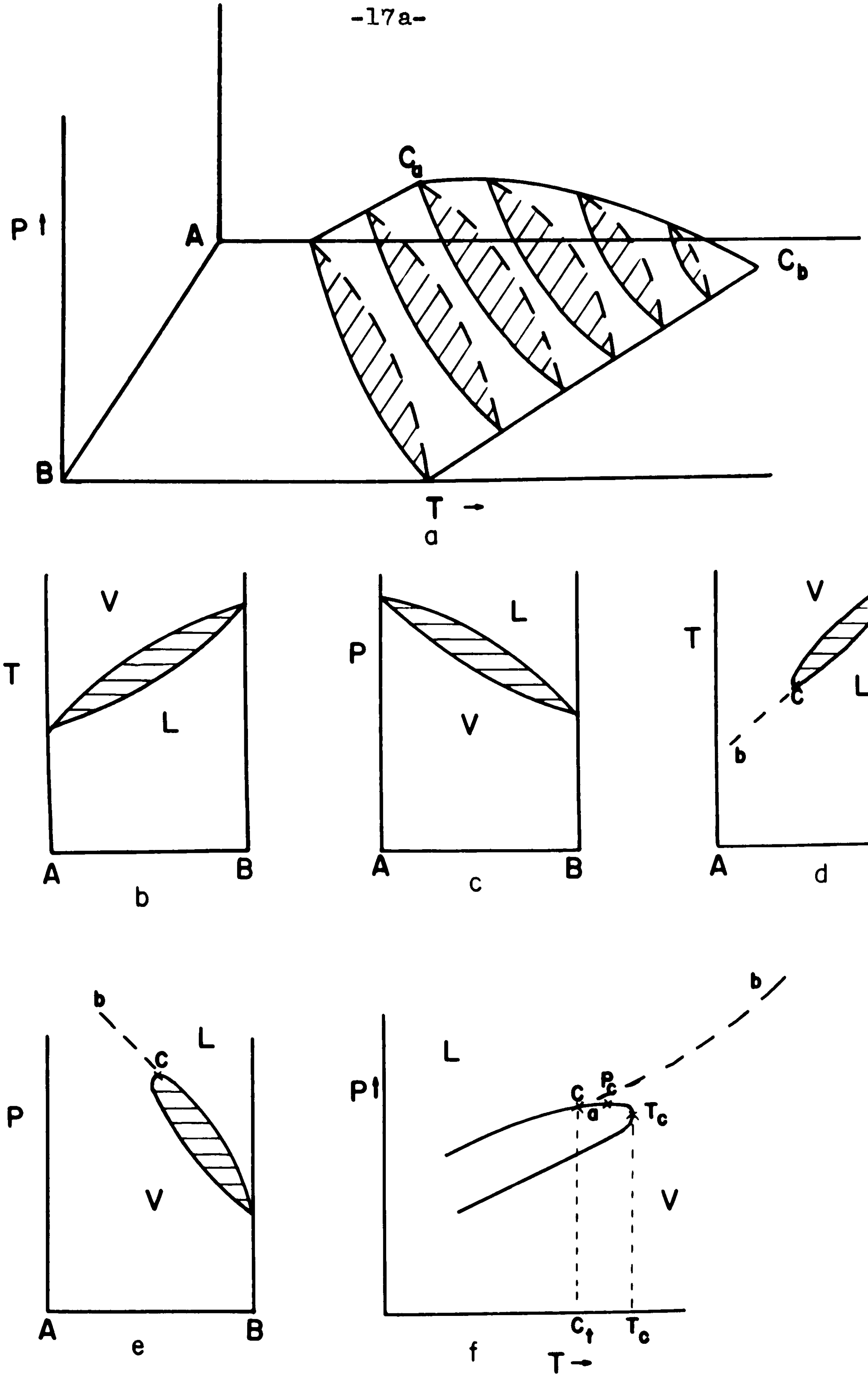
c

Figure 12

still isobaric $(\frac{\partial p}{\partial v})_T = 0$. This is shown in figure 12b. McIntire and Maass have obtained results with ethylene which agree with this theoretical conclusion. Rice prefers the interpretation shown in figure 12c and for simplicity this type of diagram will be used in subsequent drawings. It is thus by no means certain that there is a critical point as opposed to a critical region even in a one-component case. The nearly isobaric top of the liquid-vapor dome is noteworthy and it is assumed that this relation is general in polycomponent systems.

Turning to a two component system one difficulty is immediately obvious; it is not possible to represent all four variables, pressure, temperature, volume, and composition, in one diagram. Unfortunately, it develops that pressure and temperature are the two most easily plotted but the present work was done at constant volume. This occasionally necessitates the construction of special diagrams showing volume.

Liquid-vapor critical points in multicomponent systems are defined as those points at which liquid and vapor in equilibrium have identical properties. It is readily seen that this must mean identical composition, as well as density, viscosity, etc. Figures 13b and c represent the relations in a simple binary system below the critical


P↑
A
B
T →
a
C_a
C_b
V
T
L
A
B
b
P
L
V
A
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c
V
T
L
c
b
A
B
d
b
L
c
P
V
A
B
e
b
L
P↑
c
a
P_c
T_c
V
C_t
T_c
f
T→

Figure 13

point of the more volatile component. Figures 13d and e show the relations between the critical points of the two components. On a constant pressure diagram such as 13d a critical point intermediate to the two pure components must occur at the extremity of a loop, in this case at the point marked c. Likewise critical points occur at the extremities of loops such as that shown in 13e, at the point c. These relations are shown in three dimensions in figure 13a, where a number of constant pressure cross sections are indicated. Here we have a solid resembling an inflated envelope filled by tie lines. Cross-sections of this solid at constant pressure, at constant temperature and at constant composition give rise to figures 13c to f.

If we assume that the points c shown in figures 13d and 13e are the same, it is easy to see that a slight rise of temperature at constant pressure, or that a slight drop of pressure at constant temperature produces two phases. This is shown also in figure 13f, a constant composition plot of P vs. T. On this diagram Pc represents the pressure above which a fluid of this composition cannot undergo boiling or condensation. Point Tc represents the temperature above which no value of the pressure will split the fluid into liquid and vapor. The relations of Pc and Tc to each other are always the same, but the critical point c may lie counter-clockwise from Pc, as shown, between Pc and Tc, or clockwise from Tc.

Moreover if c lies counterclockwise from Tc, as in figure 13f, release of a pressure greater than Pc at some temperature between Tc and Ct produces a very interesting result. At first, as the pressure drops to some value inside the loop, vapor will condense to liquid, but further drop of pressure causes the liquid to evaporate again. The transition is then vapor ⟶ vapor + liquid ⟶ vapor. If c is clockwise of Tc, we may get the transition liquid ⟶ vapor + liquid ⟶ liquid. Either of these relations may also be produced at constant pressure and changing temperature if c, Pc, and Tc are properly oriented.

In view of the recent confusion in the literature regarding terminology it is appropriate at this point to state what is meant in this paper by the terms liquid, vapor, fluid, and gas. A fluid is defined as any substance which shows no modulus of shear. It thus includes all states except solid, glass and such unusual situations as liquid crystals. Liquid refers to a state, generally fluid, which shows short range atomic or molecular order but not long range order as in crystals. Gas refers to a fluid state which shows random order only. A vapor is a gas existing in equilibrium with a liquid. There is nevertheless a continuous transition from liquid to gas above the critical region. If there is any doubt about the nature of the state, the best term to use is "fluid". Fluid is thus an all inclusive term; liquid and gas represent special kinds of fluids.

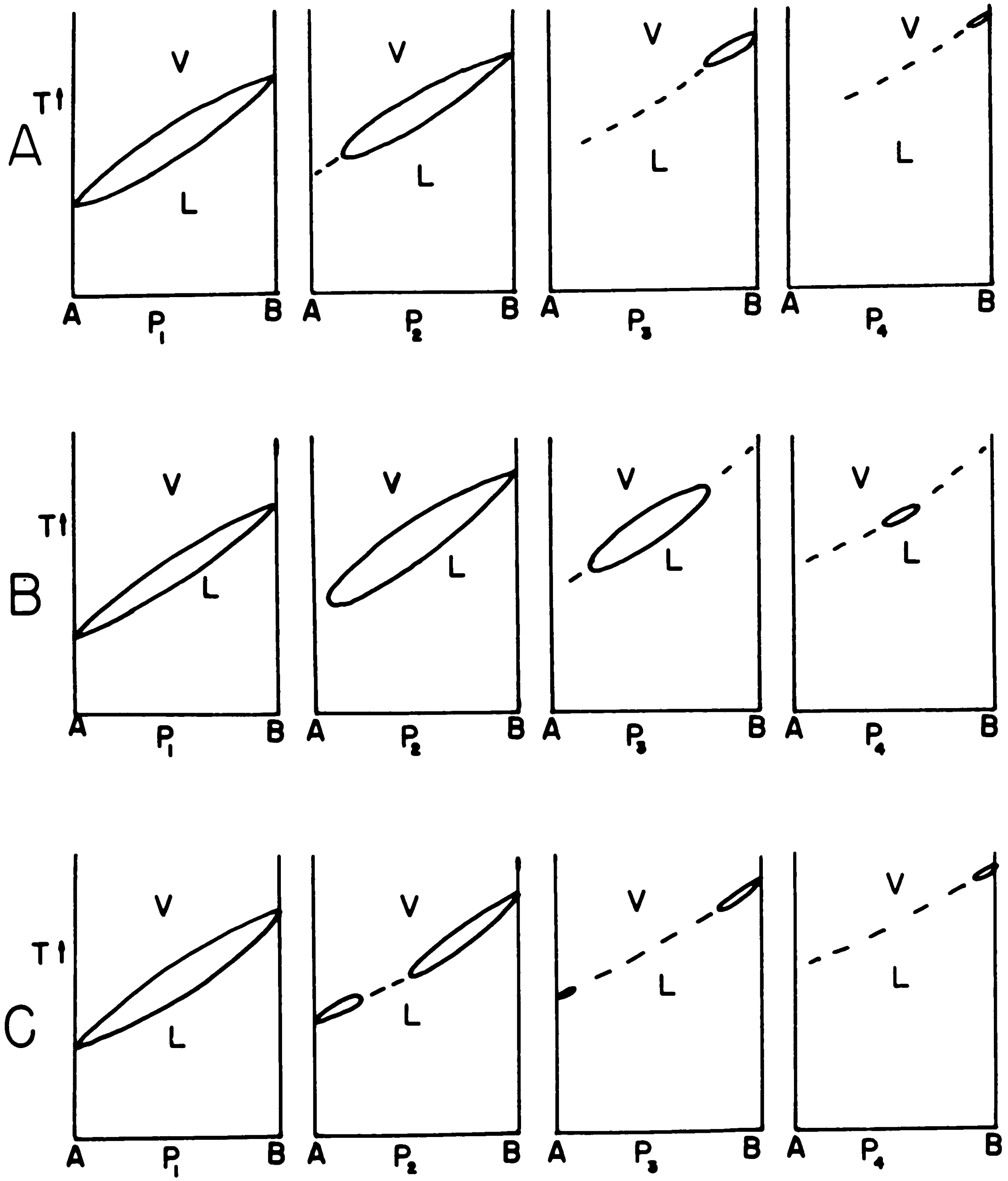
With these definitions in mind we return to the liquid vapor loop of figure 13f. If the pressure is very high at the temperature between Tc and Ct, the fluid will be a liquid. As pressure drops, this liquid will undergo a rapid expansion in some short pressure range slightly above the loop and will become gas. This transition is marked approximately by the line bc. This vapor then follows the sequence described above. The lines bc in figures 13d and e have similar significance.In the immediate vicinity of the lines bc neither of the terms liquid nor gas is appropriate; only "fluid" can be used here. Fluid is a general term; liquid and gas are specific terms representing extreme variations of fluid.

Because of the nature of critical phenomena, (cf works by Rice, Stewart, Tisza, and others), it is not thought that a point such as a in figure 13f would show liquid properties. That is, the density, viscosity, solvent power, compressibility, and other physical quantities would be more gas-like than liquid-like. There is thus no conflict with the classical concepts of liquid-vapor relations.

Liquid immiscibility has generally implied that it is possible at some point to have two liquids and a vapor in equilibrium. With the above definitions it is conceivable that liquid immiscibility could occur but that no vapor could under any conditions be in equilibrium with the two liquids. Since this lies outside the scope of the present work, this possibility has not been thoroughly investigated.

The curve connecting all the critical points in a two component system is known as the critical curve. The curve for the system shown in figure 13 rises continuously in both pressure and temperature from the critical point of component A to that of component B. This situation is represented briefly by figures 14a, and 15a. The only restriction placed on these critical curves by the theory however, is that they be smooth curves. Accordingly we can have pressure maxima, figures 14b and 15b, or pressure and temperature minima, figures 14c and 15c, or any of a number of other combinations. Roozeboom's classic work shows many of these possibilities.

These relations must now be integrated with a picture of liquid-solid relationships. The discussion of this aspect of the theory will be divided into two parts, depending on whether critical phenomena do not, or do, occur in saturated solutions.


A
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P_1
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P_2
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A
P_4
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B
T↑
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A
P_1
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P_3
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V
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P_4
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C
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A
P_1
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P_4
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Figure 14

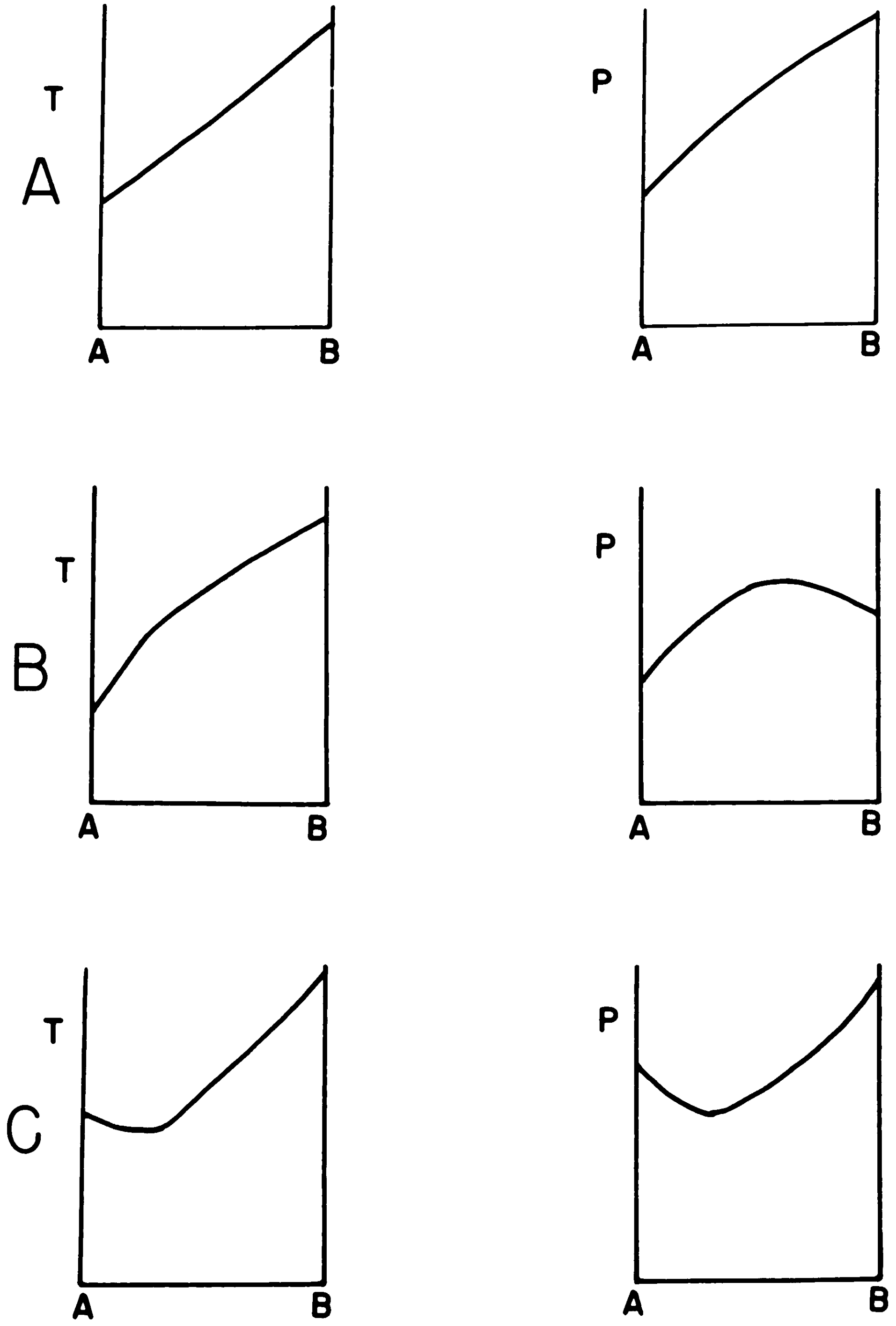
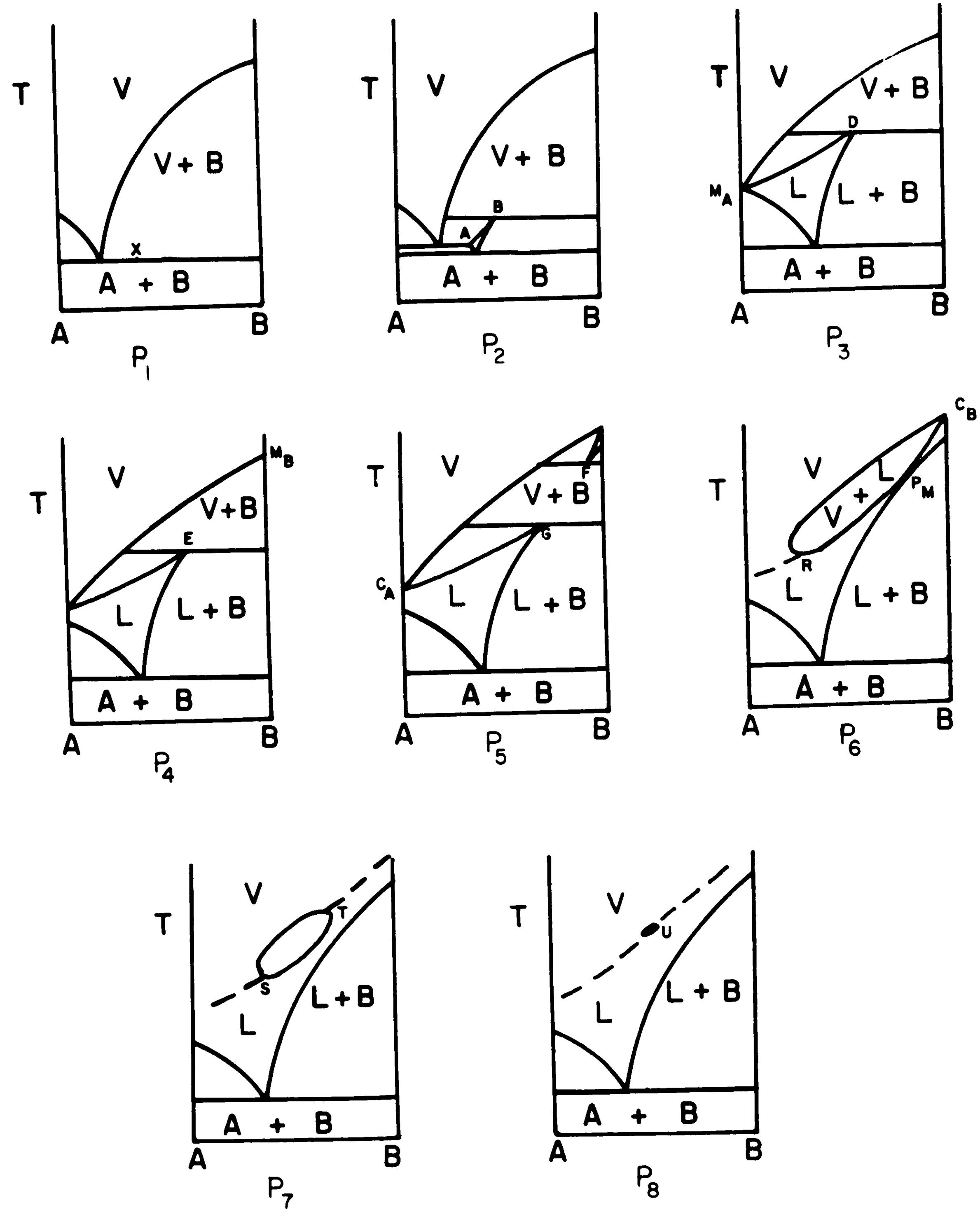


Figure 15

The case in which all critical points lie above the liquid solid region is shown in figures 16 through 20. Figure 16, P_1 to P_8 is a series of constant pressure phase diagrams outlining a simple two component system. The pressure in each succeeding diagram is higher than in that preceding so that P_1 is at the lowest pressure and P_8 at the highest. Relations similar to those in figure 16 are combined into a composite diagram in figure 17.

For definiteness the solubility curve is defined as the locus of those points which represent the composition of liquid which is in equilibrium with solid and vapor. Thus for any one temperature or pressure there is in general only one point on the solubility curve. In the event that there is a pressure (or temperature) maximum or minimum there will be a range in which two points will fall on the solubility curve (cf. figure 16b). At Point x in figure 16, P_1 liquid, vapor, solid A, and solid B are in equilibrium. This is the lowest point on the solubility curve. Other points on this curve are a, b, m_A, d, m_B, e, f, g and Pm. This curve cannot be fully represented except in a three dimensional drawing such as figure 17. Projections on the temperature and pressure axes are presented in figure 18. Points on these projections lying to the left of the point x


T
V
V+ B
X
A + B
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P1
T
V
V+ B
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P2
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V
V+ B
D
M_A
L
L + B
A + B
A
B
P3
M_B
T
V
V+B
E
L
L + B
A + B
A
B
P4
T
V
F
V+ B
G
C_A
L
L + B
A + B
A
B
P5
C_B
T
V
L
+
V
P_M
R
L
L + B
A + B
A
B
P6
T
V
T
S
L+B
L
A + B
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B
P7
T
V
U
L + B
L
A + B
A
B
P8

Figure 16

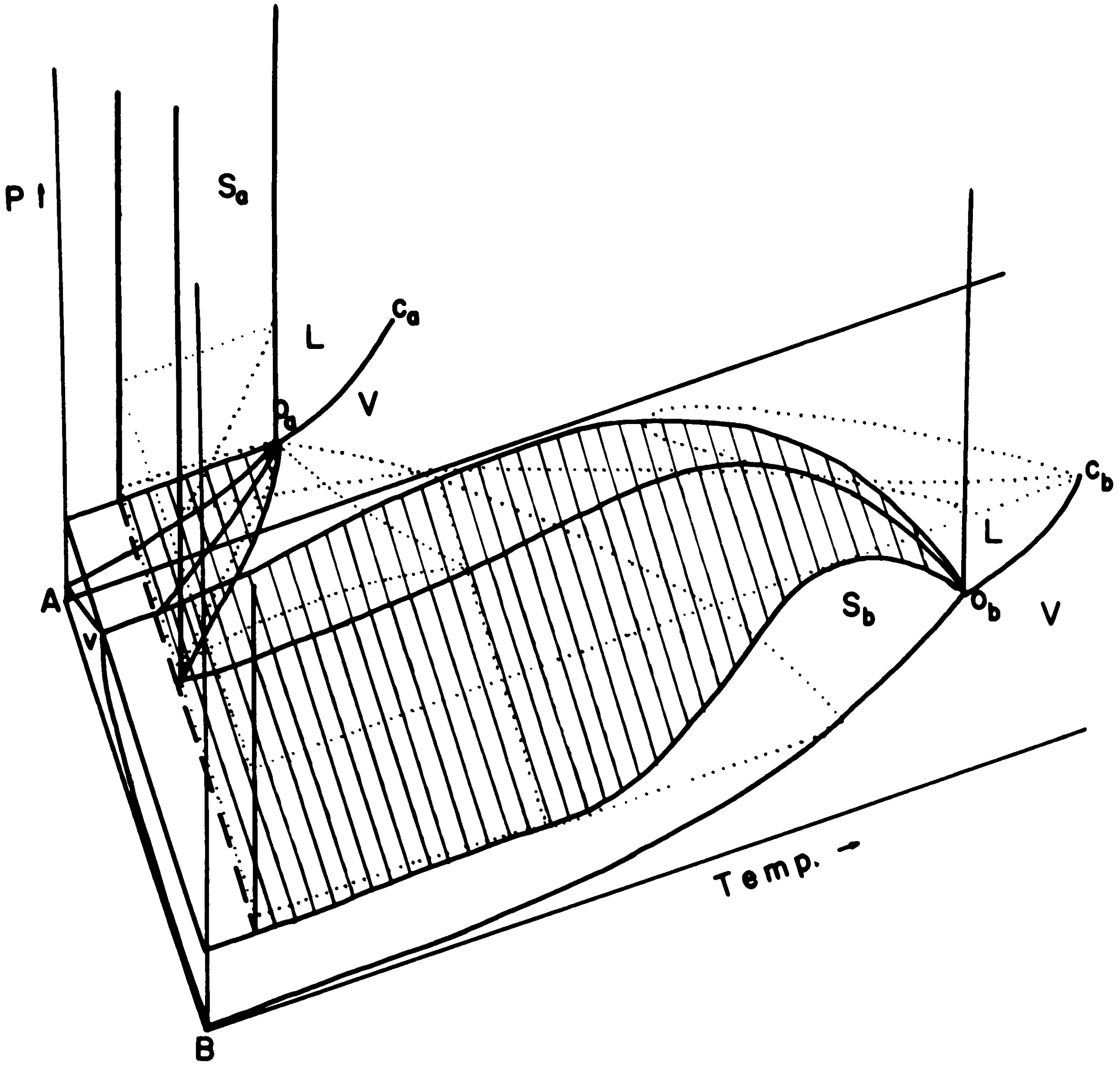
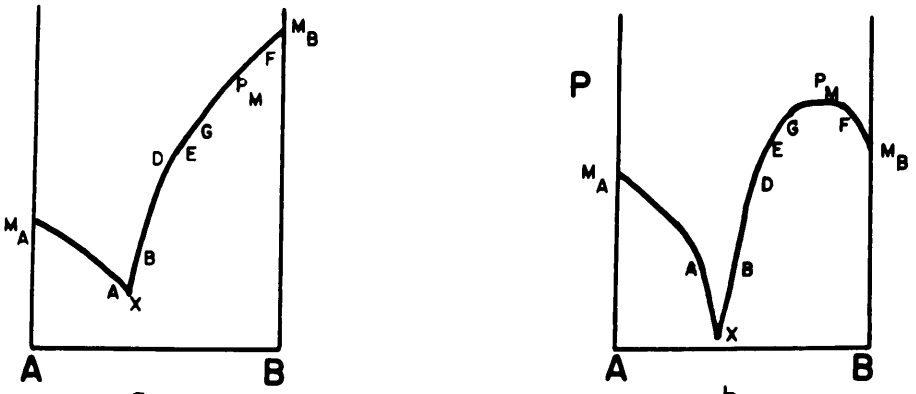


Figure 17

represent solubilities of solid A in liquid, and points to the right solubilities of B. Thus the minimum shown in figure 18b is distinctly different from the maximum.

