SOLUBILITY MEASUREMENT IN THE CRITICAL REGION

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I. HISTORICAL SUMMARY

The earliest observations of critical phenomena were made in 1822 by Cagniard de la Tour (17), who first observed the disappearance of the vapor–liquid interface, characteristic of the critical state. In 1869 Andrews (4), in his classical work on carbon dioxide, established the continuity of the gaseous and liquid phases. The thermodynamic theory of the critical phase for one- and two-component systems was carefully worked out by van der Waals (112, 113) in 1881 and later elaborated by others (88, 95, 96, 97).

Studies demonstrating the possibility of continuous change of phase from liquid to gas led Hannay and Hogarth (48, 49, 50, 51, 52, 53) to inquire whether solvent action is characteristic only of the liquid phase, or whether gases might not also be capable of dissolving solids. Their work, including the study of solutions of several inorganic salts in ethanol, demonstrated that the solution of salts is not limited to the liquid phase. In particular, it was noted that an alcoholic solution of cobalt chloride above its critical point had essentially the same absorption spectrum as in the normal liquid state, thus indicating that the usual ionic condition persists even above the critical temperature of a solution. The concentrations of solid in the supercritical phase were far higher than could be accounted for by the normal volatility of the salts concerned. Whether this is a true solution or an enhanced volatility is perhaps more a matter of nomenclature than of theory (75, 106, 118).

The observations of Hannay and Hogarth, though fairly conclusive and verified by others (19, 119, 120), were widely misinterpreted, particularly by Ramsay (86), with the result that they were largely ignored. The extreme experimental difficulties associated with such complicated critical studies discouraged extensive investigation of this field, and not until the work of Centnerszwer (20, 21, 22, 23, 124) between 1903 and 1910 was a systematic quantitative study made of the critical points of solutions of salts. Earlier observations had, however, been made of the behavior of mixtures of gases near the critical point (11, 18).

The experiments of Centnerszwer demonstrated that the presence of dissolved salts normally causes a rise in the critical point of a liquid, analogous to the rise in the normal boiling point and similarly proportional to salt concentration. The presence of dissolved material may either raise or lower the critical point of a liquid, depending on the nature of the solution. The critical point may thus, like the melting point, be used as a criterion of chemical purity (20).

Other determinations from this viewpoint are those of Büchner (16) and of Schröer (92), who reached similar conclusions, though differing somewhat in their quantitative interpretation. Schröer observed wide variations in the behavior of different salts in aqueous solution when the critical region was reached.

In 1912 Niggli (78) published the first of his works pointing out the importance of critical phenomena in geological processes, particularly as regards the formation of ores and rare minerals. This work was later expanded into a complete system of the phase relations likely to occur in natural magmas, and application of these relationships to the explanation of the formation of actual minerals (77). Such work, combined with the experimental synthesis of minerals and the study of the phase relations of magmatic components, carried on particularly at the Geophysical Laboratory of the Carnegie Institution of Washington, has added greatly to understanding of the processes resulting in the formation of ores and other characteristic end-products of magmatic activity. A large proportion of this work is not particularly concerned with critical phenomena, and hence is not within the scope of this paper. The interpretation of many of the results in terms of critical occurrences (77, 96, 97) has, however, been invaluable in the clear understanding of observations.

It seems wise to limit this paper to the type of system where, of two components, the triple point of one lies at a considerably higher temperature than the critical point of the other. This is characteristic of solutions of many salts in water or in organic liquids, as well as of the complex mixtures which make up magmas, the several components of the latter being readily classifiable as volatile and refractory substances, respectively. On the more extreme types, exemplified by combination of a "permanent gas" with a metal, metallic oxide, or other such refractory material, little conclusive information seems to be available. Systems of more nearly comparable critical constants have been reviewed elsewhere (3). These include the industrially very important mixtures of petroleum hydrocarbons, as well as the systems carbon dioxide–permanent gases (11, 64) and argon–boron trifluoride (13).

This review presents a general survey of the field from a chemical point of view. Earlier reviews of related nature (73, 75) are more concerned with hydrothermal and pneumatolytic studies of minerals.

It has been demonstrated that the solubility of salts in alcohols is not discontinuous at the critical point of the solutions. It is also shown that solubility in the single-phase region is strikingly dependent upon pressure, or perhaps more directly the density or "concentration" of the solvent (figures 4, 6, 7, 8, 9) (106, 118).

Conductivity studies (30, 33, 45, 46, 47, 63, 64, 124) substantiate solubility measurements on salt–alcohol systems and in addition show that the dielectric constants of solutions may not suffer large changes at their critical points, but may still permit dissociation of ionic salts to give electrically conducting gas-phase solutions (figures 10, 11). The recorded curves of conductivity as a function of pressure and temperature show a close resemblance to the solubility variation under similar conditions (111). This is related to the fact that the processes of solution and ionization depend to some extent upon the same solvent characteristics.

II. NATURE OF THE CRITICAL STATE

A. PURE SUBSTANCES

For any sufficiently stable substance there exists a temperature, with associated pressure and specific volume, at which the liquid and vapor phases become identical. This point, known as the critical point, is often spoken of as the temperature above which a substance can exist only as a gas. The material existing in a state not too remote from the critical state may, however, have nearly as many of the characteristics, from the conventional viewpoint, of the liquid as of the gaseous state. As was shown by Andrews (4) and later corroborated and developed from a theoretical point of view (112), a transition may be made from attenuated gas to cold liquid, passing through this region, without at any point encountering any discontinuous change of phase, as for example the formation of mist droplets, bubbles, or a meniscus. Thus water vapor or superheated steam may be heated to 400°C., above the critical temperature, compressed isothermally under several hundred atmospheres pressure, and then cooled to cold water, without condensation.

Although a substance above the critical point may be predominantly of a gaseous nature, it may still retain many of the attributes of the liquid phase. It may have comparable density, and may be capable of dissolving solids to about the same extent as liquid of that density, and of forming ionic solutions. It is perhaps not strictly correct to speak of solution properties as typical of liquids, in view of the data indicating solution and conductivity in the vapor phase even below the critical point (30, 33, 45, 46, 47, 63, 106, 111). "Solubility above the critical point," as used in this paper, refers always to solubility above the critical point of the *solution*, that is, in the gas phase.

That such dispersion is true solution in the gas phase, and not volatilization, has repeatedly been stated, although the distinction is not entirely clear-cut. If volatilization, it is at least associated with an abnormally high vapor pressure. The quantity of solute found in the gas phase is frequently far greater than could be accounted for by normal volatility (103, 106, 118). The effect of pressure on the amount of solid dispersed is much larger than that expected from normal increase of vapor pressure due to external pressure.

The spectra of such solutions have been observed to be the same as for solutions of the same solute in the usual liquid phase, and to differ from those obtained on vaporization of pure solid substances (19, 50, 51, 119). Ionic solutions of salts conduct electric current above their critical temperatures (30, 33, 45, 46, 47, 63, 64).

B. CRITICAL CURVES

It was mentioned earlier that the presence of dissolved salts causes a rise in the critical temperature of a liquid. This rise is actually (75) only the beginning of a curve connecting the critical points of solvent and solute, and representing the critical point at each intermediate concentration (curve A_cB_c, figure 1). Points A_c and B_c are the respective critical points of the pure substances. The other lines of the diagram give pressure–temperature relations under conditions of equilibrium between different phases characteristic of this system of a volatile component A and a refractory component B. "B + L + V", for example, refers to equilibrium between pure solid B, a liquid phase, and a vapor phase; that is, a solution saturated with respect to B, under its own vapor pressure. Such solubility curves run to the eutectic E from the respective triple points A_t and B_t of the two components. Diagrams similar to figure 1 may be drawn up, relating concentration to pressure, temperature, and specific volume (73, 77).

The critical points for mixtures represent, in general, neither the maximum temperature nor the maximum pressure attainable in the presence of liquid when a mixture of two components in the proper proportions is heated, but are the true critical points, i.e., the point for each mixture where the liquid and vapor phases become identical. For pure substances, the points of maximum temperature and maximum pressure coincide with the critical point, but for mixtures these points are in general all different, permitting the occurrence of retrograde phenomena (3). For solutions of salts in ordinary solvents, the critical curves show a maximum pressure at some intermediate composition and temperature, the geological importance of which is to be pointed out. This is, however, not invariably the case.

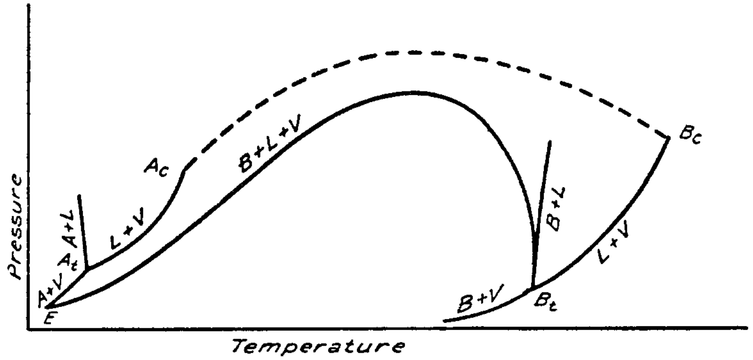

FIG. 1. Pressure–temperature diagram for a two-component system without critical end-points (after Morey and Ingerson (73)).

C. INFLUENCE OF SOLUBILITY

In the case of very soluble substances, critical phenomena may never occur for saturated solutions, that is, in the presence of solid solute. This is a result of the raising of the critical temperature by the dissolved substance, which becomes increasingly soluble as the temperature rises, allowing further increases in the temperature of liquid solution, until the composition of pure solute is attained. This is the type of system, exemplified by water–silver nitrate, of which the phenomenon of "second boiling point" is characteristic; the total vapor pressure of the mixture falling again, in general, as the composition of pure salt is approached (66). In this case the *solubility curve*, representing equilibrium between solid solute and solution, lies entirely below the critical curve, as in figure 1. The limitation of critical phenomena to unsaturated solutions under these conditions is obvious.

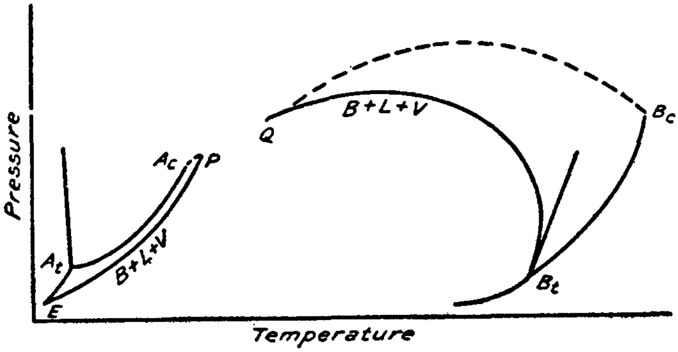

FIG. 2. Pressure-temperature diagram for a two-component system **having two critical** end-points (after Morey and Ingerson (73)).

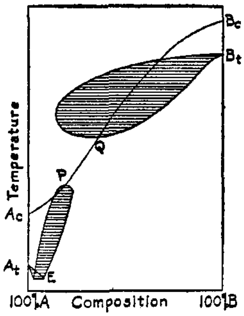

FIG. 3. Temperature-composition diagram for a two-component system having two critical end-points (after Morey and Ingerson (73)).

