THE EXPERIMENTAL DETERMINATION OF SOLUBILITIES

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I. INTRODUCTION

Although thorough reviews are available on the interpretation of solubility data (*cf.* 101), they appear to have no adequate counterpart from the strictly

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experimental point of view. Probably the best practical review to date has been that of Vold and Vold (238), in which a discussion of some of the general precautions and considerations to be observed in such work is presented, together with brief outlines of a few specific procedures. The purpose of the present article is to assemble the relatively extensive information on experimental solubility methods which is scattered in the chemical literature published since about 1870. Three important omissions from this compilation must be mentioned: (*a*) the topic of solubilities in the critical region, which was the subject of a recent review in This Journal (21), (*b*) methods of solubility determination involving gases, for which extremely specialized techniques are required, and (*c*) apparatus and procedures for obtaining solubilities under high pressure and temperature, which have also been reviewed fairly recently (157, 239). New contributions to this latter field have been limited in number (*cf.* 22, 117, 158).

The methods to be covered here will for the most part encompass those involving the solubility of solids in liquids and of liquids in liquids, with negligible reference to other possible combinations. Several ways of classifying the experiments are available. Probably the most logical of these is based on the naming of a constant factor: i.e., thermostatic, plethostatic (constant composition), and barostatic (105). Such a system has theoretical basis in the phase rule but seems not to have received general acceptance. A more usual classification is that based upon the point of whether the composition of the system at equilibrium becomes known through synthesis or analysis. When an arbitrary system of solute and solvent is prepared and the solution temperature and/or pressure is determined by adjusting these variables until all the solute just barely dissolves, the experiment is frequently termed "synthetic" (3). By contrast, a system containing an excess of solute at a given temperature and pressure is termed "analytic," since the composition of the solution phase must be determined by analysis.

Both these methods of classification appear to be defective, the former being unfamiliar and somewhat cumbersome, and the latter being not logically precise and in some cases actually ambiguous. Therefore, the present discussion will utilize a terminology based on the experimental issue of whether or not sampling or other disturbance of the equilibrium system is necessary in order to know its composition. Cases in which sampling is not required will be termed "isosystic" (243); those in which samples must be removed for subsequent analysis or which require some other disturbance of the system will be called "analytic." Thus, when composition of a solution phase is obtained either by synthesis or by analyses, such as conductivity or electromotive-force measurements, which do not disturb the equilibrium system in any way, the determination is isosystic; when the composition is obtained by removing a sample from the system or by addition of a component, the determination is analytic, even though the analytical tool be a conductivity or an electromotive-force measurement or some other procedure which might readily be applied to the original system.

II. GENERAL CONSIDERATIONS

Whatever the method finally adopted for a solubility determination, it must satisfy certain general requirements fixed by the nature of the information desired. Among the foremost of these is purity of the materials investigated. Many of the earlier data which appear in the literature for supposedly identical systems show wide disagreement, and at least a part of the discrepancies may be attributed to imperfect preparation and purification procedures (70, 126, 172). Methods such as conductivity are particularly sensitive to impurities (e.g., carbon dioxide) which therefore must be rigorously excluded (20, 186). Conditions of isomerism or allotropy have also been associated with inaccuracies in reported data (172), and even where the methods employed were otherwise satisfactory, certain intentional combinations of solutes which are capable of forming solid solutions with one another have led to serious disagreements as to the proper manner of interpreting the data accumulated (104, 226). The particle size of a solid crystalline solute has also been shown to have a very real influence on the actual solubility of the material, so that special precautions on this point are sometimes needed (57, 222).

The second important consideration is the precise regulation and measurement of temperatures, because of the sensitivity of many solubilities to thermal influences (40, 41, 172). Since the rates at which solubility equilibria are attained are often relatively slow, it is frequently not sufficient to know the temperature at only one instant; precise control and measurement must be maintained throughout the entire period of equilibration (70). Moreover, even the best thermostatic devices undergo regular variations in temperature. These, as well as the possibility of inadvertent deviations during the course of an observation, must be taken into account in planning any precise solubility experiments (20).

The third requirement to be met is the establishment of adequate solubility equilibrium. The stringency of the equilibration requirements to be satisfied varies from one system to another, but all include the need for sufficiently active agitation of the system (40, 157) or, failing that, some other means to insure complete saturation of the entire body of solvent (1). The duration of the equilibration is also a variable dependent upon the nature of the system (4, 41, 75, 172). The determination of a proper equilibration interval usually involves periodic sampling and analysis of the system (when an analytical method is employed) or a periodic measurement of some property such as conductivity or electromotive force (when the method is isosystic), but care must be exercised to insure that the criterion chosen is adequate (215). It may also happen that when equilibration is performed under unusual conditions of temperature or pressure, additional precautions are needed to make certain that samples taken are truly representative of the equilibrium situation (40, 41, 203), while in using isosystic methods involving temperature adjustments, special care must be taken in maintaining a sufficiently low rate of change of temperature (208).

Certain other factors of more restricted applicability must be considered in planning solubility measurements on special types of systems. The aqueous solubilities of the alkaline earth compounds and other substances subject to more or less advanced hydrolysis are complicated by the occurrence of this reaction (20, 75, 78, 126, 185). Generally, before any solubility is measured, the stability of the proposed solution should be verified (96). In addition, the inertness of the solubility vessel toward the components of the solution must be examined, and special steps to protect the solution from contamination by corrosion of its container may be required (25, 157, 168, 239). A less common type of instability which, nevertheless, has invalidated careful researches is the tendency of some solutes toward colloid formation at concentrations at or slightly above saturation (91, 126). In cases where oxidation by the atmosphere is a hazard, the experiments may be done in an atmosphere of nitrogen (7, 59, 81).

After the requirements described above have been fulfilled, a method of analysis or detection must be chosen which is compatible with all other conditions in the system (*cf.* 1 and 157). Upon occasion, the entire validity of the determination may hinge upon this choice (70, 126). Because of the infinite variety of systems upon which solubility studies may be undertaken, no fixed set of rules may be laid down to govern the method to be decided upon in every case. Ultimately, the choice will be determined by the peculiarities of the individual system. However, the literature (*cf.* 126, 127) does contain discussions of the broad range of applicability of some of the more common solubility methods, which may be briefly mentioned here.

For instance, electrical measurements such as those of conductivity and electromotive force are necessarily restricted to the study of electrolytic solutes (153), but where these methods are applicable, information can be obtained on very sparingly soluble substances with good precision.

Not infrequently, the order of magnitude of the solubility investigated may dictate the method to be used. If it is sufficiently high, ordinary methods of chemical analysis may be employed (20), but if it is low, or if the substances studied are not readily amenable to accurate analysis, optical methods may be required (on the assumption that one of the electrical procedures has not been found suitable) (153). Upon occasion, the ease of crystallization of the system has been found to aid materially in its study by means of the analytical method (157).

Often the deleterious influence of air or atmospheric moisture, or the limitations imposed by the availability of only small amounts of material, make particularly desirable the use of the isosystic method (206). However, in isosystic investigations such as those by Hill's isothermal volumetric method, the relative weights of the components taken for the experiments have significant influence upon the accuracy of the results. Isosystic polythermal methods, on the other hand, may involve errors because of low heat conductivity in the substances under investigation, in which event special precautions must be introduced to insure that the thermometering apparatus itself has the minimum possible heat lag and heat capacity. Use of a thermoelement, especially when composed of very fine wires, meets these requirements; and moreover it can be advantageously used when only very small amounts of materials are at hand (5).

A. TEMPERATURE

1. Liquid thermostats

The quality of thermal control and measurement required for a given experiment will usually be determined by the precision to which the experimental results are desired. Typical[2] of the design of an ordinary solubility thermostat and illustrative of the components required for it is an inexpensive apparatus (121) which consists of a jar embedded in a nest of thermal insulating material (pipe lagging, vermiculite, etc.), the whole being contained in a sturdy wooden box. Within the jar, a rigid framework is provided to support a belt-driven axle to which may be affixed the bottles containing the systems to be equilibrated. The bath is also equipped with the necessary temperature regulator, a knife-heating element, a stirrer, and where necessary a cooling coil. When properly constructed, such a bath can maintain temperatures constant to within 0.1°C.

Depending upon the specific conditions to be satisfied, numerous modifications may be introduced into this basic design. Braun (23) found that by simply packing his apparatus and solutions in melting snow, a steady temperature could be maintained for about a week, while other investigators have found a large, uninsulated beaker of water or paraffin oil over a sand bath (195), a small gas flame (210), or an electric hot-plate (233) to be sufficient for their purposes. In using such a bath for the isosystic method in its simplest form ("cloud" method), Ewins found that very efficient heating resulted from passing steam through the bath liquid (67), and Menzies used for this purpose two knife-heaters with wattage controls (147), while Harwood, Ralston, and Selby employed a "chromel" heating coil wound on the outside of the beaker and in series with a controlling rheostat (94).

TABLE 1

Precision of temperature control with various types of thermoregulators

THERMOREGULATOR	PRECISION	REFERENCE	THERMOREGULATOR	PRECISION	REFERENCE
	°C.			°C.	
Mercury	0.005	(211)	Mercury	0.1	(219)
Toluene	0.005	(36)	Mercury	0.1	(164)
Toluene	0.01–0.02	(20)	Ostwald	0.1	(6)

The chief improvements which have been made in the basic thermostat design through the years have been intended to enhance the sensitivity and precision of temperature regulation and control. The principal devices used by most workers are either mercury or toluene regulators, although in the early days when electricity was not so widely available the Ostwald gas regulator found considerable employment for this purpose. Some of the various types of control mechanisms and the precision obtained with them are listed in table 1. Important improvements which have been introduced into the conventional thermoregulator systems include the use of a thyratron relay in place of the solenoid type in order to obtain faster switching in the heating circuits (66), and the design of the toluene regulator into a "grid" form which greatly multiplies the area of the device that is exposed to thermal changes, thereby minimizing lag (36).

[2] Other thermostats not radically different from this basic type are mentioned in the following references: 6, 14, 20, 36, 48, 95, 164, 175, 211, 219.

Among the less usual methods of controlling temperature, Hildebrand and Wachter have described one which seems to be unique (102). The bath is surrounded by a jacket through which pass vapors from boiling chloroform. These vapors serve initially to heat the bath and later to maintain its temperature at the desired level. The exact value of the temperature can be varied by adjusting the boiling point of the chloroform through the use of a vacuum pump and a series of mercury pressure-regulating bottles. With this technique, it is possible to obtain with great accuracy a series of temperatures only 0.05°C. apart. The extension of this type of thermostatic control to include the use of other vapors having a greater boiling range than chloroform has great possibilities, since the method reduces the problem of temperature management to one of pressure control, which is generally capable of extreme sensitivity, particularly when one considers the possibility of using precision electronic apparatus for its regulation.