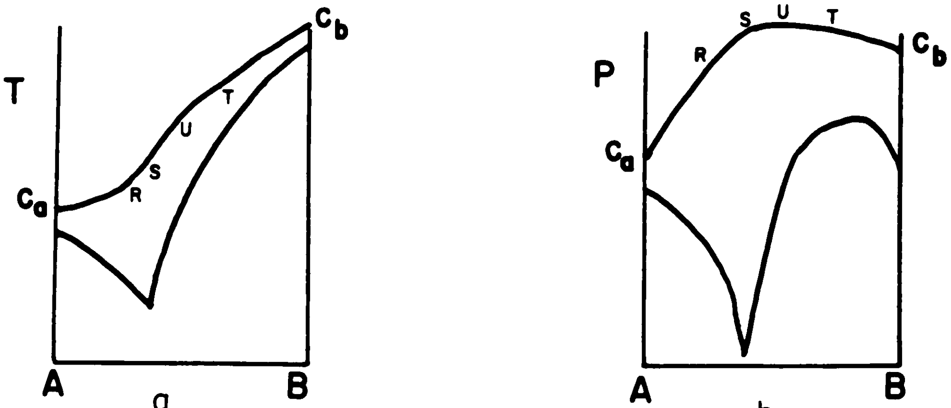
In figures 16, points which fall on the critical curve are c_A, r, c_B, t, s, and u. Figure 17 shows the three dimensional representation of the critical curve, and figure 19 shows temperature and pressure projections, of this curve as solid lines. It is to be noted that the critical curve does not intersect the solubility curve. Figure 20 shows projections of those liquid-vapor tie lines which intersect the solubility curve onto the temperature and pressure axes. In other words the right hand curves here are projections of the solubility curve itself; the left hand curves represent the vapors in equilibrium with the saturated liquids.

We now proceed to consider the case in which the solubility curve does intersect the critical curve. Diagrams corresponding to this situation are presented in figures 21 through 24. In figure 21, which is analagous to figure 16, the low pressure-temperature relations are essentially the same as in the preceding case. Figures 21, P_7 and P_8 show the only real differences, since all the others may also occur when the critical and solubility curves do not intersect. In figure 21, P_7, the lower extremity of the liquid-vapor loop is identical with the point



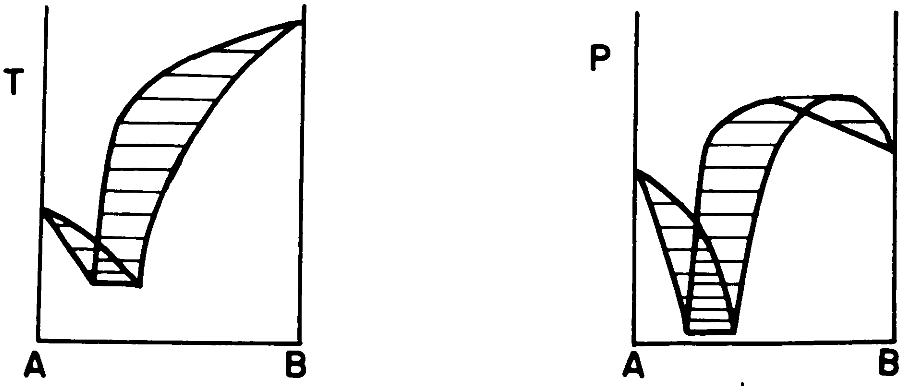
a b

Figure 18



a b

Figure 19



a b

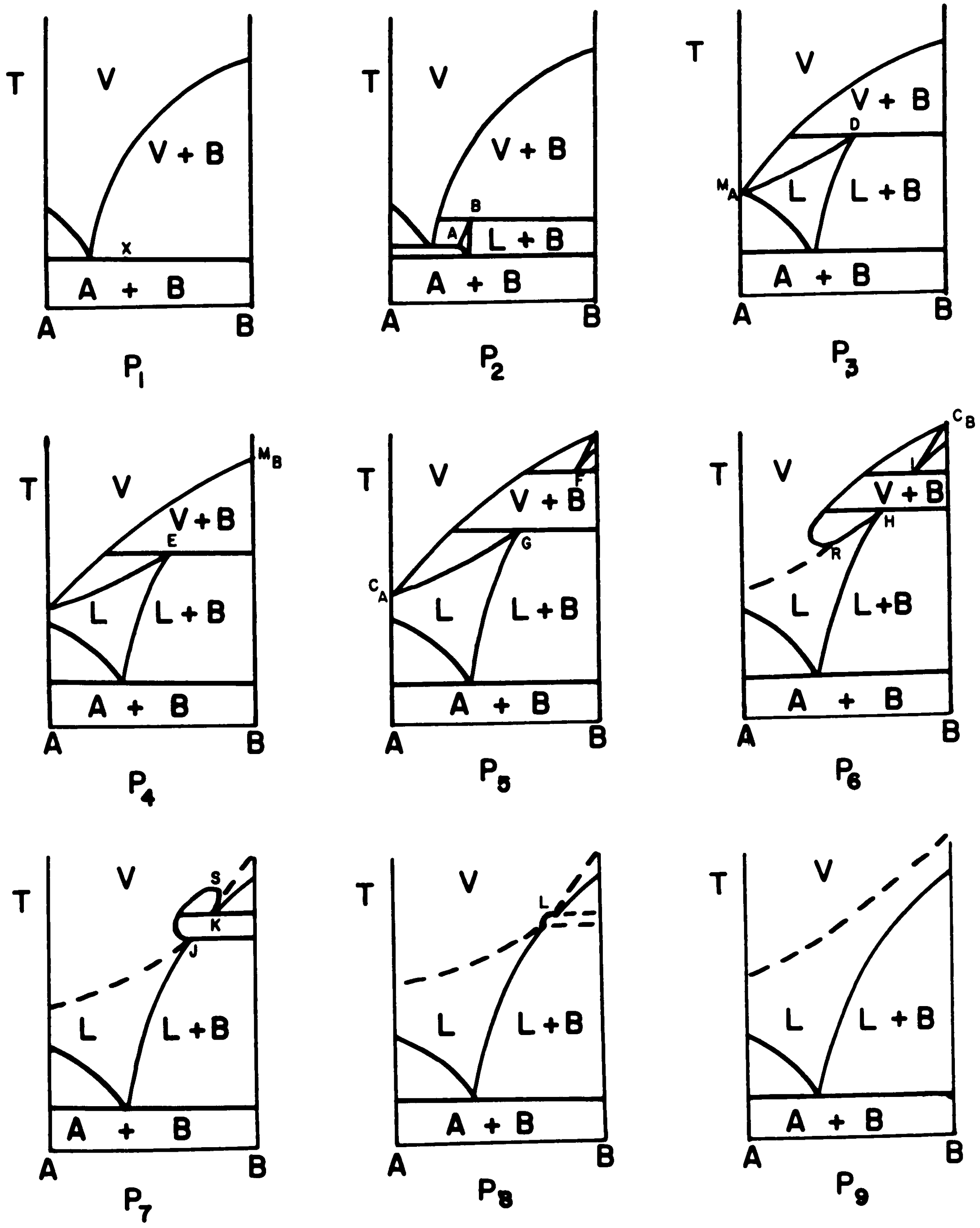
Figure 20

on the solubility curve. The point at which the upper extremity meets the solubility curve is shown in figure 21, P_8. A three dimensional representation of these relations is given in figure 22. The solubility and critical curves are plotted, in projection, in figure 23 so as to show their intersection clearly. The liquid-vapor tie lines are presented in figure 24, a commonly used diagram in discussions of critical phenomena.

The particular case shown above is only one of many possible ways in which these two curves may intersect. Other examples are shown schematically in figure 26. Many of these are essentially the same as given by Roozeboom and by Ricci.

The points at which the critical and solubility curves meet are known as critical end points. They occur when a substance is quite insoluble in some solvent and has a much higher critical point than the solvent. Examples are quartz and water, albite-water, and most probably all the common rock forming silicates plus water. Thus this phenomenon is of great importance geologically.

In order to consider volume relations we must hold constant one or more of the variables, pressure, temperature and composition and draw three dimensional diagrams such as P-V-c. Alternatively we may contour a two dimensional diagram. Figures 27 and 28 represent a liquid-


T
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V + B
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P1
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A + B
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P2
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V
V + B
D
M_A
L
L + B
A + B
A
B
P3
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M_B
V + B
E
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L + B
A + B
A
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P4
T
V
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P5
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V
C_B
I
V + B
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R
L
L + B
A + B
A
B
P6
T
V
S
K
J
L
L + B
A + B
A
B
P7
T
V
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Figure 21

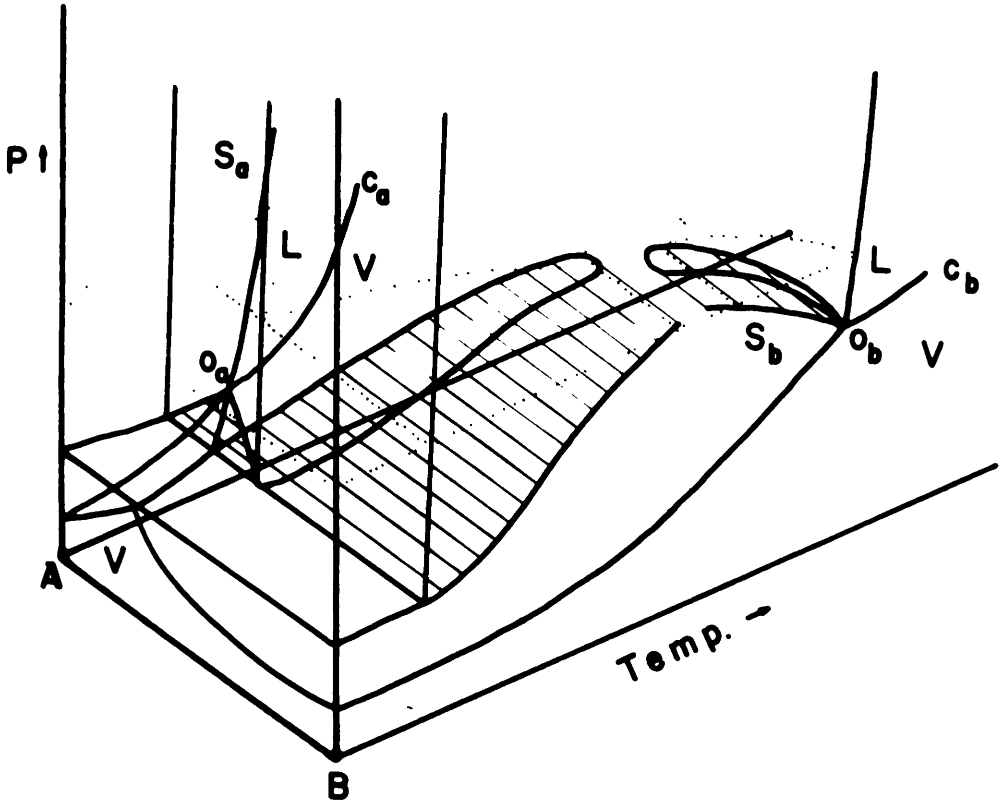


Figure 22

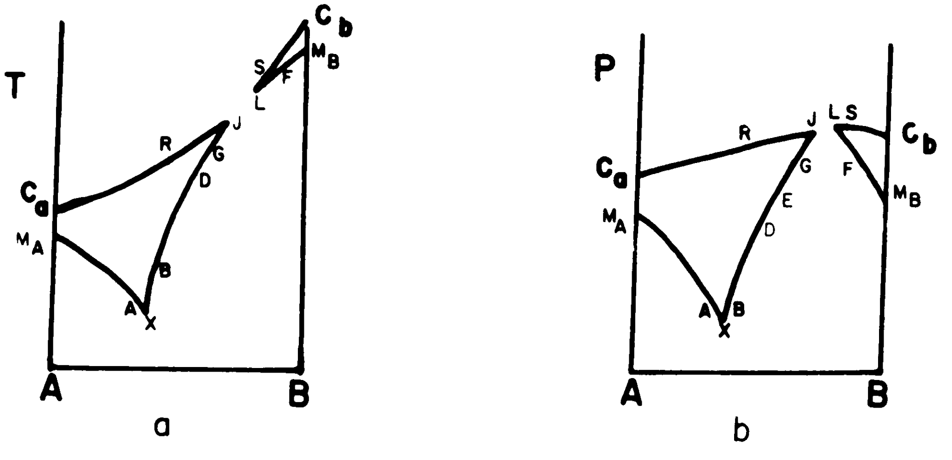


Figure 23

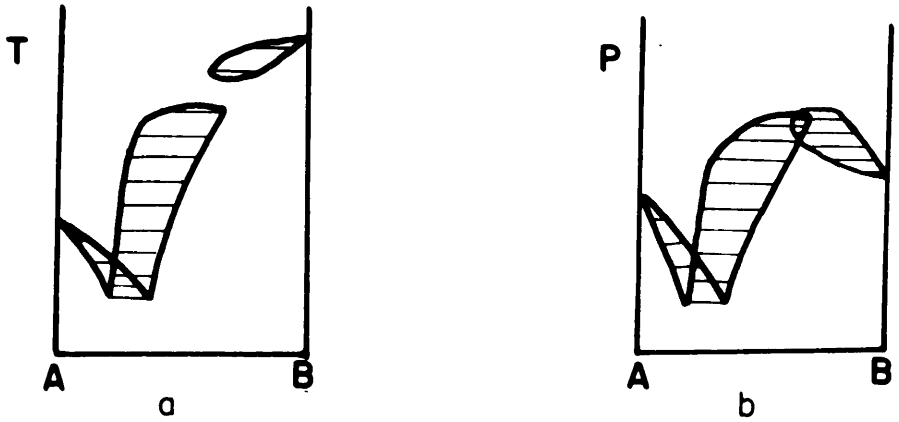


Figure 24

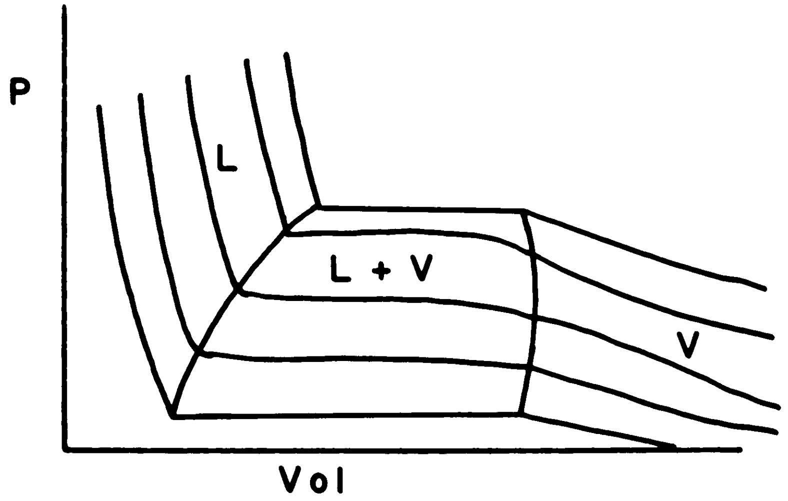


Figure 25

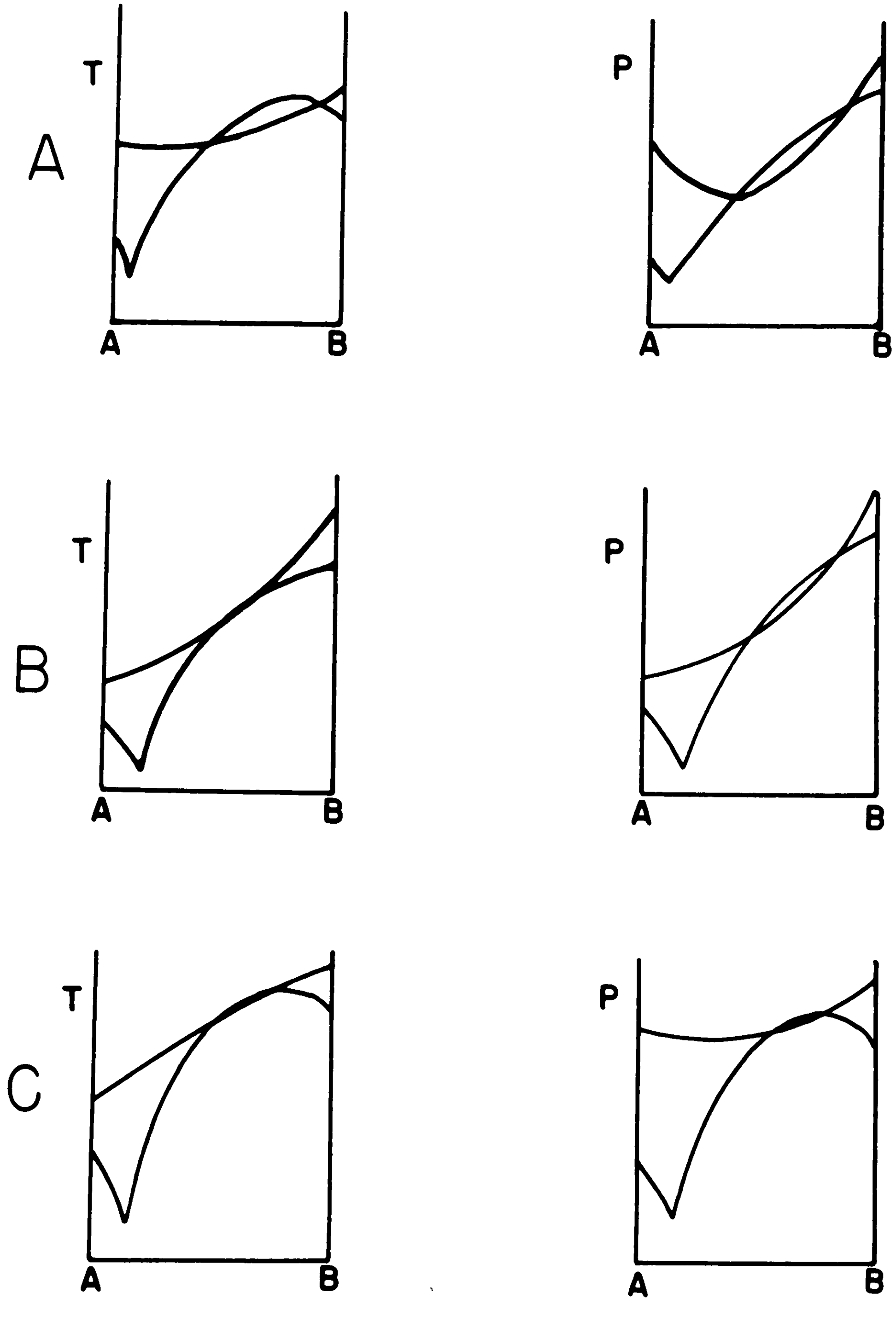


Figure 26

vapor loop at constant temperature in these two ways. To represent the picture more fully lines of constant bulk composition have been drawn in figure 27; these together with the tie lines delineate a P-V-c surface. A projection of the relations on this surface onto the V-c plane gives rise to figure 29, a type of plot used frequently by Roozeboom and by Niggli. A projection of isopleths (lines of constant bulk composition) onto the P-V plane is shown in figure 25.

In the event that the temperature chosen for constructing a P-V-c diagram exceeds the critical temperature of component A, the relations are changed to those shown in figures 30 and 31.

When the system under study is at high pressure so that experiments must be conducted inside steel bombs, these results assume considerable significance. In this case, liquid and vapor cannot be distinguished visually, but only by interpretations of P-V-T data. In a one component system one can pump a gas into an evacuated container at a temperature below the critical until the gas vapor begins to condense. At this point the pressure will remain constant until, with further pumping, the vessel is full of liquid. Forcing more material into the container causes an abrupt rise of pressure. However,

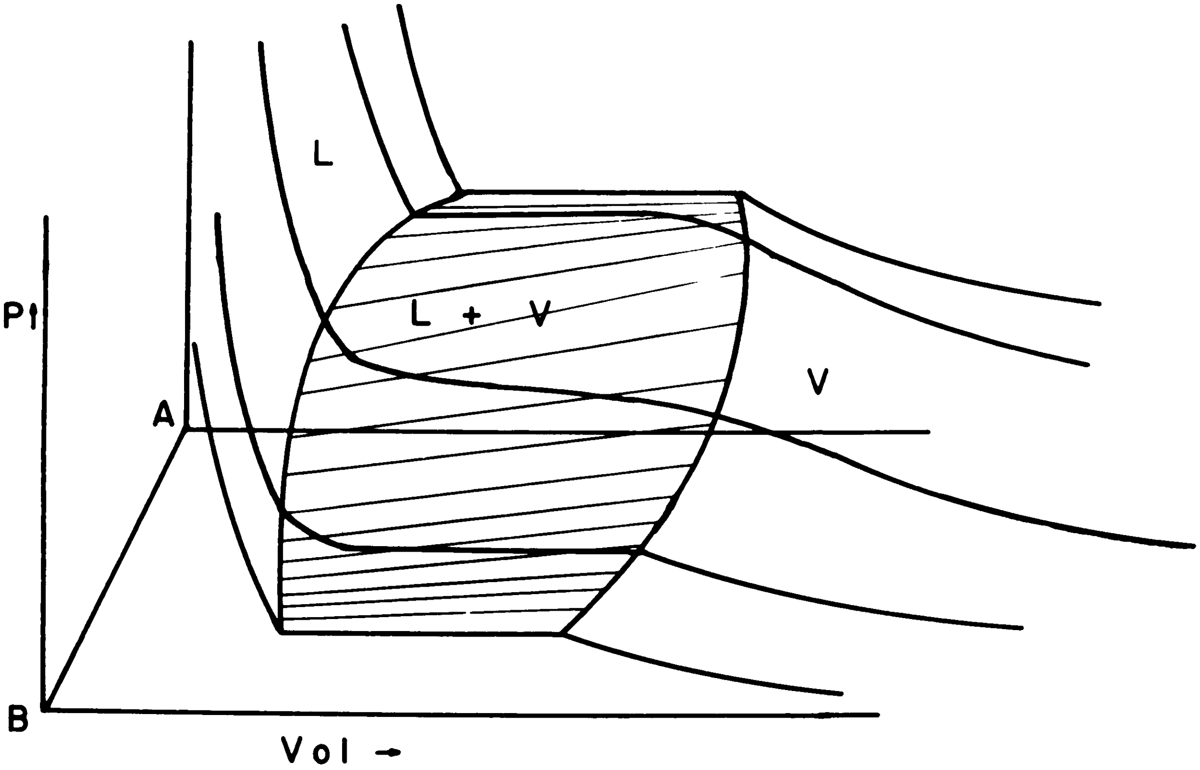


Figure 27

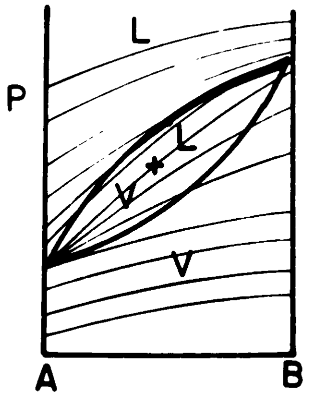


Figure 28

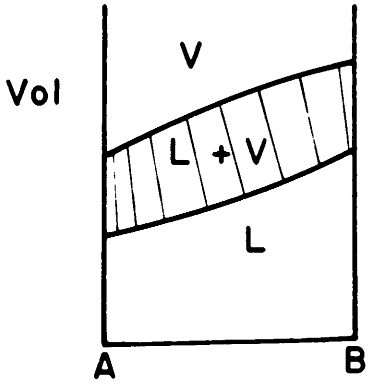


Figure 29

as examination of figure 25 clearly shows, this is not the case with a binary mixture. Here there may or may not be abrupt changes of the slopes of isopleths; in fact there may not be any isobaric portion in the entire process of condensation. It is therefore not always possible by this means to tell when liquid begins to form, nor when all the vapor has disappeared.

It should be noted that the isopleths often do show a sharp break at the compositions near the pure components and especially on the liquid side of the transition. In the case of solubility measurements where critical end points occur, it would seem at first that the following experiment would be helpful. Solid B is placed in a bomb in excess with enough liquid A so that liquid, vapor and solid are present when heated to temperature. After equilibrium is attained, pure A is pumped into the bomb, and the pressure measured continuously. If the temperature is lower than at the critical end point, it would be expected that a sharp rise in pressure would soon take place; if above the critical, only gradual rise would result. Once again, however, the result may be ambiguous. Referring to figure 30 it is seen that near the critical point of this system (no critical end points are shown here) a sharp break in the isopleth will occur at composition x if

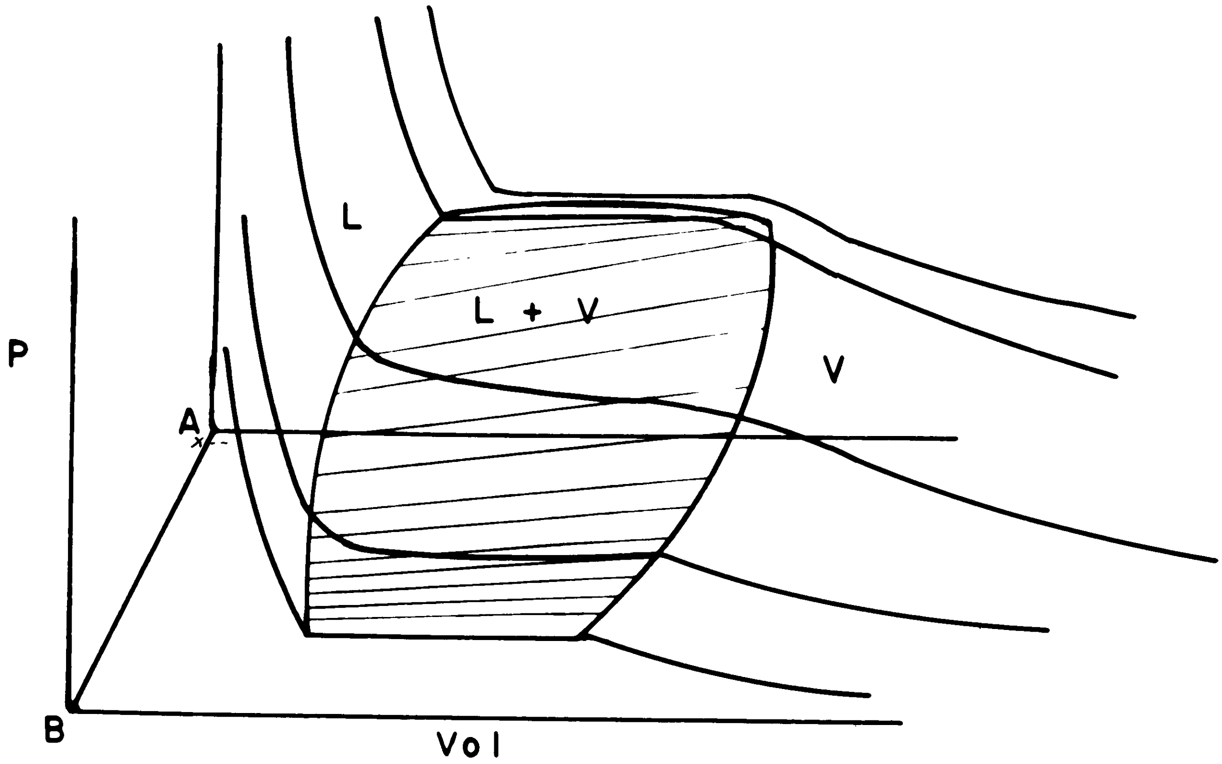


Figure 30

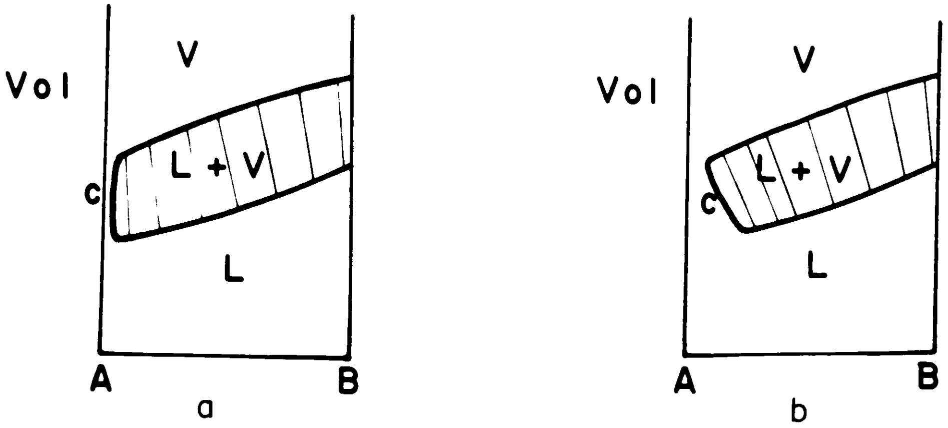


Figure 31

the added fluid is also of composition x. But if we add pure A, the bulk composition and the resulting P-V curve may slip out sideways, so to speak, and not show any discontinuity in slope. We would thus assume that the critical point had been exceeded, an obviously wrong answer. Similar remarks apply to the case of critical end points and mean that the experiment outlined above is valueless.