D. LIMITED SOLUBILITY

Of more interest in this work is the case where solubility is more limited, critical phenomena arise, and solubility in the supercritical "fluid" phase enters into consideration. This frequently occurs when the solubility of the solute falls with rising temperature. In this case the solubility curve cuts the critical curve twice, and in the intervening region both curves are discontinuous, as shown in figure 2. Two critical solution points P and Q exist, representing the upper and lower temperature limits, respectively, of two regions where equilibrium between liquid and vapor phases exists, these equilibria being represented in figure 3 by the isothermal tie-lines connecting the two phases in equilibrium with solid at the given temperatures in the loops EP and B_tQ, respectively. In the intervening region, solid component B is in equilibrium with a single fluid phase, having certain characteristics of both liquid and gas. In this phase the solubility of component B depends upon both temperature and pressure, as may best be shown (figure 4) by the experimental curves of Smits (96) for the system ether–anthraquinone: an example, under comparatively mild conditions, of the type of behavior expected of sparingly soluble solids in solution in water and other common solvents. The two loops appear, as in the general temperature–concentration diagram (figure 3), representing equilibria between liquid and vapor phases in the presence of solid anthraquinone at various temperatures. n the intermediate region of a single fluid phase isobars have been drawn in, howing the solubility of anthraquinone in ether in this phase, as dependent pon pressure. It should be obvious, however, that a rigid designation of comonents as solvent and solute, respectively, may lead to confusion; outside the ower loop of these diagrams the choice of "solvent" is often dubious. The actual situation is that of reciprocal solubilities; it would be least ambiguous to speak only of relative proportions of the two components in each phase.

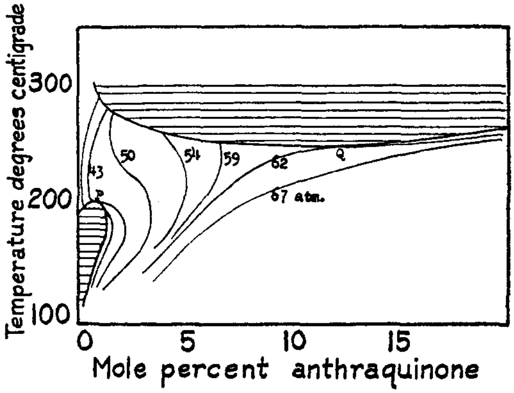

FIG. 4. Temperature–composition diagram for the ether–anthraquinone system, showing isobars (after Smits and Niggli (77)).

Other similar systems have been explored to a lesser extent than the ether–anthraquinone system, and some preliminary study (103, 118) has shown parallel behavior in a small region immediately above the critical point for the system silica–water.

In each of the two loops characteristic of these temperature–composition diagrams, three-phase equilibrium is represented between vapor and liquid phase solutions and solid B, three phases in all, with compositions fixed at the temperature in question, in accordance with the phase rule. Between P and Q, where only a single fluid phase exists in contact with solid, divariance (variation in composition with both temperature and pressure) is to be expected. In the small region A_tE (figure 3), solid component A is in equilibrium with solution and vapor, this being the region of the familiar lowering of the freezing point of a solvent.

These temperature–composition diagrams do not, of course, represent isobaric sections, but show conditions at pressures allowing multiphase equilibria. A pressure variation similar to that shown in figure 5 is characteristic of the three-phase portions of systems such as those shown in figures 3 and 4.

E. MULTICOMPONENT SYSTEMS

Where more than two components are present in a system, the relations involved are somewhat more complex, owing to the greater number of variables. No phenomena occur, however, which are intrinsically different from those already described, and those considered in elementary phase study.

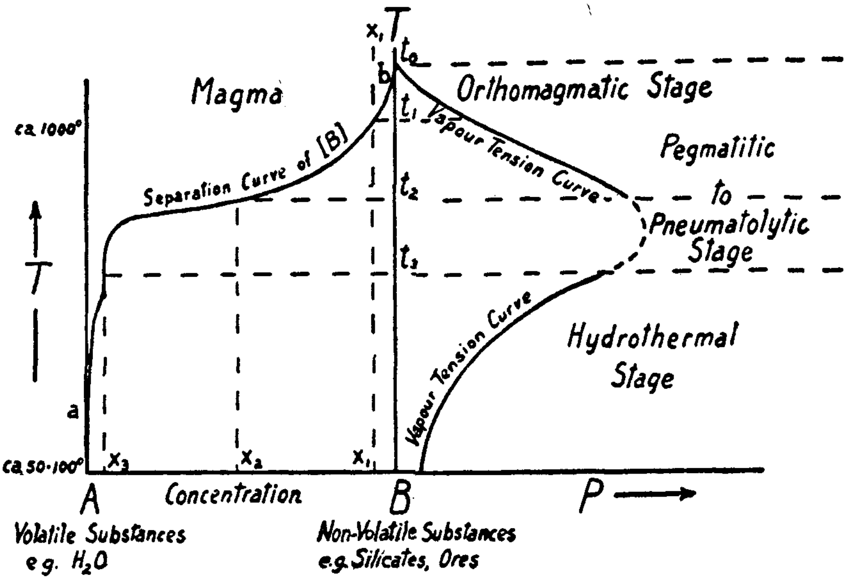

FIG. 5. Temperature–concentration and temperature–pressure diagrams for a cooling ideal magma (Niggli (77a)).

F. COMPOUND FORMATION

Under certain conditions, two or more components present in a system may interact to form compounds, as for example the various silicates and hydrates formed in the system SiO_2–K_2O–H_2O (69). An interesting example of compound formation, as occurring in systems of the type described in this paper, is the CaO–CO_2 system, which, though well known, has not generally been considered from this viewpoint.

III. GEOLOGICAL SIGNIFICANCE

A large proportion of the information on phase relations between volatile and refractory substances is the result of studies of the formation of minerals and ores, that is, from a geological viewpoint. This is related to the fact that only under the tremendous external pressure which can be exerted by hundreds of feet of rock can appreciable proportions of volatile matter be kept in intimate contact with refractory substances near their melting points, except under artificial conditions. Only the development of modern metals of high tensile strength has permitted the study of such systems.

A. NATURE OF MAGMA

A magma may be considered as a mass of fluid material in the earth's crust consisting principally of the common rock-building elements, with traces of practically all other elements in some form or other. Originally it can be considered as being an essentially homogeneous mass at something over 1000°C. Appreciable proportions of volatile materials, particularly water, hydrogen chloride, hydrogen fluoride, carbon dioxide, hydrogen sulfide, silicon tetrafluoride, and certain of their reaction products with less volatile components, are present in the normal magma, being held in solution under pressure.

B. ORTHOMAGMATIC STAGE

As the magma loses heat to the surrounding rock, the highest melting major components, in general, begin to crystallize out. As a result, the concentration of volatile components in the remaining solution rises. The total vapor pressure of the system also rises, the increase due to the increased proportion of volatile materials being greater than the decrease resulting from the reduction of temperature; there is thus observed an increasing pressure as the temperature falls (see figures 3 and 5). This is merely the generalized aspect of "second boiling point." Under these conditions, a phase containing a large proportion of volatiles tends to separate in the magma, the system now entering the state described by the upper loop of figure 3. The principal processes occurring here are crystallization of such rocks as granites, and simultaneous separation of "contact gas." This gas may (*a*) escape through fissures or other openings in the surrounding rock, (*b*) remain included in cavities in the newly formed rock, (*c*) be occluded in solid solution, (*d*) react chemically, or (*e*) redissolve in the remaining liquid magma (121). This stage in magmatic evolution, known as the orthomagmatic stage, is characterized by the presence of molten rock-forming material, and is not entirely different from early concepts of the interior of the earth.

One important result of the increase in pressure as the magma cools is the expansion of the containing space, resulting often in cracks in the surrounding rock, thus permitting escape of the more mobile phases, which may eventually produce such formations as veins, beds, and dikes. If it occurs close enough to the surface, volcanic eruption may result.

C. PNEUMATOLYTIC STAGE

As the magma cools further, the proportion of volatile material in both fluid phases becomes quite high, in agreement with figure 3; then eventually a portion of the siliceous material redissolves in the "contact gas," and the two phases become identical at the point corresponding to the upper region critical point Q (figures 2 and 3). This and the region of a single fluid phase, immediately below, constitute the region of *pneumatolytic* processes, where a considerable amount of chemical activity and transport of dissolved material is facilitated by the extremely high pressure and the action, chemically and as a vehicle, of the low-viscosity contact gas or supercritical fluid phase. The actual mechanism of the separation of phases has been a subject of considerable dispute (14).

In the cooling of the magma, those substances crystallize out first with respect to which the solution first becomes saturated. Since a few rock-building minerals are present in overwhelming proportions (99 per cent of all igneous material is said to be included under only ten mineral types), these compounds crystallize out first, along with certain isomorphic substances, concentrating rare and valuable ores and minerals in the mother liquors. These rare minerals, being by virtue of their low concentration still in solution in the pneumatolytic stage, are often carried away from the main mass of the magma, the concentration continuing during transport, and are eventually deposited in veins, beds, or dikes. Pegmatite dikes are intrusive masses of coarse-grained granite formed during this stage, usually containing an appreciable proportion of rare minerals, which tend to concentrate further during deposition of the granite, giving associated, comparatively pure deposits of these minerals. Such minerals are consequently often found in pegmatites or in fissures in the surrounding rocks. The large size characteristic of pegmatite crystals is in harmony with the concept of their deposition from relatively dilute solution.

D. HYDROTHERMAL STAGE

On further cooling, the magma enters the final *hydrothermal* stage, in which liquid and gaseous phases are again present together, but now with a greater preponderance of volatile material. The processes occurring in this stage are solution, deposition, and reaction in an essentially aqueous medium, containing, however, significant proportions of other volatiles. Minerals are deposited from dilute solution under these conditions, large deposits being built up by continued flow of the cooling saturated solutions. Hydrothermal reactions, being closest to ordinary chemical experience, are comparatively well understood, and many of the postulated or proven reactions will be included in the next section.

E. INFLUENCE OF VOLATILE CONSTITUENTS

As suggested earlier, mineral deposition depends to a considerable degree on the action of volatile substances, of which perhaps the most important are water, carbon dioxide, hydrogen sulfide, hydrogen chloride, hydrogen fluoride, sulfur dioxide, and silicon tetrafluoride (25, 77, 127). These substances are known as "mineralizers," because of their action in promoting mineral concentration and crystallization during the solidification of rock-forming material, particularly in pegmatite dikes. They, or more commonly their ultimate reaction products, such as hydrated minerals, carbonates, sulfides, halides, and oxides, are found as constituents of, or associated with, minerals and ores, frequently those of commercial value. Thus, for example, fluorspar is often found with sphalerite (ZnS), galena (PbS), and chalcopyrite ($CuFeS_2$).

Volcanoes, fumaroles, and hot springs are all surface manifestations of magmatic activity, and represent the ultimate separation and dispersal of volatile constituents. The sampling of substances from these sources gives valuable information toward the better understanding of geological processes, although it must be understood that the ejected material is in many cases heavily contaminated with foreign substances (127). Gases such as those mentioned above, associated often with well-defined solid minerals, have frequently been detected in these exhalations (1, 93, 126, 127, 128).

Mineralizers may include, however, not only such highly volatile substances, but a complete range of compounds, ranging from the most volatile to such materials as fluorspar, with melting points above 1000°C. The characteristic behavior of mineralizers is a type of solvent action, associated in some cases with chemical reaction. Any substance can be a mineralizer which appreciably increases the mobility of a system, allowing more rapid attainment of equilibrium and thus promoting the separation of pure phases. Fluorides, in fact, owe their name to the viscosity-lowering properties of fluorspar, commonly used as a flux.

The extent of the influence of fluorides, characterized as "*mineralisateurs par excellence,*" on geological processes has perhaps been underestimated because of the difficulty of determining gaseous fluorides in samples, both because of their high reactivity, particularly on glass, and because of the difficulty of precise analysis in the presence of other reactive gases and of each other. Large proportions of fluoride gases were collected at the fumaroles of the Valley of Ten Thousand Smokes (126, 127, 129).