Less general in usefulness but equally precise in control of temperatures is a method in which solubilities are determined at the boiling point of the solvent. Two versions of this procedure appear in the literature. In one, use is made of the Mammut pump principle. Solid solute is placed in a small open tube attached to the thermometer, which is then immersed in the solvent contained in a cell equipped with a coiled side tube connecting the bottom of the cell with a point at the top level of the solvent. Application of heat to the coil produces vapors which drive the solvent up the side arm, while solvent from the bottom of the cell takes its place, thus producing continuous circulation of solvent until saturation equilibrium has been attained (217). Applicability of the method is limited chiefly by the thermal stability of the system and the magnitude of the solubility to be studied, which must be small. This latter limitation is avoided by the second version, in which saturation equilibrium is attained under conditions of constant reflux (37, 201). Again, a variety of temperatures may be employed by controlling the pressure and thereby varying the boiling temperature of the solution at will.

In addition to the heating methods already discussed, mention should also be made of two internal heating techniques of limited applicability. In one of these, involving the solubility of iron in mercury, induction heating by means of a high-frequency coil has given good results (141); in the other a resistance heater which can be inserted into the solution itself is prepared by winding Nichrome wire on an asbestos form and encasing the coil in a test tube, a variable transformer and mercury thermoregulator being used to control the temperature (46).

The thermometry problems involved in solubility work assume two aspects. For precise thermostatting, it is mandatory that the constancy of the bath be accurately known. This information is obtained by plotting the readings from a differential thermometer, such as the Beckmann, as a function of time for a period long enough to disclose the extreme variations of temperature which may occur (36, 211, 219). For accurate measurements of the actual temperature, once thermal constancy has been verified, an ordinary mercury thermometer graduated in tenths or fifths of a degree usually serves satisfactorily if calibrated against a reliable thermometer, such as one certified by the National Bureau of

Standards. As an alternative the thermometer may be calibrated against known reference points, such as the boiling point and freezing point of water and the transition point of sodium sulfate (6). When such a thermometer is used, it is advisable to conduct the measurements at all temperatures with the entire thread of mercury immersed in the bath (67, 233) in order to avoid the necessity of stem corrections (45).

Under conditions such as those which obtain in solubility studies at high pressures, where direct observation of a thermometer is not possible, temperatures may be determined by means of either a resistance thermometer or a thermocouple. Construction and calibration of the former have been described in detail by Cohen and Sinnige (41), the platinum resistance thermometer used in their work giving temperatures accurate to within 0.2°C. The possibility of significant amounts of heat being developed from such a resistance thermometer at the lower temperatures sometimes makes it advisable to use a thermocouple instead (66). Further, the thermocouple is advantageous when minimum heat capacity, heat conductivity, and temperature lag are required (5) and when the space occupied by the thermometer must be as small as possible (224). A final factor which must be considered when solubilities are to be determined by the method of cooling curves is the temperature head between the solution (or "melt") and the bath. This head should be kept constant, and it can usually be measured with both convenience and accuracy by means of thermocouples (5).

Another modification useful when it is inadvisable to immerse the solubility cell directly in the thermostat is the employment of a cell fitted with a water jacket, the jacket being supplied from the thermostat by means of a circulating pump. With such an arrangement, care must be taken to correct for thermal losses occurring between the bath and the jacket.

When solubilities are to be determined at temperatures below 0°C., the range as far down as −78.5°C. can be satisfactorily attained with a dry ice-cooled bath in a Dewar flask (136).

2. Vapor thermostats

Probably the simplest air bath which can be used to maintain the desired temperature in the equilibrium vessel consists of a spiral steam coil which is mounted around a horizontal saturation tube. Temperature within the tube is maintained at a variety of values by adjusting its position with respect to the coil, the narrow part giving the higher temperatures (189). Such thermal regulation is very rough and has not received wide use. Other baths which are useful at moderately elevated temperatures consist of vapor jackets, the solubility apparatus being placed in a tube bathed in steam or other vapors under reflux conditions (149). By attaching the exit of the reflux condenser to a water pump and maintaining constant pressures with a manostat, a whole range of temperatures may be explored with such a jacket (232).

Vapor jackets are principally useful as substitutes for the more common liquid baths. When very high temperatures (of the order of a few hundreds of a degree Centigrade) are required, the use of an air bath becomes essential. Such thermostats present characteristic problems, two of which may be mentioned here. Because of the high temperatures involved, they must be designed so that damage, as from accidental bursting of solubility vessels, is minimized. They must be sturdy enough to prevent undue danger to the investigators if such accidents should occur. In addition, the attenuated nature (low heat capacity) of the bath fluid and the high temperatures for which such baths are used multiply the difficulties of maintaining a high degree of thermal constancy.

Illustrative of the construction of an air thermostat is an apparatus which consists (231) of a concentric series of six sheet-iron cylinders, through all of which are cut two pairs of opposing windows. The innermost shell fits loosely in the second shell and may be turned on its axis to close the windows. It is also fitted on the ends with thick iron screw-caps through which a movable thermometer well may pass. The second and third shells give laminar strength and serve as radiators for heat. The bath is heated electrically by a resistance coil wound between layers of asbestos on the outer side of the fourth shell. The two outermost shells serve as containing walls for a thick layer of asbestos wool which provides the principal insulation, and the windows in them are fitted with glass to assist in retaining heat in the interior. These shells are fitted at the ends with sheet-iron plates covered with asbestos board, serving completely to enclose the bath. The equilibration cell is attached directly to the thermometer well, and the bath itself is fastened to an axle so that it can be turned end-over-end during operation. The movable thermometer well permits measurement of temperature at any geometric position in the bath, and although no provision is made for internal air circulation or control of the heating element other than use of ordinary external rheostats, thermal constancy of between ±0.1°C. at moderate temperatures and ±0.3°C. in the vicinity of 350°C. is obtained. A less sturdily constructed air bath for use at temperatures of 20–30°C. ±0.1°, which is controlled by a thermoregulator and in which the mechanism for shaking the saturation vessels also serves to circulate the air, has also been described by Beier and Brintzinger (11).

In another type of air bath for high temperatures, a 500-watt heater is placed in each corner of the interior, three being controlled by switches and the fourth by a rheostat. Circulation is accomplished by a fan, turning at 600 R.P.M., located at one end of the chamber. The thermometer dips into a small cup of bismuth, and the part of it which projects from the bath is surrounded by an electrically heated shield in order to minimize stem corrections. Temperatures with this bath are maintained to within 0.2°C. (220). Morey and Burlew have also given the details of a refractory-lined furnace which is electrically heated under the control of a manually operated variac and suffers thermal variations of no more than 0.1°C. (158). Their temperatures were accurately measured by means of platinrhodium thermocouples, whose calibrations were subjected to periodic rechecks.

Adaptations of the air-thermostat procedure have been carried over to the use of air jackets thermally controlled by an outside source, both for elevated and for subzero temperatures. For the higher temperatures, the air jacket is connected to a hot-air manifold which is controlled by a regulator actuated from a thermocouple located in the jacket. This arrangement is said to give thermal constancy to within 0.056°C. For subzero work, the entire air bath is placed in an acetone–dry ice bath and temperatures measured with an iron–constantan thermocouple. This arrangement has reportedly been used only for solubility determinations by the "cloud" method but has given results reproducible to within 0.1°C. (107).

Finally, mention should be made of an aluminum-block thermostat, outfitted with the usual control and observation attachments (16). This device has been used in solubility studies up to temperatures of about 500°C.

B. EQUILIBRIUM

1. Agitation and mixing

One of the foremost problems in attaining true saturation equilibrium is that of achieving thoroughly intimate mixing between the solute and all parts of the solvent. The difficulty of the problem is once again dependent somewhat on the nature of the system in question—its stability, order of magnitude of the solubility to be measured, etc. Numerous mixing techniques are available, and often the final choice is merely a matter of preference or convenience. Generally, all methods of mixing may be classified into two groups, external and internal, the former being those in which agitation is accomplished by motion of the saturation cell itself, and the latter those in which the cell contents are set in motion without moving the cell.

Among the external techniques, the use of a rocking or pendulum-like movement is probably the most popular. In one such device, a lever resting upon a cam is caused to move up and down by rotation of the cam-wheel, and this type of impulse is translated into the rocking motion by a suitable arrangement of pivot points (52, 55, 147). Depending upon the vigor of movement which is required, other devices may also be used: the cell may be attached to the hammer of an electrically actuated bell (45, 233), it may be fastened to the arm of an automobile windshield wiper (219), or it may be placed in an oscillating cradle designed to accommodate either a single cell at a time (13, 113, 239) or a whole battery of cells which are to be equilibrated simultaneously (220).

External mixing devices involving complete rotation of the saturation cell have also received wide use. The prototype of all these is an apparatus wherein an axle is passed horizontally through the thermostat and is equipped with clamps so that the cells or bottles may be securely fastened to it (167). With this arrangement, agitation may be continued over long periods with maximum convenience. In a simple modification of the method, Schröder used a wheel, to which the cells could be attached, turned by a wheel-and-pulley array (200), while to secure more thorough agitation other workers have fastened the cells to their rotating device at an angle (e.g., about fifteen degrees from the perpendicular) (94).

Internal mixing techniques which have been described exhibit a much wider range of ingenuity. These vary all the way from the simple, manually operated loop stirrer (151) to relatively complicated electromagnetic devices. Stirrers driven by an axle passing out of the cell are of two chief forms: the worm-shaped "blade" which gives thorough agitation to the whole mass within the cell (115, 211), and propeller-type "blades" which impart a vigorous whirlpool motion to the cell contents (203). Among the electrically driven agitation devices several interesting versions also appear. In one, stirring is accomplished by an internal rotor, mounted on a central shaft and consisting of an iron ring pressed onto drilled aluminum disks. A rotating field is produced by three electromagnets just outside the cell, all mounted on a circular laminated iron core and connected to a three-phase, 60-cycle power supply. This rotor can be made to spin at about 200 R.P.M., giving excellent dispersion (85). Another effective mixing method is to place within the cell a small electric vibrator (5), which gives quite adequate stirring when the amount of material used is small. A third electrical technique which is particularly useful when the saturation is to be carried out in an inaccessible container, such as a compression bomb, has been described in great detail by Cohen and Sinnige (41). In their method, the solute is confined within a small basket which is suspended in the solvent; an electromagnet then actuates a lever arm which moves this basket up and down in the solvent. Thus, the solute is thoroughly exposed to solvent, and at the same time the motion of the basket keeps the solvent well mixed.

In studies of the solubility of a liquid in a liquid, it is sometimes of value to include in the cell a small globule of mercury. Then, when the cell is repeatedly inverted, the mercury will travel along its length, giving turbulent mixing (14). A similar technique has also been used to stir solid–liquid systems (43).