Another approach to the problem of introducing volume into present considerations is to construct a P-V-T diagram at constant bulk composition. In this case the pressure, volume, and temperature of the system can all be adequately represented in the three dimensional representation, but in all the two phase regions the compositions of both phases are different from the bulk compositions and cannot be shown. In figure 32b, such a P-V-T diagram is presented for some such composition as x of figure 32a. It is to be noted that the isotherms in the liquid-vapor region are not isobaric, as was the case in a one component system (of figure 10). Likewise the isobars are not isothermic, nor do all the isochors have the same slope at the same temperature as in the case with a single component. Comparison of figures 32c and 32d with figures 10b and 10c respectively shows the

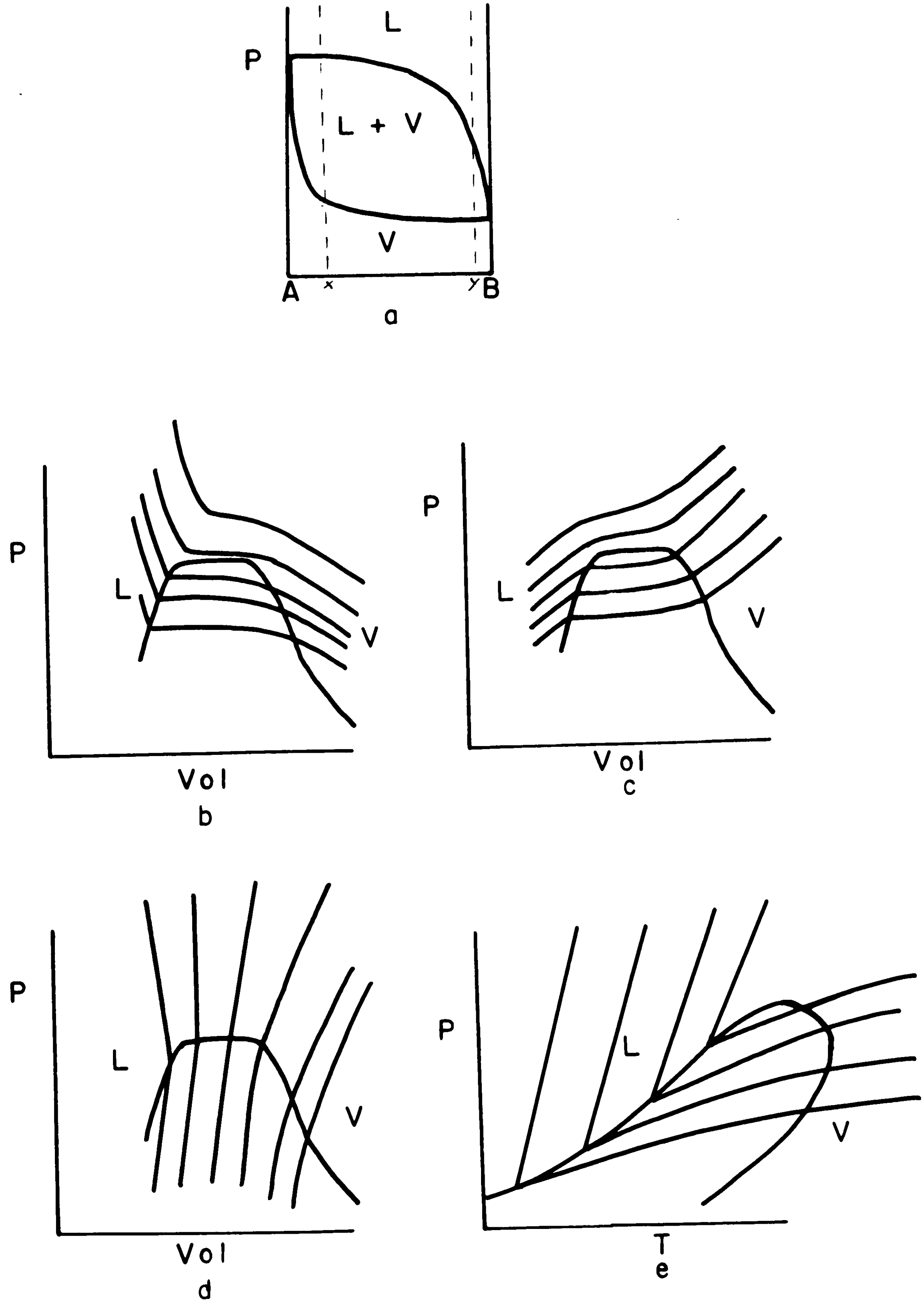


Figure 32

difference between the two cases. Figure 32 shows a projection of these relations onto the P-T plane. In these diagrams the points Pc and Tc have the same significance as in figure 13. If instead of the compositions some such value as y were chosen from figure 32, the curvature on the isotherms, isobars, and isochors would occur on the left of the liquid-vapor region instead of on the right. This is shown for isotherms in figure 33.

Other V-c diagrams are shown in figures 34, 35, and 36. If to figure 29 we add the solid-liquid relations, assuming a simple eutectic, we obtain figure 34. Figure 35a shows a more complex case in which liquid, vapor and solid are in simultaneous equilibrium; this is the diagram resulting when the temperature is dropped from that shown in figure 34. If, however, the critical point of pure A is exceeded at some temperature below the triple point of pure B, we obtain the relations shown in figure 35b. Finally all volume composition plots falling at temperatures between the upper and lower critical end points of the system have the form of figure 35c. To obtain a complete picture of the system in T-V-c coordinatès, we have merely to superimpose diagrams of the types shown in figure 35. To avoid confusion the only boundary lines used are those surrounding regions in which solid B or solid A is one of the phases. Thus all tie lines are omitted, and

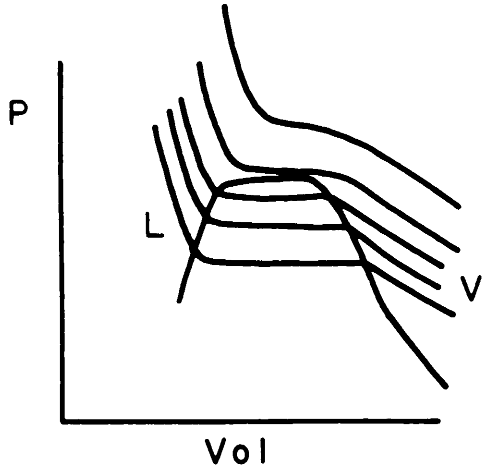


Figure 33

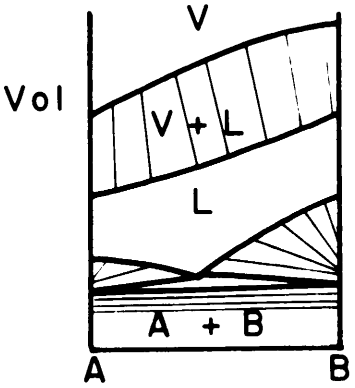
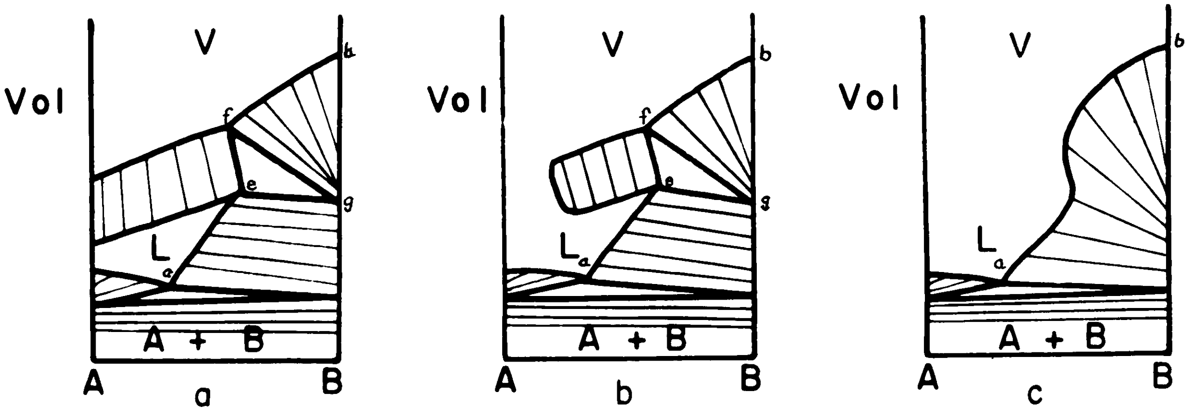


Figure 34



a b c

Figure 35

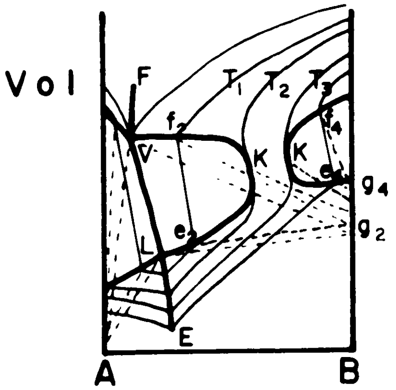


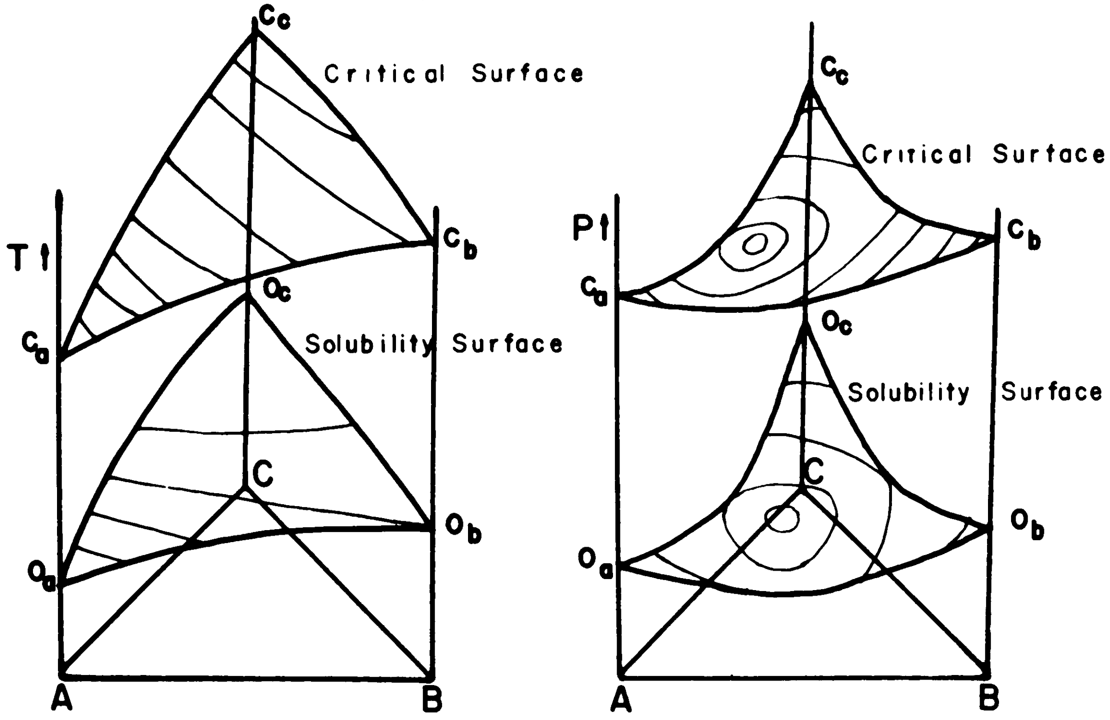
Figure 36

the boundary lines of the liquid-vapor field are omitted. Then for a temperature T_1 above the upper critical end point the lines af, fg, ef, eg, and eb from figure 35a or b are plotted in figure 36. Next a curve of the form ab in figure 35c and passing through the upper critical end point is plotted. Proceeding in this way, taking successively lower temperatures, the complete T-V-c diagram is constructed. Isotherms to the left of the line FVLE represent solid A in equilibrium with vapor or liquid; those to the right solid B plus vapor or liquid. The line EL is the liquid eutectic line and VF the vapor eutectic.

Before proceeding to the three component case, it would be well to point out the general trend of relations as the number of components is increased. With only one component we are faced with only one critical point; with two components we have a critical line. Phase changes in single component systems are generally marked by sharp changes in isotherms, isochors, and isobars; with two components this is by no means general. A critical point may be located as the limit of the isothermal-isobaric tie lines in a one component case, but with two components there may be no isotherms that are also isobaric. Thus in passing from one to two chemical components points become lines, lines go to surfaces, and solids go to four-dimensional "solids;" it becomes more difficult to locate phase transitions, and in particular to find critical points. Adding a third component may therefore be expected to transform the points of the one component system into surfaces, lines into solids, and so on. We are then dealing with critical surfaces and critical end point lines. It becomes more difficult yet to locate transitions from one phase to another, and the occurrence of smooth curves, as opposed to cusps and discontinuities, becomes more common. Fortunately for the present work, certain characteristics of the particular system under study enable the determination of phase changes with a greater degree of accuracy than is indicated by this discussion.

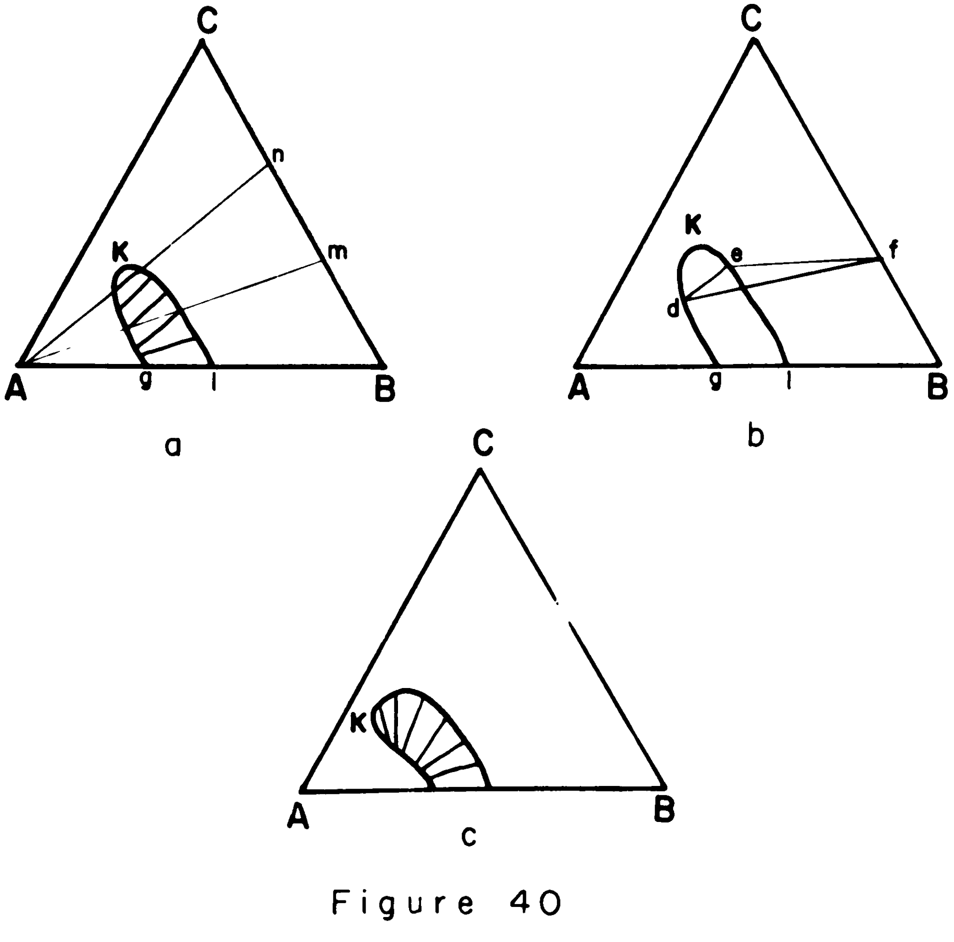
Having discussed the two component cases in considerable detail, we may now proceed to three components. It has already been mentioned that now we must deal with a critical surface; in like manner we have a solubility surface. As with two components we can distinguish two cases; those in which saturated solutions do not show critical phenomena, and those in which they do.

Figure 37 shows a case in which these surfaces do not intersect. The particular situation represented exhibits a regular variation among the three components with respect to temperature, but shows a ternary minima in both surfaces. There are, of course, a great variety of



a b

Figure 37

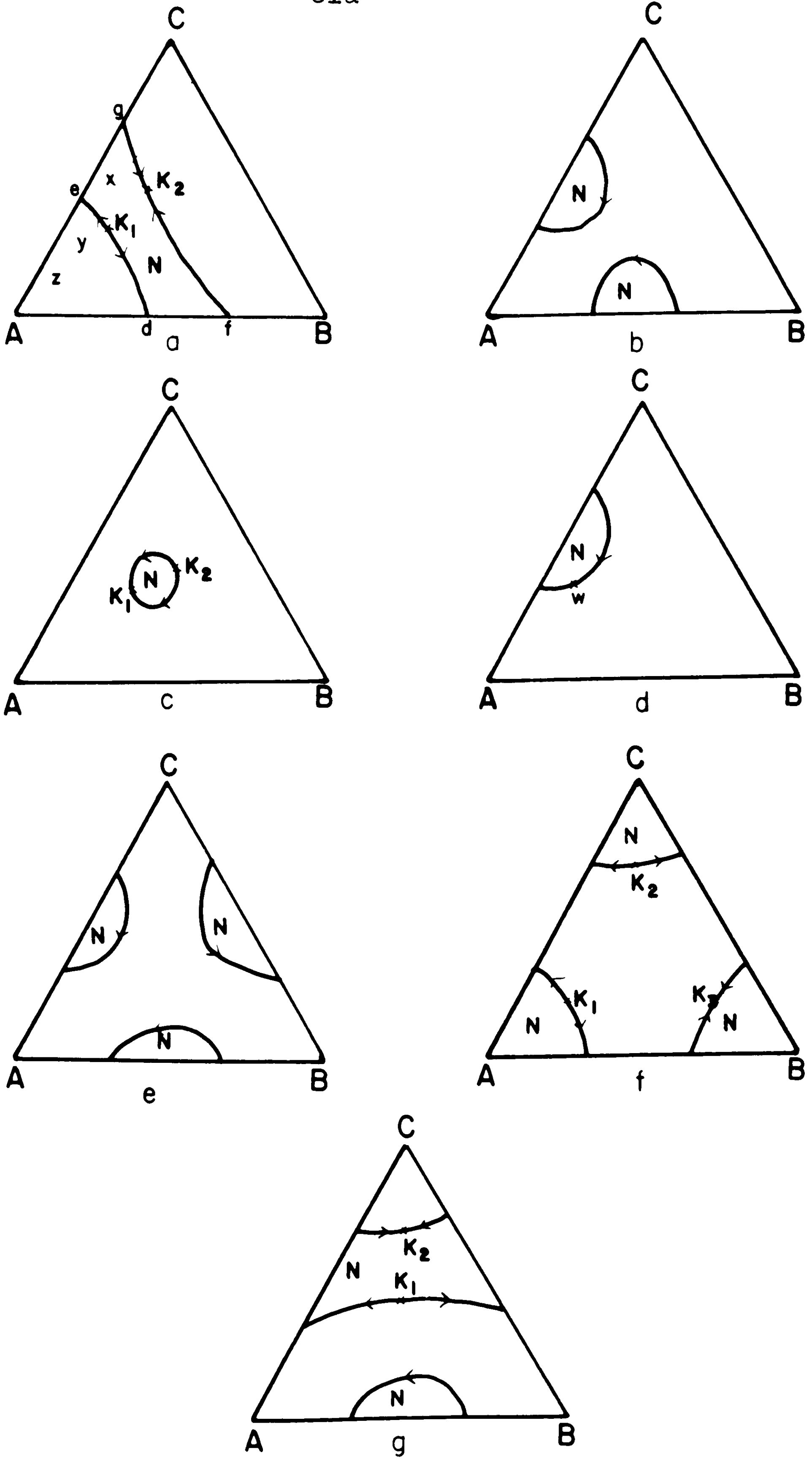


a b c

Figure 40

other cases showing various combinations of binary and ternary maxima and minima. A situation can arise in which components A and B exhibit a maximum, B. and C a minimum, and A and C a simply ascending relation.

Such complexities being possible, it is easy to see that a great variety of curves could result from the intersection of the critical and solubility surfaces. Rather than discuss all conceivable cases, only a few of the more usual examples will be given. Attention will then be turned to the particular types of most value in the present work. In figure 38 projections onto the ternary composition plane of six different cases are shown. It will be noted that, in each case where a binary system is involved, there is an upper and a lower critical end point. The example represented by figure 38a is described in great detail by Niggli. Here there are two binary systems showing critical end points. The non-volatile substances show complete solid solution, and since the properties of the solid solution are essentially the same as the pure components both the upper and the lower critical end point curves extend completely across the ternary field. Point K_1 represents the highest temperature point on the lower critical end point curve, and K_2 the lowest temperature on the upper critical end point curve. A similar case is


C
g
x
K2
e
K1
y
N
z
A
d
f
B
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B
C
N
K2
K1
A
c
B
C
N
w
A
d
B
C
N
N
N
A
e
B
C
N
K2
K1
K3
N
N
A
f
B
C
K2
N
K1
N
A
g
B

Figure 38

shown in figure 38, but here the intermediate solid solution (or compound) is sufficiently more soluble in A so that critical phenomena do not occur in the saturated solution. Figure 38c shows the result when two ternary maxima or minima intersect. If critical end points occur in only one of the three binary systems, a figure such as 38d arises; if all three binary systems show critical end points, some such diagram as 38e, f, or g may arise. In figures 38 a to g the areas marked N represent regions between or "inside" the critical end point curves. These are therefore areas in which the critical end point and solubility surfaces do not exist. Blank regions represent those portions of the system in which these surfaces do exist.

These statements do not mean that it is impossible for a bulk composition which plots within an area N to have liquid, vapor, and solid in equilibrium. For instance, in figure 38a the bulk composition x may consist of a solid solution of composition a, liquid y and vapor z. In this case the temperature would have to be below the lower critical end point for that composition. It would not be possible to have a liquid lying between this critical end point and x in equilibrium with vapor and solid.

To obtain a fuller understanding of the significance of critical points in three components, we now proceed to construct composition-volume triangular cylinders. For this purpose use is made ofthe binary composition-volume diagrams presented above. Following the method of Niggli a temperature is chosen between the lower critical end points of the system AC and AB shown in figure 38a. A diagram similar to figure 35b must then be constructed along the AB side of the prism, and one like 35c along the AC side. The temperature must be well below the triple points of components B and C, so the diagram on the third side consists of a diagram similar to that of figure 29, except that it represents vapor-solid relations. The completed representation is given in figure 39; solid lines outline the relations on the three faces, and dashed lines in the interior.

This diagram can be greatly abbreviated by projecting the curve gKl onto the composition plane. In figure 40a the result is shown together with the projection of those liquid-vapor tie lines which are in equilibrium with solid. If the curve gKl and the triangle def are projected onto the triangular base, figure 40b is obtained. Here it is seen that the ratio of B to C is different in general in each of the three phases. However, the ratio of B to C in the liquid and the vapor becomes identical as the point K is approached. This is easily seen in figure 40a where line An coincides with a

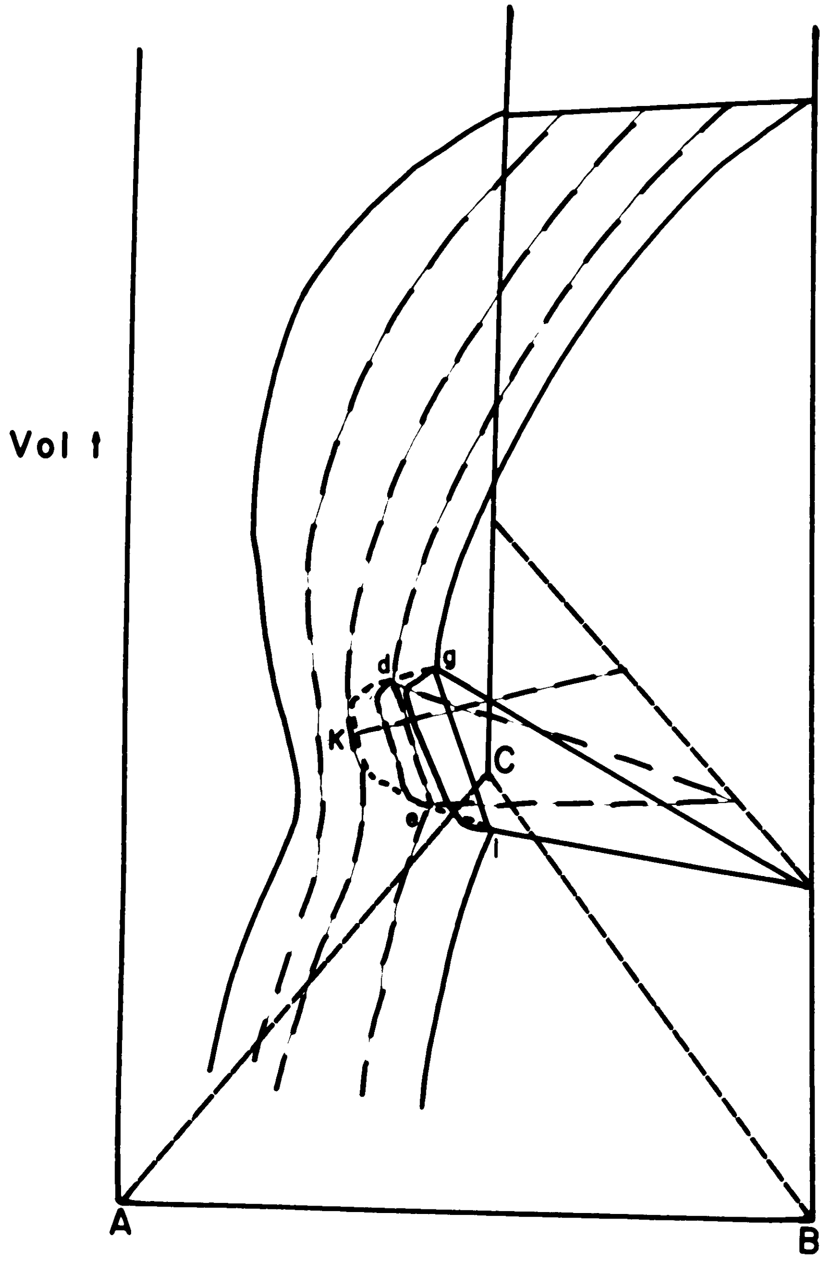


Figure 39

tie line, but where line Am does not do so. In this figure point K lies at that point where a line through A is tangent to the liquid-vapor loop. Since K may also lie at other points on this loop another more complex case arises (figure 40c) and this is in fact the relation which most probably occurs in the system under study.

With the use of diagrams such as that shown in figure 40a it is easy to construct the sequence of relations at successively higher temperatures. The sequence for the example of figure 38a is shown in figure 41. Here temperature is continually rising from a through i. Points K_1 and K_2 are the same in both cases. The curve de in figure 37a is the locus of all points K, K', and K'': the curve fg is the locus of points K''', K'''', and K''''' in figure 41. Figure 38b can be built up similarly by using the sequence of figures 40a, b, c, g , h, and i. --figures 41d, e, and f are omitted. The situation shown in 38c corresponds to the sequence 41d, c, g, f-- provided that the loops in c and f are moved somewhat to the right.