Many systems and reactions have been studied, and others postulated, for the formation of minerals, particularly through the action of mineralizers as reagents (128). A few examples are given below (1, 26, 77, 127).

$$\begin{aligned}
&Fe_2Cl_6 + 3H_2O \rightleftharpoons 6HCl + Fe_2O_3\\
&Fe_2Cl_6 + 2H_2O \rightleftharpoons 4HCl + 2FeOCl\\
&Fe_2Cl_6 \rightleftharpoons Fe_2Cl_4 + Cl_2\\
&6Fe_2O_3 \rightleftharpoons 4Fe_3O_4 + O_2\\
&4HCl + O_2 \rightleftharpoons 2H_2O + 2Cl_2\\
&SnCl_4 + 2H_2O \rightleftharpoons 4HCl + SnO_2\\
&TiF_4 + 2H_2O \rightleftharpoons 4HF + TiO_2\\
&CaF_2 + H_2O \rightleftharpoons CaO + 2HF\\
&BeCl_2 + H_2O \rightleftharpoons BeO + 2HCl\\
&2AlF_3 + 3H_2O \rightleftharpoons 6HF + Al_2O_3\\
&3SiF_4 + 2Al_2O_3 \rightleftharpoons 3SiO_2 + 4AlF_3\\
&SiO_2 + 4HF \rightleftharpoons SiF_4 + 2H_2O\\
&PbCl_2 + H_2S \rightleftharpoons PbS + 2HCl\\
&4AsCl_3 + 2CoCl_3 \rightleftharpoons Co_2As_4 + 9Cl_2\\
&FeSO_4 + H_2S + S \rightleftharpoons FeS_2 + H_2SO_4\\
&3FeO + H_2O \rightleftharpoons Fe_3O_4 + H_2\\
&3S + 2H_2O \rightleftharpoons 2H_2S + SO_2\\
&H_2S + 2H_2O \rightleftharpoons 3H_2 + SO_2\\
&2H_2S \rightleftharpoons 2H_2 + S_2\\
&S_2 + 4CO_2 \rightleftharpoons 2SO_2 + 4CO\\
&2NaCl + H_2O \rightleftharpoons 2HCl + Na_2O
\end{aligned}$$

Many of these are noticeably high-temperature reactions, particularly if equilibrium is regarded as occurring in the presence of appreciable proportions of the several substances concerned. There may be some doubt whether magmatic emanations often contain low enough concentrations of water to permit the extensive transfer of such elements as aluminum and titanium in the form of their halides.

It has been stated that the gaseous emanations from certain incandescent lavas may consist principally of sodium chloride (28). How generally this may be true, however, is in doubt (1).

There is increasing acceptance of the concept of simple solution in volatile substances, frequently in the gas phase, as the principal medium in the transfer and concentration of ore minerals, rather than the formation of volatile compounds. These solutions are generally primarily aqueous, though the presence of other compounds acting as solvent is not excluded, but at lower temperatures water is usually present in far larger proportion than other potential solvents (56).

With respect to the occurrence of solutions above their critical points, it is believed that the normal concentration of mineralizers of moderate volatility (alkali and alkaline earth halides, for example) in normal magmatic mixtures may be high enough to make true critical phenomena indeed of rare occurrence in the presence of the main body of the magma, the liquid phase of the magma then consisting, as it cools, of solutions in a series of increasingly volatile mixtures of compounds, but with no principal solvent substance above its critical point, as altered by the presence of other components, at any time. This does not necessarily apply, however, to fluid "emanations" separated from the magma, which, with their dissolved solids, are probably frequently above the critical temperature.

The potentialities of sodium chloride as a solvent, or mineralizer, are shown by its use as such in industrially practicable syntheses (10, 11b, 11c, 11d). Fluorides have frequently been used in syntheses difficult or impossible in the absence of mineralizing action (27, 125).

Although much information has been acquired through the study of minerals and volcanic activity, no complete picture of mineral-forming processes can be built up until a great deal of further experimental study has been made of solutions and reaction equilibria at temperatures and pressures similar to those encountered in nature.

IV. ENGINEERING SIGNIFICANCE

It has frequently been observed that a solid deposit appears on steam turbine blades, in spite of precautions to prevent entrainment (24, 65, 70, 104, 105, 106). These deposits are observed to occur particularly at regions of falling pressure, such as the convex sides of turbine blades, and consist principally of quartz, amorphous silica, and sodium salts.

It has been the object of some study to prevent the formation of these deposits, since the efficiency of a turbine is appreciably impaired by their presence. The deposition of silica is particularly undesirable, since it requires the use of either caustic or mechanical cleaning for removal.

Reviews and criticisms have been written (70, 106) on the limited number of studies made, from an engineering point of view, of this problem. In some cases (24, 70, 106) turbines were examined, and the nature and quantity of the deposits ascertained. An effort was made to correlate these observations with operating conditions.

Of a somewhat more fundamental nature are experiments in which saturated or superheated steam is passed over dry solids or saturated solutions, and the effluent vapor analyzed (104, 106). In other experiments steam from a boiler containing known concentrations of salts was analyzed, the primary objective being the prevention of the carrying over of silica by adjustment of operating conditions and addition of salts to form compounds less easily dissolved in steam (106).

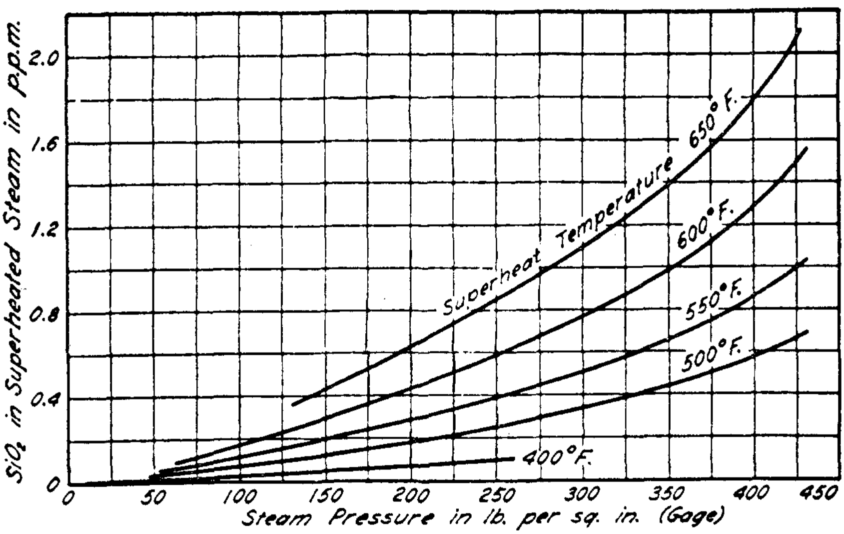

FIG. 6. Solubility of silica in superheated steam as a function of temperature and pressure (Straub (106)).

Since these experiments were carried out under such conditions as to exclude entrainment except as a known very minor source of error, it is established that many substances have a measurable solubility in steam (70, 106). This solubility, first becoming prominent in the region of 50 atm., rises sharply with increasing pressure (figure 6), agreeing in this respect with measurements by different techniques above the critical point in the silica–water (118), anthraquinone–ether (97), and other systems (23, 97, 111). The high solubility of silica, or silicic acid, in both liquid and gaseous water as the critical region is approached is noteworthy.

V. Experimental Methods

A. INTRODUCTION

Owing to the experimental difficulties encountered, studies involving critical conditions have been very limited in number and in scope. Studies of critical phenomena of mixtures as such have been largely limited to non-aqueous systems, because of the extreme corrosiveness of water at those temperatures, which is not likely to be decreased by the presence of dissolved salts. Ordinary construction metals and most glasses are attacked by water near its critical point.

B. HYDROTHERMAL SYNTHESIS

A large proportion of the work involving solutions above the critical point has been from the viewpoint of the hydrothermal synthesis and alteration of minerals. These procedures involve, in general, the heating of a mineral or a known mixture of pure chemicals with water and perhaps other reagents at the temperature of interest until equilibrium has been attained, the purpose being to simulate natural geological processes. Some type of pressure vessel is, of course, usually necessary as a container. The pressure vessel and contents are cooled rapidly, often quenched, to room temperature, preserving the phases formed under the experimental conditions. The crystals and glass (representing the liquid phase) from the bomb are analyzed chemically and microscopically. The techniques and history of these investigations, extending back to 1845, have been reviewed (55, 73, 75).

From the various combinations of phases found stable at various temperatures, pressures, and proportions of components, a complete phase diagram describing the system can be drawn up. Many of these reactions are carried out at temperatures well above the critical point of water. Over a hundred minerals have thus been synthesized.

As one possible variation, carbon dioxide may be introduced into the hydrothermal bomb as an additional component, the action of carbonic acid at lower temperatures simulating the weathering of rocks (81), as well as taking part in syntheses.

The results of hydrothermal reactions and more direct solubility measurements may supplement each other in the complete analysis of a system.

1. Refinements of hydrothermal methods

Much of the more recent hydrothermal work (74) has been done with a highly complex apparatus in which steam is introduced into the reaction vessel from an external boiler. The outer parts of the container are kept at a desired temperature, say 500°C., and an internal furnace heats the charge, wrapped in platinum foil, to the test temperature. The charge is suspended from fusible wires and is quenched by simply passing a current through the wires, which then allow it to fall into the cooler lower part of the container. It will be seen that great flexibility is attainable by the use of such an apparatus. Other gases, as well as steam, may of course be introduced at controlled temperatures and pressures.

For the study of the oxidation of minerals in water, a bleed-off valve attached to a hydrothermal bomb permitted the escape of evolved hydrogen, thus adding another variable to the simulation of magmatic conditions (31).

C. DIRECT SOLUBILITY MEASUREMENTS

1. Sampling methods

Since the direct chemical analysis of the contents of a container at high pressures presents unusual experimental difficulties, it is desirable, in order to determine the solubility of a substance under such conditions, to withdraw a portion of the saturated solution from the bomb. Since the solution is exposed to considerable changes in both temperature and pressure upon leaving the bomb, it is usually necessary to separate the solution from the undissolved solid phase *before* it leaves the container. This requires, in general, some type of filter *inside* the pressure vessel.

A popular technique is the intersection of a sintered filter stick through the top of a pressure vessel to a point near the bottom. Such apparatus was used to measure the solubility of calcium sulfate (107) in water to temperatures somewhat below the critical. The liquid in this case was drawn off into a smaller pressure vessel, originally at atmospheric pressure.

For measurements of the solubility of silica to 360°C., a filter in the base of the container, consisting of graded particles of the solute, was used. The solution was drawn off into a water-cooled condenser, a procedure said to be usable only where the solute is not deposited rapidly from supersaturated solution, or where it may be removed easily from surfaces (55).

2. Internal filters

In many cases it may be expected that an appreciable change in the constitution of the solution will occur on passing through the filter, resulting in deposition of solute in and near the filter itself. In work close to the critical point, appreciable changes may also occur in the nature of the solution remaining inside the pressure vessel, even while sampling. It is often of interest to examine this material in the equilibrium state.

To effect the separation of solution from solid phases under equilibrium conditions, the *internal filter* was developed (108). In this type of apparatus the container is divided essentially into two sections by a filter or screen, the solid solute being restricted to one side. During the time equilibrium is being attained, usually with agitation, the solution is on the lower side of the partition, in contact with the solid phase. Filtration is effected by simply inverting the container, the solution then passing through the filter. Subsequent cooling may cause part of the solute to precipitate, but the entire contents, solid and liquid, of that part of the bomb will in general give the solubility at the equilibrium temperature. With this type of apparatus, unlike some sampling devices, only one sample may be taken for each filling of the bomb.

A disadvantage of internal filters is the difficulty with which vapor passes through pores blocked with liquid or solid. This may perhaps often be alleviated by tilting the container slowly enough so that only part of the filter is, at any time, immersed in the solution. An improved design (60, 61, 62) has a small tube inserted through the filter, itself equipped with a filter disk. The displaced gas rises through this tube unhindered and passes out through the small filter, under an appreciable hydrostatic head, into the now uppermost compartment.

A greatly refined and modified design of internal filter (72) includes a stirrer which, when equilibrium has been attained, is lowered to cut a gold diaphragm. The charge above the diaphragm can then pass through to a filter crucible. Steam pressure in the upper chamber is externally controlled, and that below made approximately the same, by the presence of a small, calculated amount of water placed there at the beginning of the experiment.