If for any reason one does not wish to employ any of the various mechanical mixing devices already mentioned, internal mixing may still be accomplished by bubbling air through the system (177). When using this procedure, especially if it is continued for any great interval or is used at the higher temperatures, it is often necessary to take into account errors due to evaporation of the solvent (95). Such errors may, of course, be minimized by presaturating the air by first passing it through an approximately saturated solution of the system in question. When the presence of atmospheric oxygen in the system is undesirable, the bubbling technique may still be carried out using purified nitrogen (113), a procedure which also serves to sweep out all previously dissolved oxygen.

Finally, mixing may be accomplished through various kinds of circulating arrangements. A study by Frear and Johnston (71) which required that a saturated solution of calcium carbonate be in intimate contact with a carbon dioxide atmosphere used a special cell which included a bubble of carbon dioxide, this bubble serving to force solvent through a compartment containing the solute every time the cell was rotated through 180 degrees. Circulation of solvent through a bed of solid solute may also be achieved by alternations of pressure in the closed arm of the cell shown in figure 1 (35). In addition, automatic circulation may be obtained by convection (80) or by gravity, using the cell shown in figure 2. There, solid solute is initially placed in both the top and the bottom compartments; whenever the solution concentration is less than the equilibrium value, solution will occur at the top, and the denser solution will sink to the bottom; if the solution becomes supersaturated, solid will crystallize out at the bottom, and the lighter solution will then rise. Hence equilibrium conditions are maintained at all times (1).

2. *Saturation equilibrium*

A final problem of general applicability in any solubility study is the determination of the length of the equilibration period necessary to attain total saturation. This interval is usually shortened when a solid solute is involved by making certain that the solute is present as small crystals. Especially in determinations by the isosystic method it is often desirable to precede the actual measurement by a cycle of heating to achieve complete solution, followed by rapid cooling to precipitate the solute in a finely divided state (19). In some types of work, such as solubilization studies, it is sometimes necessary to keep the amount of solid solute used at the lowest level feasible to minimize unwanted adsorption effects (142), while in others (e.g., solubility of various hydrates) it is necessary that the system be kept seeded with traces of the particular solute form in question in order to avoid supersaturation errors (235).

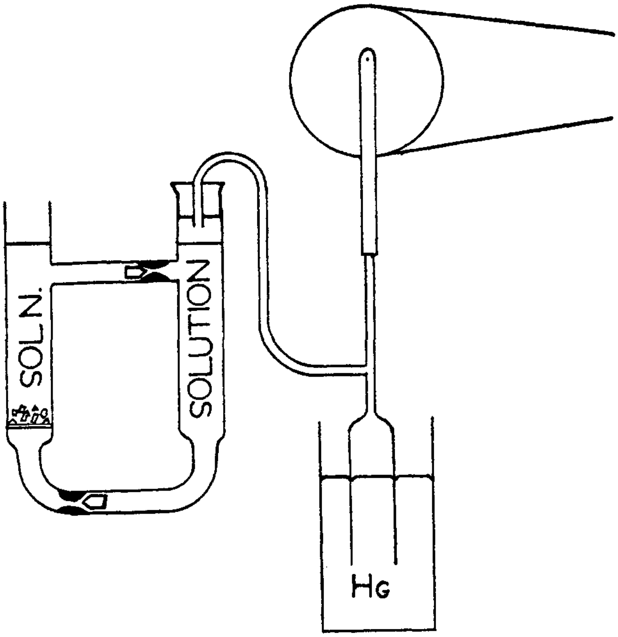

FIG. 1.

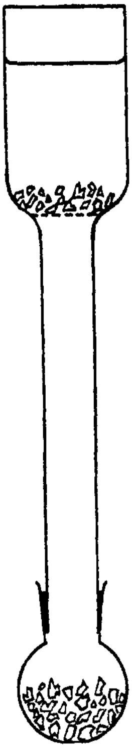

FIG. 2.

FIG. 1. Circulating apparatus making use of alternate pressure and suction
FIG. 2. Circulating arrangement making use of differences in specific gravity

In determining the length of time to be allowed for equilibration, Limpricht

(134) has advocated that it be as great as possible to ensure complete saturation. For measurements by conductivity, on the other hand, Böttger (20) recommends that it be as brief as possible both to minimize the effect of dissolution of glass from the vessel and to decrease the influence of transference phenomena. Careful independent study of the changes which may occur in the system with passage of time is also necessary when possible hydrolysis has to be considered (185).

The determination of the point at which saturation has been reached is best made by approaching the equilibrium from both undersaturation and supersaturation. Sometimes the nature of the system makes possible an approach from only one side (166), and in other cases the saturation point may best be reached by a stepwise approach of trial and error (111). Generally a most satisfactory criterion of saturation is the observation that the system has reached a stable condition. Thus the attainment of a constant electrical potential (179) or a constant conductivity (20) is often useful in isosystic studies, while in many analytic determinations the fact that repeated analyses of the solution give constant results is frequently employed (36, 44, 181). In any case, the law governing the approach to saturation is necessarily a simple exponential one (1), whose parameters are determined by both the nature of the system and the temperature at which the study is made (136, 191). Some indication of the duration of the equilibration period may be gained from table 2, which lists a few of the systems described in the literature together with the saturation intervals used for them.

III. Basic Methods

A. CONSTANT-COMPOSITION METHODS

1. Cloud method

The cloud method of determining solubilities is the form in which the isosystic procedure was first proposed by Alexejew (3). The principle is to prepare a solute–solvent system of known composition, confine it in such a way as to prevent loss of either component, and then vary the temperature in order to determine that temperature above which only the solution phase exists and below which the two phases, solute and saturated solution, are coexistent. The chief problems to be solved in using this method are the following: maintenance of near-equilibrium conditions by suitably adjusting the rates of heating or cooling and by giving attention to the crystal size of solid solutes, correction for the fraction of solvent which may be in the vapor phase at the saturation temperature, and problems posed by the influences of pressure generated by vapors, as well as those introduced by unusually low temperature coefficients of solubility. On the other hand, the method presents genuine advantages in that the influences of air and moisture can be readily eliminated, as well as in the fact that it can be utilized when only very small amounts of material are available for study (206). Because of its great popularity in solubility work, many modified forms of apparatus and procedure are available. In outlining these, many of the methods of handling the special problems and sources of error mentioned above will be considered.

In its simplest form, the cloud method can be applied by using merely a flask or a test tube as the saturation vessel. Thus, the solubility of aniline in aqueous solutions of its hydrochloride was measured by placing known weights of aniline and of hydrochloric acid in steamed-out Jena flasks whose necks had been constricted to inhibit condensation of vapors into drops. The mixture was heated to homogeneity and then allowed to cool slowly, being constantly shaken. The point of separation into two phases was observed by noticing the temperature at which a small gas flame became obliterated when observed through the liquid. Saturation temperatures were reproducible to within 0.2°C. with this procedure (210). Similar precision has also been obtained for studies of the solubility of urea in

TABLE 2

Equilibration periods for various systems

TIME	SYSTEM	REFERENCE
20 min.	Rare earth salts in water	(189)
30 min. to 1 week	Magnesium sulfate in water	(191)
1 hr.	Alkali and ammonium perrhenates in water	(213)
1–6 hr.	Alkali iodides in acetone	(66)
2 hr.	Orthophosphoric acid and its hydrates in water	(211)
2 hr.	Silver halides and thiocyanate in water	(103)
2 hr.	Silver sulfate in water	(36)
2–3 hr.	Fatty amines in water	(184)
3 hr.	Arsenic trioxide in water (by a graphical method)	(140)
4 hr.	Calcium carbonate in water	(89)
4 hr.	Water in organic solvents	(17)
5 hr.	Sodium sulfate in aqueous ethylene glycol	(235)
5 hr.	Potassium and ammonium nitrates in aqueous 2-propanol	(227)
6–7 hr.	Gold in mercury	(220)
6–8 hr.	Silver in mercury	(219)
12–48 hr.	Various salts in deuterium oxide	(166)
14 hr.	Silver nitrite in water	(48)
16 hr.	Various salts in ethanol	(205)
16 hr.	Fatty acids in water	(59)
18–24 hr.	Amino acids in aqueous alcohol	(44)
1 day	Potassium thiosulfate in water	(110)
1 day	Uni-bivalent salts in water	(92)
1 day	Rotenone in various solvents	(111)
1 day	Various dyes in aqueous detergent solutions	(142)
1–2 days	Iodine in water	(93)
1½–2 days	Indium in mercury	(175)
2 days	Dotriacontane in various organic solvents	(25)
4–10 days	Dimethylglyoxime in aqueous ammonia and alcohols	(218)
5 days	Lead sulfate in water	(183)
7 days	Calcium carbonate in water under carbon dioxide atmosphere	(73)
10–14 days	Arsenic trioxide in water (single-stage determination)	(4)

water at elevated temperatures, the cells in that case consisting of air-jacketed Pyrex tubes provided with manually operated glass-loop stirrers, and the heating rate near saturation being not greater than 1°C. per minute (151). In this latter case the cloud method was found especially valuable because the rapid measurements which it affords minimized the effect of the hydrolysis of urea, which is relatively rapid at the temperatures under study. Solubility temperatures in the subzero region which were reproducible within 0.1°C. and considered accurate within 0.2°C. have also been obtained with the same type of cells, using an iron–constantan thermocouple set within the sample for the thermometry (107). Less satisfactory results were obtained with such cells for the solubility of naphthalene in aromatic hydrocarbons, the transition-point temperatures for rising and falling temperatures disagreeing in that case by about 1°C. (187). However, results accurate to within 0.1°C. for this system were observed when the rate of thermal change was decreased nearly to zero by the following technique (187): two glass bulbs were filled with solutions identical in composition, and one was cooled until two phases were coexistent, while the second was heated to assure total homogeneity. Both bulbs were then maintained for 2 hr. in a thermostat at an estimated correct temperature obtained from the approximate results described above. If both solutions were alike at the end of this time (i.e., both were homogeneous or both were alike containing two phases), the temperature was adjusted to a new value in the indicated direction and the procedure repeated until a temperature was found at which the first bulb retained two phases at the same time that the second remained homogeneous. A related static-type method has also been used to determine solubilities of rotenone, the composition of the system being varied by trial and error to obtain solubilities at a fixed temperature (111).