The last case to be considered is outlined in figure 42, a constant temperature prism, and is believed to correspond to the conditions encountered in the present experiments. For definiteness water, quartz, and potassium hydrogen disilicate have been entered at the corners of the triangle. The relations do not represent the

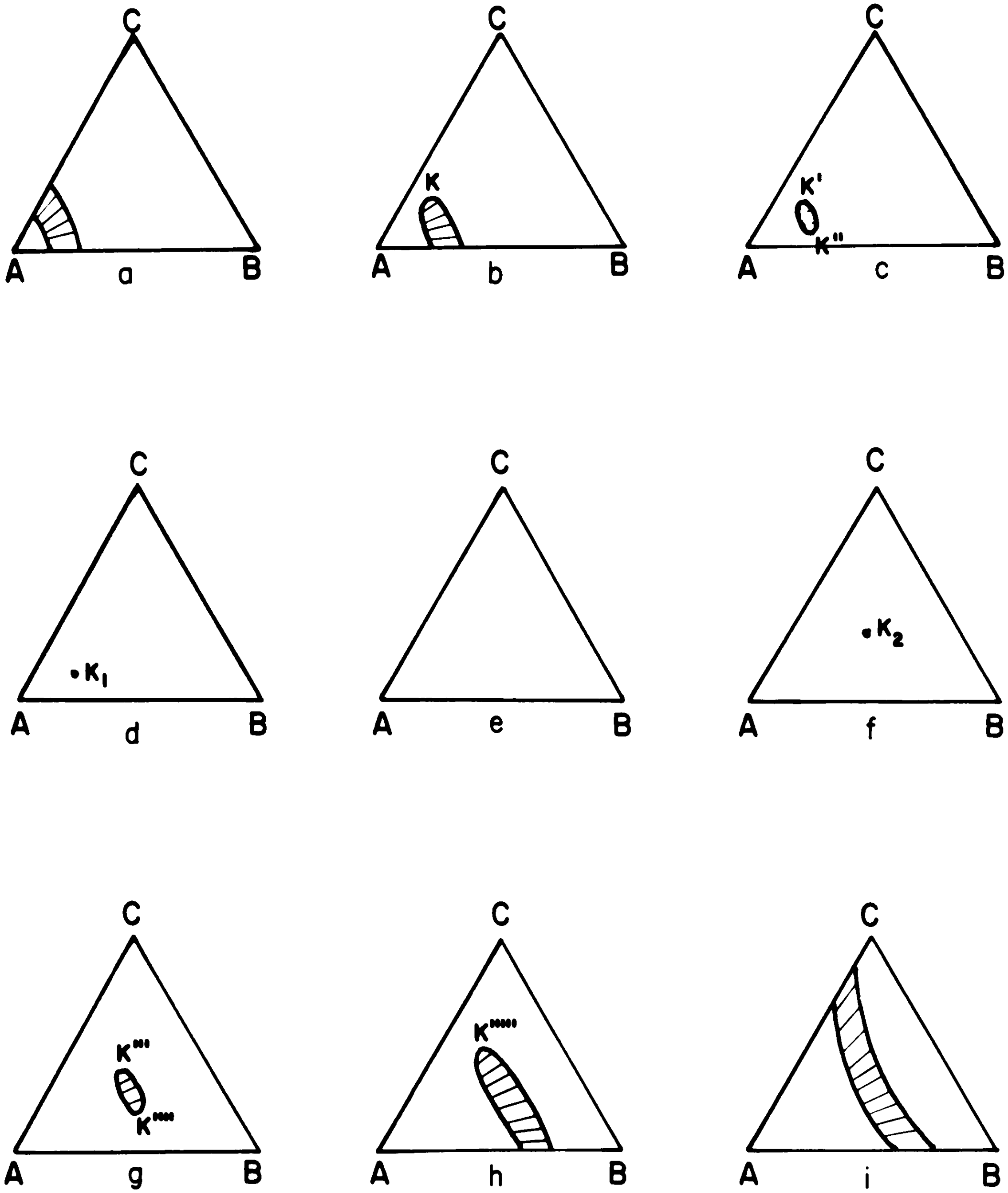


Figure 41

accurate plotting of the compositions found in the system, but they do give a qualitative answer. In the tetrahedron jmnop liquid, vapor, and solid $KHSi_2O_5$ are in equilibrium. In the tetrahedron jgmn solid $KHSi_2O_5$ quartz, liquid n and vapor m are in equilibrium; the pressure is constant throughout this solid. The volume gmbeKn represents that region in which quartz, liquid, and vapor are in equilibrium. The point K represents the critical end point at the temperature chosen.

The lines aK, bc, gf, and others of the same nature have been drawn at a constant ratio of potash to silica. The tie lines in the plane pmbeKno connect liquid and vapor in equilibrium and do not have a constant ratio of potash to silica. The curved lines such as orp also connect points where liquid and vapor are in equilibrium. The solid orpmbqeKn represents that region in which liquid and vapor are in equilibrium and is filled by tie lines.

Let us then start a process under high pressure at some such composition as x, where x has the same ratio of potash to water as does point K. We then maintain the temperature constant, and lower the pressure (increase the volume). At the start the system consists of liquid in equilibrium with quartz. As the pressure is decreased the solubility of the quartz is decreased* along the line

---

*The diagram actually shows that the solubility increases. This is done because of the greater ease of drawing and because the diagram is easier to visualize when drawn in in this manner.

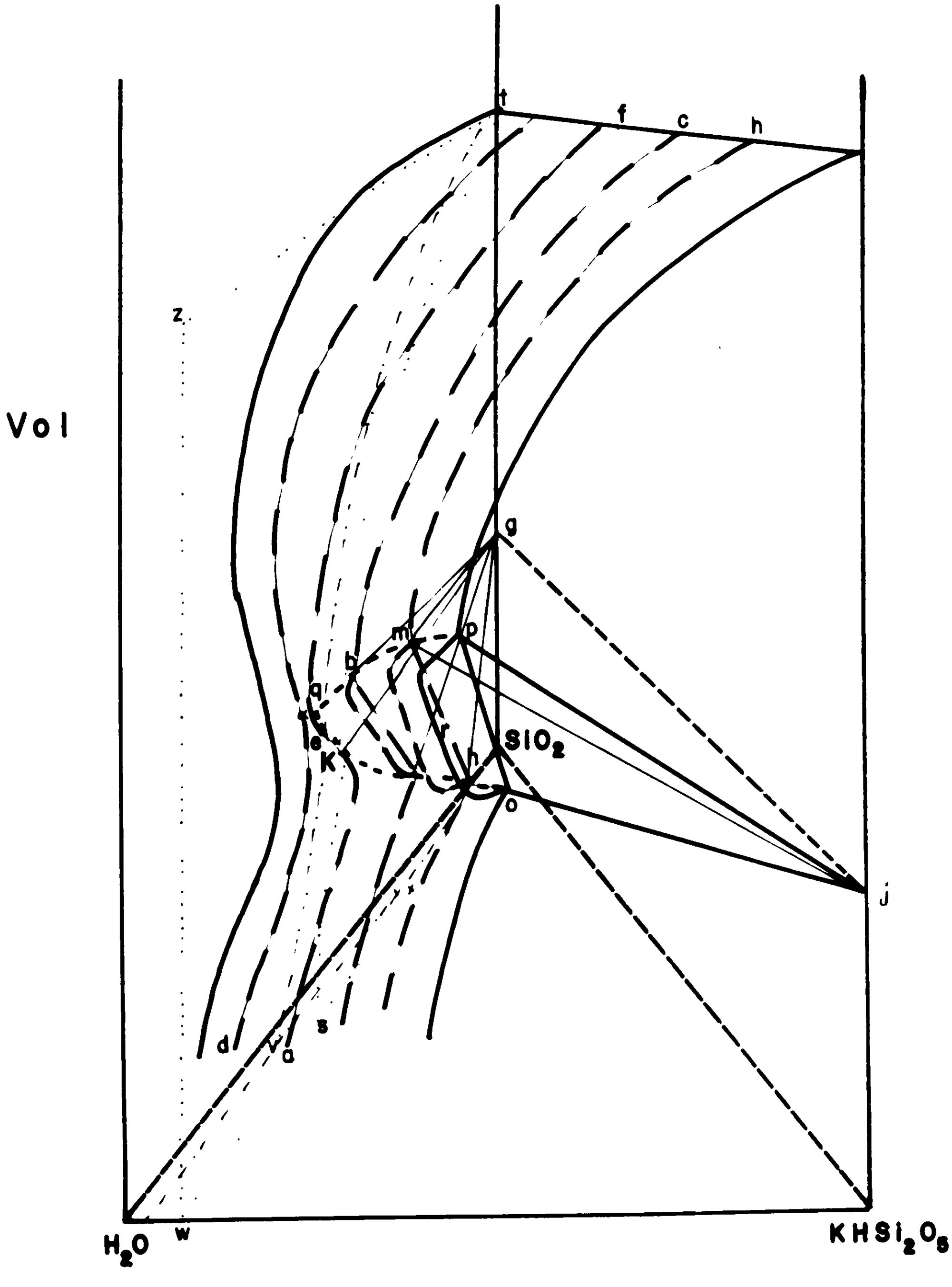


Figure 42

sK. At K liquid and vapor of the same composition are in equilibrium with quartz. This is the critical end point at this temperature. Decreasing pressure further produces a liquid and a vapor of different compositions both in equilibrium with quartz. On reaching point b, all the fluid is vaporized. Further decrease of pressure causes more and more silica to enter the vapor phase until only vapor is present. Another experiment starting with bulk composition y may be performed in the same manner. Here the composition of liquid in equilibrium with quartz rises along ve. The critical end point in this case has been exceeded (assuming a critical end point curve of the form 38d). The fluid at e is thus a vapor having attained this state without undergoing boiling. At point e the vapor splits into liquid and vapor. Decreasing the pressure still more first increases the amount of liquid and then decreases it. At point g all the fluid is vapor once again. This sequence of transitions is exactly analogous to that described in the liquid-vapor loop of figure 13f. Following this to its logical conclusion, it is readily seen that it is possible under appropriate conditions to have liquid, vapor, and solid in equilibrium at all temperatures between the critical end point lines as well as above and below them! In a four component system it would be possible to have two solids, liquid, and vapor in equilibrium in the entire range between the critical end point

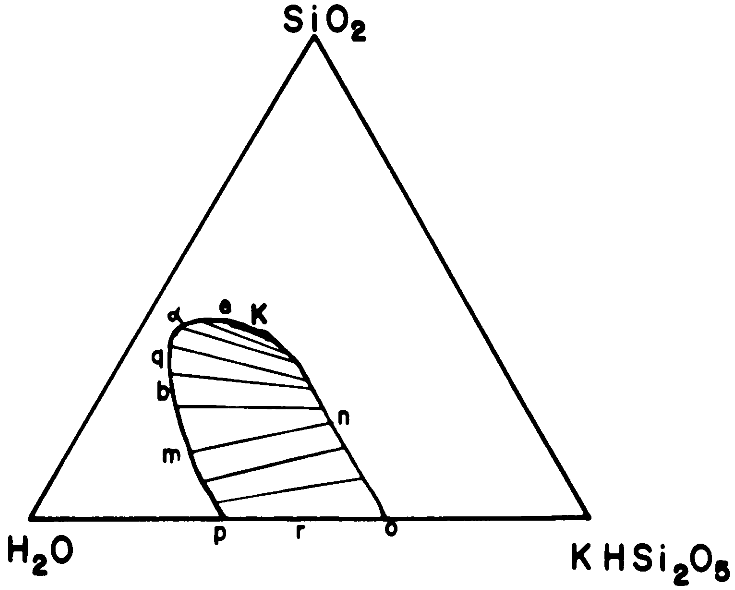


Figure 43

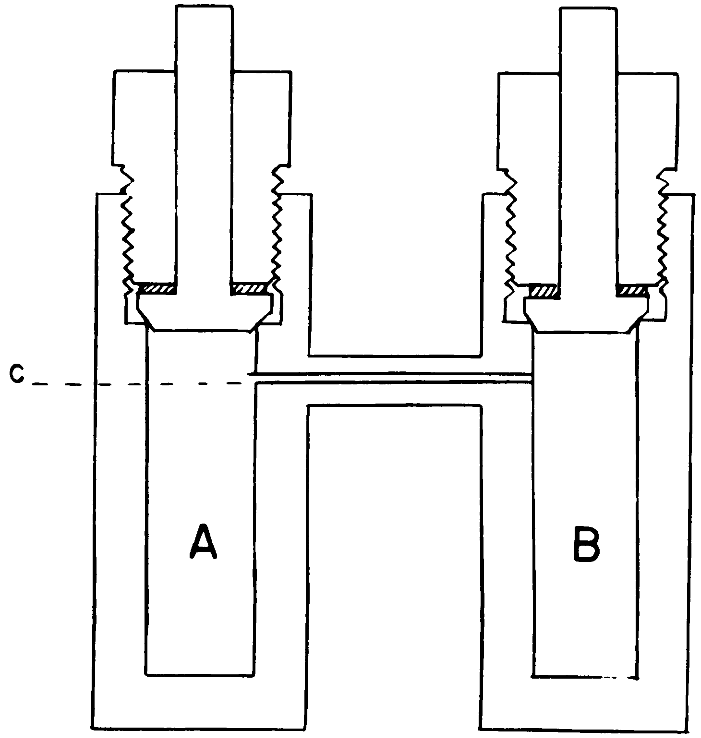


Figure 44

surfaces. In view of the importance assigned to critical phenomena in the recent geological literature, this result is of great importance. Under magmatic conditions, for instance, it would probably be possible to produce a vapor in equilibrium with a partly crystallized pluton at any temperature.

In view of the discussion given above of the non-isobaric nature of an isothermal evaporation it is apparent that the transition here from liquid-solid to vapor-solid, at constant temperature, is also non-isobaric. It is therefore not possible to locate the critical end point by means of P-V-T data. In fact it is not easy to detect the change from liquid-quartz to liquid-vapor-quartz. Fortunately a special property of the present system facilitates recognition of this transition.

Referring to figure 42 again we see that a liquid in equilibrium with quartz and an infinitesimal amount of vapor will lie along line Kn. Decreasing the pressure from there it is seen that the evaporation causes a very rapid increase in the potash content of the liquid. Although not clearly shown this increase in potash more than compensates for the fact that there is now less volume of liquid. There is thus more weight of silica in solution at the lower pressure. This increase was found to be extremely sharp if the temperature was near or above the critical point of water (cf fig. 64). If therefore a number of experiments are run at increasing specific volumes at the same temperature, the weight of quartz dissolved per gram of fluid first drops until the line Kn is reached, then increases abruptly. Unfortunately because of the relative position of K, it is impossible by this method to locate the critical end point, or even to tell whether there is a critical end point at the concentration of KOH in question.

Yoder of the Geophysical Laboratory in Washington has suggested a method of locating the critical end point in such cases, and this appears to be the only method available. A bomb such as shown in figure 44 is used, always in an upright position. In compartment A quartz plus KOH solution is added. The amount of solution added must be regulated so that when hot, the expanded liquid will not rise above the level c. The chamber B will then be filled with vapor. On cooling the vapor will condense to a liquid in compartment B, and the liquid will contract to partially fill compartment A. The separate liquids are then analyzed; if the compositions are identical, the system was at the critical end point.

To study the solubility relations at different potash to water ratios we may take cross-sections of the prism in figure 42, such as the plane tvwz. This plane intersects the boundary between fluid plus quartz and homogeneous fluid in a single line. The composition of the fluid in equilibrium with quartz can thus be shown simply on the plane, provided the three phase region is avoided.

We now take the single point where the fluid first splits into two phases on releasing a high pressure, and plot the composition of this point against the temperature. Proceeding in this manner for all different temperatures we obtain the curve α Kc of figure 45 and 46. In figure 45, liquid of compositions along Kc is in equilibrium with quartz and vapor of a composition lying along Kb. The vapor is poorer in silica and potash than the liquid. At temperatures above that at K, a vapor of composition lying on αK is in equilibrium with quartz and a liquid lying along aK. This liquid is richer in potash and silica than the vapor. The point α corresponds to the highest temperature in the lower three phase field at which two fluid phases can exist in equilibrium with quartz at the concentration of KOH chosen. As the temperature approaches the upper critical end point, three phases will appear again.

It may happen that the composition chosen shows no such points as α. In this case the situation in figures 47 and 48a arises. Lastly if the concentration is sufficiently great, no critical end points will arise (in this system), and the graph of figure 48b is obtained. A graph

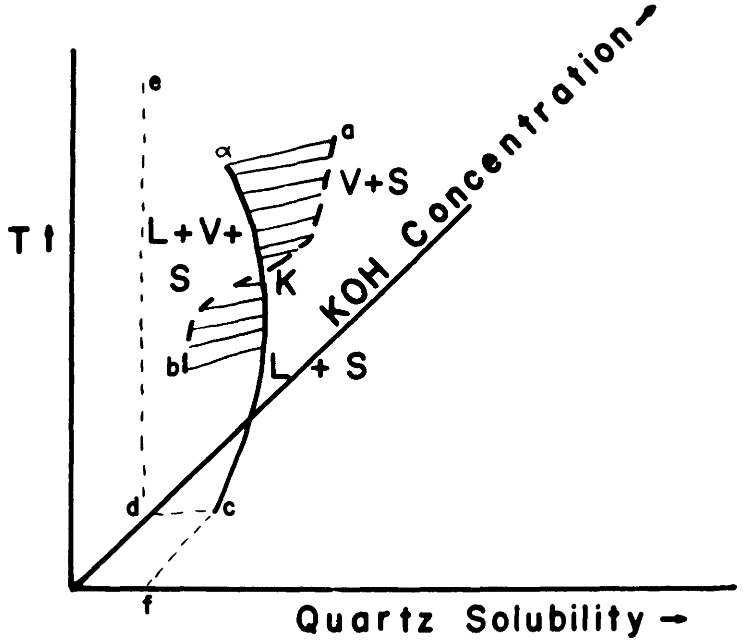


Figure 45

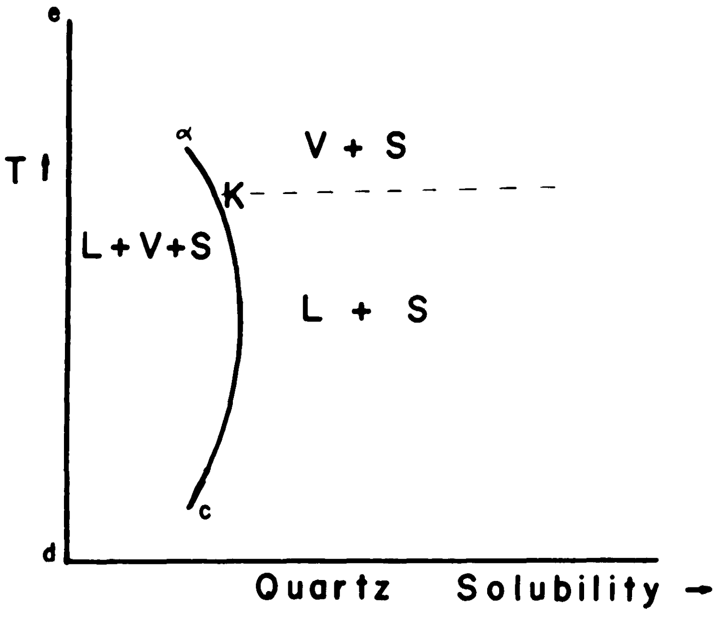


Figure 46

of this nature is used to show the experimental data. Isochors and isobars have been added in the liquid-solid region.

One further observation is worthy of mention in this section. It has been noticed by Cailletet and Mathias that, if the densities of liquid and vapor in a one component system are averaged and plotted against temperature, a nearly straight line passing through the critical point results. For water this relation is shown in figure 49. For systems of more than one component there is of course a range of values of density for liquid and vapor in equilibrium. It is therefore not possible to make much use of a plot of this nature. However, the experimental data for work with 0.05 molal KOH, the densities of liquid in equilibrium with quartz and a minute amount of vapor can be plotted. Since this graph shows no indication of a rapid increase of slope toward higher temperatures, it has been concluded that there is probably no critical end point at this concentration. This conclusion may be in error however.

The reader may perhaps wonder why no use has been made of the extensive theory of solution and thermodynamics in this work. The reason is simply that almost all of this theory is based on the use of thermal data such as heats of reaction, heats of solution, entropies, and the like.

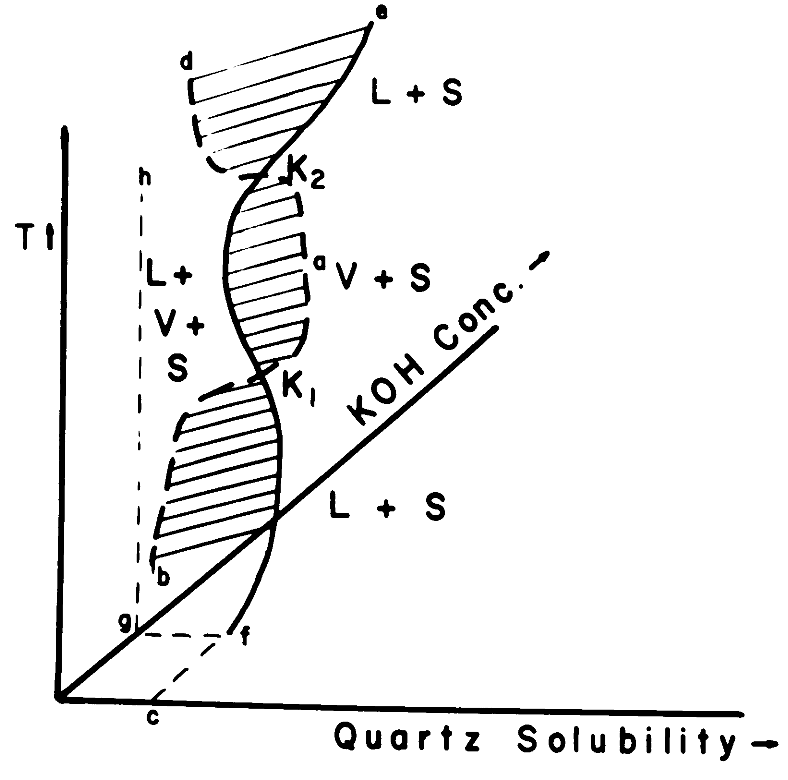
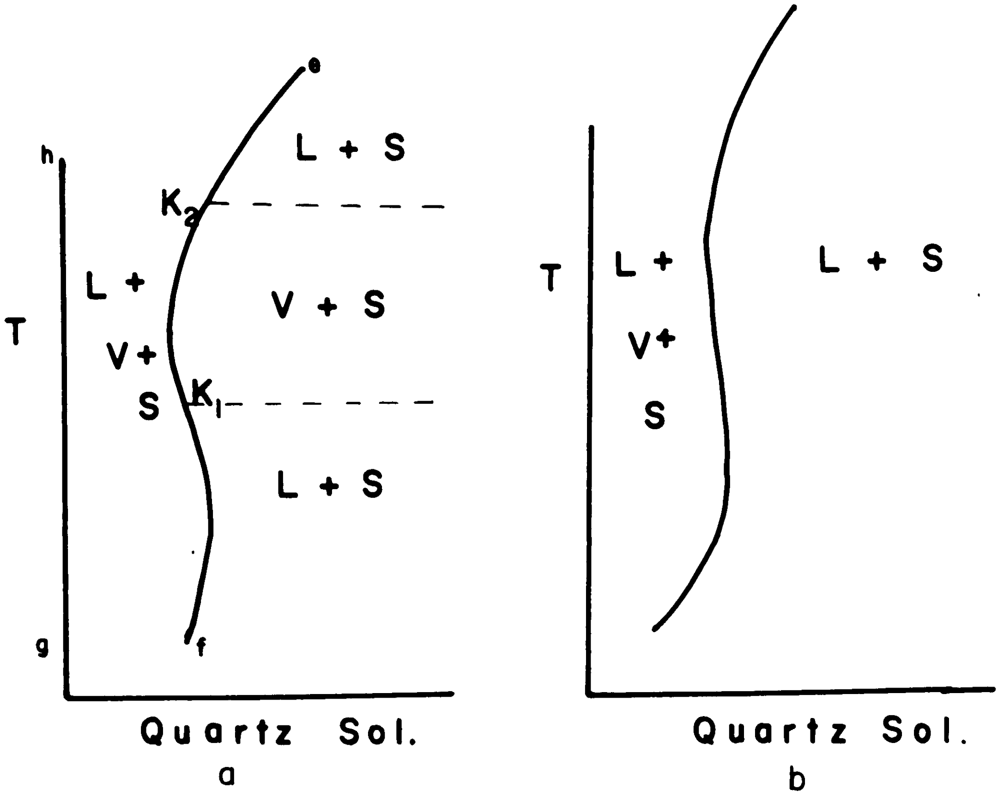


Figure 47



a

b

Figure 48

At the present time it is very difficult to obtain such data under high temperature conditions, with high pressure and high temperature the situation becomes much more difficult. No attempt was made therefore to obtain such data. Furthermore no such information is available in the literature. It is thus unfortunately true that these tools of thermodynamics cannot be used.

EXPERIMENTAL DIFFICULTIES

In addition to the many problems already discussed, four others of importance have yet to be mentioned. The first of these concerns leakage of the solution from the bomb. With the cone-in-cone type bomb experience has shown that once a leak has started for any reason, that all or nearly all of the solution is lost at once. If the seal is almost tight, it sometimes develops that solution will leak out until the pressure has dropped to a certain value. Not infrequently this pressure is in the neighborhood of 100 bars.

With the unsupported area type seal the situation is quite different. In this case too rapid heating may cause a slow leak to start between the heated wall and the still cool copper washer. However, the pressure is building up on the inside, and soon the washer deforms to fill the crack. In this event only part of the solution is lost.

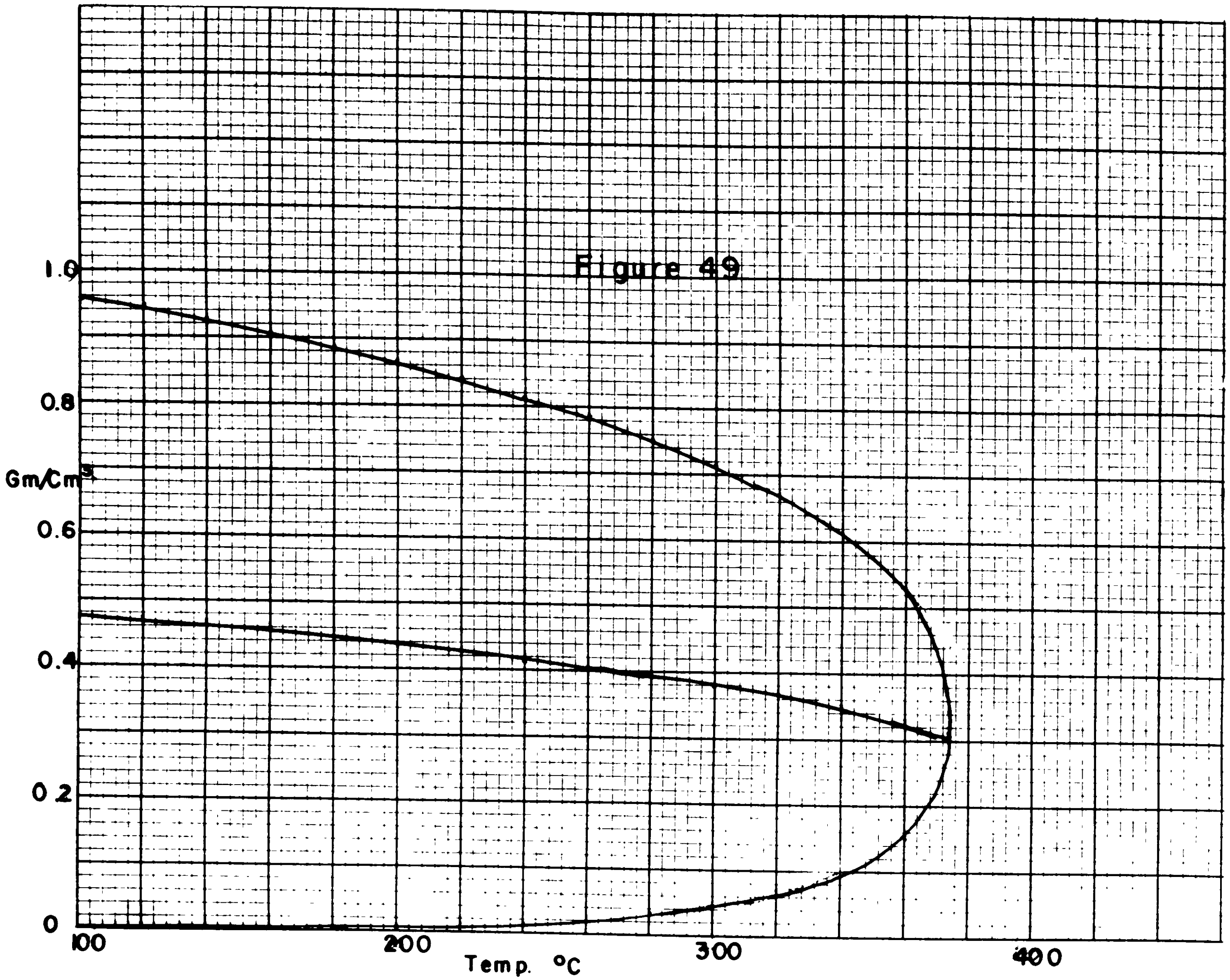


Figure 49

A second possibility is that a slow leak will be present throughout the course of the run. This is detected by measuring the pressure at regular intervals. A steady drop of pressure indicates that there is leakage. These problems can be avoided by carefully annealing the copper washers and by relatively slow heating.