3. Sampling of solutions near the critical point

Sampling methods and internal filters are applicable to solubility measurements, in general, which are made appreciably below the critical point. Above the critical, however, there exists only a single homogeneous fluid phase, and there is consequently no driving force to cause the liquid to pass through an internal filter, unless possibly some external force is applied to one side of the filter. In the case of external sampling, this is essentially the situation. The application of force, however, changes the state of the system, and equilibrium conditions then no longer exist. While this is of little importance at ordinary temperatures and pressures, a negligible amount of solvent being evaporated or condensed, with a corresponding small temperature change, in the critical region and above a large change in the density of solvent occurs under external influences. The solubility of a solid in this region has been shown (97, 106, 114, 118) to vary considerably with pressure, and therefore with the density of the solvent.

Under these conditions, it is to be expected that as soon as a portion of the solution is removed, the remaining solution will become appreciably supersaturated. It is then likely that a part of the dissolved salt will precipitate, either in the container or in the pores of the filter itself. The extent of this deposition may be difficult to estimate.

Where pressure is applied to an internal filter, the compressed fluid will in general tend to dissolve more solute. This will often lead to negligible error, owing to the slowness of the dissolving process.

Apparatus not necessarily subject to these difficulties has been developed (8, 122, 123). In these the sampling chamber is an integral part of the pressure vessel.

Both upper and lower phases of a two-phase mixture can be sampled by a technique involving displacement with mercury. In one such apparatus (55a) two smaller bombs were connected at the sides of the main pressure vessel. Tubes connected the tops of these two bombs with, respectively, the upper and lower parts of the large chamber. The lower ends of the two were both connected through tubes, closed by valves, to the bottom of the larger container. When a valve was opened, mercury flowed down into the main chamber, displacing a sample of its contents into the space formerly occupied by mercury, in the top of one of the small bombs. Solubilities above the critical point are, of course, thus measurable. Since there is no change in pressure or volume, the equilibrium conditions are maintained while sampling. Filters could, if necessary, be inserted in the lines.

4. Synthetic method

One of the more successful procedures for the determination of solubilities in closed systems, where transparent containers may be used, is the synthetic method (21, 111). Known quantities of solvent and solute are enclosed in the system, and, sufficient agitation being supplied, the points are observed at which the solute is completely dissolved and at which it begins to crystallize out again. These temperatures can be very precisely observed, in the case of an anisotropic solute, by the use of polarized light, the crystals shining brilliantly against a dark field (11a). The synthetic technique has been successfully used above the critical point (23, 95, 111).

D. PHYSICAL MEASUREMENTS

Although chemical determinations on solutions above the critical point are very difficult, certain physical methods have more promise. The methods which have been used in this and related fields are (*1*) spectrometric or colorimetric and (*2*) electrical conductivity.

1. Spectrometric measurements

The observation of visible color and qualitative spectroscopic examination of solutions of cobalt chloride, ferric chloride, a chlorophyll extract, and alizarin in ethanol (7, 50, 51, 52, 53), and of iodine in carbon dioxide (19, 119) were used to indicate the presence and physical state of dissolved material in liquid, vapor, and "fluid" phases. A similar technique has been used on aqueous solutions of potassium dichromate, copper sulfate, cobalt chloride, and cupric chloride (7, 92). These methods have apparently not yet been used for precise quantitative measurement.

2. Conductivity measurements

The use of electrical conductivity measurements for the determination of solubilities of sparingly soluble salts in ionizing solvents has been recommended (82, 87). Although excellent conductivity and dielectric constant measurements have been made above the critical point on solutions of known concentration (30, 33, 45, 46, 47, 63, 64, 124), the somewhat more tedious determination of solubility in this region by such means has apparently not been carried out.

For solutions in alcohols, ammonia, and sulfur dioxide at the critical point, glass capsules with sealed-in electrodes were found satisfactory. For other, more corrosive, solvents, such as water and hydrogen fluoride, metal apparatus modelled after that used by A. A. Noyes and his colleagues (82) for their classic studies on conductivity and ionization of water and aqueous solutions at elevated temperatures should be suitable.

The limitation of most chemical thought to "beaker chemistry" is well demonstrated by the fact that in the forty years since the conductivity measurements of Noyes, no attempt has apparently been made to check or extend the observations (54), in spite of improved available techniques and materials of research. Though these studies did not extend to the critical point, there is at present no apparent reason why such apparatus could not be used.

E. LOSS OF WEIGHT METHOD AND VAPOR-PHASE TRANSPORT

If a substance shows no tendency to deposit back on the original charge when cooled, the solubility may be obtained from the loss of weight of that charge (58), which may be isolated from the rest in a capsule or crucible. This principle was applied (44, 58) to the determination of the solubility of silica. If there is some intermediate state of maximum solubility which must be passed through to reach the temperature and pressure of interest, heating and cooling must be rapid to minimize errors from this source. At one laboratory, at least, the bomb containing the charge is quenched in 1 min. to near room temperature. Silica was observed in most cases to remain in colloidal solution in water; occasionally flakes were observed to separate out (44).

A modification of this method was used for the determination of the solubility of silica in water above its critical point (118). In this apparatus the silica was supported in a crucible near the top of an autoclave, this location minimizing, though not eliminating, error due to flooding by the expanding liquid just below the critical point.

By the use of a similar apparatus, the *transport* of silica through the supercritical fluid phase was observed (68, 115, 116, 117). The silica was here dissolved from one crucible, and absorbed by reaction with zinc oxide in a second crucible.

Similar experiments were carried out with chromium (59b) and molybdenum (59d) compounds, using ferric hydroxide as a "getter" for chromium, and calcium and lead oxides to absorb molybdate ions. In these investigations, flooding by liquid was avoided by using less than the critical volume of solution.

In the course of pneumatolytic experiments using a furnace *inside* the autoclave (57, 74), under conditions encouraging some convection, the gas-phase transport of several refractory substances from the furnace and charge at temperatures above 450°C. was observed. Deposits of sillimanite, rutile, corundum, quartz, and amorphous silica were identified.

It is obvious that measurements of solubility by weight loss cannot be carried out accurately if temperature differences exist in the autoclave, resulting in circulation and the deposition of dissolved material at cold spots, and consequent positive error in solubility values.

F. BALANCING METHOD

One apparatus for establishing the critical points of solutions and rough measurement of solubility at the critical point consisted of a steel tube mounted on knife edges, the whole being heated in an air bath (59c, 59e). When two phases co-existed in the tube, it was unbalanced and tilted, with the denser phase in the lower end. When the contents of the tube, on passing through the critical point, became homogeneous, the tube assumed a horizontal position. When a small amount of solute remained in the solid phase or was precipitated, the tube did not become horizontal, but assumed some intermediate angle. Since the angle of tilt could be fairly accurately measured, the final tilt could be observed, giving the critical temperature of the saturated solution. The critical solubility could be approximated by varying the concentrations of solid in successive tests.

A modification of this method, in which the tube was attached to one arm of an analytical balance (9), has been used for the determination of the critical temperatures of pure liquids, and could no doubt be adapted to solutions.

G. AGITATION

Agitation, or the introduction of any mechanical motion into a high-pressure vessel, is a difficult problem. Leakage along a shaft or chemical action on packing is nearly unavoidable. Filter autoclaves with externally driven stirrers have, however, been developed for use to above 200 atm. pressure and 400°C. (72, 110).

In most hydrothermal experiments the use of stirrers has been avoided. A small charge is ordinarily used, and sufficient time given for equilibrium to occur through diffusion. The filter autoclave of Königsberger and Müller, however, was agitated by simply rocking the entire furnace containing the bomb (60, 61, 62).

The apparatus used at Western Reserve University (11, 11a, 12, 13) for agitation in most high-pressure studies is the magnetic stirrer. This consists of a small piece of iron, commonly sealed into glass, placed inside the high-pressure cell, and activated by the intermittent magnetic field of a solenoid surrounding the cell. This type of stirrer should be usable for other than glass cells. The design of a system can, of course, be much simpler when a magnetic stirrer is used, eliminating leaks due to entering shafts.

H. MATERIALS

Pressures and temperatures encountered in critical studies do not always present the greatest experimental difficulties; the critical points for most stable organic compounds can be observed in sealed borosilicate glass tubes and by other methods (9, 12, 13). Ordinary carbon steel containers could be used, except where ionizable substances are concerned. With water and many other inorganic materials, however, corrosion presents a serious problem.

Most glasses are disintegrated within a few hours by the action of pure water under elevated pressure at 300° to 500°C., although glasses containing large amounts of lead and barium are somewhat more resistant. Borosilicate and soda-lime glasses are very susceptible to such corrosion (71). Although fused quartz is observed (55, 68, 118) to have an appreciable solubility in water at temperatures near the critical point, it has been used successfully (92) for observations on the behavior of aqueous solutions in the critical region. Crystalline quartz, used for electrical insulation (82) at elevated temperatures, was observed to be little affected by long exposure to usually somewhat milder conditions, although hydrated silica under like circumstances was rapidly dissolved.

Several early investigators (73) overcame both the fragility of glass and contamination due to corrosion of metal by sealing the sample in a glass capsule which was enclosed in a steel pressure vessel. In the steel container, outside the glass tube, was placed some of the solvent used in the sample, the effect being to equalize approximately the pressures inside and outside the glass. This principle was used again recently (72) in an intricate filter autoclave.

Ordinary steels are, in general, too easily corroded for use with water in the critical region. Earlier workers used tool steels, soft steels (82), or nickel steels (60, 61, 62), lined with gold, platinum, or platinum–iridium alloy. A silver-plated copper–nickel alloy calorimeter was used (83) in the measurement of thermal properties of water to 270°C. Later work was done with a special chrome–nickel alloy steel (84). Alloys based on 18-8 stainless steel have been used commonly by recent investigators, in particular by Keyes (59) in his well-known studies of the thermodynamic properties of steam. A tendency of pure nickel to creep and crystallize was reported (59).

The problems of gaskets for closures and valve packing have been among the most serious encountered in all but the sealed-tube systems. Ordinary gasket materials are too soft, and usually chemically unsuitable, for most critical determinations. Gold and annealed copper have been used successfully; a gold–copper alloy was, however, discarded (82) in favor of pure gold. At temperatures above 250°C. gold welds under pressure to noble metals, and hence is often not usable as gasket material when the autoclave is lined or plated with such metals (82, 44). This difficulty is eliminated in the recent common use of unlined alloy steel containers.

A metal-to-metal cone joint (6, 15, 59) eliminates altogether the use of gaskets in contact with chemicals. In this design a tight joint is made by a 57–59° cone fitting into a 60° conical seat, leaving nothing but the resistant metal in contact with the charge. This closure requires very precise machining and somewhat more complex design to give a tight seal and to avoid abrasion of the units.

Sampling devices, although they may have a metal-to-metal joint at the valve seat itself, usually require some type of packing on the valve stem. For temperatures not too elevated, ordinary packing materials may suffice for some systems. With water in the critical region, however, none of these is satisfactory. A packing consisting of alternate layers of talc and graphite, precisely cut, was used successfully for aqueous solutions near the critical point (55).

I. MISCELLANEOUS INVESTIGATIONS

A number of studies, while not strictly solubility measurements of the type stressed here, are, however, of fundamental importance and essential to a complete picture of these processes.

Most closely related are investigations concerned with the solubility of water in rock-forming minerals near their melting points, essentially a study of the upper loop of figure 3 (37, 38, 39, 40, 41, 42).

Studies have been carried out relating volume changes due to temperature, pressure, and admixture of various solutes in aqueous systems (34, 35, 36). In connection with this it was noted, for example, that the solubilities of calcium carbonate and sulfate in water were increased 50 per cent by an external pressure of 1000 atm. It is suggested, however, that the reverse may be true for certain magmatic components. Further information has been obtained concerning solubility as a function of temperature and pressure (58).

Of a similar nature is the careful measurement of pressure–volume–temperature relations for salt solutions of different concentrations (6).

VI. Systems Reported in the Literature

A. INTRODUCTION

In this chapter are reviewed the most important systems described in the literature, and those most prominent in the development of the solution above the critical point. The arrangement of systems is alphabetical, the name of the more volatile component coming first. Studies of the electrical properties of solutions in the critical region are reviewed together at the end of the chapter.