When only small amounts of material are to be used for an investigation, the use of a sealed bulb or capillary tube as the solubility vessel is very satisfactory (33, 108, 200, 212). Such a cell is especially useful where physical isolation of the solubility system during the determination is desirable (76). By a suitable provision, the seal of the bulb may be broken after one set of observations, additional solvent added, and the bulb resealed for another run (69). When the determination is to be made under conditions which provide significantly high solution vapor pressures, care should be taken that the cell is constructed strongly enough to withstand them (51). Use of the bulb or capillary cell also often requires special techniques and care in the process of charging the cell. Thus, Groschuff (86) found it necessary to use a micropipet graduated in 0.005-ml. divisions and equipped with a long fine capillary exit to charge his cells with accurately measured amounts of liquid solute and to prevent accidental spattering of the liquid onto the outer surface of the delivery pipet. Ewins used a special capillary funnel for the same purpose but had to take additional special precautions to exclude moisture because of the hygroscopic nature of his materials (67). When the substances under study are highly volatile, special calibrated pipets made from 2-mm. capillary tubing have been found very satisfactory, the charging operation being immediately followed by freezing in liquid nitrogen in order to permit the cell to be sealed (99). Alternatively, it may also be possible to distill solute into the cell and then add the solvent from a calibrated and thermostatted buret under an inert atmosphere, followed by freezing of the cell contents to facilitate sealing (19).

Because of the fact that most determinations by the cloud method cannot be classed as measurements at true saturation equilibrium, the degree of dispersion of the solute is of greatest importance, even when the solute is a liquid. For example, in studying the solubility of water in benzene and certain paraffins it is necessary that the "cloud" point be reached relatively quickly in order to prevent coalescence of finely divided water particles into drops (86). Should such drops appear, they can be removed by heating. Moreover, as noted previously, the size of the solid crystals often influences the actual solubility of the material. Hence it is usual to subject the system to a preliminary cycle of rapid heating and cooling in order to assure uniformly small crystals for the final determination (19, 208, 233).

Of equal importance where temperature is normally not constant is the precise value of the rate of thermal change. The value which is permissible in a given case is governed by the rate at which equilibrium is approached after each shift in temperature, and this, in turn, is governed both by the order of magnitude of the solubility under study and by the temperature coefficient of solubility of the system. Benrath and Braun are of the opinion that the cloud method is quite unsuitable for the study of salts or systems with small, or with negative, coefficients (15). On the other hand, Merriman has reported that accurate results could be obtained when the coefficient was small but that a negative coefficient led to unreliable measurements (148), but Eddy, Machemer, and Menzies were able to get good results by this method for the retroflex solubility curves in the systems magnesium sulfate–water and magnesium sulfate–deuterium oxide (58). It can only be concluded therefore that, while small or negative temperature coefficients of solubility present special problems in the application of the cloud method, proper precautions can make their study in this way entirely feasible in particular cases. The choice of a sufficiently slow heating rate thus is determined chiefly by the nature of the system. Table 3 gives some of the heating rates used for data reported in the literature and serves to indicate how they vary from one system to another.

Greatly superior to the sealed bulb or tube in flexibility is the apparatus described by Menzies (147), which permits accurate cloud-point determinations at a whole series of consecutive concentrations without opening the solubility cell. The construction of the cell is shown in figure 3. Solid solute or a known solute–solvent combination is placed in the equilibration compartment, A, and extra solvent is placed (usually by distillation) in the calibrated reservoir, D. Connecting tube C is equipped with a small amount of a fused mixture of silver chloride and iodide. Tubes B and C are then sealed together, the sealing mixture in C is heated and manipulated so as to produce a complete closure between A and D, and the entire apparatus is sealed at E. The cloud point of the mixture in A is then determined. Additional determinations at new compositions may thereafter be made by opening the seal in C, distilling into A a quantity of solvent which can be measured by means of the graduations on D, and then resealing the closure in C, followed by the temperature adjustment to obtain the new cloud point. This device is suitable for work at temperatures up to 200°C.

TABLE 3

Heating rates and precision of measurement in some systems studied by the cloud method

RATE	PRECISION	SYSTEM	REFERENCE
°C./min.	*°C.*		
1.0	0.2	Urea in water	(151)
0.2	0.2	Aluminum bromide in hexane	(19)
0.05	0.2	Nitroanilines in "various liquids"	(45)
0.05	0.2	Mannose derivatives in alcohols	(233)
0.05	0.2	Aliphatic amine hydrochlorides and acetates in ethanol and benzene	(94)
0.017	0.1	Magnesium sulfate monohydrate in water and monodeuteriate in deuterium oxide	(58)
0.01	0.1	Naphthalene in aliphatic alcohols	(208)
0.007	0.1	Amines in water	(184)

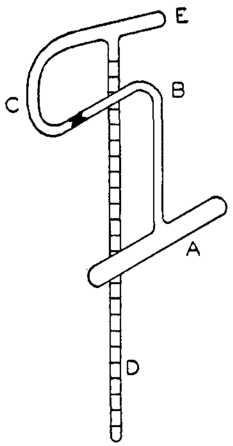

FIG. 3.

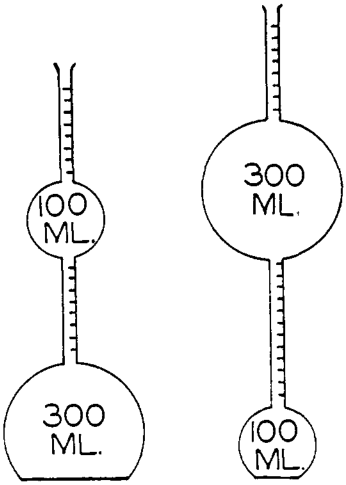

FIG. 4.

FIG. 3. Cloud-point apparatus for studying a system with serial dilutions by measured quantities of solvent.

FIG. 4. Apparatus for studying mutual solubilities of liquids by the volume method, utilizing large quantities of materials.

Particularly at such elevated temperatures, the possibility of error due to the vapor pressure generated by the solution must be considered. Moles and Jimeno (156) have found that the influence of the pressure itself on the solubility of acetamide in benzene is negligible, and most investigators have operated on the basis of similar assumptions. Errors resulting from the transfer of definite amounts of solvent into a vapor phase which is inoperative insofar as the solution process is concerned are, however, far from negligible, and one must correct for their effect. One procedure is to provide the solubility tube or bulb with a minimum of excess space in which vapors may exist (45). Another method is to assume Raoult's law to be applicable for calculating the quantity of solvent present as vapor (58, 150); and a third method (the most satisfactory of all where applicable) is to determine experimentally the vapor pressure of a saturated solution at the temperature in question, using this result and the volume of the vapor space to estimate the necessary correction in the weight of the solvent (147, 209).

2. Method of cooling and heating curves

This method, while not widely used for ordinary solubility studies, is practically identical with that commonly used in complex phase studies such as those in the field of metallurgy. It is especially useful when easily supersaturated solutions are under investigation, or when high viscosity or some other property of the saturated solution makes sampling in an analytical method unusually difficult. The principle lies in the fact that the slope of the heating or cooling curve of the system of known composition undergoes a relatively abrupt change at the saturation temperature (or cloud point). Thus, the general procedure is to observe the rate of cooling (or heating) of the system under a constant thermal head as a function of time (108, 184, 235). Refined techniques for obtaining such data and utilizing them to derive precise transition temperatures have been developed in recent years at the National Bureau of Standards (84, 139, 225) for use in melting-point determinations, but the methods are equally applicable to solubility studies. In order to maintain suitable control over the thermal head, it is desirable in precise work to record both the temperature of the bath and that of the solubility system as a function of time. Thermocouples are very satisfactory for this purpose (5).

3. Volume methods

The volume method for determining the mutual solubilities of two partially miscible liquids was first worked out by Aignan and Dugas in 1899 (2). The procedure was to place V_a ml. of liquid A in one tube and V'_a ml. in a second tube, add V_b ml. of liquid B to the first tube and V'_b ml. of B to the second, mix the liquids in the respective tubes intimately, allow the layers to separate, and measure the volumes, V_1 and V_2 of B in A and of A in B, respectively, in the first tube and the volumes V'_1 and V'_2 in the second. Assuming no volume change on mixing, the solubility coefficients, α and β, of A and B were then given by the relations:

$$\alpha = \frac{V_1 V'_a - V_a V'_1}{V_1 V'_b - V_b V'_1} \tag{1}$$

$$\beta = \frac{V_2 V'_b - V_b V'_2}{V_2 V'_a - V_a V'_2} \tag{2}$$

Relations were also worked out for cases in which volume changes do occur on mixing, and it was noted that the method in this form is unworkable in the event that either liquid loses its original identity upon going into solution in the other. Methods were also given for distinguishing which case obtains in a given system.

At that time, the method was of little help in determining solubilities on a weight basis, and the calculations were cumbersome in all but the simplest cases. However, by determining the densities of the two saturated phases at the temperature under study, it later became possible to calculate the weight of liquid A dissolved in a given weight of liquid B and *vice versa* (148). Further development of the volume method appeared when the phase rule was applied to the two phases in equilibrium at a fixed temperature (105, 114). Assume the following notation: m and m' are the weights of one component used in each of two experiments. x is the concentration of this component in, say, the upper phase in each experiment, while y is its concentration in the lower phase. a and a' are the measured volumes of upper phase in the respective experiments, and b and b' the respective volumes of the lower phase. Then it follows that the two simultaneous relations,

$$ax + by = m \tag{3}$$

and

$$a'x + b'y = m' \tag{4}$$

may be written for the component in question, and a similar set for the other component. Solution of these equations for x and y will give the concentration of the component considered in each phase, in grams per milliliter of solution.

While it is possible to perform the measurements to a fair degree of accuracy using simple graduated cylinders as solubility vessels, for accurate work it is desirable to use cells of special design. Figure 4 shows the form of apparatus which was used in the earlier work for study of large quantities of materials (105). The two graduated necks may be designed in such a way as to give a precision of 0.01 ml. (114). The principal errors which may occur with this method include (*a*) possible undersaturation, (*b*) incomplete separation of the phases (emulsification), (*c*) errors in weighing the components, (*d*) errors in reading the meniscuses, (*e*) retention of a thin layer of one of the phases on the surface of the bulb containing the other phase, and (*f*) possible vapor losses of one or both components (105, 114). The effects of all these error sources may be avoided by taking obvious measures. In addition, Hill and Malisoff have developed a mathematical analysis useful for deducing the optimum quantities of the components which may be taken to minimize weighing and reading errors (106).

For studying solubilities of small amounts of material, Bennett and Philip (14) have developed the two forms of solubility cells shown in figure 5, which are constructed from 5-mm. glass tubing and can be completely sealed. Other satisfactory cells have made use of Babcock test bottles or oil centrifuge tubes (65, 82). When this latter type of cell is employed, it is possible to subject the sample to centrifuging in order to obtain clean separation of the phases, but such a practice is open to severe criticism because of the lack of temperature control which it entails (119). Another development of the volume method worth noticing is its reported utility in the study of polycomponent systems (162).