The second difficulty mentioned above is the occurrence of glass firmly welded to the quartz if the specific volume is very large. If such a run at temperatures near or above the critical point of water is quenched rapidly in water, a highly siliceous glass is found on the bomb walls, and especially between the platinum wires and the quartz plates. Since it is impossible to remove this glass without breaking the plate, the weight of quartz dissolved cannot be determined. Sometimes the glass forms a "mud-cracked" surface film on the quartz; this film is securely attached to the quartz in some places and not attached in others. The resultant appearance is that the quartz seems to be peeling off the plate much as does old cracked point from a wall. Crystal faces are often built up around the wires, often partly enclosing the wire. It was found that these problems could be avoided by slower cooling of the bomb. A quench in air, taking 1 1/2 to 2 hours, allowed the condensing water vapor to completely redissolve the glass (a dense liquid when hot).

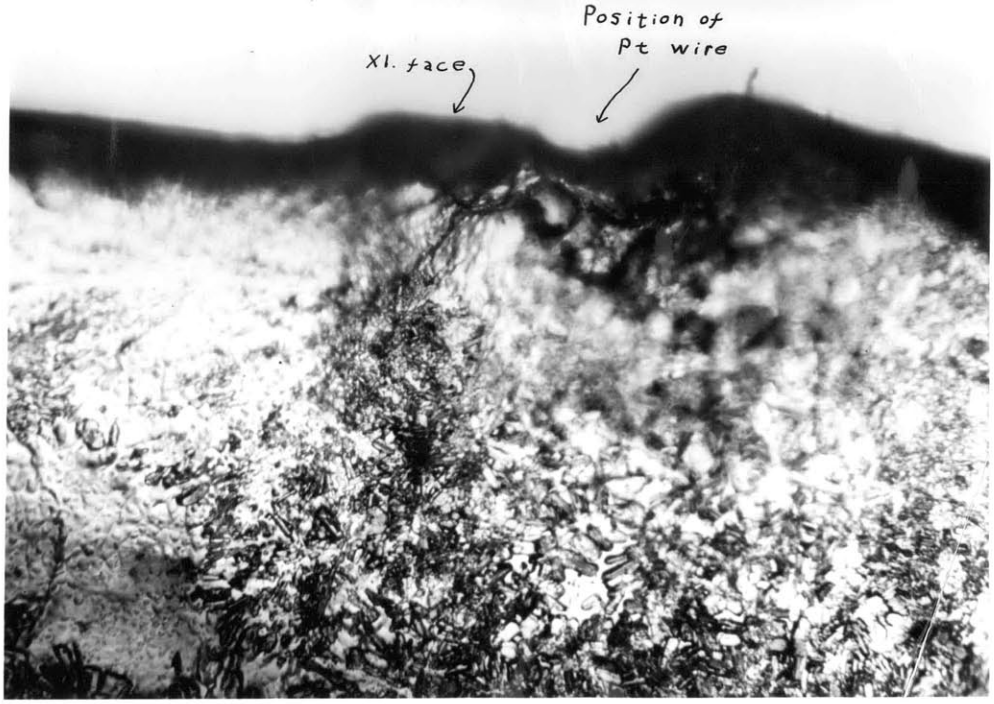


Plate 7

Quartz crystal faces grown around platinum wire

It has been suggested by several persons that the newly formed crystal faces were formed because of temperature variations next to the platinum wires. Since the wires are good conductors, the immediate vicinity of the wire would be the first place to show the effects of a slight temperature drop. This would cause precipitation of quartz. On the other hand a slight temperature rise would produce exactly the reverse effect. Fortunately, it was not necessary to investigate the basis of this local quartz growth since it did not occur in any of the runs which were of value to the present work.

Whenever possible the solution remaining in the bomb after being taken from the furnace was recovered. In most of the runs at high temperature with the unsupported area type seal this was not possible. This was a consequence of the difficulty of opening the bomb. The stem attached to the "head" of the bomb was threaded so as to provide a means of pulling the seal apart. If firmly stuck, however, this procedure was of no avail. In such a case the bomb had to be opened by loosening the nut and pumping water into the bomb until the pressure had built up to a high enough value to force the head out. The nut was kept loosely in place to prevent the head from flying violently about the room. The best procedure in this case is to pump water into the bomb until the pressure begins to rise. Then the valve leading into the bomb is shut off and the outside pressure is built up to a high value. On reopening the valve the head will pop out. If the pressure is built up slowly, a leak may develop so that the bomb will no longer hold pressure, but the head is not moved far enough to completely free it. Needless to say the KOH solution is greatly diluted in this case and is of no further value.

One last difficulty develops when the KOH content is high and the temperature upwards of 400°C. Under these conditions the KOH solution is sometimes so corrosive that it will dissolve tiny pinholes through an inch of stainless steel. The bomb is then of no more value than a sieve to hold pressure. If this happens, it is sometimes possible to recover the use of the bomb by filling it with a mixture of finely powdered aluminum oxide and water and pumping to a considerable pressure. The alumina tends to clog the holes. Neutral or slightly acid solutions can then be retained, but alkaline liquids quickly dissolve the alumina.

EXPERIMENTAL RESULTS

Previous to the present investigation, much work has been done on various parts of the system under study.

The work of Kennedy and of Morey and Hesselgesser on the solubility of silica in water has already been mentioned. The results of Kennedy's work are shown graphically in figures 50 and 51. The solubilities obtained by Morey and Hesselgesser are virtually identical.

In addition to this work Morey and Fenner have investigated a large part of the system K_2SiO_3 - H_2O-SiO_2. Their study was aided greatly in the organization of thought concerning phase relations. Their description of the potassium silicates enabled the identification of a crystalline compound encountered early in the present set of experiments. The fact that this compound occurs at so dilute a concentration of potash and the fact that it is not stable here at temperatures below about 350°C indicate certain changes in the curves drawn by Morey. The results of the previous study are given in figure 52 along with the suggested modifications. It is to be noted that Morey had no experimental data in the region of the proposed changes.

The related system H_2O-Na_2O-SiO_2 has been studied by Tuttle and Friedman. No direct use of these results has been made in the present work. Because of the appearance of liquid immiscibility, and a more extensive critical end point region it is probable that the relations to be found in very dilute NaOH solutions in

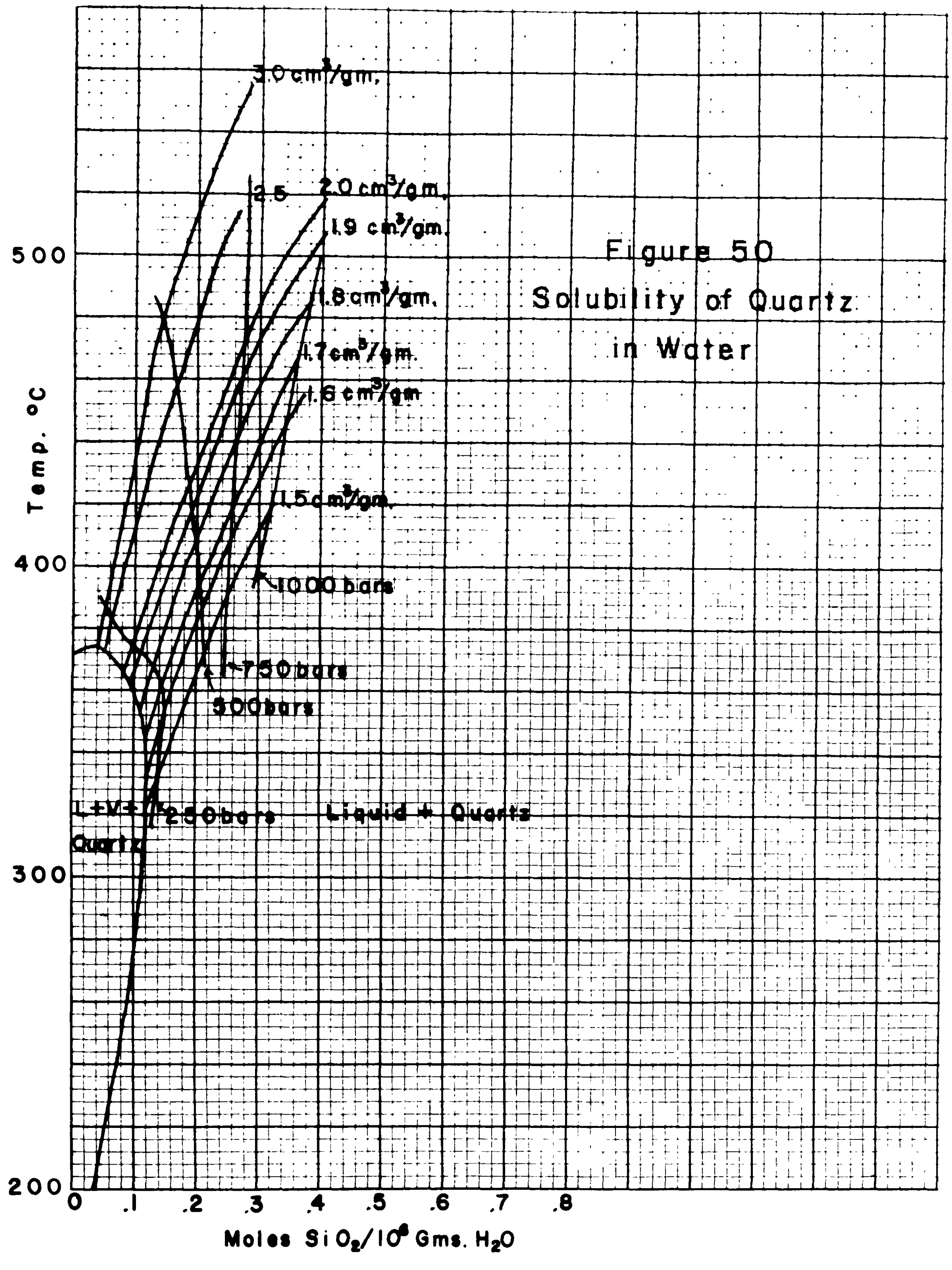


Figure 50 Solubility of Quartz in Water

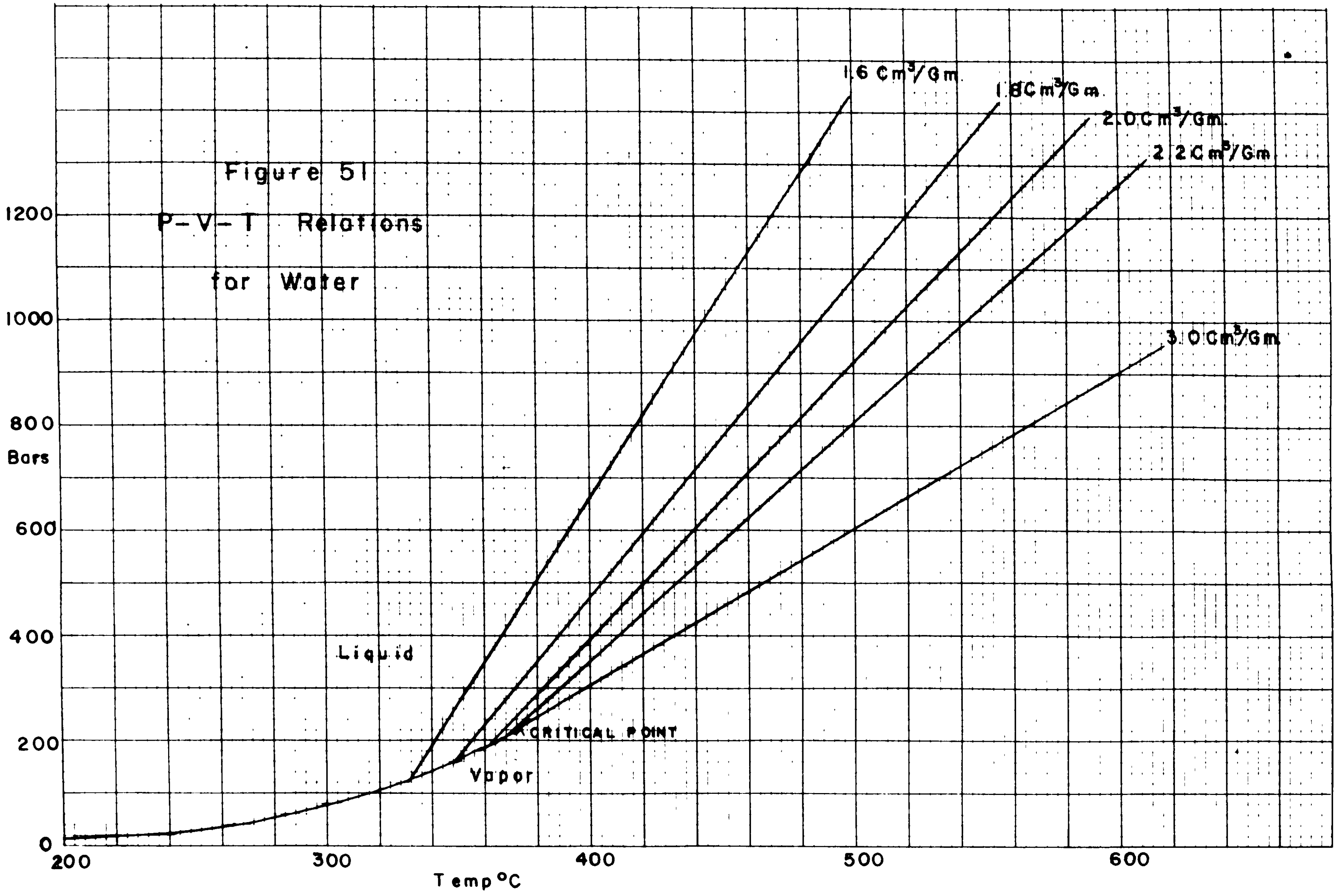


Figure 51

P-V-T Relations for Water

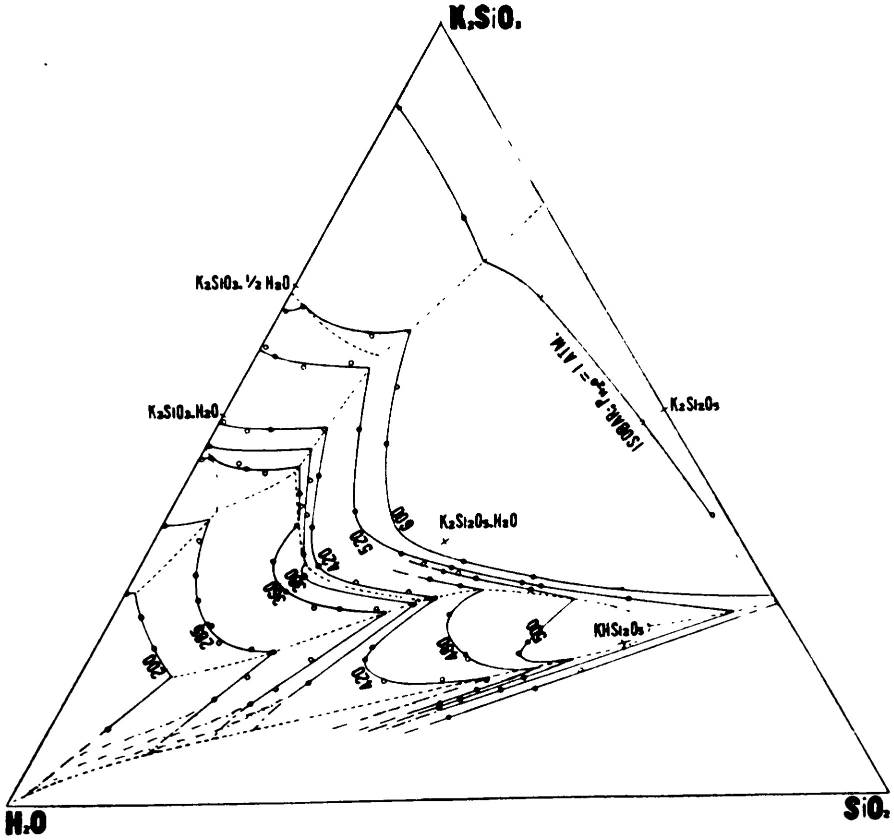


FIGURE 52

The solubility surface for the system H_2O-K_2SiO_3-SiO_2 (after Morey).

equilibrium with quartz under high pressure and temperature will differ considerably from those found in the KOH system. Friedman has determined a few solubilities and they seem to be about 2 1/2 times as great as in KOH at a concentration of .16 moles/1000 gh_2O at 300°C.

Experimental data for the present investigation are presented in Tables I to V, to be found in Appendix I. The most complete set of data was obtained for 0.010 m KOH solutions. The solubility relations for this concentration are presented in figures 53, the corresponding P-V-T data in figure 54. The similarity to Kennedy's results may indicate a critical end point. An outline such as shown in figure 53 proves nothing, however, concerning the presence of critical end points. At this concentration retrograde pressure solubility is shown much more markedly than in the work by Kennedy. Very high pressure will produce normal solubility relations, and this does occur at the highest temperature pressure conditions determined. Since the P-V-T data are very nearly as for water, it is permissible to assume that these relations are essentially the same in hydrothermal solutions and water.

The somewhat more limited results at a concentration of 0.015 m KOH are shown in figure 55. Much of the infor-

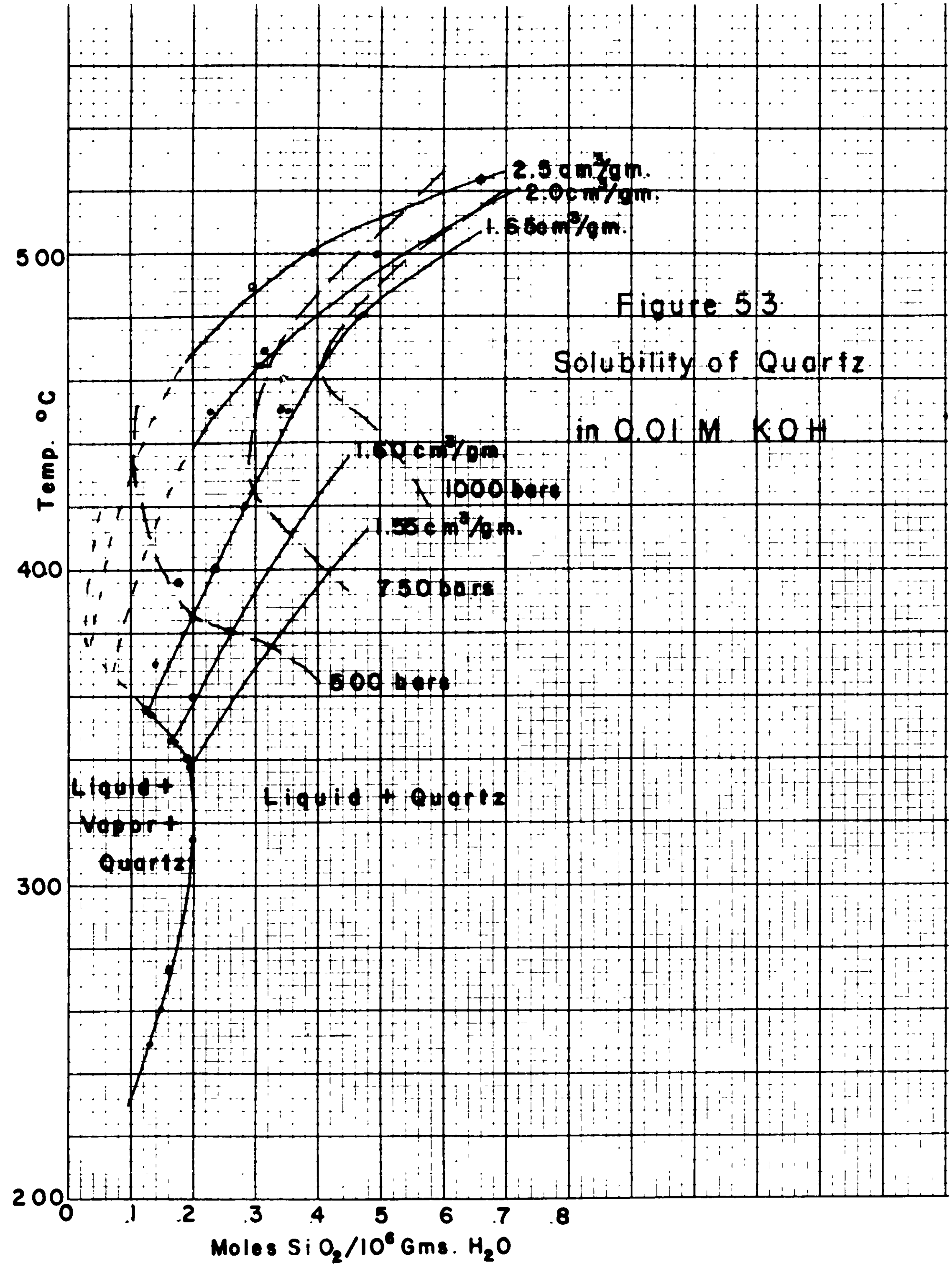


Figure 53
Solubility of Quartz
in 0.01 M KOH

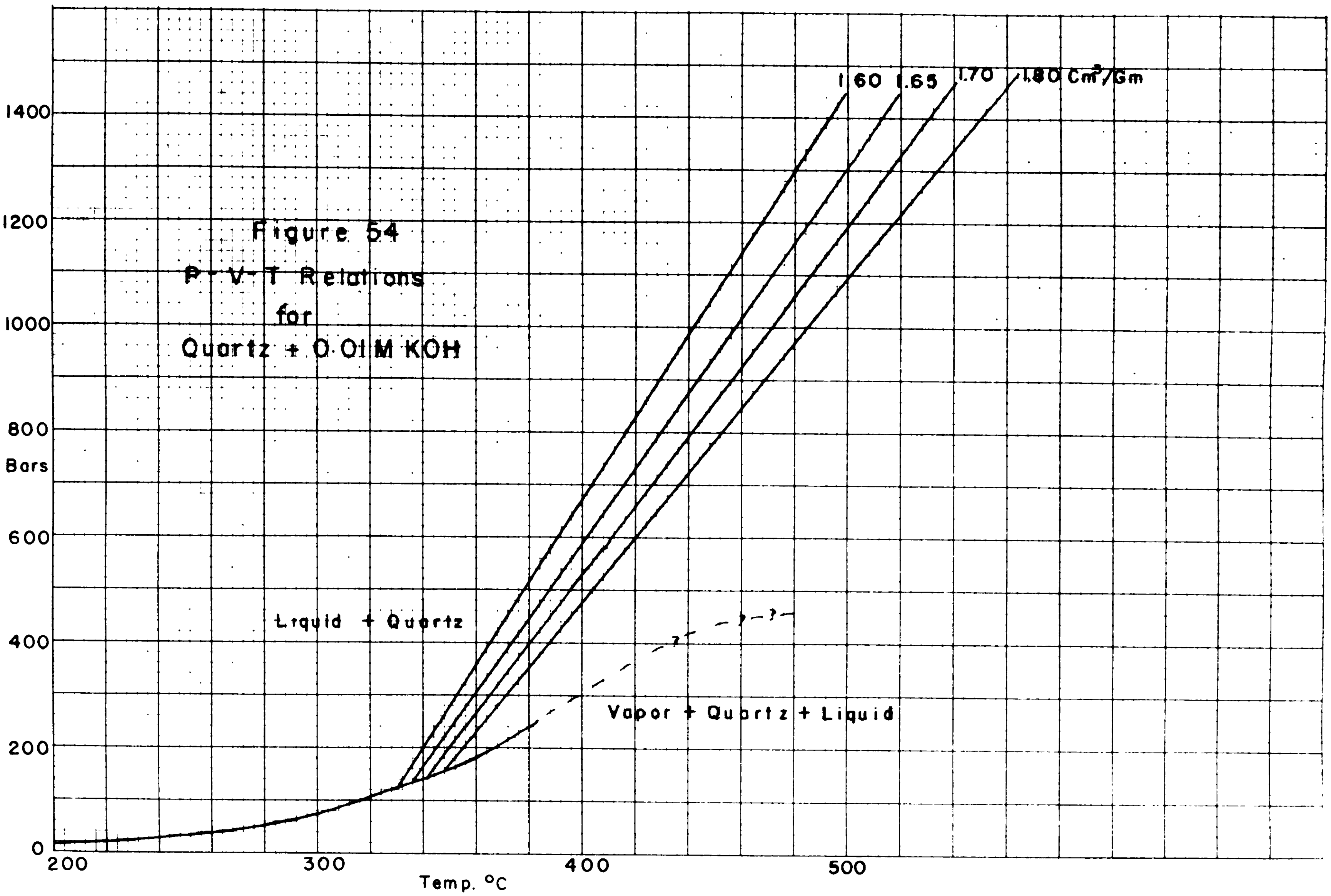


Figure 54
P-V-T Relations
for
Quartz + 0.01M KOH

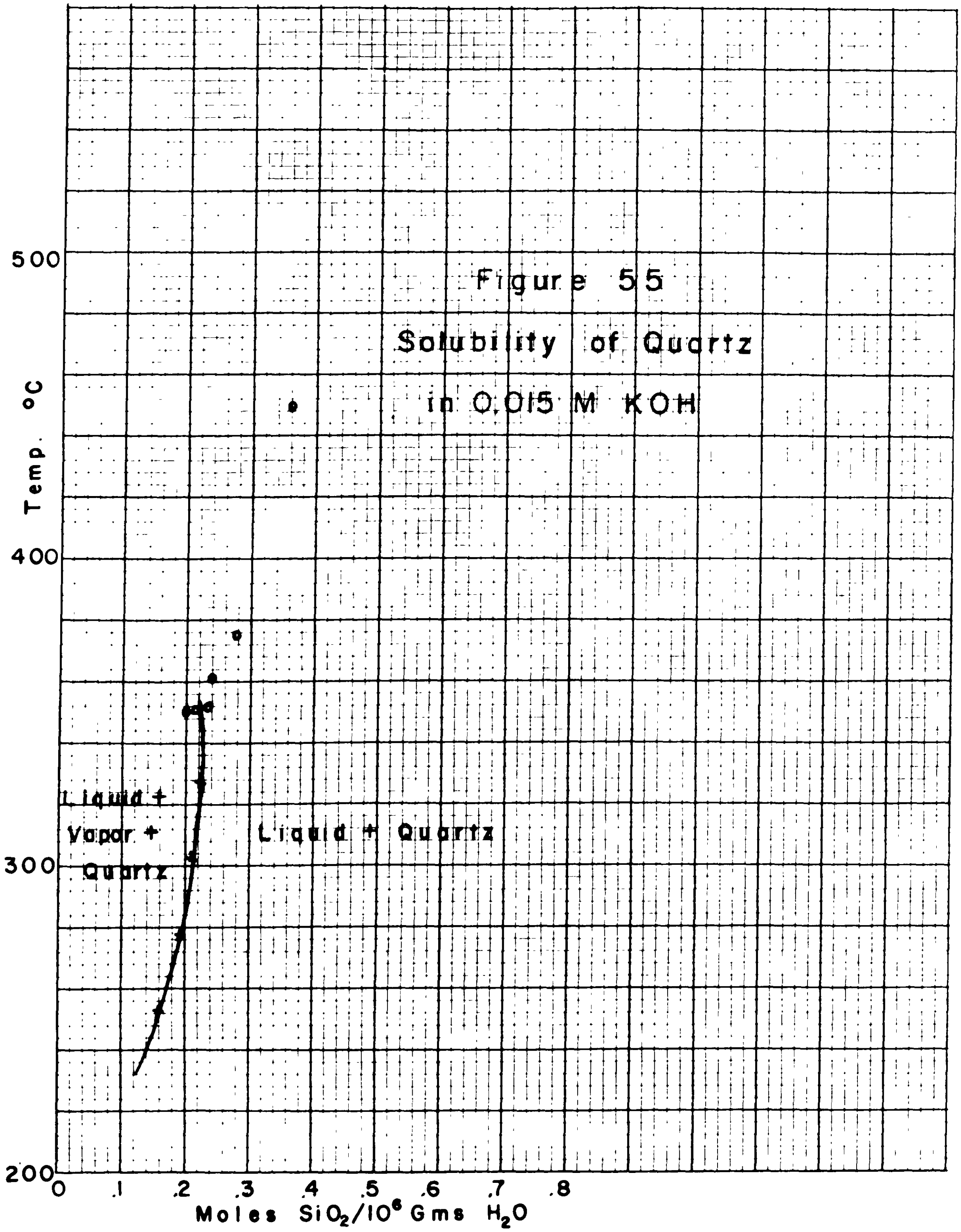


Figure 55
Solubility of Quartz
in 0.015 M KOH
Temp. °C
500
400
300
200
0
.1
.2
.3
.4
.5
.6
.7
.8
Moles $SiO_2/10^6$ Gms H_2O
Liquid +
Vapor +
Quartz
Liquid + Quartz

mation plotted on these graphs has been obtained by plotting solubility of quartz against concentration of potash. Such plots are shown in figures 56 and 57. In regions where more than three points (0.000m KOH, 0.010 m KOH, and 0.050 m KOH) seemed to be required, determinations were made at intermediate values. The representation is thus believed to be fairly accurate, but all relations are less certain than in figure 53.