B. INDIVIDUAL SYSTEMS

1. Systems with ammonia

The solubilities of a number of organic compounds in ammonia, extending up to the critical point, have been measured by Centnerszwer and others (20, 23). The synthetic method was used, known quantities of solute and ammonia being placed in sealed tubes. In no case were true critical phenomena of the saturated solutions observed. The solutes tested included diphenylmethane, triphenylmethane, naphthalene, anthracene, phenanthrene, α-naphthol, β-naphthol, resorcinol, diphenylamine, α-naphthylamine, β-naphthylamine, benzil, anthraquinone, camphor, dimethyl-*d*-tartaric acid, and urea. The raising of the critical point of ammonia due to dissolved substances was found to be 13.0°C. per mole per cent of solute.

2. System: carbon dioxide–iodine

Cailletet and Colardeau (19) dissolved iodine in liquid carbon dioxide in a sealed tube. When the solution was heated past its critical point, the rose color of dissolved iodine remained in the lower part of the tube. The spectroscope showed the absorption spectrum characteristic of dissolved iodine, not the fluted spectrum of iodine vapor. The interpretation of these data was that although the meniscus had disappeared, the liquid state persisted above the critical point.

The more thorough experiments of Villard (119, 120) led to a more logical and more complete explanation of this system. Upon agitation or long standing of the iodine–carbon dioxide system above its critical point, the iodine coloration became uniform throughout the entire tube. Diffusion of iodine into the vapor phase did not occur in the presence of liquid except with considerable agitation. Any coloring of the vapor phase was in general considerably fainter than that of the liquid, the difference approaching zero as the critical point was approached. Crystals of iodine in the top of the tube dissolved in the vapor, sometimes making the vapor temporarily more highly colored than the liquid phase.

Experiments with iodine in compressed, but unsaturated, carbon dioxide at 20–25°C. showed that an unsaturated vapor may dissolve solids. It is not necessary to postulate liquid dissolved in vapor to explain the solubility of solids in the gas phase.

Spectroscopic examination by Villard of solutions of iodine in both saturated and unsaturated carbon dioxide vapor also showed only the spectrum of dissolved iodine, not of iodine vapor.

3. Systems: carbon dioxide with various solutes

The solubilities of a large number of organic and inorganic substances in carbon dioxide in the region of the critical point were measured by Büchner (16). Many organic compounds, particularly the more volatile, were found to give a complete range of solubilities, eliminating critical phenomena, except of unsaturated solutions. Many other organic compounds, however, and almost all inorganic compounds except gases had more limited solubility, passing through critical points in saturated solution. Organic compounds giving critical points with carbon dioxide included naphthalene, phenanthrene, methyl iodide, *p*-dibromobenzene, borneol, substituted phenols (except nitrophenol), *p*-chloronitrobenzene, *p*-bromonitrobenzene, 1,2,3-dichloronitrobenzene, 1,3,2-dichloronitrobenzene, phthalic anhydride, succinic anhydride, α-naphthylamine, urea, and benzamide. The inorganic compounds tested were not listed. The compounds giving unbroken solubility curves included *p*-dichlorobenzene, acetic acid, camphor, ethanol, carbon disulfide, ethyl ether, pentane, amylene, acetylene, benzene, and *p*-xylene.

The raising of the critical point of carbon dioxide by dissolved substances was found to be 8.8°C. per mole per cent of solute. Comparison of this result with the data of Centnerszwer (20, 23) led to an interesting approximate empirical relationship between the absolute critical temperatures of the pure solvents ammonia, sulfur dioxide, and carbon dioxide, and the changes in these temperatures due to the presence of 1 mole per cent of dissolved material:

$$\Delta T_c = 0.029 T_c$$

4. Systems with carbon disulfide

Hannay and Hogarth (50, 51, 52, 53) observed no deposition of sulfur from solution in carbon disulfide 50°C. above the critical point. Arsenic was also soluble in this region, apparently as a sulfide.

5. System: ethane–hexachloroethane

Holder and Maass (55a) measured the solubility of hexachloroethane in ethane in both liquid and vapor phases, as well as above the critical point of the solution. Solubilities were determined by sampling the solutions in the upper and lower parts of the phosphor bronze bomb used, the material being displaced by mercury, a technique avoiding the disturbance of equilibrium. The proportions of the two components and the partial density of ethane in each phase were obtained by weighing the small sampling bombs, evaporating out the ethane, and reweighing.

It was observed that a difference in the proportions of hexachloroethane in solution in the upper and lower regions of the container, respectively, persisted for 4°C. or more above the previously observed point of disappearance of the meniscus of a saturated solution, the two solubilities approaching each other asymptotically. This was interpreted as a persistence of liquid-like structure over a limited range above the conventional critical point defined by the disappearance of the meniscus.

The partial densities of the ethane in the upper and lower parts of the bomb were found to give curves very similar to the solubility curves, though covering a narrower percentage range of variation. A direct relation between solvent power and partial density of solvent is indicated.

Good precision in solubility measurements in this system is made possible by the solubility of about 14 per cent by weight of hexachloroethane in ethane at the critical point, and in general by the ease of handling and lack of corrosive properties of the substances. The consistency of results and the use of a Podbielniak column in the purification of the ethane, as well as other refinements, suggest that the unique results of Holder and Maass be seriously considered, particularly in view of their support of certain recent theories favoring a critical *region* of finite extent, rather than a critical point (54a, 65a).

6. Systems: ethanol–inorganic compounds

The pioneer studies of Hannay and Hogarth (50, 51, 52, 53) on solutions above the critical point included solutions of several inorganic salts in ethanol. Potassium bromide, potassium iodide, cobalt chloride, and ferric chloride all gave clear gas-phase ethanol solutions far above the critical point. Observations extended to about 380°C., 150° above the critical temperature. Solubility was observed to depend upon both temperature and pressure.

The absorption spectrum of cobalt chloride in ethanol solution was the same at 300°C. as at 15°C., indicating no change in electronic structure on passing into the critical region.

The rather complex behavior of calcium chloride–ethanol solutions above their critical points, including the re-formation of two fluid phases at an elevated temperature, was said to give evidence of compound formation. The later interpretation of Smits (96), however, is that the observed phenomena are typical of a system of the ether–anthraquinone type, having two critical end-points. Smits also believed the potassium bromide and potassium iodide solutions in ethanol to be of this type.

Ramsey (86) heated a solution of potassium iodide in ethanol to above its critical point. Observing that solute crystallized out under these circumstances, and that solution above the critical point failed to dissolve iodide crystals, he concluded that the solubility reported by Hannay and Hogarth was simply solution in hot liquid, the liquid phase persisting above the critical point. This position was strengthened by his critical experiments with presumably pure compounds in sealed tubes. In these experiments the refractive indices in the upper and lower parts of the tubes were found unequal after the disappearance of the meniscus.

Hannay (48) ascribed the results of Ramsay to traces of impurities, particularly water, which, he had observed, lead temporarily to appreciable differences in properties between the upper and lower parts of the contents of a sealed tube.

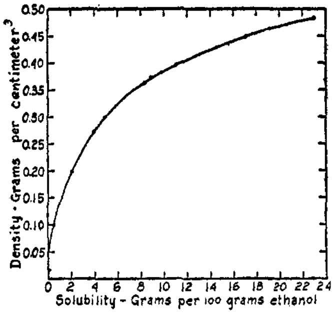

FIG. 7. Solubility of sodium iodide in ethanol above the critical point as a function of solvent density (Tyrer (111)).

Saturation with potassium iodide was found to raise the critical temperature of ethanol by 0.8°C. On the basis of his summed observations, Hannay (49) concluded that solvent power increases with temperature in the single-phase region, at constant specific volume.

Tyrer (111) determined the solubilities of potassium iodide in methanol and sodium iodide in ethanol up to and above the critical temperatures of the saturated solutions. The synthetic method was used, known quantities of salt and alcohol being heated in sealed glass tubes with agitation, and the temperatures of disappearance and reappearance of crystals being noted.

The solubilities were observed to reach a maximum some distance below the critical temperature, and dropped very rapidly in the neighborhood of the critical point. A sharp break occurred at the point where one of the phases disappeared, whether with or without critical phenomena. In the single-phase region, the solubility at constant volume decreased slowly with increased temperature, and was dependent upon the density of the solvent and therefore upon the pressure (figure 7). Solubility in the vapor phase a few degrees below the critical temperature was measured in some cases.

The rapid fall in the solubility of salts in the liquid phase just below the critical temperature was explained by the large dilation of the liquid phase in that region, a corollary of the effect of "solvent concentration" on solubility above the critical point.

7. Systems: ethanol–organic compounds

The solution of a chlorophyll extract in ethanol was observed spectroscopically by Hannay and Hogarth (50, 51, 52, 53) above its critical temperature. The spectrum of the solution at 300°C. was the same as at 15°C., indicating that no change in electronic structure occurred on passing through the critical region.

Pictet (85) used a solution of alizarin in ethanol to demonstrate that a solid remains in solution above the critical point. The vapor phase remained colorless until the meniscus disappeared, after which uniform diffusion throughout the tube occurred.

The same result was obtained by Bertrand and Lecarme (7). They observed also the raising of the critical point of ethanol by the dissolved solid, which for a 5 per cent solution of alizarin amounted to 7°C.

8. System: ethyl ether–anthraquinone

The ether–anthraquinone system, investigated principally by Smits (95, 96, 97, 102), is the classic example of a system having two critical end-points (figures 2, 3, 4). When ether is heated with excess anthraquinone, the liquid and vapor phases coalesce at critical point P, at 203°C., with 0.15 mole per cent anthraquinone in solution. Upon further heating more anthraquinone is dissolved, and eventually two fluid phases are again formed, this second critical point Q occurring at 247°C. and 13 mole per cent anthraquinone. Upon further heating increased solubilities of anthraquinone occur in the liquid phase, up to the triple point of anthraquinone.

In some of the later experiments (97) pressure and volume, as well as temperature, measurements were made, permitting the drawing of isobars (figure 4) giving concentration of anthraquinone as a function of both temperature and pressure in the region of a single fluid phase.

The phase relations for this type of system were graphically developed, and used to design a space model (96, 102).

9. Systems with ethyl ether

The system ethyl ether–ferric chloride was one of those used by Hannay and Hogarth (50, 51, 52, 53) to show visually the persistence of the solution above its critical point. In this state the yellow color remained, diffused uniformly through the tube, but eventually disappeared as reaction with the solvent occurred.

A number of ethereal solutions were investigated by Pictet (85), who measured the raising of the critical temperature by the dissolved solute. His data were apparently not sufficiently precise for the establishment of any general relationship between temperature rise and concentration. The solutes studied in ether solution included borneol, cineole, terpineol, phenol, guaiacol, and iodine.

Smits (96) found saturated solutions in ether of mercuric iodide, silver nitrate, potassium nitrate, cadmium iodide, and alizarin to be of the ether–anthraquinone type, having critical end-points. The ether–anthraquinone system is described separately in this paper. Saturated solutions of *p*-hydroxybenzoic acid and borneol in ether showed no critical phenomena.

10. Systems: hydrogen–alkali metals

Hannay and Hogarth (49, 50, 51), after their initial success in demonstrating the solubility of solids in gases, investigated certain more extreme systems: solutions of alkali metals in hydrogen gas at high pressure. Samples of sodium, potassium, and lithium were placed in high-pressure containers, also containing mercury, not in contact with the alkali metals. Dry hydrogen was then admitted up to pressures of from 300 to 1000 atm. The alkali metal gradually disappeared, and the mercury became pasty, owing to the formation of amalgam. This process occurred in about half an hour at room temperature and within a few seconds at 100°C. The alkali metals were presumably transported through solution in hydrogen to the mercury.