Finally, mention should be made of a modification in which determination of the volume of solid residues in a saturated system may be used to determine solubility. A quantity of solute is weighed into a Goetz tube, and enough solvent is added to give a fixed total weight. The tube is then closed and brought to equilibrium, and is finally centrifuged to obtain uniform packing of the residual solid. The volume of this residue is noted, and the experiment repeated for a number of system compositions both above and below the solubility limit. A plot of residue volume against system composition is then found to consist of two straight lines which intersect at a composition equal to the solubility limit of the most soluble component of the solute preparation (if it be a mixture) (234). This technique has the advantage of permitting determinations with relatively impure "solute" preparations, but it also suffers from the lack of thermostatic control during centrifugation mentioned before.

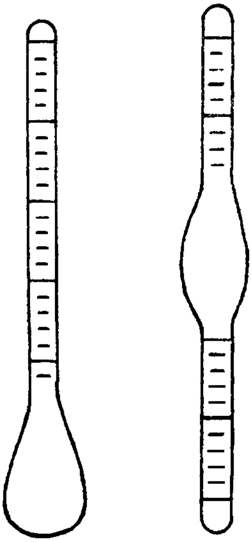

FIG. 5. Apparatus for studying mutual solubilities of liquids by the volume method, utilizing small quantities of materials.

4. Electrical methods

The chief electrical methods for studying solubilities by isosystic methods involve the measurement of electromotive force on the one hand and of conductivities on the other. Both types of measurement may frequently find use in determining concentrations of electrolytic solutes in the saturated solutions of a sealed system, and both have been excellently reviewed by Pinkus and Martin (181) in a general discussion of theory, practice, and precision. These workers find that the maximum errors which may be encountered in the isosystic use of the electromotive method are 3 per cent for a monovalent metallic salt, 3.7 per cent for a bivalent one, and 4 per cent for a trivalent one, while use of the conductivity method leads to errors whose magnitude depends upon the order of magnitude of the solubility itself. If solubility is less than about 10^{-5} mole per liter, this error is greater than 5 per cent for monovalent metallic salts and 10.5 per cent for bivalent salts, at which point the method of conductivity measurements becomes quite useless.

It should be reëmphasized that both these methods depend upon the presence of ions of the dissolved substance. When the concentration of these ions does not reflect a true picture of the concentration of solute at saturation because of significant hydrolysis, incomplete dissociation, or the effect of high concentrations on activity coefficients, for example, then such electrical measurements will produce misleading results. Thus, Neuhausen has even suggested the extreme view that the solubilities of sulfides, for instance, determined from electromotive-force measurements should not be taken literally but rather considered merely as measures of the activities of the ions in the solutions studied (163). On the other hand, the electrical methods are very useful in studying systems where solubility is so low that analytical procedures are worthless or where interference from colloid-formation tendencies makes cloud-point techniques impracticable (60, 109, 126, 186).

Considering briefly the electromotive-force method in particular, it is noteworthy that it may generally be employed without recourse to any but ordinary electrochemical apparatus. Occasionally it is necessary to take precautions to prevent mixing of anode and cathode compartment liquids (165) and special cells may be required to eliminate the effects of diffusion potentials (180). Also, a special flat cell has been designed to facilitate agitation of the contents and bubbling with nitrogen to eliminate the influences of dissolved oxygen (113).

The electromotive-force method is also very useful in prosecuting investigations under high pressure, where the confinement of the saturated system in a bomb precludes its direct observation (42). The electromotive force of a cell at constant temperature and high pressure depends both on the direct influence of pressure on the potential and on the solubility as influenced by the pressure. These effects may be expressed by the thermodynamic relation

$$\left[\left(\frac{\mathrm{d}E}{\mathrm{d}P}\right)_T\right]_a = \left[\left(\frac{\mathrm{d}E}{\mathrm{d}P}\right)_T\right]_b + \left(\frac{\mathrm{d}E}{\mathrm{d}C}\right)_{T.P}\left(\frac{\mathrm{d}C}{\mathrm{d}P}\right)_T \tag{5}$$

which may be rearranged to the form:

$$\left(\frac{\mathrm{d}C}{\mathrm{d}P}\right)_T = \frac{\left[\left(\frac{\mathrm{d}E}{\mathrm{d}P}\right)_T\right]_a - \left[\left(\frac{\mathrm{d}E}{\mathrm{d}P}\right)_T\right]_b}{\left(\frac{\mathrm{d}E}{\mathrm{d}C}\right)_{T.P}} \tag{6}$$

Independent measurements may be performed to determine the values of

$$\left[\left(\frac{\mathrm{d}E}{\mathrm{d}P}\right)_T\right]_a, \quad \left[\left(\frac{\mathrm{d}E}{\mathrm{d}P}\right)_T\right]_b, \quad \text{and} \quad \left(\frac{\mathrm{d}E}{\mathrm{d}C}\right)_{T.P}$$

so that the potential method can be employed directly to determine the effect of pressure on solubility. The potential measurements so obtained are superior to most other procedures for this particular purpose, because they leave no opportunity for any disturbance of saturation equilibrium during operations such as sampling. If dC/dP is negative, the present method is reliable only when the supersaturation occurring at the lower pressure remains steady during the measurement. Use of the method is also limited by the availability of suitable electrochemical couples for a particular investigation, a restriction common to any employment of the potential method.

For such studies at high pressures, the conductivity method is also very useful. Noyes and Coolidge have described, with minute detail, the design and construction of a bomb suitable for such measurements, together with a full description of the operations required for the measurements and also an evaluation of the errors involved in them (168). Conductance of a saturated solution can often be readily measured to a high degree of accuracy, and when the solubility is small it provides an excellent means of obtaining the concentration of dissolved solute through the well-known relation between concentration and conductivity (20, 38, 109, 123).

In addition to such straightforward applications, it has also been shown possible to construct a calibration curve of specific conductance as a function of an empirical polynomial in terms of concentration of the salt in question. When the pressure on a solution of that salt is altered, a new value for conductivity is obtained because of the change in solubility, and the concentration may then be found by interpolation on this curve (38). This approach is particularly suitable to investigations under very high pressures. In addition, a new, modified procedure has recently been advanced which is said to be particularly useful in studying systems with strong tendencies toward colloid formation (60). In it, the conductivity of the subject solution as a function of concentration is compared with the sum of the ionic conductivities of its positive and negative members as obtained from measurements on solutes without colloidal tendencies. A sharp break is observed in the former curve, whereas no such break occurs in the curve from the summed ionic contributions. The concentration corresponding to this sharp break is taken as defining the solubility limit.[3]

In addition to its advantage of making possible the study of solubilities of a very low order of magnitude, the conductivity method, in common with the potential method, requires little in the way of special apparatus. It is superior insofar as its application is independent of the availability of suitable electrochemical couples (123), and the presence of particles of solid solute in an equilibrium system causes no interference (125, 189). Moreover, the existence of the equilibrium state can be determined with certainty merely by observing the point in time at which conductivity becomes constant (20, 125, 189). Another procedure, which verifies both the existence of equilibrium and the purity of the solute,

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[3] New studies on this method, published from the same laboratory as the work discussed above, indicate in some detail the errors inherent in it and cast considerable doubt on its reliability as a general procedure.

is to expose the solute repeatedly to fresh quantities of solvent until successive trials give the same conductivity (124, 146).

On the other hand, it must be remembered that, unless calibration curves are employed, the conductivity determinations are sometimes subject to serious errors, since use of the method implicitly assumes complete ionization of the solute (109, 123, 125). Where this assumption is not justified, as may frequently occur when polyvalent ions are concerned, the degree of ionization must be determined separately and inserted into the calculations of results (20, 57, 123, 185). Moreover, occurrence of hydrolysis may constitute a problem which must be given special attention (125, 185). The method is extremely sensitive to conducting impurities, so that the solvent must be purified with special care (109, 185) and its contribution to the conductivity must be known as accurately as possible (20, 189). Inadvertently dissolved carbon dioxide is the commonest solvent impurity, and specific precautions must be taken to exclude it (20, 125, 186, 189).

An interesting adaptation of the conductivity method to the indirect determination of the solubility of nonelectrolytes which perhaps deserves more attention than it has received has been proposed by Lannung (133), who has found that the solubility of an electrolyte, such as sodium chloride, in acetone is proportional in a linear way to the water (or also methanol) content of the acetone. Since the solubility of the salt can be determined by conductivity, it would appear that this method might provide the means for a rather wide variety of related investigations into the solubility of nonelectrolytes.

The potentiometric method has also been adapted to the indirect determination of the solubility of magnesium hydroxide by taking advantage of the relationship between the solubility of the base and the acidity of the resulting solution, measurement of the pH by means of a hydrogen electrode–calomel couple giving a direct measure of solute concentration in the saturated solution (83).

5. Special methods

Before leaving the solubility procedures applicable in systems at constant composition, several minor methods which are sometimes applicable in special circumstances should be mentioned. Closely allied in principle to the simple cloud technique is the microscopic method, in which the temperature of the saturated system is adjusted until a very small crystal located under the objective of a microscope reaches a stable condition, neither waxing nor waning in size. The method is said to be very precise, although great care is required in measurement and control of the temperature (224).

In cases where the effect is of sufficient magnitude to yield the necessary precision, measurements of surface tension have been useful in determining concentrations of nonelectrolyte solutes (159, 223). An empirical calibration curve is first constructed to determine the influence of surface-active solute upon the surface tension of the solvent. Then, the same relative degree of influence being assumed to persist at saturation, the measurements provide direct determinations of concentration at that point. The analysis of surface-tension curves has also been suggested as a means of studying the solubility of colloidal materials (120), but no extensive applications of this technique appear to have been recorded up to the present time.

For solubility studies involving, as solvent, a condensed gas or other very volatile material, measurements of vapor pressure have found use as methods of determining the degree of solubility (74, 135). This method is also one which requires the use of calibration curves. It finds its chief merit in the fact that it can be employed in closed systems in which observations could be carried out otherwise only with difficulty and the contents of which cannot readily be sampled for the application of an analytical method. As used for solubilities in condensed gases, a weighed quantity of solute is placed in the saturation cell, and the entire system is evacuated. A cold well is then placed around the cell and a measured quantity of the gas is allowed to enter and become condensed. The cell is then raised to the desired temperature, and the pressure measurements are made. The method is subject to relatively serious errors because of the facts that (*a*) the pressure-measuring methods are not always of the highest precision, (*b*) the sensitivity decreases at the lower temperatures, and (*c*) relatively large corrections are required for the quantity of solvent found in the vapor phase (74, 135, 207). The method of vapor pressures has also been used to study the solubilization of an insoluble volatile liquid in aqueous detergents (144). Again, however, it suffers because of a lack of sensitivity (145).

In addition, solubilization of hydrocarbons in aqueous media may be studied by means of x-ray measurements, the spacing of a given band increasing as solute is added, until at saturation this increment either increases no further or increases by a negligible amount (120).