Figures 58 and 59 show the situation at 0.050 m KOH. The data for this concentration are not so complete as for 0.010 m KOH, but are nevertheless sufficiently good to warrant the interpretation given. Part of the higher temperature range is based on the assumption that critical end points do not occur. No retrograde solubility was found at this concentration.

The very limited work at the highest concentration, 0.150 m KOH is shown in figure 60. No pressure data were obtained for these runs, but it is assumed that the pressures are essentially the same as those encountered in the corresponding positions at lower concentrations. At about 350°C the crystalline phase $KHSi_2O_5$ becomes stable. The relations above this temperature can therefore not be determined by the present method. No attempt has been made to extrapolate results from lower concentrations to cover the high temperature region. Potassium hydrogen

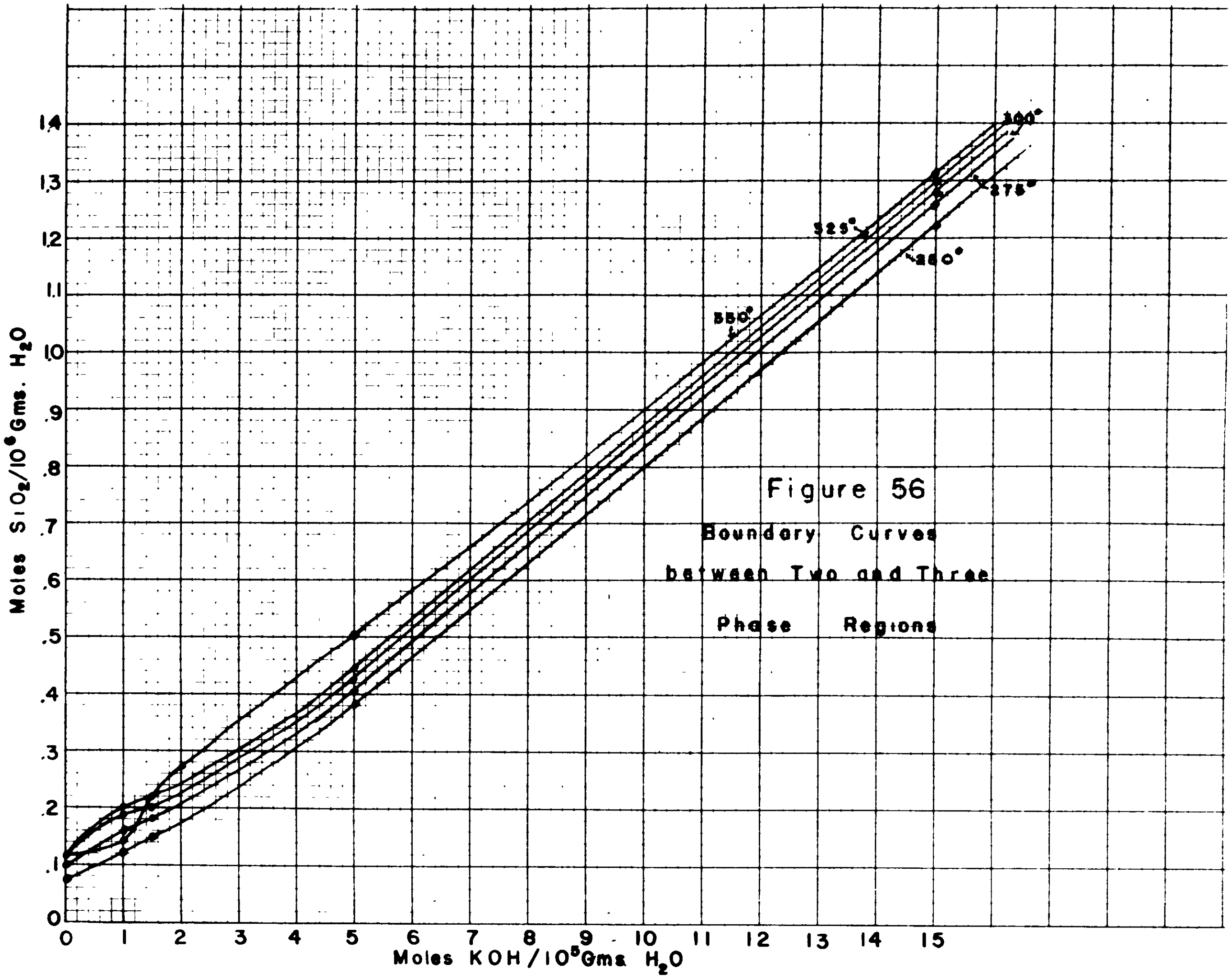


Figure 56

Boundary Curves between Two and Three Phase Regions

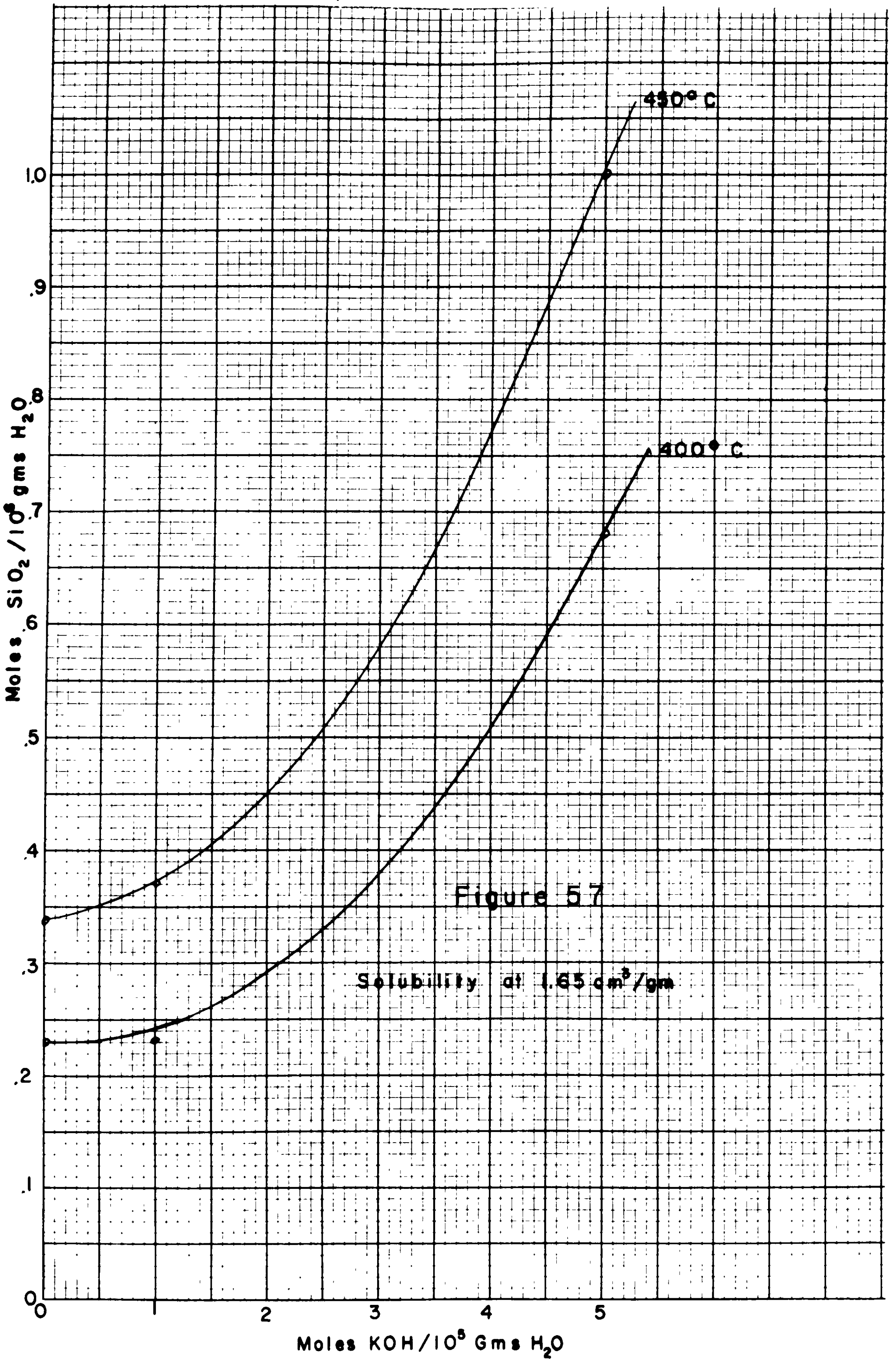


Figure 57

Solubility at 1.65 cm^3/gm

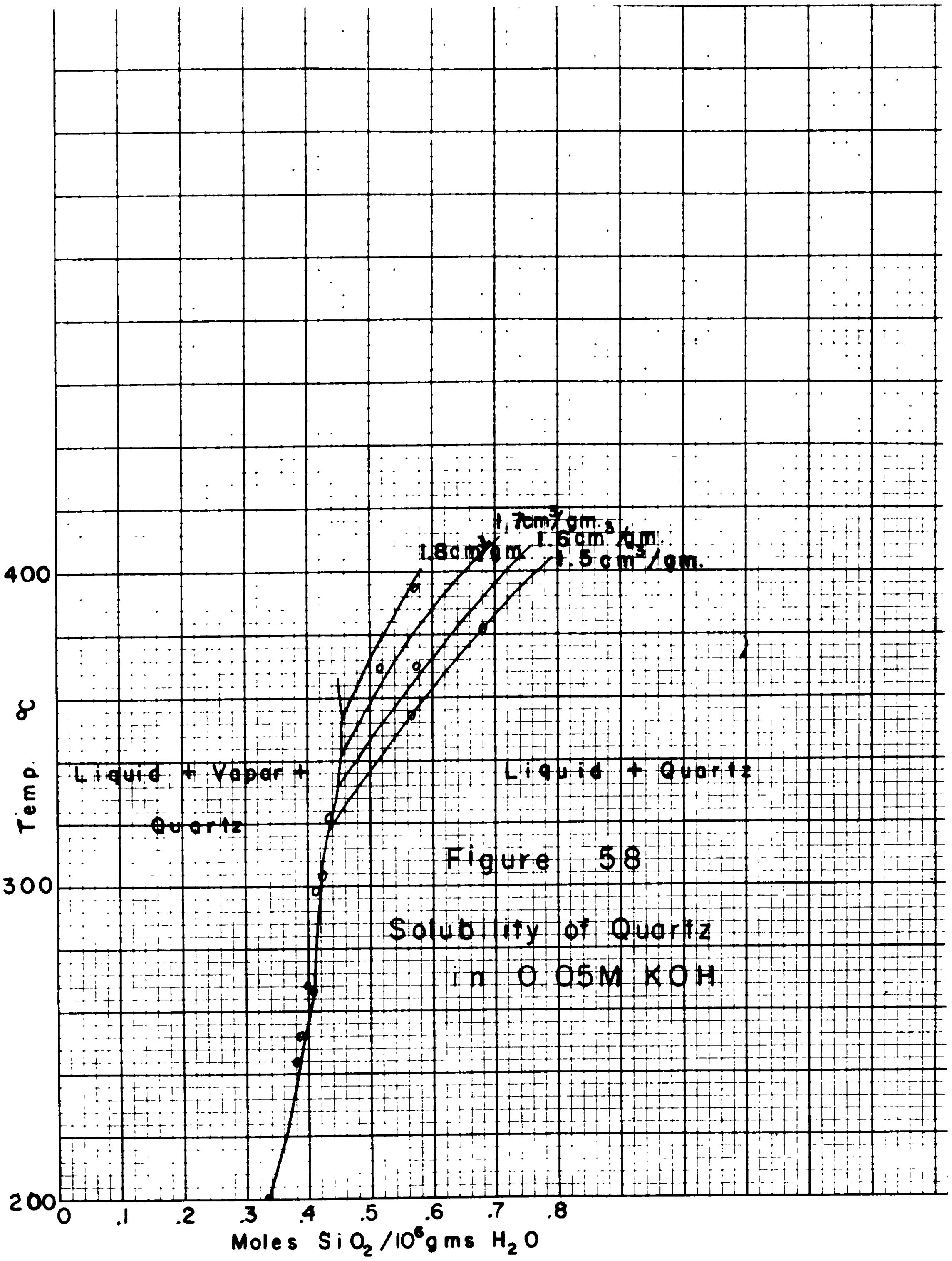


Figure 58

Solubility of Quartz in 0.05M KOH

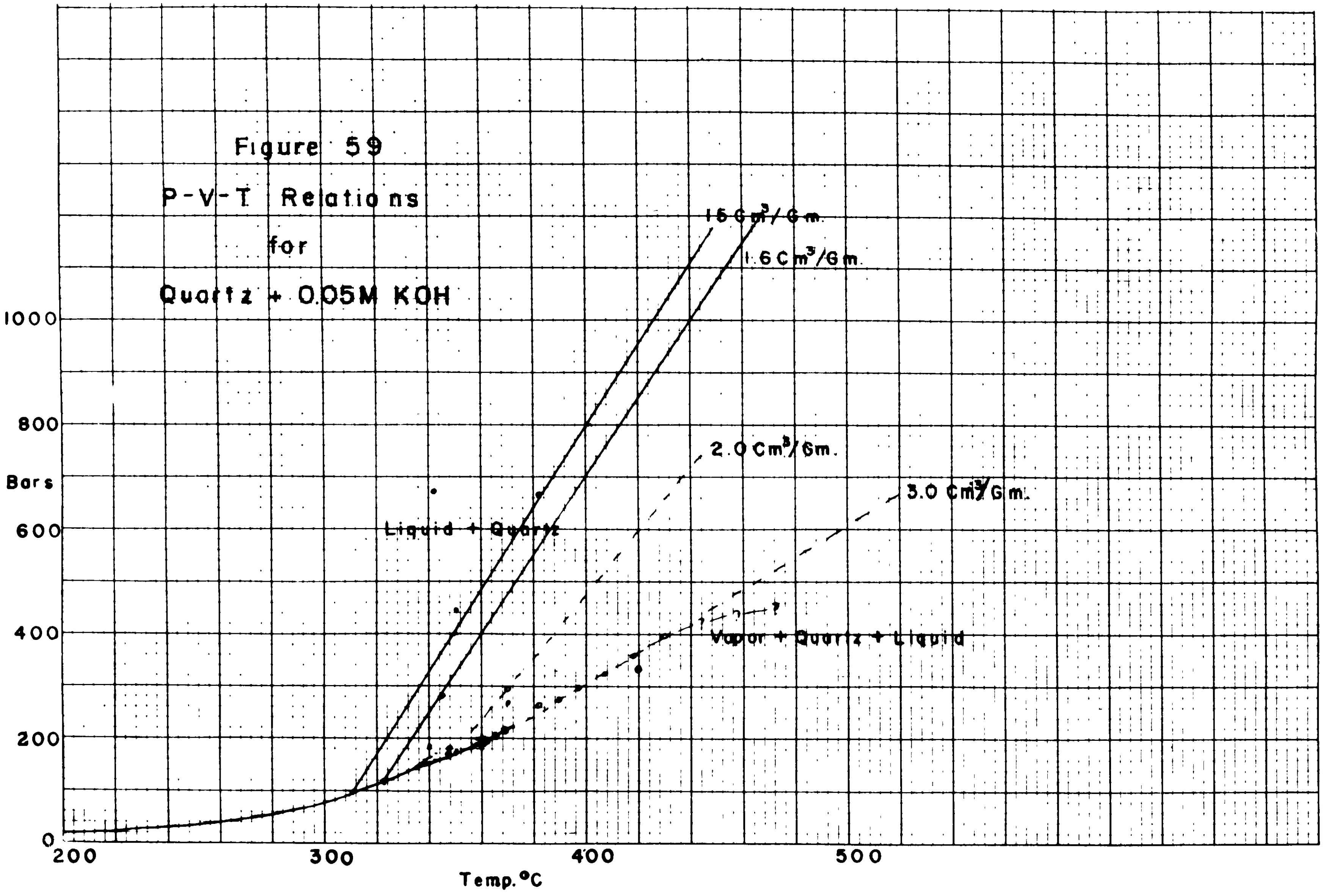


Figure 59

P-V-T Relations for Quartz + 0.05M KOH

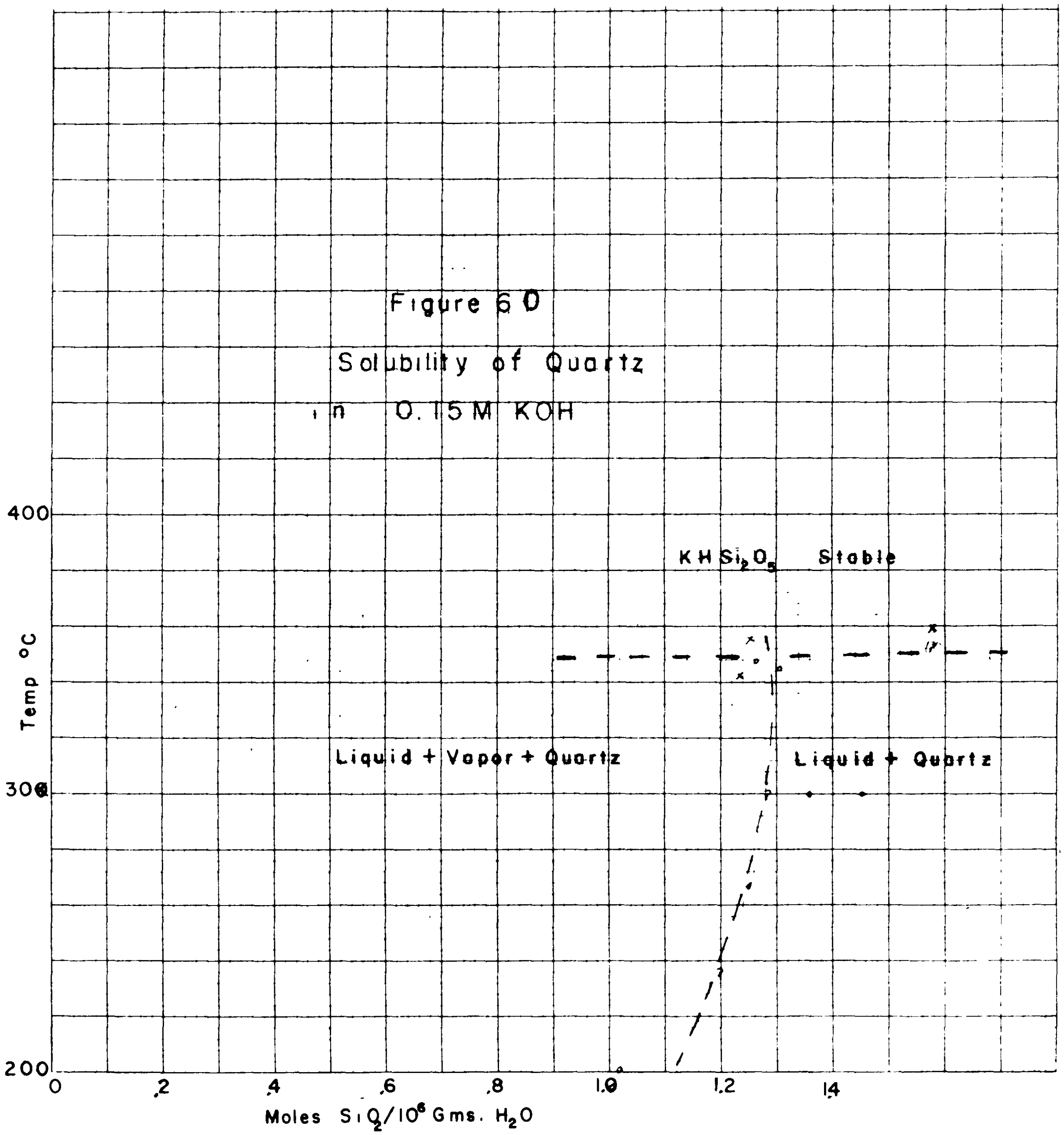


Figure 6 D
Solubility of Quartz
in 0.15 M KOH
400
300
200
Temp °C
KHSi$_2$O$_5$ Stable
Liquid + Vapor + Quartz
Liquid + Quartz
0
.2
.4
.6
.8
1.0
1.2
1.4
Moles SiO$_2$/10^6 Gms. H$_2$O

disilicate was found to be unstable at a concentration of 0.098 m KOH at a temperature of 360°C. The limit of its stability is estimated to be at about a concentration of about 0.12 m KOH. Referring to figure 52, it is seen that at 360°C Morey has estimated that $KHSi_2O_5$, quartz, liquid, and vapor would be in equilibrium at a concentration of 7.5% K_2SiO_3, or a molality of KOH equal to 0.683. As observed in these experiments the actual molality is only about one seventh of this amount. Moreover the concentration of silica in solution is much less than shown by Morey. This must mean that the 360° isotherm should be changed to lie in some such position as shown by the line ab in figure 52. Adjacent isotherms should be changed accordingly.

A plot of solubility against the logarithm of the specific volume has been made for water for 0.010 m KOH and for 0.05 m KOH in figures 61 62, and 63. These correspond to the diagram of Kennedy where he plotted solubility against specific volume to obtain exponential curves. The curves in the present case are very similar and in part identical to those of Kennedy.