11. Systems: methanol–inorganic salts

Centnerszwer (21) measured the solubilities of several inorganic salts in methanol up to, but not above, the critical points of the solutions by heating known quantities in sealed tubes. The system methanol–potassium iodide was studied with particular care. The raising of the critical point by dissolved salts was found to be proportional to the molality of the salt. Of the many salts investigated, most were found to be very insoluble in methanol, having no appreciable effect on the critical temperature. The salts having measurable solubility at the critical point were sodium chloride, potassium bromide, barium bromide, sodium bromide, mercuric chloride, cadmium chloride, potassium iodide, mercuric bromide, mercuric iodide, and cadmium iodide, in order of increasing solubility at the critical point.

The observations of Tyrer (111) on potassium iodide in methanol are described under "Systems: ethanol–inorganic compounds."

12. Systems with sulfur dioxide

The solubility measurements on organic compounds in ammonia, carried out by Centnerszwer and others, were repeated on the same compounds with sulfur dioxide as solvent, hydroquinone being added to the list (20, 23). Similar results were obtained, no system showing critical phenomena in the presence of free solute. The critical point of sulfur dioxide was raised 11.3°C. per mole per cent of dissolved material.

13. Systems: water–inorganic compounds

The high critical temperature and pressure of water, and its corrosiveness in that region, have discouraged many investigators from the study of aqueous systems, despite their outstanding importance in natural processes. Bertrand and Lecarme (7), however, observed that potassium dichromate remained in solution in water on passing through the critical point, although it deposited if the water all vaporized before the critical temperature was attained. This is in harmony with the low vapor-phase solubility below the critical point noted for alcoholic (111) and other solutions. The dichromate in solution above the critical point diffused throughout the entire tube and was still in solution at 20°C. above the critical point.

Bertrand and Lecarme postulated, as an explanation of their observations, a solution of liquid in gas in equilibrium with a solution of gas in liquid, the two becoming identical at the critical point, and the liquid in gaseous solution persisting for a considerable distance above the critical temperature.

Schröer (92) made a careful study of the raising of the critical temperature by salts in aqueous solution. Solutions of alkali and alkaline earth halides in water at various concentrations were heated to above the critical point in sealed fused-quartz tubes. The behavior of the solutions on heating and cooling was observed. Unambiguous results were obtained only with alkali halides, and only up to 0.684 M. Complex phenomena were observed in the case of alkaline earth chlorides, where the solubility curve cuts the critical curve. In some cases two liquid phases were formed.

The dispersion of solute in the gas phase above the critical point was demonstrated by colored solutions of cupric chloride and cobaltous chloride. Prolonged heating of these and other substances led to decomposition.

The raising of the critical point of water by dissolved salts was found to follow the law:

$$\Delta T_c = x^{1/n} + C$$

where n is greater than 1. Schröer gave a theoretical development of this formula, which disagrees more in form than in quantitative evaluation with the linear relation of Centnerszwer (20, 23). Observations were made on aqueous solutions of sodium chloride, potassium chloride, potassium bromide, potassium iodide, rubidium chloride, calcium chloride, strontium chloride, barium chloride, cupric chloride, and cobaltous chloride.

No quantitative observations of solubility in the gas phase were made by Schröer.

Khitarov and others (59b) heated aqueous solutions of chromic acid, sodium chromate, and chromic sulfate to above their critical points in a steel tube. The chromium compound in the gas-phase solution was absorbed in ferric hydroxide in a crucible at the top of the tube. The volume of solution placed in the tube was carefully calculated, to avoid flooding of the crucible by liquid. In all cases a considerable quantity of the chromium compound was transported through the gas phase, to react with the ferric hydroxide. The possibility of pneumatolytic transfer of chromium in any of the forms tested was thus established.

Sodium molybdate solutions were heated in the same apparatus (59d), the crucible at the top of the bomb containing either calcium oxide or lead oxide, to absorb molybdate ion. Although only a trace of molybdenum was transported through the gas phase from pure sodium molybdate, the presence of silica gel greatly enhanced the transfer, to give concentrations of up to 21 per cent molybdic oxide in the crucible after 5 days at 430°C. This transport was greatly diminished by the addition of alkali. These observations agree with the postulated geochemical transport of molybdenum with silica in the form of a heteropoly acid.

In connection with the same project (59a, 59c, 59e) aqueous solutions of a number of compounds and mixtures were heated to above the critical point of water in a silver-plated steel tube balanced on knife edges. The tube was heated in an air bath, its angle of tilt indicating the state of its contents. A horizontal position showed the contents to be a homogeneous gas or gas-phase solution. Presence of solid or liquid phases was indicated by deviations from the horizontal.

When no excess solid phase was present, the critical point of the solution in the tube could be determined directly. In the presence of excess solute the critical point of the saturated solution was observed, and the critical solubility could be estimated from a series of runs, including concentrations above and below that at the observed critical point.

The accuracy of the apparatus was checked by comparison with the observations of Schröer (92). The raising of the critical point of water by a number of inorganic solutes was measured. By comparing the raising of the critical point by a number of acidic substances, notably silica, boric acid, alumina gel, molybdic acid, and chromic acid, with that produced by their alkali salts, it was seen that the effect of a salt was much greater than that of an equal molarity of the corresponding acid. From this it was concluded that alkali ions have an effect on the structure of water, inhibiting gasification. It was not made clear why this effect could not be interpreted in terms of the respective degrees of ionization and association of the several substances, the raising of the critical point being considered as a colligative property.

Solutions containing both sodium metasilicate and boric acid in varying proportions, with constant total molarities of solute, showed a minimum critical point at near-equal mole concentrations, indicating formation of a complex (59a). The same phenomenon was observed for solutions containing molybdic oxide and silica, giving additional support to the heteropoly acid concept (59d).

Solubilities in steam of compounds of importance in boiler chemistry were measured by Spillner (104). The solubilities of sodium chloride, sodium hydroxide, sodium sulfate, and potassium chloride in saturated and superheated steam at various temperatures and pressures were determined. Solubility became appreciable at about 75 kg. per square centimeter pressure. Salts were found nearly equally soluble in saturated and in superheated steam. In general, solubility at a given pressure decreased with temperature increase. The techniques used were the passing of superheated steam over dry solute, and the boiling of solutions of known concentration.

The experiments of Spillner and others were criticized by Straub in his review on turbine blade deposits (106). Straub, in his much more complete and more precise measurements of solubilities in steam, found that the solubilities of sodium chloride, sodium hydroxide, potassium hydroxide, sodium sulfate, and silica in steam varied sharply with both temperature and pressure. Respective solubilities in vapor and liquid phases were seen to approach each other as the critical region was approached. No data were taken close to the critical point. Measurements above the critical temperature were made on superheated steam, that is, at a lower pressure.

Hydrothermal and pneumatolytic syntheses of minerals, many of which involved critical transitions, were reviewed by Morey and Niggli (75) and Morey and Ingerson (73). In the papers reviewed, however, the emphasis was on the products of the reactions, and little information was obtained relative to solubilities in the gas phase.

14. System: water–silica

Because of its outstanding importance, both geologically and from an engineering viewpoint (70, 106), the silica–water system has been studied more frequently and in greater detail than systems of other substances involving critical phenomena or solution in the vapor phase (56a).

In 1930 van Nieuwenberg and Blumendal (115) observed gas-phase transfer of silica. Two crucibles, containing silica and zinc oxide, respectively, were supported near the top of a pressure vessel containing a calculated quantity of water. The apparatus was heated to 400°C. and 300 atm. for several hours. On cooling, the weight of silica was observed to have decreased, the weight of the zinc oxide crucible having correspondingly increased. Zinc silicate (willemite) was detected in the second crucible. The transport of silica through the gas phase, presumably through the medium of solution, was thus demonstrated.

The above experiments were interpreted by Smits (103) in terms of phase study. The silica–water system is of the same type as the ether–anthraquinone system (96, 97) (figure 4), but complicated by the several crystalline modifications of silica. Phase diagrams comparing pressure–temperature–composition relations of the two systems were drawn.

The experiments of van Nieuwenberg and Blumendal were repeated by Morey (68). The experimental conditions were similar, except that the volume of water was carefully chosen to avoid flooding of the crucibles by the dilated liquid just below the critical point. A small loss in weight of silica was observed, presumably due to vapor-phase transport, but of lesser magnitude than in the earlier experiments.

van Nieuwenberg and Blumendal (117) explained this discrepancy by the greater relative quantity of water used in their experiments. The capacity of their container was actually less than the critical volume of the contained water, a result of which was a transitory flooding of the crucibles by liquid during both heating and cooling. That this flooding was merely a source of error rather than the prime vehicle of transfer was established by runs of varying lengths in a later experiment (118). In this experiment, as well as others, the dependence on pressure of solubility in the gas phase was amply demonstrated, explaining the disagreement of Morey's results.

The solubility or volatility of silica with steam having been demonstrated, a quantitative measurement of it as a function of temperature and pressure was made by van Nieuwenberg and van Zon (118). Runs were made essentially as in the earlier experiments, but with only a single crucible, containing quartz. Temperatures were varied from 380° to 420°C., and pressures from 293 to 500 kg. per square centimeter, adjusted by the quantity of water placed in the container.

The solubility of quartz was determined from the loss of weight of the contents of the crucible. Runs of varying lengths established the error due to flooding of the crucible by liquid, which was used as a correction factor, depriving the final results of any great precision. Results (figure 8) are in agreement with the theory of Smits, and correlate well with the similar ether–anthraquinone system.

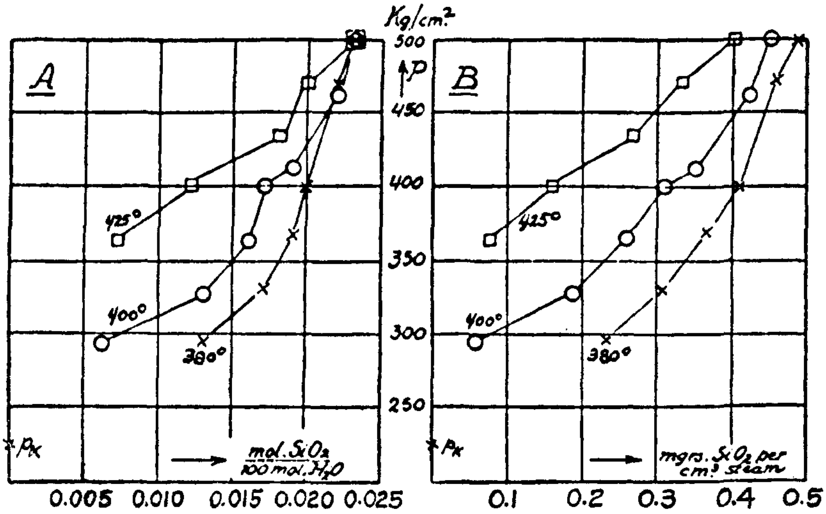

FIG. 8. Solubility of silica in water above the critical point as a function of temperature and pressure (van Nieuwenberg and van Zon (118)).

Ingerson and Morey (57, 70) heated samples of quartz and amorphous silica with approximately the critical volume of water in a hydrothermal bomb. Approximate measurements of solubility at 300°, 400°, and 500°C. were made. At 500°C. 0.5–1.0 per cent of amorphous silica dissolved in the gas phase, and at 400°C. half as much. The solubility of quartz at each temperature was half that of the amorphous silica. The solubility at 300°C. agreed with the 0.17 per cent of Hitchen (55).

Kennedy (58) made a series of solubility measurements on fused quartz along the 300-atm. isobar from 200° to 420°C., by the method of weight differences. Reconnaissance measurements up to 500°C. and 1000 atm. were made. Results suggested that the solubility of silica in steam is an inverse function both of temperature and of specific volume. As the density of the gas phase approaches that of a liquid, the solvent power approaches that of liquid.