B. VARIABLE-COMPOSITION METHODS AND TECHNIQUES

In this classification will be included all those solubility methods which do not make use of the condition of constant composition. Although a few such methods are based on nonanalytic principles (e.g., the formation of a slightly soluble solute by reaction between two soluble salts), the great majority of them may be classed as clearly analytic procedures. For procedures of this latter type, the general plan is to obtain saturated solutions at equilibrium with the undissolved solute, making use of the considerations mentioned previously, remove a sample of the solution, and subject it to a suitable analysis.

1. Sampling and filtering

The chief problem to be settled at the outset of most analytic methods, therefore, is that of obtaining a sample which truly reflects the equilibrium situation. The applicability of any given sampling technique must be judged in relation to the nature of the system to be sampled (*viz.*, viscosity, relative stability of the solution constituents, etc.) and to the conditions under which the equilibrium to be studied exists (i.e., unusual conditions of temperature, pressure, etc.). There are three methods of getting saturated solution samples from an equilibrium system: (*a*) percolation of solution through a confined portion of solute, (*b*) decantation, and (*c*) filtration of the heterogeneous saturated solution.

The percolation technique is really one of extracting or leaching, consisting in principle of repeatedly exposing the pure solid to its solution until full saturation is reached. The plan differs from most analytic arrangements in that the solid solute is confined to one chamber throughout the experiment, the solution circulating repeatedly through that chamber. Various devices to perform this function have been proposed, e.g., a stopcock-fitted cylinder surmounting a narrow-necked funnel, the latter issuing into a receiving cylinder, and the upper and lower cylinders being connected by tubing to provide pressure equalization as well as a route for transferring the solution for repeated passes through the confined solute (202). A less elaborate apparatus may also be constructed from ordinary glass tubing and test tubes, as shown in figure 6. Tube A is plugged with an asbestos filter, D; the solid is placed in A and is followed by solvent. The liquid then percolates down into B, tube C providing for pressure equalization and recycling when desired (72). When the study of the solubility of a moderately to slightly soluble solute which is also volatile and relatively reactive (such as iodine) is to be performed, the percolation technique permits the establishment of equilibrium rather rapidly and in addition is extremely simple to manipulate (28), since circulation may be accomplished by employing the pressure of an

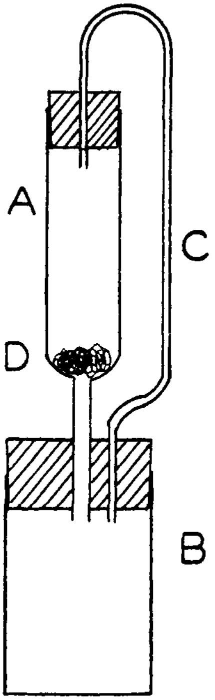

FIG. 6. Simple percolation apparatus for solubility studies

inert gas which simultaneously minimizes the evaporation of the solute. Moreover, the method is well adapted to the precise determination of solubilities for very slightly soluble solutes, having been successfully used by Brønsted and his coworkers in the classical confirmations of the Debye–Hückel theory by means of solubility studies (26, 27). Alternative types of apparatus employing the same principle are illustrated in figures 7a and 7b. The former includes the neck, B, in which the solid solute is placed, joined through filters to the bulbs, A and A′. Circulation of the liquid phase is accomplished by intermittent oscillation and, after equilibrium is reached, a sample of the saturated solution may be withdrawn at the stopcock, C (73). The apparatus shown in figure 7b is designed to be situated in a pressure bomb. Crystals of the solid are confined in the chamber A, and the liquid phase occupies both A and B, the equilibrium condition being attained by means of convection (80).

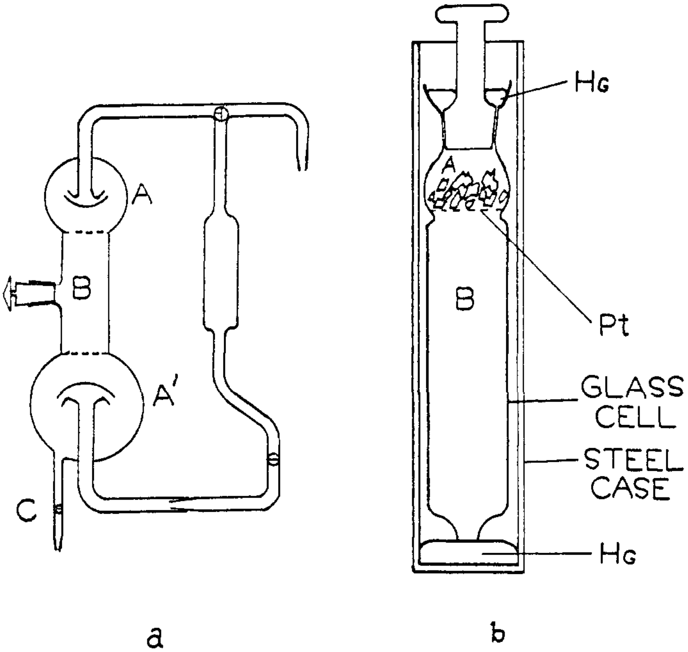

Fig. 7. Devices for determining solubilities while keeping solid solutes isolated in a single chamber of the system.

Separation of the phases by decantation is sometimes useful when the saturated solution is sufficiently fluid and the solid phase sufficiently granular to permit the latter to settle readily from the supernatant liquid. Some cells which may be used for such separations are illustrated in figure 8. In using the arrangement shown in figure 8a, the apparatus, after equilibration, is tilted so that the exit tube is vertical, and a part of the solution is forced upward into the pipet by gentle gas pressure applied through the side-arm (100). After equilibration, the cell of figure 8b is manipulated so that the excess solid is brought into the narrower of the arms. The solution in the wide arm then constitutes a representative sample which can be used for analysis (245). The cell shown in figure 8c combines both decantation and filtering procedures, the insertion of a small glass-wool plug as indicated making this latter possible. As indicated by the plan view, it is possible with this cell to take up to three samples, either from the same system or from three systems at conditions varied consecutively by sealing off the arm to each

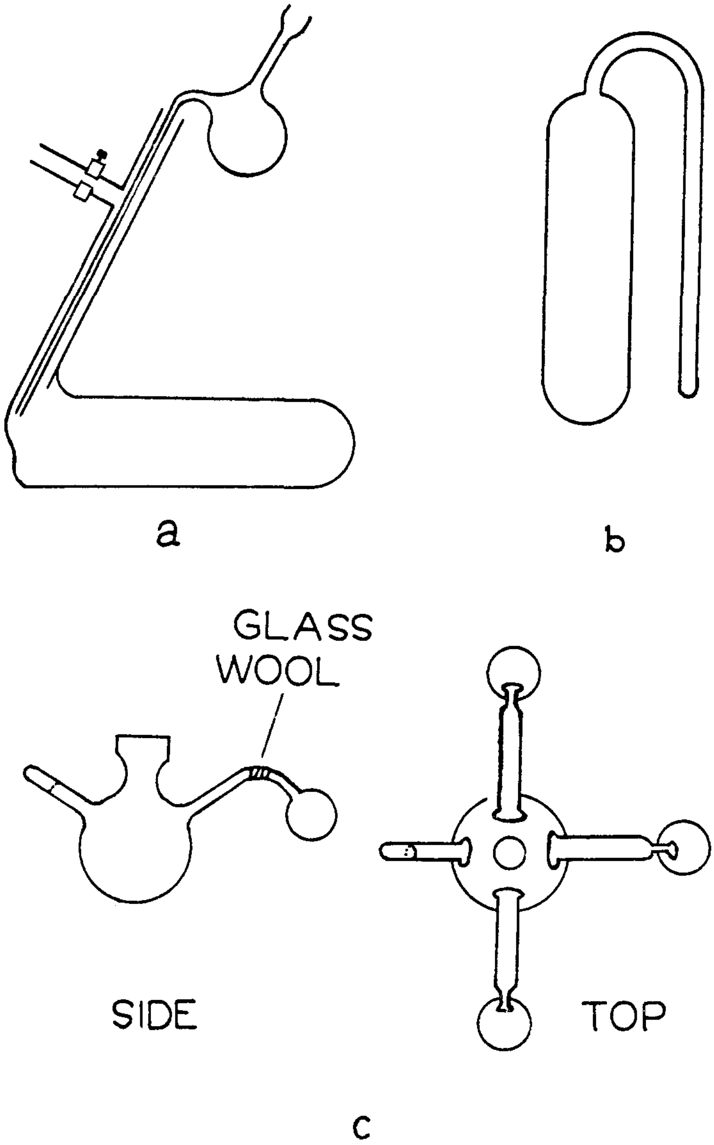

FIG. 8. Devices for separation of the solution phase from solid solute by decantation

sample bulb at the time of its removal. A modification of the decantation approach is to centrifuge the system in order to obtain a clear supernatant liquid (96, 140). This method may be employed when close temperature control is not necessary, but again it should be recognized that such lack of thermal regulation is usually a fatal impediment to such an approach (119).

Direct filtration is the method most widely used for separations of phases in solubility studies. Since the chief requirement upon the filter itself is that of efficient filtration (i.e., pore fineness) (29), as well as inertness toward the system under study, a great variety of filtering media are available, the choice depending mainly upon the nature of the system. Among the filter media which one finds mentioned in the literature are cloth fabrics (68, 190, 195), cotton plugs (43), asbestos (92, 131), glass wool (12, 48, 77, 174), and mixed glass wool and cotton (236), all of which should be incorporated into removable filter tips for removal after the filtration is complete in order to obtain best results (25, 194). In addition, filtration through an alundum disk has been found useful in studies of solubilities at very high pressures (191), while sintered-glass filters have also been used for filtration under pressure (36, 70, 136), in one case the filter having been made an integral part of the solubility cell by fusing it into the bottom of the vessel (155). The chief difficulty encountered with sintered filters is found in the removal of highly divided (colloidal-type) solids, but this trouble is common to most filter systems (70). So far as can be determined at this time, the best filter medium for such troublesome materials is cellophane (143), the filtration being accomplished under mild pressure.

In addition to these more or less conventional types of filters, one is also available which is said to be particularly useful for handling small amounts of materials (47). A flared glass plug is made so that it just fits in the constricted part of a funnel or partially collapsed test tube. By means of carborundum grinding powder, the plug is then ground into the constriction so that the narrow edges of contact between the constriction and the flared portion form a close, ground-glass joint of extremely small pore size. The system under study is then filtered very effectively as it seeps through this ground edge. In addition to its utility for small quantities, the simplicity and rigidity of the device recommend it for use in a closed system, and it may be fabricated in a considerable variety of forms.