It should be realized that the curves on these diagrams are based on high temperature points and are therefore uncertain. They should be used only as a

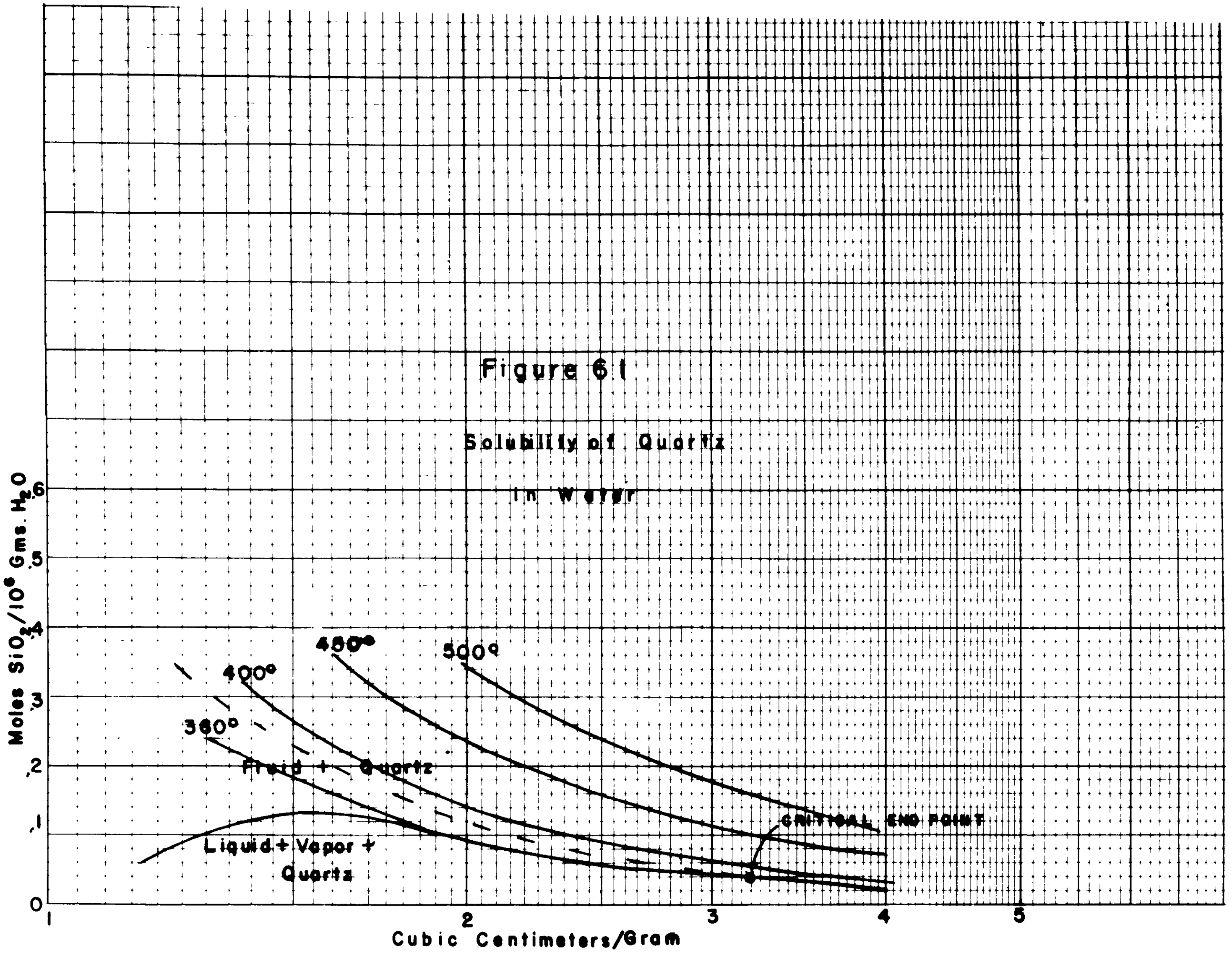


Figure 61

Solubility of Quartz

in Water

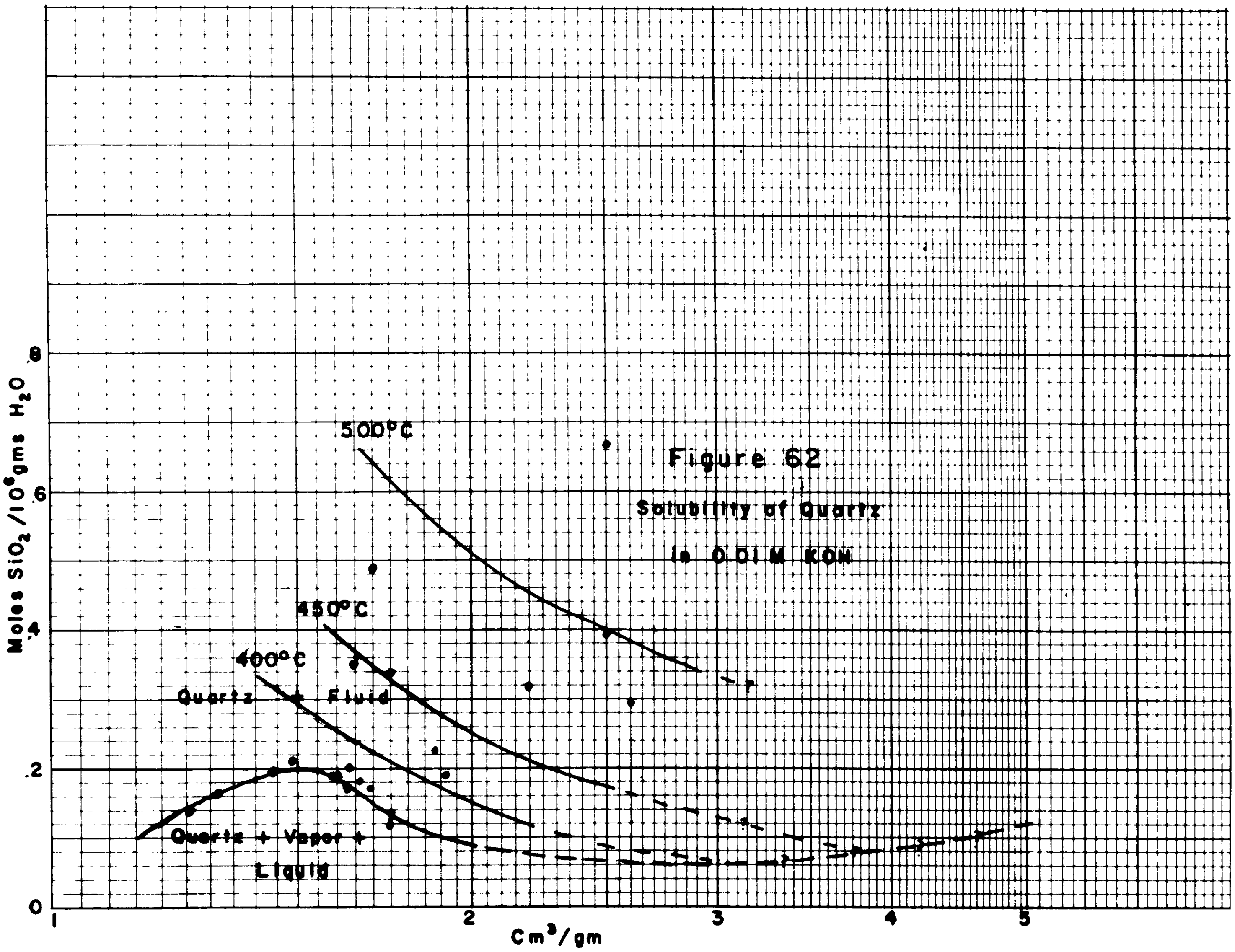


Figure 62

Solubility of Quartz

in 0.01 M KOH

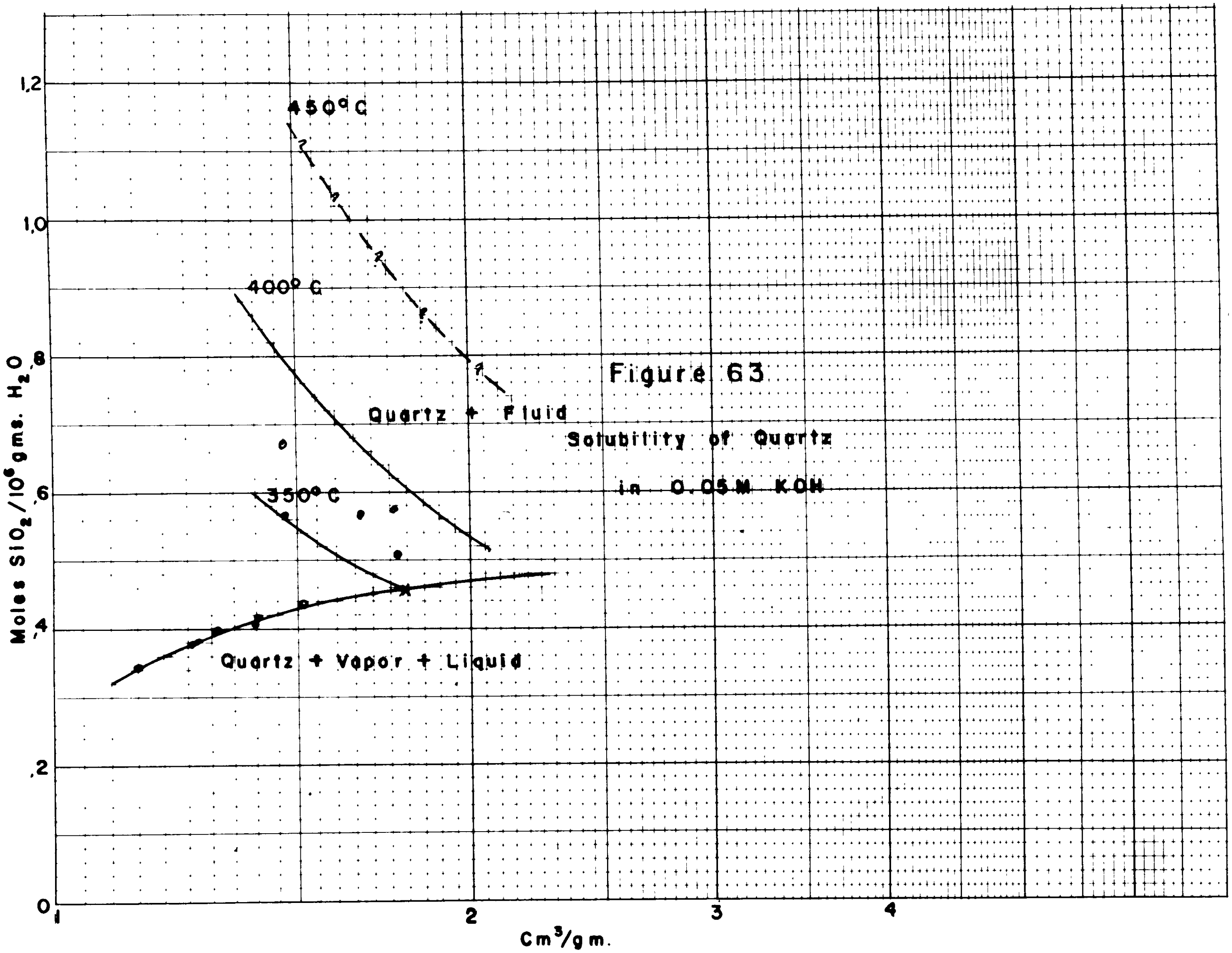


Figure 63

Solubility of Quartz

in 0.05M KOH

reasonable approximation to the probably existent conditions.

A plot of solubility of quartz versus concentration is shown in figure 56 for several temperatures below the critical point of water. The solubilities plotted all lie on the boundary between the liquid-quartz region and the liquid-vapor-quartz region. It is to be noted that as the critical temperature is approached the solubility drops if the concentration is below about 0.015 m KOH. This would lead us to expect critical end points at a concentration of 0.01 m KOH. A plot of solubility against concentration of KOH at 450°C and at 400°C and a specific volume of 1.65 is shown in figure 57. These curves are, of course, not the only ones that can be drawn. Using the relations at the three principal concentrations investigated, nearly complete diagrams could be constructed with fair accuracy for any desired potash content in this range.

Due to the many complicating factors entering into the work, it cannot be proved that the interpretation given to the data in figures 53 through 63 is correct. In view of Kennedy's work, and in view of the theoretical possibilities, the present interpretation seems the easiest and most reasonable. Much more reliance can be placed on the postulated relations below 360°C than on those above that temperature. Nothing definite can be said in regard to the occurence of critical end points, although it is thought that they are entirely lacking. Below 360°C the data are probably accurate to within one to two percent. At the highest temperatures, the data may be in error by as much as 10% to 15%.

The properties of the crystalline phases encountered are given in Appendix II. The difficulty of obtaining pure samples of $KFeSi_3O_8$ limited the amount that could be used for spectrographic analysis. Consequently the determination of potash in particular was hampered. The very small size of the crystals of this compound prevented the observance of good interference figures. For the compound $KHSi_2O_5$ an approximate determination of the "d's" is given in order of decreasing intensity. Optical data are much better for this substance.

It was originally thought that the critical end point in the silica water system would be little affected by the addition of a small amount of potassium hydroxide. Consequently several runs at high specific volumes were tried at temperatures over 374°C. These gave such high results that many more determinations were made before it was realized that these high values were caused by the appearance of a dense and very concentrated liquid. Unfortunately all the data obtained are somewhat erratic. Many attempts have subsequently been made to use this information, but no satisfactory results have been obtained. A few typical runs have been recorded in Appendix I. A few plots of solubility against specific volume are shown in figure 65, the cusp corresponds to the boundary between the two and three phase regions. A notable and significant phenomenon is that on cooling a run at high specific volume to room temperature a great deal of colloidal silica is formed. In many instances a thick slush of siliceous material collects at the bottom of the recovered liquid. If such conditions exist in nature as did inside the bombs, a rapid expansion and cooling could very easily precipitate large quantities of colloidal silica.

The reaction rate in these KOH solutions appears to be very different than in the water system. Kennedy found that at the higher temperatures equilibrium as attained in a period of 6 to 8 hours. At the corresponding positions in the present work, it seems to require 100 hours as a minimum. Furthermore there is some evidence for a very complex reaction mechanism during the process of solution.

The explanation for the greatly increased time required probably lies in the field of catalysis. It seems probable that a very thin surface film of $KHSi_2O_5$ forms on the surface of the quartz. This substance is quite insoluble in water, but less so **than** is quartz. Nevertheless it could have an important effect on the rate of reaction since it introduces an extra step into the process of solution. First the quartz would react to form $KHSi_2O_5$ and then this would dissolve in the surrounding fluid.

There are a number of instances where the equilibrium solubility was apparently attained in less than 50 hours, and other cases where equilibrium was apparently not attained in more that 200 hours. There is insufficient data on which to base an explanation for these relations and consequently they must for the present be classed as anomalous.

A plot of time versus solubility is presented for three typical cases in figure 65. The reaction rate seems to be faster at the higher temperatures as would be expected. However, in view of the probably complex relations no attempt was made to calculate activation energies.

In several cases it was found that a very long run of some 200 hours would give a lower solubility than one under the same conditions for 100 hours. This happened frequently enough to warrant consideration of an explanation. If we assume that silica can be held in

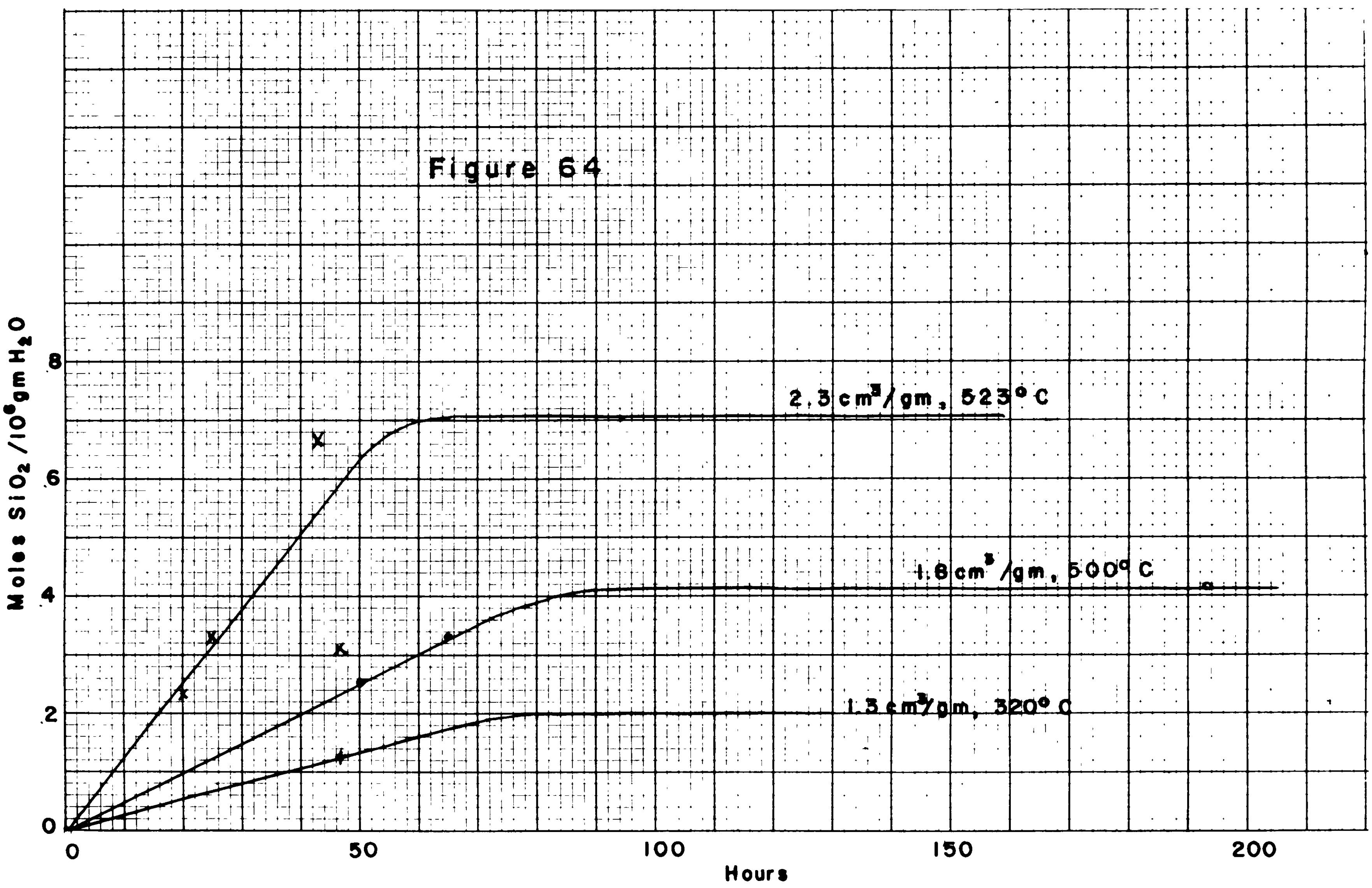


Figure 64
Moles SiO_2/10^6gm H_2O
Hours
0
50
100
150
200
0
.2
.4
.6
.8
2.3 cm³/gm, 523° C
1.6 cm³/gm, 500° C
1.3 cm³/gm, 320° C

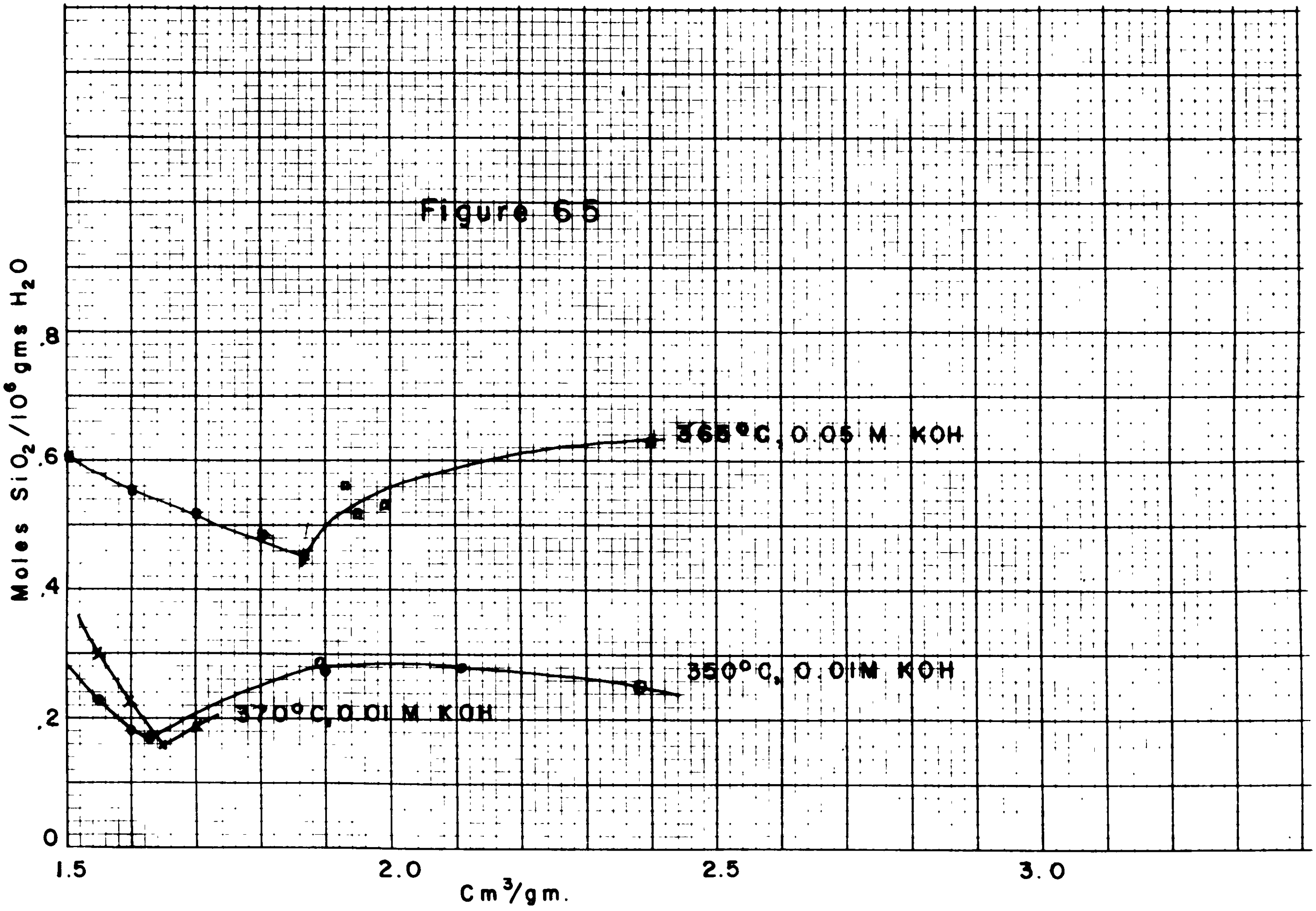


Figure 65

Moles $SiO_2/10^6$ gms H_2O
0
.2
.4
.6
.8
1.5
2.0
2.5
3.0
Cm³/gm.
365°C, 0.05 M KOH
350°C, 0.01M KOH
370°C, 0.01 M KOH

solution two different forms, it seems that a complicated situation should arise. Let us suppose that the following reactions take place.

1) $2\ SiO_2\ (qz) + KOH\ (aq) = KHSi_2O_5(surf)$

2) $KHSi_2O_5\ (surf) = KHSi_2O_5\ (aq)$

3) $KHSi_2O_5\ (aq) = KOH\ (aq) + 2\ SiO_2\ (aq)$

4) $SiO_2\ (aq) = SiO_2\ (qz)$

For the purpose of illustration it is not important whether these are the actual reactions; it matters only that there can be such a sequence of reactions. For each of the reactions there are associated two reaction rates, one for the processes as written and one for the reverse relation. For the first reaction in the forward sense, the rate constant is K_1. The constant for the reverse reaction is K_1'. K_1 / K_1' is equal to the equilibrium constant for the reaction. Correspondingly we have K_2 and K_2', K_3 and K_3' and K_4 and K_4'. Reaction 1 can be considered as of first order in the forward direction and zero order as reversed. Reaction 2 is zero order forward and first order reversed., Reaction 3 first order and third order, and Reaction 4 first order and zero order respectively.

Let us then call aqueous silica component x, potassium hydroxide component y, $KHSi_2O_5$ (aq) component z, and $KHSi_2O_5$ (surf.) component w. Since we can assume the solid and water to have constant concentrations we may then formulate the governing differential equations as follows:

For the aqueous solution:
$$dx/dt = K_3 z - K_3' x^2 y - K_4 x + K_4'$$
$$dy/dt = -K_1 y + K_1' + K_3 z - K_3' x^2 y$$
$$dz/dt = K_2 - K_2' z - K_3 z + K_3' x^2 y$$

Reaction 1 presumably takes place rapidly in the forward direction. It may react very slowly in the reverse direction, however, and may in fact be so slow as to virtually not take place at all. Reaction 2 would be rather slow and would give rise to the long period required for attaining equilibrium. It is to be noted that this reaction in the forward direction is zero order; this should give a straight line plot of solubility versus time, a relation actually observed initially in curves of figure 65. Let us assume that reaction 3 takes place quite rapidly in both directions. Reaction 4, judging from Kennedy's work would normally be moderately fast. However, the surface coating of $KHSi_2O_5$ could retard the reaction to a rate less than the forward rate of reaction 2. The reverse direction of reaction 4, being endothermic is presumably slower yet. Under these assumptions, the bulk of the silica enters the solution by way of the disilicate. However, virtually no silica can leave by this means since the reverse of reaction 1 is so exceedingly sluggish. The silica must then leave by means of reaction 4. As the concentration of aqueous silica builds up, it may inhibit the forward rate of reaction 2. We then have essentially the same relations as described by Daniels, and it is possible to build up the silica content of the solution to a maximum, with subsequent slow decrease with time. Some such complex situation possibly involving also complex ions of the nature $Si(OH)_6^=$ could explain the apparent slow drop of silica in the solutions described above.

It has been found that attainment of equilibrium in regions near the critical point is very difficult. Sometimes a supposedly metastable state is seemingly stable. In view of the closeness of some of the runs to critical regions, some of the difficulties may perhaps be explained best on this basis.

GEOLOGICAL APPLICATIONS

The experimental results are of considerable importance for discussions of natural hydrothermal solutions. It must be realized, of course, that natural solutions differ in many important respects from those encountered during this work. To illustrate the large degree in which they do differ, analyses of several mineral springs are given in table VI. Further evidence is presented by the composition of liquid inclusions in ore minerals; table VII gives some typical examples. Presumably the salt content of these liquids is a closer approximation to the solutes present in hydrothermal solutions than those investigated in these experiments. In spite of these differences, however, it is thought that these natural waters may exhibit properties similar to those encountered in the potash-quartz-water system. We shall therefore assume for the present that this is the case and investigate the meaning of this assumption for geology.

In recent years the processes operative in rising ore solutions have been discussed primarily by Niggli, Bowen, Fenner, Ross, Lindgren, Graton, Morey, Ingerson, Fersmann, Neumann, Smith, Emmons, Bandy, Bichan, Landes, Sales and Meyer, and Kennedy. A large part of the discussion has been concerned not so much with how the ore minerals have precipitated, but with how the solutions developed. It has been pointed out repeatedly that pegmatites generally do not contain sulfides, and that hydrothermal veins do not contain pegmatite minerals. Yet both are presumed to be derived from residual solutions arising from a cooling magma. The question has therefore been asked how two such seemingly different solutions can develop simultaneously in essentially the same way from the same parent.

This question has been answered in various ways. The reply given by Fenner, Bowen, and others is that there has been boiling of the residual solution and that the ore minerals have been removed from the residual solution by entering the vapor phase. Other workers, among them Ross and Graton, seem to believe that, whereas boiling may take place, this method is ineffective; the ore solutions are then liquids and have at no time been in a vapor state. It is probably true, as pointed out by Bowen and Fenner, that the vapor evolved from a boiling magma will be richer in acid components such as HCl, HF, H_2S, and CO_2.* On recondensing to a liquid, as it must do in most cases before reaching the surface, this solution will be acid. On the other hand liquids residual from cooling magma will almost certainly be alkaline. Thus the question over origin has come to be a controversy over an alkaline versus an acid nature of ore solutions. It should be pointed out, however, that all who propose an acid condition agree that this acid will react with the wall rocks and will become alkaline. Thus the last solution to be active in an ore deposit (excluding supergene effects) is believed to be alkaline by all who have considered the question.

Niggli, Fersmann, Landes, and Graton have pointed out that in most cases ore mineralization has followed

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*Some experimental work by Smith suggests the opposite conclusion.

the formation of pegmatites. According to Niggli the normal sequence of events in a crystallizing magma is gradual rise of vapor pressure along with crystallization (this is also emphasized by Morey). By the time the temperature has dropped to about 800°C pegmatites have begun to develop and continue to form down to 600°C. By then the vapor pressure may have risen enough to exceed the confining pressure, and pneumatolytic deposits can be formed by the escape of gases.. By this is meant primarily tin veins, tungsten,veins, and the like. At 400°C the pressure has again fallen and the hydrothermal stage starts. This last stage may last down to surface temperatures. Niggli emphasizes the influence of critical phenomena on this relationship ascribing the pneumatalytic phase to supercritical conditions. However, it is not necessary to assume that critical phenomena occur in order that his sequence be valid.

Fersmann does not have much to say on this subject, but does mention that pegmatites which do contain sulfides seem to have formed at low temperatures. He also states that there is considerable question whether the sulfide is primary or introduced later through replacement. In another place he states that a high water content is favorable to sulfide occurrence in pegmatites. In addition to this he arranges his sequence of pegmatite and mineral deposit types in such a manner as to suggest that he visualized much the same conditions as those proposed by Niggli. The temperature which he proposes for the formation of some pegmatite types is considerably below that proposed for the highest vein deposits.

Landes and Emmons have been concerned with the relations of pegmatites and vein deposits to their position in or near igneous masses. Emmons has pointed out that sulfide-bearing pegmatites occur only in the so-called "hoods" of batholiths. This is a region near the top of the igneous mass and is presumably the first part to crystallize. Ore bearing veins also occur in these hoods and in the surrounding rocks. Many veins, however, show no obvious connection with an igneous body. Landes continues from Emmons' observation and emphasizes that the sulfides in the pegmatites found in the hood all seem to be late replacements. He also notes that in no case has a pegmatite been observed to grade into an ore vein, although cases are known where a pegmatite grades into a barren quartz vein. Landes then concludes that the sulfides in pegmatites are derived from a solution formed at much greater depths and penetrating upward. To the present writer this does not explain why the surrounding granite is not similarly replaced, or why parts of the associated quartz veins, if present, are not also affected.

Bandy and Sales and Meyer deal with zonal distribution of ore minerals. Since this is a finer distinction than is here in question, it is important to note only that they conclude that zoning can be explained on the basis of one through-going solution. It is not necessary to have several different solutions at different times or places.

Bichan has proposed that hydrothermal veins are formed from a solution having properties intermediate between the supposedly dilute hydrothermal solutions and the magma. The temperatures of deposition would then be higher than has generally been supposed. This assumption of higher temperatures runs into some conflict with those presumed to correspond to the pegmatitic stage, but Bichan has apparently not considered this of enough importance to mention. In spite of this objection the present experiments gives some support to the idea of higher temperatures.

For present purposes it is unnecessary to become involved in the arguments over the origin of ore solutions. It need merely be noted that by the time the solutions reach the surface (except in the case of volcanic fumaroles they are alkaline. It is therefore pertinent to discuss what may occur in an alkaline solution and in particular to apply the results of the experimental work described above to this discussion. Nevertheless, a few remarks will be made concerning the genesis of ore fluids.