Grieg, Merwin, and Shepherd (42) heated pieces of rock, ranging from basalts to obsidians, to 600° to 1200°C. for periods of from 16 hr. to 2 weeks in evacuated silica tubes. Silica evaporated from the tubes, to deposit as fine crystals on platinum foil wrapped around the rock. When no platinum was present, a glassy coating formed on the rock. These phenomena were explained by the dissolving of the silica of the tube by water vapor liberated from the rock, with subsequent deposition (*a*) in the *less soluble* crystalline form, or (*b*) in a solution or compound with the elements of the rock, having a lower vapor pressure of silica than pure fused silica. This hypothesis was proven by later experiments with dry synthetic minerals in the presence or absence of water. The presence of a very small quantity of water greatly increased the quantity of such crystalline or glassy deposits.

Additional evidence of the transfer of solids through vapors was obtained by Morey and Ingerson (74) with a hydrothermal bomb having a furnace inside the bomb. Silica was observed to deposit at colder points of the container and around any leak, where a release of pressure occurred.

In a run of several days' duration, refractory substances were observed to deposit on the refractory furnace core and on platinum leads, the deposit being zoned as the temperature dropped from estimated levels of 1000° to 500°C. The successive deposited materials were sillimanite, rutile, corundum, quartz, and amorphous silica. The steam pressure was 200 atm. The deposited materials were believed to have dissolved in the steam, to be re-deposited at points where their solubilities decreased owing to lowered temperature.

With the recent development of steam turbines operating at pressures of the order of 75 atm., the deposition of silica on turbine blades has become a serious problem. Silica and certain salts are carried from the steam boiler through the superheater in the vapor phase, and deposit on the turbine blades as the temperature and pressure become lower. As mentioned earlier in this paper, a number of studies have been made with the object of preventing this deposition. Although none of these observations extend above the critical point, they are of interest and are related to the problem, since they concern solubilities in the gas phase. The work done on this subject was reviewed by Morey (70) from a phase study viewpoint. A later review by Straub (106) is more concerned with the engineering features of the problem, and presents the results of his extended experiments, as well as their interpretation in terms of the various theories of turbine blade deposits.

The experiments of Straub involved a variety of boilers and bombs, in which saturated or superheated steam was brought in contact with solid silica and solutions containing silica or silicates in known concentration. The steam leaving these containers was condensed and analyzed for silica. The solubility of silica in superheated steam was found to vary with both temperature and pressure (figure 6). The ratio of the solubility of silica in steam to its solubility in the liquid with which it was in contact was found to vary inversely with pH.

C. ELECTRICAL PROPERTIES OF SOLUTIONS

Conductivity measurements of both liquid- and vapor-phase solutions of sodium iodide and sodium bromide in sulfur dioxide were made by Hagenbach

(45, 46) at temperatures extending to above the critical point. The resistance of the liquid solutions increased rapidly up to the critical point, but only a slow increase in resistance occurred above that point. Conductivities of liquid and vapor phases approached each other with rising temperature, becoming identical at the critical point.

The conductivities of solutions of cadmium chloride, calcium chloride, and acetic acid in ethyl ether were measured, but the increasing conductivity of glass made it impossible to continue to the critical region.

Eversheim (30) made conductivity and dielectric constant measurements on ethyl ether, ethyl chloride, and sulfur dioxide, and solutions in these solvents. The conductivity measurements on sulfur dioxide were in complete agreement with those of Hagenbach (45, 46). The dielectric constants were measured by a sealed-in condenser of four concentric cylindrical plates. An abrupt, though not large, change in dielectric constant occurred at the critical point, but little change was observed in the single-phase region at constant volume.

Walden and Centnerszwer (124), in the course of extensive investigations of the properties of sulfur dioxide, observed the conductivity of sulfur dioxide and its solutions to become zero at the critical point. This is, of course, in disagreement with Hagenbach (45, 46). A conclusion from this observation was that the dissociating power of solvents depends upon their *surface tension*, as well as other properties. Electrolytes used in these determinations included hydrogen chloride, quinoline, triamylammonium iodide, benzylammonium chloride, and trimethylsulfine iodide.

Hagenbach (47) explained the discrepancy between his results and those of Walden and Centnerszwer by the greater sensitivity of his apparatus, which was capable of measuring small currents which seemed equal to zero with less refined equipment.

Kraus (63, 64) made a series of very precise determinations of the electrical conductivities of solutions of potassium iodide and ammonium chloride in methanol, and reconnaissance measurements on potassium iodide in ethanol. Both solute concentration and degree of filling of the tubes were varied. Conductivities were measured for some distance above and below the critical point, and were determined in both liquid and vapor phases, where both existed (figures 9 and 10).

Conductivities above the critical point, and of the vapor phase below the critical point, were observed. Though a sudden change in the temperature coefficient of conductivity was observed when liquid was present up to the critical temperature, no abrupt change in the conductivity itself occurred at that point. Unsaturated vapor-phase solutions showed no discontinuity in conductivity at the critical temperature. The conductivity where a single phase existed was found to increase with the density or "concentration" of solvent, and consequently with the pressure. Conductivity fell off slowly with increased temperature above the critical point.

Although most solutions show a maximum in conductivity at some distance below their critical points, the conductivity then monotonically diminishing with further temperature rise, certain solutions show a minimum conductivity in this region (33, 124). Since these solutions have not been carried to the critical temperature, their behavior at that point is unknown.

An electrolytic cell using dry sulfur dioxide as solvent was set up by Hagenbach (47). The E.M.F. values in the liquid- and vapor-phase solutions were found equal at all temperatures, and no singularity of E.M.F. marked the critical point of the solution.

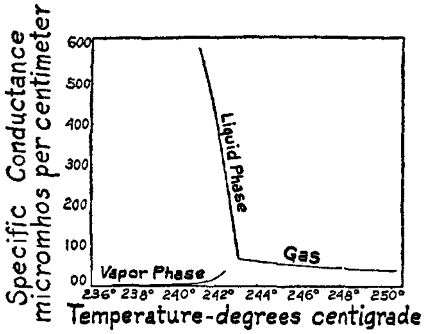

FIG. 9

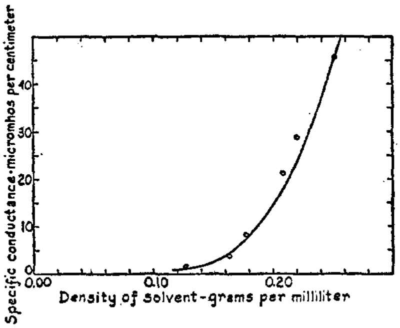

FIG. 10

FIG. 9. Conductance of ammonium chloride in methanol as a function of temperature in the critical region (Kraus (64)).

FIG. 10. Specific conductance as a function of solvent density for 0.00463 *N* potassium iodide in methanol at 245°C. (after Kraus (64)).

VII. CONCLUSION

An effort has been made, in this review, to present to the chemist and the chemical engineer a field of endeavor of which, despite its wide potentialities, comparatively little systematic study has been made. The solubility of solids in vapors and above the critical point has been presented both for its own intrinsic interest, as a challenge in pure research, and from the points of view of its geological and industrial applications. The work in this field on the more important systems reported has been reviewed.

Proper control of the phenomena described here is capable of increasing the over-all efficiency of certain power installations and of prolonging the useful life of turbine and superheater units. The contribution of such study to the understanding of the mechanism of ore deposition may well aid in the more efficient location and exploitation of valuable ore deposits.

Certain synthetic processes may be found to occur more readily under the conditions of high solvent mobility occurring in the critical region (110a). It is possible that further information obtained from these studies may lead to a modification of present concepts of solution, ionization, and association, and may be used as a basis for the growing of large crystals of various substances for optical and other scientific purposes (57a).

It is true that comparatively careful machine work and moderately expensive construction materials are often required for studies at elevated temperatures and pressures, yet the cost can be small as compared with, for example, a recording potentiometer, which is a useful, though not essential, accessory. The principles of the design of such equipment (15, 76, 109) are well understood, and the day is past when the experimenter with high pressure would build his equipment as strongly as he knew how, and then hope for the best. The materials of construction are readily available, and the compounds of greatest interest are among the commonest.

New industrial applications for knowledge of solubilities in the gas phase will probably appear as soon as such knowledge becomes available. The possibilities of this comparatively unexplored field are large, and may be quite unexpected.

VIII. REFERENCES

(1) ALLEN, E. T.: J. Franklin Inst. **193**, 70 (1922).
(2) ALTSCHUL, M.: Z. physik. Chem. **11**, 577 (1893)
(3) AMERICAN INSTITUTE OF PHYSICS: *Temperature, Its Measurement and Control in Science and Industry*, pp. 1079–89. Reinhold Publishing Corporation, New York (1941).
(4) ANDREWS, T.: Trans. Roy. Soc. (London) **A159**, 547 (1869).
(5) BECKMANN, E.: Z. physik. Chem. **44**, 161 (1903).
(6) BENEDICT, M.: J. Geol. **47**, 252–276 (1939).
(7) BERTRAND, G., AND LECARME, J.: Compt. rend. **141**, 320 (1905).
(8) BOND, P. A., AND STOWE, V. M.: J. Am. Chem. Soc. **53**, 30–4 (1931).
(9) BOND, P. A., AND WILLIAMS, D. A.: J. Am. Chem. Soc., **53**, 34 (1931).
(10) BOOTH, H. S.: U. S. patent 2,112,903 (April 5, 1938).
(11) BOOTH, H. S., AND CARTER, J. M.: J. Phys. Chem. **34**, 2801–25 (1930).
(11a) BOOTH, H. S., AND MARTIN, D. R.: Chem. Revs. **33**, 57 (1943).
(11b) BOOTH, H. S., AND POLLARD, E. F.: Ind. Eng. Chem. **40**, 1983 (1948).
(11c) BOOTH, H. S., AND POLLARD, E. F.: Ind. Eng. Chem. **40**, 1986 (1948).
(11d) BOOTH, H. S., POLLARD, E. F., AND RENTSCHLER, M. J.: Ind. Eng. Chem. **40**, 1981 (1948).
(12) BOOTH, H. S., AND SWINEHART, C. F.: J. Am. Chem. Soc. **57**, 1337–42 (1935).
(13) BOOTH, H. S., AND WILLSON, K. S.: J. Am. Chem. Soc. **57**, 2280 (1935).
(14) BOWEN, N. L.: *The Evolution of the Igneous Rocks*. Princeton University Press, Princeton (1928).
(15) BRIDGMAN, P. W.: *The Physics of High Pressure*. G. Bell and Sons, Ltd., London (1931).
(16) BÜCHNER, E. H.: Z. physik. Chem. **54**, 665 (1906).
(17) CAGNIARD DE LA TOUR, C.: Ann. chim. phys. [2] **21**, 127, 178 (1822).
(18) CAILLETET, L.: Compt. rend. **90**, 210–11 (1880).
(19) CAILLETET, L., AND COLARDEAU, E.: Ann. chim. phys. [6] **18**, 269 (1889).
(20) CENTNERSZWER, M.: Z. physik. Chem. **46**, 427 (1903).
(21) CENTNERSZWER, M.: Z. physik Chem. **72**, 431 (1910).
(22) CENTNERSZWER, M., AND PAKALNEET, A.: Z. physik. Chem. **55**, 303 (1906).
(23) CENTNERSZWER, M., AND TELETOW, I.: Z. Elektrochem. **9**, 799 (1903).
(24) CLEVE, K.: Z. Ver. deut. Ing. **84**, 789–95 (1940).
(25) DAUBREE, A.: Compt. rend. **29**, 227 (1849).
(26) DAY, A. L., AND ALLEN, E. T.: *The Volcanic Activity and Hot Springs of Lassen Peak*. Publication No. 360, Carnegie Institution of Washington, Washington, D. C. (1925).
(27) DEVILLE, H. ST-C., AND CARON: Ann. chim. phys. [4] **5**, 104 (1865).