Arrangements for accomplishing the filtration are almost as varied as the number of investigations of solubility. Of these, various styles of pipets are the most usual. When the system contains two liquid phases, of which it is desired to sample the lower, a removable cap may be fitted to the pipet tip in order to introduce the pipet without contamination from the upper layer (41). Such a cap, as well as the filter-tip itself, may be attached advantageously by means of a ground-glass joint (131). In sampling solutions whose viscosities may vary widely from one to another, Rourneux and Pernot (194) have recommended that the pipet bulb lie horizontally for the mobile solutions in order to prevent reëntry of solution into the cell upon removal of the suction, while for the more viscous solutions, the pipet may safely be held vertically. In either case, removable filter-tips were used, and the samples weighed directly in the pipet (the latter having been previously tared). This technique of weighing the sample directly in the pipet has also been used elsewhere with good results (13, 198, 228). Since there is a possibility that in any filtering operation, adsorption upon the filter will alter the concentration of the first portion of the solution to pass through it, it is advisable to reject this first portion as a matter of routine (61, 92). Chloupek and Danes (36) have designed a special pipet to facilitate this rejection by incorporating in the lower stem a bulb to receive the first few milliliters of solution withdrawn. When solubilities are studied at somewhat elevated temperatures, it is often necessary to take special precautions to avoid troublesome precipitations of solute during and immediately after sampling. The usual method of doing this is to preheat the pipet just before the sample is taken (*cf.* 174). Creighton and Ward, however, found that it was necessary to encase the pipet in a hot-water jacket while studying silver nitrite solutions in order to prevent premature crystallization (48), while Schimmel found it advisable to equip his pipets with double stopcocks in order to permit draining of the narrow lower stem immediately after the sampling (198) and thereby prevent it from being clogged by crystallization. For special problems, additional modifications in the design of the pipetting apparatus may also be called for. Thus, in the sampling of amalgams (solubilities in mercury), a special, flared filter-tip with a wide end opening is desirable (174), while in sampling a saturated solution under high pressure, it is sometimes desirable to fill the pipet by displacing an inert and immiscible liquid from it under pressure (43). Still another form of the weighing pipet provides an overflow type of inlet so that, after filtration of the sample, the filter may be removed without danger of any loss of the solution, and both the upper and lower openings may subsequently be sealed by attaching glass rods by means of short sections of rubber tubing (216).

When crystallization from a heated saturated solution is an especially great danger, it may be entirely impracticable to obtain samples by pipet, whereupon it becomes necessary to maintain the entire apparatus for the sampling at the temperature of the equilibrium. This may be done in several ways. Forbes (71) has arranged the solubility cell so that it takes the form of a small, straight-walled separatory funnel with filter and stopcock in the lower portion. The stopcock is closed during equilibration. After saturation, the lower stem of the cell is fastened to one opening of a double-necked weighing bottle, the other opening leading to a suction tube. Opening of the stopcock and application of gentle suction gives filtration into the bottle, the whole arrangement being maintained in the thermostat during the entire time. Similarly (177, 190), two vessels may be located in the thermostat and connected by a U-tube, both vessels being fitted with reflux condensers to avoid loss of volatile materials. After equilibration of the system in the first vessel, an application of either pressure through its reflux condenser or mild suction through the condenser tube of the receiving vessel causes the saturated solution to pass through the U-tube into the receiver, which may then be removed and weighed. The pressure transfer is to be preferred when dealing with easily volatile materials (24). Yet another method of obtaining a filtered sample involves the insertion into the equilibrated solution of a small sampling bottle fitted with a filter-equipped inlet tube and an exhaust tube to allow the escape of displaced air. The simple act of immersion causes the solution to pass through the filter into the sampling bottle (8, 195). The same principle has also been used by other investigators in employing partial immersion of a filter thimble (240) and a hollow stirring shaft fitted with a filter over its lower, open end (68).

Assemblies making use of simple gravity filtration are also available. Meyer has fitted the sampling bottle to the saturation cell by way of a funnel (149). During saturation, filtration is prevented by closing the air inlet to the cell with a glass rod, subsequent removal of which allows filtration to proceed, air being vented from the receiver by a connection to a drying tube. This apparatus has been modified by Koehler to incorporate reflux condensers for volatile materials as well as more effective protection from the atmosphere by means of drying tubes (122). A more compact apparatus which may be readily fitted into even a small thermostat utilizes two small bottles as saturation cell and receiver, respectively. Both are fitted with double-bore rubber stoppers and are then connected head-to-head by means of tubes through these bores. One tube constitutes a filter-capillary, and the other is a vent. Saturation is accomplished with the entire contents of the apparatus in the first bottle; inversion of the assembly then permits filtration into the receiver to proceed (31). A somewhat similar device consists of a narrow-necked cell for saturation, fitted over the top with the filter. A small wide-mouthed receiving bottle fits loosely over the narrow neck during equilibration. When equilibrium is reached, inversion of the apparatus permits filtration to occur, the process being assisted by the presence of a vent tube situated in the side of the saturation cell (89). This latter arrangement is particularly designed for use in an autoclave or similar pressure device.

Another device making use of a hollow stirring shaft has been described by Weimarn (241) and improved by Kuznetzov (130). In it, two glass cylinders are attached side by side with a filter tube, the first cylinder being the saturation cell and the second containing the weighing bottle for receiving the sample. The stirrer consists of a wide tube which, after equilibrium is reached, is raised above the surface of the solution, closed at its upper end, and pushed back into the solution. This produces sufficient pressure to force the solution through the filter tube and into the weighing bottle in the second cylinder.

An apparatus in which a column of mercury supplies pressure to displace the saturated solution and force it upward through a filter is also available (39).

Devices for determining the solubilities of various substances at the boiling points of the solutions make use of essentially the same principles already discussed. Thus, Schroeder reached equilibrium in a saturation cell equipped with a reflux condenser and a side-arm accommodating an immersed filter tube. Application of pressure through a second side-arm permitted him to expel any desired quantity of filtrate into a receiving vessel (201). Chugaev and Chlopin, on the other hand, included in the saturation cell a sampling bottle equipped with filter tube and vent. Opening of the vent at the conclusion of the experiment allowed the clear solution to filter into the bottle (37).

2. Analysis and detection

After a sample of the saturated system has been obtained, the whole repertoire of physical and chemical techniques is available for the determination of its composition. The discussion which follows, however, will be confined to the mention only of some examples of those techniques which from time to time have been specifically used in solubility work, and the list of possible approaches will therefore be necessarily incomplete.

(a) Residue weight

The simplest and most straightforward method of determining the amount of solute dissolved in the solvent at saturation is to evaporate a weighed sample of the solution to dryness and to determine by weight the solid residue remaining (62, 227, 244). This procedure is often especially useful whenever the solute is a stable nonvolatile solid which can be quantitatively recovered by such a treatment. When the method is employed, it is usually advisable to keep the evaporation temperature at the lowest practicable level (6) and, particularly when the solute is an organic material, it is well to carry out the operation at room temperature, using a fan to aid the evaporation (204). If the system is one which is adversely affected by the small amounts of moisture present in the atmosphere, the evaporation should be carried out in a closed container, special evaporation bottles being available (232) which provide a large surface area over which dry air may be drawn. Should the system also be sensitive to oxidation by the air, an inert gas such as nitrogen may be used (230). The residue-weight method has also been refined by Noonan (166) to permit recovery of the solvent. The technique consists in placing the saturated solution in a platinum crucible, the latter being enclosed in a gas-tight system whose lower part consists of a receiver. The closed system is evacuated, and the crucible contents are heated by irradiation with infrared light, while the receiver is protected from the rays by means of an aluminum shield. Under a good vacuum, the solvent quickly distills from the solution and is recovered in the receiving vessel.

In addition, the evaporation procedure has been used for the determination of the solubility of metals in mercury by distilling the solvent mercury slowly under a vacuum. The residual amalgam is then washed from the distilling bulb with acid and the metal content determined analytically (141, 219).

(b) Chemical analysis

Next to the measurement of weight of residue, the chemical analysis of the saturated solution is the most usually employed method of determining solute content (*cf.* 205). Moreover, powerful chemical methods are available for estimating quantitatively a great number of classes of materials. Thus, volumetric acidimetry may be used when the solute is an acid or a base of fairly large solubility (184, 211), but its use has also been reported in the study of slightly soluble acids (178); iodometry has been the method for studying solubilities of iodine (93), thiosulfates (110), and arsenic trioxide (140); the Volhard method was used for the solubilities of difficultly soluble silver salts (103); the solubility of orthophosphoric acid was found by gravimetric measurement as magnesium pyrophosphate (211); and slightly soluble lead salts have been investigated by concentrating large samples of the saturated solutions and recovering the lead as chromate (183). Potentiometric titration (*cf.* 128) is also a valuable standard method, and it has been found especially useful for the study of systems in which exposure to the atmosphere must be avoided (50).

Particularly in collecting data for the description of a complete phase diagram, it is necessary to conduct an analysis of the residue, as well as of the saturated solution, as has been pointed out by Vener and Thompson (235) among many others. The procedure of analyzing the undissolved residue rather than the solution has also been found most practicable in determining the solubility of a hydrocarbon in a solvent such as water. In such a situation, a measured quantity of the hydrocarbon is allowed to come into equilibrium with a known quantity of solvent. The hydrocarbon remaining undissolved at saturation is then withdrawn into a Haldane gas-analysis system and determined by combustion, the dissolved portion thus being determined by difference (152).

One solubility problem which differs considerably from most is that of the solubility of water in an organic solvent. For the analysis of such a saturated solution for water content, three methods offer themselves. The first of these is an analysis by the well-known Karl Fischer method (17), which requires no extensive discussion here. The second method requires the use of calcium hydride, which is dropped into the sample, the water content being found by measurement of the volume of hydrogen liberated (192). Since considerable amounts of gas may be adsorbed on the calcium hydride used as reagent, precautions must be taken to remove it as far as possible by heating the reagent before use, and the use of constant blanks is desirable in order to avoid error from this cause. The third method for water solubility is an indirect one, in which the solubility of an appropriate salt in the wet organic solvent is studied (154). Since the solubility of a salt such as silver perchlorate in organic liquids is markedly increased by even trace amounts of water, a standard (or reference) curve of salt solubility as a function of water content may first be constructed. The presence of the salt extends the solubility of the water far beyond its normal limit, so that the normal solubility may readily be obtained for the normally saturated solution by interpolation (105).

(c) Electrical methods

(*i*) *Conductometry:* Conductometric analytical procedures have been found useful in following the course of the equilibrium process, the attainment of constant conductivity in successive samples giving an indication that saturation conditions have been reached (24). This method is superior for this purpose to most others in many cases because of the ease and rapidity with which it may be performed. The actual analysis of the dissolved solute (when it is a salt) may also be done in the same way. The saturated solution is evaporated to dryness, and the solute is converted into a stable salt such as the nitrate or chloride, the conductivity of which in a known volume of water will give a measure of the amount of solute originally dissolved (181). The errors accompanying this method are about twenty times those attending the determinations by conductivity at constant composition. The determination of solubility directly by a conductometric titration has also been described (197). The procedure is exemplified in its use in determining the solubility of manganese hydroxide, which is difficult to study directly since the hydroxide usually contains indeterminate amounts of the oxide. The titration solutions consisted of standard barium hydroxide and manganous sulfate, the products of the reaction being manganous hydroxide and the very slightly soluble barium sulfate. The conductance curve so obtained gives a minimum, the conductance at that end-point being the summed conductance of the two product salts. If the conductance of the barium sulfate be known from independent measurements, that of the manganous hydroxide may be determined by difference and the solubility of the latter substance determined from this value by the Kohlrausch method.