To the author it seems that a fact of prime importance has often been neglected in previous discussions. This fact is that at a given temperature and pressure a slightly soluble compound will be more soluble in a liquid than in a vapor in equilibrium with it. To be sure this relation has often been mentioned, but only Graton, to my knowledge, has pointed out its true significance. This relation still continues to be valid under the most rigorous conditions described above in the section of theoretical considerations, except at critical end points. Because of the very limited field of critical end points in the system under study and because of the work of Morey at the Geophysical Laboratory, it seems unlikely that critical end points occur in magmas or in ore solutions. Therefore, at equilibrium the vapor will contain less "solid" substance such as PbS, ZnS, CuS, Ag_2S, and so on, than the vapor. It is to be doubted that the presence of HCl will reverse this relation. This being the case it would be necessary to pass enormous volumes of sulfide free gas through the magma in order to remove the sulfides (or chlorides). In this case the gas entering always has less sulfide content than the magma and therefore dissolves some sulfide from the liquid. In no case does the gas contain more than the equilibrium amount of sulfide.

In the event that the gas is evolved by boiling of the magma the situation is vastly different. Here the initially formed gas contains a considerable fraction of the equilibrium amount of sulfide. It will pick up little more on its upward journey. Since the solubility is less in the gas, more sulfide is left behind than is taken out for each bubble that is formed. It is also to be noted that, as heat is absorbed by exsolution of water and other volatiles, the temperature will drop. This means that the vapor becomes ever less capable of dissolving sulfides. If now we consider the solubility relations in terms of weight percent, the full meaning of the above discussion becomes apparent. Let us assume that all the water is separated as vapor at the temperature at which boiling begins. Since some of the water is evolved at lower temperatures, the amount of sulfide that can be dissolved in this case is undoubtedly more than in fact would be disolved. Under the postulated conditions the weight percent of sulfide in the vapor is less than that in the liquid. Let us assume further, with Fenner, that the ore solutions are evolved as gases before the formation of pegmatites. This latter assumption means that water forms at most 10% by weight of the magma. It must then follow that the vapor at equilibrium has dissolved less than one tenth of the sulfide and that more than nine tenths still remains in the liquid. If the weight of vapor were many times that of the liquid, as in the case where gas is passed through a liquid, a nearly complete separation could be achieved. Coupled with the other arguments presented by Graton, this relation has convinced the author that separation by boiling is exceedingly unlikely.

On the other hand we may consider the possibilities of separation by simple crystal fractionation. On the basis of the results of crystal chemistry we know that ions with similar properties often form similar compounds and exhibit solid solution. The less the similarity, the less the solid solution. It is also true that during a rapid crystallization some of these similar ions, attracted to the growing surface, may be included in the structure even at the expense of some distortion. Under conditions of slower growth, these ions would be replaced by others which produced less or no distortion.

In particular we may consider the pairs zinc-magnesium and lead-calcium. It has been found that up to 2% zinc may occur in biotite and hornblende, apparently replacing magnesium and iron, but the affinity is not strong. Moreover, zinc tends to form tetrahedrally distributed bonds whereas magnesium and iron do not. This would lead us to expect, where cooling is fairly rapid and where hornblende and biotite are stable, that zinc would enter the structure rather by permission than by choice. This could correspond to the case in a granitic batholith. On the other hand crystallization in a slightly viscous slowly cooling environment where iron and magnesium are largely absent would lead to rejection of the zinc. In this case the zinc would either be removed completely from the vicinity as the solution moved on, or would much later precipitate as a sulfide. Presumably the high temperature would prevent the formation of sulfide at an earlier time. This latter situation describes the probable relations in a pegmatite. Exactly analogous statements apply to the lead-calcium relations in feldspar. It may be argued that there is still feldspar present in pegmatites, but it should be remembered that it is poor in calcium.

According to Goldschmidt the average zinc and lead contents of granite are 0.0150% and 0.0030% respectively. Fersmann reports 0.002% zinc and less than 0.001% lead in a typical high temperature pegmatite. These results are therefore in accord with the postulate presented above.

The above discussion therefore presents an adequate explanation for the absence of sulfides in pegmatites. As for the contrary argument that pegmatite minerals do not occur in ore veins, it should be noted that temperatures are much lower. We would therefore expect to arrive in that region where low temperatures silicates are stable. These silicates are indeed found and correspond to those found in deuteric alterations and in weathering. There is thus nothing unusual about the lack of feldspar or the other rarer pegmatite minerals.

We now turn to the particular applications of the experimental results to ore deposits. The conclusions to be drawn from this work closely parallel those of Kennedy in his work on the silica water system. In addition the significance of boiling adds a great deal of depth in understanding certain replacement phenomena. As in Kennedy's work it is found that pressure has a large effect on the solubility of quartz. In many regions the effects of isothermal expansion and of isobaric cooling are nearly equivalent in the amount of quartz precipitated. If the concentration is not too great, isobaric cooling will cause quartz to be dissolved (retrograde solubility) in the temperature range from about 500°C to 350°C.

As with Kennedy's work it can be concluded that the release of pressure as a fluid enters a permeable horizon is likely to cause precipitation.

Other interesting possibilities appear if the pressure on the solution should drop enough to cause boiling at some temperature above about 350°C. Such a situation could for instance arise as the liquid emerges through a tight orifice in a fault stone. At first the boiling might cause some quartz to precipitate. As the concentration in the residual liquid increases, however, the solubility might increase so rapidly as to cause quartz to dissolve (of. above). This could easily produce greatly corroded and even cellular masses of quartz as in Plate VIII. Furthermore this boiling produces just that type of concentrated solution from which it was so easy to produce great masses of colloidal silica in the experimental work. If the pressure should for any reason experience a sudden decrease, expansion would cause rapid cooling and possible precipitation of colloidal silica. This in effect would amount to colloidal replacement of the wall rocks. Alternatively the pressure might increase because of blocking of the channel further up. This would probably result in dilution of the concentrated solutions and precipitation of new quartz where the old was dissolved. Successive changes of pressure could produce a great series of re-

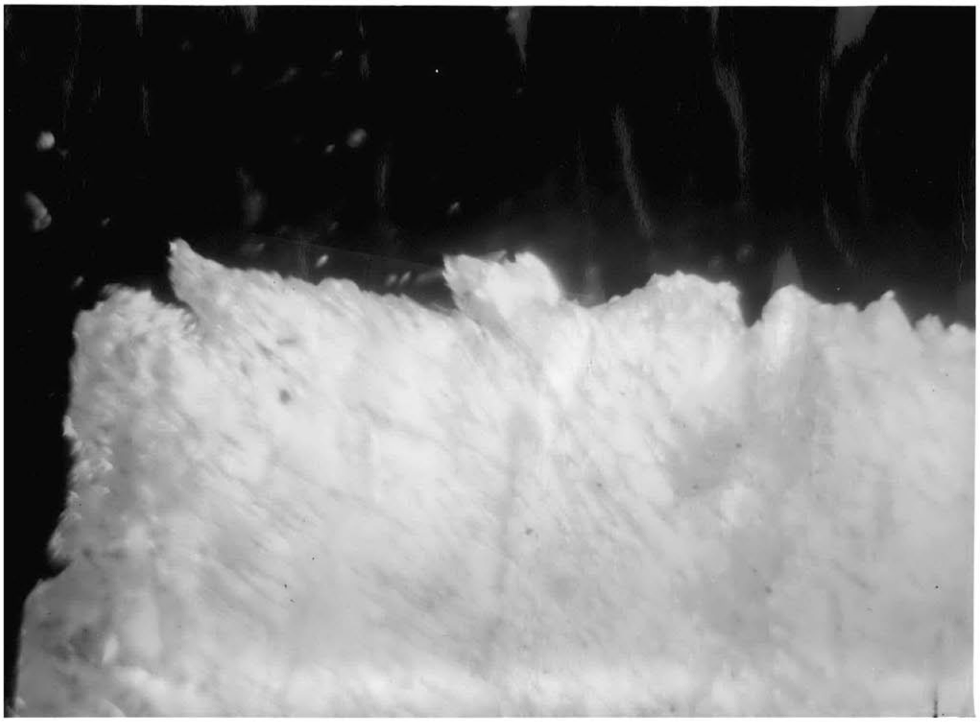


Plate 8

Highly etched quartz plate

placements and precipitations, including formation of colloids.

The reader is doubtless aware that the near surface regions most likely to give rise to these fluctuations of pressure are also the regions where colloidally deposited ores and extensive replacements are most common. As depth is increased these phenomena are likely to become of less importance until the hypothermal they should be almost absent. Even here, however, pressure changes could give rise to successive periods of mineral deposition. The principal difficulty with this explanation is that it assumes a temperature of over 350°C for the epithermal. If we are to believe Bichan, this is probably permissible, but Lindgren assumes that the epithermal starts at about 200°C and extends down to 50°C. Also the pressures (less than 100 bars) are much too low. If we are justified in contending that tight fissures will maintain higher pressures locally and in maintaining that the ore solutions enter the epithermal zone very hot, then the explanation given above is sound. If not, we had best seek another explanation.

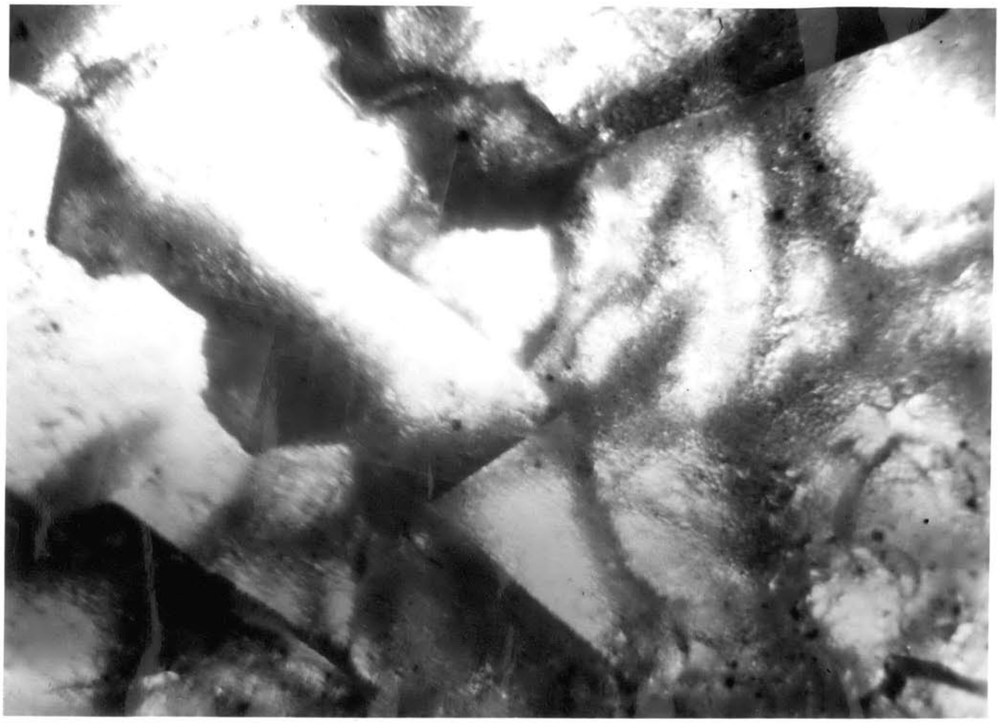
Further support is given to Bichan's hypothesis by the slight solubility of quartz in dilute alkaline solutions. Bichan points out that it would be almost impossible to dissolve the requisite amount of quartz

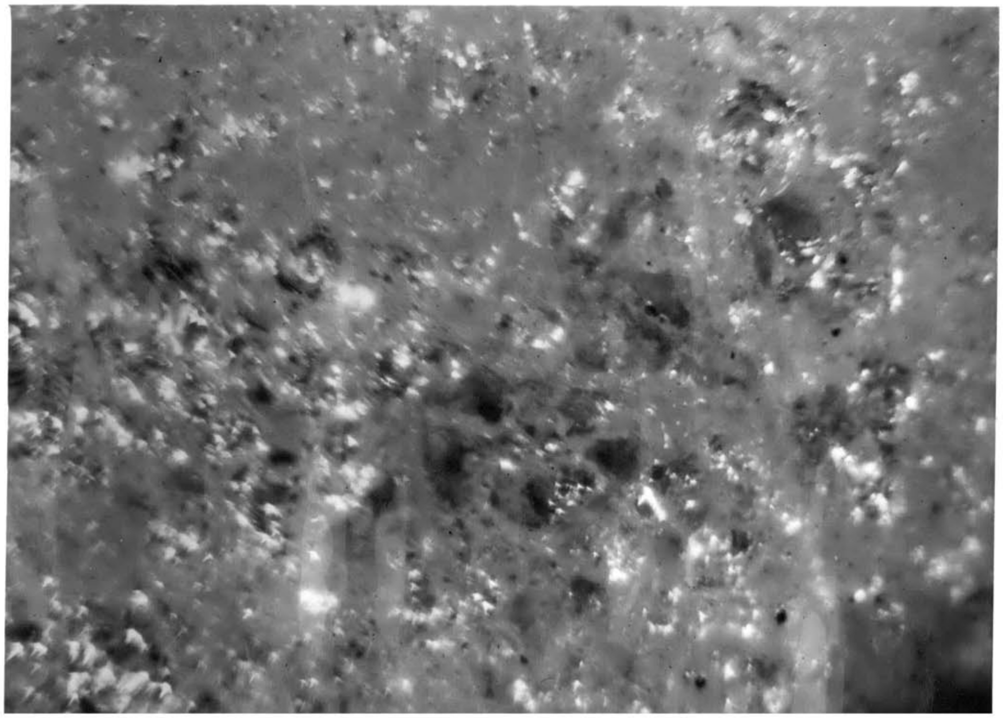
Plate 9a

Quartz plate fractured by
sudden release of pressure (about 20x)

Plate 9b

Quartz plate fractured by
sudden release of temperature (about 20x)





or sulfides in the amount of water available. Since the solubility in moderately alkaline solutions (such as might reasonably correspond to natural pH conditions) is also slight, the presence of alkalis does not help the situation.

It must be remembered, in spite of the ease with which many observations in ore bodies are explained, that the solutions whose behavior suggests this simple answer, are radically different in composition from what is presumably the constitution of natural ore solutions. The importance of critical phenomena is greatly reduced in this discussion, but it should be mentioned that the retrograde solubility along the isobars is due primarily to the proximity to a critical region. As explained elsewhere it is not known from the present experimental work how great a concentration of potash is needed to eliminate critical end points.

In conclusion it appears from the present work, and from previous work elsewhere, that practically all the observed features of ore deposits can be explained by one solution moving continuously upward and outward. It is not necessary to assume as many have done that the composition of the solution is continually changing, or that successive mineralizations are caused by stoppage of flow followed by a new flow at a later period. This concept is much more satisfying than some of the complex relations postulated in the past.

BIOGRAPHY

The author was born at Orono, Maine, on February 6, 1929. He was educated in the public school system of Orono and graduated from Orono High School as Valedictorian in 1947. He received many school prizes (mathematics award, science award, Bausch & Lomb science award, and several others) in his senior year. His principal activities were participation in the school orchestra, the debating team, the preparation of the school yearbook, and the National Honor Society. Also in his senior year he competed in the Sixth Annual Science Talent Search, won a trip to Washington, and received one of the top ten awards. During his junior and senior years he played in the second violin section of the Bangor Symphony Orchestra.

During the period 1937 to 1947 the author studied violin at the Northern Conservatory of Music in Bangor, Maine, and in 1947 received a certificate signifying that he had completed the preparatory course.

On application to Harvard the writer was awarded the Henry B. Humphrey scholarship which he held for four years. At Harvard he majored in geological sciences and graduated Magna cum Laude in 1951. His extra-curricular activities included the Pierian Sodality of 1808, the Harvard Orchestra (treasurer in 1950), the Geology Club, and the Congregational-Presbyterian Student Fellowship. Other activities were of lesser importance.

In the summer of 1945 the author was employed briefly by the Maine Geological Survey. This employment was continued in the summers of 1946 and 1947. In 1948 he was hired by the U. S. Geological Survey as a field assistant and continued in this capacity in the summers of 1948, 1949, and 1950. Until 1949, all of the field work was in Maine, but in 1949 the author worked on a reconnaissance party in Colorado and Wyoming. In 1950 the work was in a volcanic area of New Mexico near Los Alamos. In the summers of 1951 and 1952, he continued work in this same region as a geologist.

Since 1951, the author has been attending Massachusetts Institute of Technology pursuing study leading to the degree of Doctor of Philosophy. For the academic year 1951-1952 he was employed as a teaching assistant in optical crystallography and petrology; in the spring of 1952 he was elected to the M. I. T. chapter of the Society of Sigma Xi. Also that spring he was awarded a fellowship by the National Science Foundation for the year 1952-1953. This enabled him to stay in Cambridge during the summer of 1953 and to complete a large portion of the experimental work. For the year 1953-1954 the author received a tuition scholarship from Massachusetts Institute of Technology, but the last half of this was relinquished in favor of a teaching assistantship in mineralogy.

ACKNOWLEDGMENTS

The author wishes to express his appreciation for the assistance given him by all those who have offered assistance. In particular he wishes to thank Professor Harold W. Fairbairn and Professor George C. Kennedy for their aid during the course of the work, and for permission to use their apparatus for the experiments. Special mention should also be extended to Professor Carl W. Wagner of the Department of Metallurgy at M. I. T. for his interest in the work and for his many valuable suggestions concerning difficult points in the work. Thanks are also due to Dr. Hattan S. Yoder, Dr. Joseph C. Boyd, and Dr. George W. Morey of the Geophysical Laboratory in Washington for their criticisms and suggestions. Lastly the author wishes to thank the many others who have contributed ideas and helped in various ways, especially Miss Margaret Canty, who typed the manuscript.

APPENDIX I

Table I

Solubilities of Quartz at 0.010 moles KOH/1000g. H_2O

cm^3/g	Temp. °C	Pressure, bars	Moles $SiO_2/10^5 g.$ H_2O	Hours of Run	Fluid Phases
1.21	191	17	0.02	66	L,V
1.24	274		1.62	66	L,V
1.31	252	50	1.38	119	L,V
1.32	320	124	1.69	47	L
1.32	341	347	2.84	17	L
1.48	313		2.12	64	L,V
1.50	361	390	1.94	43	L
1.55	337	208	1.94	44	L,V
1.55	336	182	1.96	38	L,V
1.58	306	100	1.92	65	L,V
1.63	347	169	1.69	188	L,V
1.63	347		1.61	42	L,V
1.63	348		1.25	118	L,V
1.63	349		1.46	64	L,V
1.63	361	261	2.00	68	L,V
1.63	370		1.49	22	L
1.64	448	881	3.48	43	L
1.67	397		1.77	93	L
1.69	448	843	1.68	72	L
1.70	498	1253	4.85	47	L
1.70	370	297	1.90	70	L,V?
1.72	477		2.24	63	L
1.75	450	812	3.46	107	L

Table I (cont.)

cm^3/g	Temp. °C	Pressure, bars	Moles SiO$_2$/10^{5}g. H$_2$O	Hours of Run	Fluid Phases
1.79	463		1.80	137	L
1.79	463	783	1.98	46	L
1.80	474	916	1.61	233	L
1.79	498	1065	2.57	50	L
1.80	500	1168	4.05	193	L
1.79	502	1117	3.34	65	L
1.88	448	725	2.27	69	L
1.88	338		2.21	22	L,V
1.89	348		2.87	63	L,V
1.88	350		0.08	94	L,V
1.90	350	174	2.71	66	L,V
2.2	466	645	3.09	47	L
2.1	506	871	1.39	28	L
2.1	355	184	2.29	188	L,V
2.1	348	169	2.76	66	L,V
2.1	380	230	2.59	48	L,V
2.2	523		2.27	18	L
2.2	524		3.14	47	L
2.4	349	168	2.52	188	L,V
2.6	489	650	2.96	43	L
2.5	502	733	3.98	42	L
2.3	523	886	3.27	23	L
2.5	523	802	6.64	43	L
3.2	470	491	2.84	38	L,V?

Table II

Solubilities of Quartz at 0.015 moles KOH/1000g. H_2O

cm^3/g	Temp. °C	Pressure, bars	Moles $SiO_2/10^5g.\ H_2O$	Hours of Run	Fluid Phases
1.60	348	209	1.97	120	L,V
1.64	448	845	2.10	145	L
1.64	448	1100*	4.47*	18	L
1.70	362	235	2.35	65	L,V
1.70	374		2.71	84	L
1.78	350	175	2.25	69	L,V

*Pressure was accidentally raised; solubility is therefore high.

Table III

Solubilities of Quartz at 0.050 moles KOH/1000g. H_2O

cm^3/g	Temp. °C	Pressure, bars	Moles $SiO_2/10^5g.\ H_2O$	Hours of Run	Fluid Phases
1.18	198		3.35	263	L,V
1.28	245		3.79	96	L,V
1.29	248		3.78	47	L,V
1.33	343	670	5.60	43	L
1.35	271		4.02	119	L,V
1.36	274		3.99	234	L,V
1.44	299		4.05	137	L,V
1.47	355	447	5.68	117	L.
1.47	382	705	6.79	311	L
1.58	303		4.12	310	L,V
1.57	340	192	4.62	48	L,V
1.57	355	280	4.90	43	L

Table III (cont.)

cm^3/g	Temp. °C	Pressure, bars	Moles $SiO_2/10^5$g. H_2O	Hours of Run	Fluid Phases
1.65	323	122	4.36	115	L,V
1.66	353	188	6.23	48	L
1.66	370	276	4.79	43	L
1.67	370		5.72	46	L
1.77	370	290	4.18	46	L
1.77	370		5.06	68	L
1.77	395	315	5.73	93	L
1.91	356	191	9.85	41	L,V
1.95	361	191	5.19	46	L,V
1.93	361	194	5.65	111	L,V
1.92	389	318	5.22	38	L
1.99	368	204	5.26	111	L,V
1.99	383	258	5.61	39	L,V?
2.4	527	812	11.12	47	L
2.4	442	511	9.46	41	L
2.5	432	436	13.88	87	L
2.9	459	495	12.67	48	L
2.4	368	204	6.28	119	L,V
2.5	414	325	9.10	90	L
2.6	365	200	6.51	91	L,V
2.9	420	329	11.14	138	L,V
3.4	300	100	3.58	45	L,V
5.48	462	345	11.38	22	L,V
5.48	463	345	9.48	16	L,V
5.48	464	345	16.04	23	L,V
5.42	469	350	16.80	210	L,V
5.37	474	330	13.70	69	L,V
5.37	481	337	13.33	67	L,V
5.39	485	343	14.68	45	L,V
5.39	487	420	15.80	69	L,V
5.39	487	350	15.80	63	L,V
5.04	618	684	14.98	211	L,V
5.50	647	600	11.78	25	L,V

Table IV

Solubilities of Quartz at 0.150 moles KOH/1000g. H_2O

cm^3/g	Temp. °C	Pressure, bars	Moles $SiO_2/10^5g.\ H_2O$	Hours of Run	Fluid Phases
1.18	200	16	10.33	266	L,V
1.31	258	46	12.50	135	L,V
1.50	299	85	13.56	163	L,V
1.76	343	152	11.78	170	L,V
1.76	347	159	13.32	119	L,V
1.76	348	162	12.75	119	L,V
1.76	361	189	12.28	28	L,V
2.80	369	208	17.95	452	L,V

Table V

Solubilities of Quartz at intermediate concentrations

$\frac{\text{Moles KOH}}{1000g.\ H_2O}$	cm^3/g	Temp. °C	Pressure bars	$\frac{\text{Moles } SiO_2}{10^5g.\ H_2O}$	Hours of Run
0.0050	1.94	358	182	1.50	65
0.0120	1.64	341		1.75	121
0.0125	1.86	448	722	1.38	93
0.0138	1.64	351		2.18	30
0.0207	1.64	350		2.56	46
0.1965	1.46	302	88	14.82	451
0.1965	1.76	362	191	21.75	140

Table VI*

Composition of salts contained in Mineral Springs

Constituent	A	B	C
Cl	35.0	36.6	8.9
SO_4	4.6	1.8	5.8
S	0.2	---	---
CO_3	5.1	0.2	41.9
B_4O_7	8.9	2.2	0.2
Na	30.4	21.4	38.1
K	3.8	4.5	1.2
Li	0.3	0.2	0.1
Ca	0.3	0.4	0.9
Mg	---	0.1	0.4
Al_2O_3	---	0.8	---
SiO_2	11.4	31.7	2.3
Others	---	0.1	---
	100.0	100.0	100.0
Salinity parts per million	2,850	1,830	2,614

A. Steamboat Springs, Nevada.

B. Coral Spring, Norris Basin, Yellowstone Nat'l Park

C. Ojo Caliente Spring, near Taos, New Mexico

*after Lindgren, W., *Mineral Deposits*, 4th ed., McGraw-Hill Book Co., Inc., New York, 1932, pp48, 54.

Table VII*

Composition of Liquids in Inclusions

Constituent	Bachistock	Aaremassiv	Mississippi Valley
H_2O	83.4%	85.0%	80-90%
CO_2	9.5	5.0	
Na	2.0	1.5	
K	0.7		
Li	0.2	0.3	
Ca	0.3	1.5	
Cl	1.6	0.7	
SO_4	0.5	3.5	
CO_3	1.8	2.5	
NaCl			10-20
	100.0%	100.0%	100.0%

*after Newhouse, W. H., <u>Econ</u>. <u>Geol</u>. 27, 1932, pp419-436.

APPENDIX II

PROPERTIES OF POTASSIUM HYDROGEN DISILICATE, $KHSi_2O_5$.

Physical Properties: Commonly no crystal faces are present, but when they are developed (100), (010), and (001) faces are prominent. Perfect cleavage is present along (001), and good cleavage along (010). The crystal system is monoclinic; twinning is very common. This compound is nearly insoluble in water.

Optical Properties: X = 1.490, variable, Y = 1.490, variable, Z = 1.531. Y-X = 0.004. 2V (+) = 45°. Extinction is parallel. Orientation is X = c, Y = b, Z = a.

"d" spacings have been determined approximately as follows:

d in angstroms	Relative intensity
4.11	2
3.56	2
3.09	½
2.44	½
2.08	9
1.924	9
1.893	10
1.845	9
1.654	1
1.605	1
1.544	5
1.505	7
1.409	5
1.354	½
1.331	½
1.296	1
1.270	1
1.221	½
1.126	1
1.103	7
1.084	½
1.038	½
1.016	½
1.003	½

d in angstroms	Relative intensity
0.985	$\frac{1}{2}$
0.962	$\frac{1}{2}$
0.937	$\frac{1}{2}$
0.925	$\frac{1}{2}$
0.913	$\frac{1}{2}$
0.891	1
0.858	$\frac{1}{2}$
0.835	$\frac{1}{2}$
0.811	$\frac{1}{2}$
0.798	$\frac{1}{2}$

PROPERTIES OF POTASSIUM IRON SILICATE, $KFeSi_3O_8$

Habit: Potassium iron silicate (iron orthoclase) commonly occurs as tiny (0.01 mm) rhomb shaped crystals; occasionally it is in long needles. Almost invariably it is attached to some surface.

	Properties of synthesized material	Properties reported for $KFeSi_3O_8$
X =	1.590	1.601
Y =	?	?
Z =	1.610	1.609
	Twins fairly common	Twins on (100),(001), (021)
	Xl angles of 65° and 115°	$(100) \wedge (001) = 64^\circ$ $KAlSi_3O_8$
	$X(?) \wedge a(?) = +2^\circ$ to $+11^\circ$	$X \wedge a = +7^\circ$ to 8° in (010)
	Mono.?	Mono. and Tric.
	Colorless	Yellow
	$(+?)\ 2V = 60^\circ$ to 70°	$2V = ?$

Spectrographic analysis of synthesized material:

K = ?

Fe = ca. 50%

Si = ca. 50%

Theoretical analysis of $KFeSi_3O_8$ recomputed to 100% after subtracting oxygen:

K = 21.8%

Fe = 31.2%

Si = 47.0%

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