(28) Deville, H. St-C., and Leblanc, H. E.: Bull. soc. geol. France [2] **13**, 606 (1855-56).
(29) Dewar, J.: Proc. Roy. Soc. (London) **30**, 538 (1880).
(30) Eversheim, P.: Ann. Physik [4] **8**, 539 (1902).
(31) Fenner, C. N.: Am. Inst. Mining Engrs. **1933**, 72.
(32) Foreman, F., and Gruner, J. W.: Econ. Geol. **24**, 825 (1925).
(33) Franklin, E. C., and Kraus, C. A.: Am. Chem. J. **24**, 83 (1900).
(34) Gibson, R. E.: Am. J. Sci. **35A**, 49 (1938).
(35) Gibson, R. E.: *The Nature of Solutions and their Behavior under High Pressures.* Supplementary Publication No. 35, Carnegie Institution of Washington, Washington, D. C. (1938).
(36) Gibson, R. E.: Trans. Am. Geophys. Union **19**, 273 (1938).
(37) Goranson, R. W.: Am. J. Sci. **22**, 481 (1931).
(38) Goranson, R. W.: Trans. Am. Geophys. Union **12**, 163 (1931).
(39) Goranson, R. W.: Am. J. Sci. **23**, 227 (1932).
(40) Goranson, R. W.: Trans. Am. Geophys. Union **17**, 257 (1936).
(41) Goranson, R. W.: Trans. Am. Geophys. Union **18**, 246 (1937).
(42) Goranson, R. W.: Trans. Am. Geophys. Union **19**, 271 (1938).
(43) Grieg, J. W., Merwin, H. E., and Shepherd, E. S.: Am. J. Sci. **25**, 61 (1933).
(44) Gruner, J. W.: Econ. Geol. **25**, 697 (1930).
(45) Hagenbach, A.: Physik. Z. **1**, 481 (1900).
(46) Hagenbach, A.: Ann. Physik [4] **5**, 276 (1901).
(47) Hagenbach, A.: Ann. Physik [4] **8**, 568 (1902).
(48) Hannay, J. B.: Proc. Roy. Soc. (London) **30**, 478 (1880).
(49) Hannay, J. B.: Proc. Roy. Soc. (London) **30**, 484 (1880).
(50) Hannay, J. B., and Hogarth, J.: Proc. Roy. Soc. (London) **29**, 324 (1879).
(51) Hannay, J. B., and Hogarth, J.: Proc. Roy. Soc. (London) **30**, 178 (1880).
(52) Hannay, J. B., and Hogarth, J.: Chem. News **40**, 256 (1880).
(53) Hannay, J. B., and Hogarth, J.: Chem. News **41**, 103 (1880).
(54) Harned, H. S., and Owen, B. B.: *The Physical Chemistry of Electrolytic Solutions*, p. 492. Reinhold Publishing Corporation, New York (1943).
(54a) Harrison, S. F., and Mayer, J. E.: J. Chem. Phys. **6**, 87 (1938).
(55) Hitchen, C. S.: Bull. Inst. Mining Met. **1**, 364 (1935).
(55a) Holder, C. H., and Maass, O.: Can. J. Research **18B**, 293 (1940).
(56) Ingerson, E.: Econ. Geol. **29**, 454 (1934).
(56a) Ingerson, E.: Econ. Geol. **42**, 560 (1947).
(57) Ingerson, E., and Morey, G. W.: Trans. Am. Geophys. Union **22**, 504 (1941).
(57a) Ingerson, E., and Tuttle, O. F.: Am. J. Sci. **245**, 313-19 (1947).
(58) Kennedy, G. C.: Econ. Geol. **39**, 25 (1944).
(59) Keyes, F. G.: Proc. Am. Acad. Arts Sci. **68**, 505 (1933).
(59a) Khitarov, N. I.: Soviet Geol. **9**, No. 7, 71 (1939).
(59b) Khitarov, N. I., and Ivanov, L. A.: Soviet Geol. **6**, 1098 (1936).
(59c) Khitarov, N. I., and Ivanov, L. A.: Zentr. Mineral. Geol. **A1936**, 46.
(59d) Khitarov, N. I., and Ivanov, L. A.: Compt. rend. acad. sci. U.R.S.S. **27**, 694 (1940).
(59e) Khitarov, N. I., Ivanov, L. A., and Rotman, L. E.: Soviet Geol. **9**, No. 2, 98 (1939).
(60) Königsberger, J., and Müller, J. W.: Zentr. Mineral. Geol. **A1906**, 339.
(61) Königsberger, J., and Müller, J. W.: Chem. Zentr. **1906**, **II**, 268.
(62) Königsberger, J., and Müller, J. W.: Zentr. Mineral. Geol. **A1912**, 413.
(63) Kraus, C. A.: Phys. Rev. **18**, 40, 89 (1904).
(64) Kraus, C. A.: *The Properties of Electrically Conducting Systems*, pp. 167-75. The Chemical Catalog Company, Inc., New York (1922).
(65) Lupberger, E.: Stahl u. Eisen **53**, 1080 (1933).
(65a) Maass, O., and Geddes, A. L.: Trans. Roy. Soc. (London) **A236**, 303 (1937).
(66) Mellor, J. W.: *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. II, p. 327. Longmans, Green and Company, London (1922).

(67) Morey, G. W.: J. Wash. Acad. Sci. **12**, 219 (1922).
(68) Morey, G. W.: Trans. Am. Geophys. Union **13**, 269 (1932).
(69) Morey, G. W.: *The Properties of Glass*, p. 103. Reinhold Publishing Corporation, New York (1938).
(70) Morey, G. W.: Proc. Am. Soc. Testing Materials **42**, 980–1022 (1942).
(71) Morey, G. W., and Bowen, N. L.: J. Soc. Glass Tech. **11**, 97 (1927).
(72) Morey, G. W., and Burlew, J. S.: Am. J. Sci. **35A**, 193 (1938).
(73) Morey, G. W., and Ingerson, E.: Econ. Geol. **32**, 607–760 (1937).
(74) Morey, G. W., and Ingerson, E.: Am. J. Sci. **35A**, 217 (1938).
(75) Morey, G. W., and Niggli, P.: J. Am. Chem. Soc. **35**, 1086 (1913).
(76) Newitt, D. M.: *The Design of High-Pressure Plant and the Properties of Fluids at High Pressures*. The Clarendon Press, Oxford (1940).
(77) Niggli, P.: *Das Magma und seine Produkte*. Akademisches Verlagsgesellschaft, Leipzig (1937).
(77a) Niggli, P.: *Ore Deposits of Magmatic Origin*. T. Murby and Company, London; D. Van Nostrand Company, New York (1929).
(78) Niggli, P.: Z. anorg. allgem. Chem. **75**, 161 (1912).
(79) Niggli, P.: Z. anorg. allgem. Chem. **77**, 321 (1912).
(80) Niggli, P.: Zentr. Mineral. Geol. **A1912**, 321.
(81) Norton, F. H.: Am. Mineral. **22**, 1 (1937).
(82) Noyes, A. A., *et al.*: *The Electrical Conductivity of Aqueous Solutions*. Publication No. 63, Carnegie Institution of Washington, Washington, D. C. (1907).
(83) Osborne, N. S., Stimson, H. F., and Fiock, E. F.: Bur. Standards J. Research **5**, 411 (1930).
(84) Osborne, N. S., Stimson, H. F., Fiock, E. F., and Ginnings, D. C.: Bur. Standards J. Research **10**, 155 (1933).
(85) Pictet, R.: Compt. rend. **120**, 64 (1895).
(86) Ramsay, W.: Proc. Roy. Soc. (London) **30**, 323 (1880).
(87) Reilly, J., and Rae, W. N.: *Physico-Chemical Methods*, pp. 598–9. D. Van Nostrand Company, New York (1925).
(88) Roozeboom, H. W. B.: *Die heterogenen Gleichgewichte vom Standpunkte der Phasenlehre*. Friedrich Vieweg und Sohn, Braunschweig (1901–1918).
(89) Schroeder, W. C., Berk, A. A., and Gabriel, A.: J. Am. Chem. Soc. **58**, 843 (1936).
(90) Schroeder, W. C., Berk, A. A., and Gabriel, A.: J. Am. Chem. Soc. **59**, 1783 (1937).
(91) Schroeder, W. C., Gabriel, A., and Partridge, E. P.: J. Am. Chem. Soc. **57**, 1539 (1935).
(92) Schröer, E.: Z. physik. Chem. **129**, 79 (1927).
(93) Shepherd, E. S.: Bull. Hawaiian Volcano Observatory **9**, 83 (1921).
(94) Shepherd, E. S.: Am. J. Sci. **35A**, 311 (1938).
(95) Smits, A.: Z. Elektrochem. **9**, 663 (1903).
(96) Smits, A.: Z. physik. Chem. **51**, 193 (1905).
(97) Smits, A.: Z. physik. Chem. **52**, 587 (1905).
(98) Smits, A.: Z. physik. Chem. **54**, 498 (1906).
(99) Smits, A.: Z. physik. Chem. **54**, 513 (1906).
(100) Smits, A.: Z. physik. Chem. **67**, 454 (1909).
(101) Smits, A.: Z. physik. Chem. **67**, 464 (1909).
(102) Smits, A.: Z. physik. Chem. **76**, 445 (1911).
(103) Smits, A.: Rec. trav. chim. **49**, 962 (1930).
(104) Spillner, F.: Chem. Fabrik **13**, 405 (1940).
(105) Splittgerber, A.: Vom Wasser **15**, 271 (1940).
(106) Straub, F. G.: Univ. of Illinois Bull., Eng. Expt. Sta. Bull. Ser., No. **364** (1946).
(107) Straub, F. G.: Trans. Am. Soc. Mech. Engrs. **1932**, F. S. P. -54-17, p. 221.
(108) Tilden, W. A., and Shenstone, W. A.: Trans. Roy. Soc. (London) **A175**, 23 (1885).

(109) Tongue, H.: *The Design and Construction of High Pressure Chemical Plant.* D. Van Nostrand Company, Inc., New York (1934).
(110) Tongue, H.: Trans. Inst. Chem. Engrs. **8**, 81 (1930).
(110a) Toriumi, T., *et al.*: J. Soc. Chem. Ind. Japan **49**, 1-2 (1946).
(111) Tyrer, D.: J. Chem. Soc. **97**, 621 (1910).
(112) van der Waals, J. D.: *Die Continüität des gasförmigen und flüssigen Zustandes.* Johann Ambrosius Barth, Leipzig (1881).
(113) van der Waals, J. D., and Kohnstamm, P.: *Lebrbuch der Thermodynamik.* Johann Ambrosius Barth, Leipzig (1912).
(114) Reference 113, Vol. 2, pp. 552ff.
(115) van Nieuwenberg, C. J., and Blumendal, H. B.: Rec. trav. chim. **49**, 857 (1930).
(116) van Nieuwenberg, C. J., and Blumendal, H. B.: Rec. trav. chim. **50**, 129, 989 (1931).
(117) van Nieuwenberg, C. J., and Blumendal, H. B.: Rec. trav. chim. **53**, 476 (1934).
(118) van Nieuwenberg, C. J., and van Zon, P. M.: Rec. trav. chim. **54**, 129 (1935).
(119) Villard, P.: Compt. rend. **120**, 182 (1895).
(120) Villard, P.: Ann. chim. phys. [7] **10**, 409 (1897).
(121) Vogt, J. H. L.: J. Geol. **30**, 659 (1922).
(122) Waldeck, W. F., Lynn, G., and Hill, A. E.: J. Am. Chem. Soc. **54**, 928 (1932).
(123) Waldeck, W. F., Lynn, G., and Hill, A. E.: J. Am. Chem. Soc. **56**, 43 (1934).
(124) Walden, P., and Centnerszwer, M.: Z. physik. Chem. **39**, 513 (1902).
(125) Winkler, H. G. F.: Am. Mineral. **32**, 131 (1947).
(126) Zies, E. G.: Natl. Geographic Soc., Contributed Tech. Papers, Katmai Ser. **3**, 159 (1924).
(127) Zies, E. G.: Natl. Geographic Soc., Contributed Tech. Papers, Katmai Ser. **4** (1929).
(128) Zies, E. G.: Chem. Revs. **23**, 47 (1938).
(129) Zies, E. G., and Allen, E. T.: Natl. Geographic Soc., Contributed Tech. Papers, Katmai Ser. **2** (1923).