(*ii*) *Electromotive force:* Electromotive-force measurements may also be used for the analysis of a saturated solution of a salt. The principle is the same as that used for the similar measurements under conditions of constant composition. However, by evaporating the sample to dryness and converting the salt, by displacement of the original anion, into one which gives a stable electromotive behavior that can be readily interpreted, it is possible to eliminate any errors due to the mode of dissociation of the original solute (181). The method does not eliminate errors due to diffusion potentials, variations of activity coefficients, etc. This type of measurement may also be used to determine the precipitation curve of a solute potentiometrically, the basic idea being similar to that of the related conductometric titration described above. In addition, the solute content of a saturated sample may also be determined by amperometric titration (218).

(*iii*) *Polarography:* Polarography as an analytical tool for solubility work possesses the advantages that it is capable of giving accurate analyses of traces of reducible material down to concentrations as low as 10^{-5} or 10^{-6} molar and, in addition, is superior to the conductivity method by virtue of the fact that small quantities of many ions can be determined even in the presence of a great excess of other electrolytes (98). Although it has been employed for a few solubility studies (*cf.* 116, 129), the polarographic method seems not to have received the degree of application in this field which its ease and precision seem to recommend.

(*iv*) *pH determinations:* Determinations of the pH as an indirect means of getting at solubilities and solubility products, especially of hydrolyzable materials, have been recognized as useful in a limited way (126), but seem never to have received any widespread attention. In addition, Baumberger and Davidson (9) have described some observations on the influence of the solubility of phthalic acid on the pH of some potassium acid phthalate buffers, and these suggest the possibility of utilizing such an effect in studying a variety of related systems.

(d) Optical methods

(*i*) *Colorimetry:* Colorimetry as a reasonably accurate and convenient method of determining the solute content of a saturated solution is particularly adapted to studies in any system which absorbs visible or ultraviolet light so long as the absorption follows Beer's law. The chief practical drawback to its utilization occurs when the solute fails to follow Beer's law because of changes in its nature due to ionization, complex formation, hydrolysis, etc. When a good colorimetric comparison instrument is used for the measurements, subjective factors usually lead to errors of the order of 1 per cent, but the use of a spectrophotometric device largely eliminates the subjective element and reduces the error markedly. The method is further recommended by its great sensitivity to minute quantities of dissolved material (181). In work with highly colored dyes, the method of course achieves its greatest advantages from this sensitivity, but frequently the color is so intense that considerable dilution is required before an observation can be made (54, 120, 142), the inevitable dilution errors somewhat counteracting the advantages of the method. In addition to dyes, salts capable of being transformed into colored modifications and derivatives may also be studied by colorimetry, as has been shown, for example, by Smith for potassium perrhenate (213) and by Lanford and Kiehl for lead iodide (132), while even the very small solubility of silica may be measured by means of the intensely yellow silicomolybdic acid (119).

(*ii*) *Turbidimetry and nephelometry:* These methods have been employed in the study of solubilities, the former for determining solubility limits and the latter for analyzing suspensions to determine amounts of undissolved solute. Considering first the applications of turbidimetry for systems of variable composition, it may be noted that one method is to add solvent slowly to a nonhomogeneous system, observing turbidity until an amount of solvent has been introduced sufficient to make the cloudiness almost disappear (63, 118). This technique is to be recommended more for its simplicity than for its accuracy. A procedure which is used somewhat more frequently is that of preparing solutions containing, respectively, the positive and negative ions of the substance to be studied, and mixing them until a turbidity due to undissolved product is just noticed. This method is closely related to that noted when discussing conductometric procedures. Depending upon the manner in which the solute precipitates itself, the experiment may be performed either by adding one of the solutions dropwise to a known quantity of the second solution (90) or by adding alternate drops of the two solutions into a known quantity of solvent (10). Detection of the end-point for such a titration may be facilitated by the employment of a Tyndall beam (182). The solubility of a sparingly soluble organic liquid in water may be determined by this method also, and the sensitivity of the observation is enhanced by including in the system a trace amount of a dye soluble in the organic material but not appreciably soluble in water. The merest excess of organic material will then show up clearly because of the color imparted to it by the dye (214).

For solubilization studies, the turbidimetric method of plotting degree of opacity against composition provides an excellent means of making accurate measurements and has been discussed in some detail in a recent review by Klevens (120). Solubilities of an extremely low order may be determined by the nephelometric observation of serial dilutions of a suspension of the solute in the solvent and noting the composition beyond which further dilution causes no further reduction in light scattering (46, 53).

The use of nephelometry for the analysis of suspensions is described in several places in the literature (e.g., 179). The measurements may be made by visual comparison of the unknown opalescence with a standard, much as in the colorimetric method (188, 242), or by measurement of the intensity of scattered light by means of a photoelectric cell (46). Chief disadvantages of the nephelometric method as an analytical procedure lie in the fact that the measured turbidity depends heavily upon the mode of preparation of the precipitate, its age, its nature, and amounts of foreign ions in the solution, etc. All these factors influence the size of the suspended particles and tend to produce variable results unless carefully controlled (18, 188).

(*iii*) *Refractometry:* Refractometric measurements provide another means of determining the composition of a saturated solution of a nonelectrolyte. For many binary systems, the curve of refractive index as a function of composition is a straight line, and the construction of a calibration curve makes possible the determination of the saturation composition either by graphic extrapolation (111, 171) or by substitution into the linear formula derived from the calibration curve (34, 79). Osaka has proposed a quadratic relation for the calibration curve which purports to give somewhat more accurate results (169, 170), but Getman and Wilson, after a comparison of the quadratic and linear relationships, report that no appreciable advantage is gained thereby (79). At best, it appears that refractometry yields only good approximate results, and it is not recommended for highly precise work (79, 111). Use of the schlieren effect has also been tried for solubility studies (199, 229) but only qualitative results are reported from it.

(*iv*) *Interferometry:* Interferometry provides yet another optical method for studying the solubilities of sparingly soluble nonelectrolytes. Gross (87) and Gross and Saylor (88) have described the principles of this method in great detail, and no purpose would be served by repeating their discussion here. It may be noted, however, that since the relationship between composition and instrument reading is usually linear, it is generally sufficient, after verification of this fact for a particular case, to calibrate for the given system by determining a single point at a known composition (153). Should it be found that the relation is not linear, an entire series of such calibration determinations is necessary, and the method loses most of its advantage of simplicity.

(*v*) *Polarimetry:* Polarimetry, although restricted to the study of solutes possessing optical activity, has been successfully used in the analysis of saturated samples by Lowry (137) and by Lowry and Robertson (138). The chief assumption involved with this method of analysis as used in that work is that the optical rotation is directly proportional to the solute concentration, but the construction of a calibration curve should remove any uncertainty on that score in any given case.

(*vi*) *Microscopy:* Microscopy in the examination of solutions to determine the solubility limit is claimed by Biltz (18) to be superior to nephelometry because, when an ultramicroscope is used, the errors due to variability in particle size for undissolved material are sensibly eliminated. The procedure utilized with this method is to examine successive dilutions of a suspension of the solid solute in the solvent until a composition is reached at which the system becomes devoid of solid matter (18). Kolthoff (126) has criticized the accuracy of this method for very slightly soluble substances, pointing out that it is subject to errors from supersaturation phenomena and from the necessity of having a certain minimum number of particles present in the solution in order for them to be detected, this minimum being itself a function of the particle size. In view of these considerations, it appears that the chief value of microscopic examinations in solubility work lies in its utility as an aid in identifying the various solid phases which may be present in the saturated system.

(e) Radioactive tracer methods

First proposed and tested as a method for the analysis of solubility samples by Hevesy and Paneth (97, 173), the use of radioactive tracers received little attention in the years immediately following its introduction, but has twice been discussed in considerable detail in review articles (64, 193). The recent burgeoning of interest in the field of radioactivity has, however, led to a marked increase in its employment during the last few years. For example, the solubility of trivalent cobalt salts has been determined with radioactive cobalt tracer (30), and the solubility of water using tritium as a tracer (112), of silver bromide using radiobromine (196), and of ytterbium oxalate using active ytterbium (49) have all recently been subjects of careful studies.

The principle of the method requires simply that one include in the substance whose solubility is to be studied a known proportion of a radioactive form of one of the elements in the material. After saturation, the radioactivity of a suitable aliquot is then accurately determined with standard apparatus for the purpose, and the solute content deduced therefrom. Alternatively, the solute may be isolated by a physical method, such as evaporation of an aliquot of the solution to dryness, and the activity of the residue may be measured. With reasonably sensitive detection equipment, it is possible in this way to obtain accurate solubility values at levels of the order of micrograms per liter.

(f) Special methods

(*i*) *Float method:* A float method of determining the concentration of a saturated solution constitutes a novel approach to the problem of analysis which is worthy of brief discussion despite the fact that it has been used but little in the solubility field. The device employed consists of a float of known weight and volume which acts as a cartesian diver when placed in a solution of appropriate density. The determination may be carried out in either of two ways: (*a*) A float, which may be very simply constructed from an inverted Florence flask with an iron rod sealed in its neck, is placed in the saturated solution, the float being constructed so that it will just ride upon the surface of the liquid at a constant, known density. In the saturated solution, this float will ride quite high in the solution. Pure solvent is then added up to an amount just sufficient to cause the top of the float to sink to the surface. Since the density of the solution at this point is then known, as well as the quantity of additional solvent necessary to attain it, the solute content at such a point may be determined from a previously constructed calibration curve, and the original concentration of the saturated solution deduced from that value (56). (*b*) The determination may also be carried out by using a glass float to which small amounts of mercury may be added through a capillary. The float is placed in the saturated solution, and mercury is added until the "equilibrium" position is reached. From the known weight and volume of the float and the amount of mercury added, the density of the solution may be determined in this way at a temperature at which the solution is no longer saturated, and its solute concentration again obtained from a calibration curve (236).

(*ii*) *Ebulliometry:* Ebulliometry has been suggested as a method of possible utility in determining saturation concentrations of solute by measurements of boiling-point elevations (221). In order for the method to be useful, however, the solute must be nonvolatile and rather highly soluble, and the ebulliometric constant of the solvent would probably have to be relatively large. It is suspected that such a method would not be especially precise for these reasons, but no data obtained by it seem to be available to confirm such a judgment.

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