Summary

1. The osmotic pressures of phenol solutions have been determined throughout the solubility range at 30.0°.

2. From the results so obtained the degree of association of phenol in aqueous solution has been calculated, and it is found that the percentage of simple molecules existing in the dimolecular form varies from 86% for 0.1 *M* solution to 99% for 0.9 *M* solution. The pure material is entirely associated.

3. It is suggested that the variance in the chemical compounds formed on direct bromination of aqueous phenol solutions of varying concentration is attributable to the different molecular combinations present.

4. The great absorption of heat attending the solution of phenol is due to the partial decomposition of higher molecular forms, the reaction $(C_6H_5OH)_2 \longrightarrow 2C_6H_5OH$, being endothermic.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY]

IMPROVEMENTS IN THE MODE OF MEASUREMENT OF OSMOTIC PRESSURE

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Introduction

Of the various experimental physicochemical methods, none is of greater importance than the measurement of osmotic pressure. The thermodynamic considerations of solutions are based on the concept of an osmotic pressure and all other properties of solutions are derivable from osmotic-pressure data. Of paramount importance is the fact that osmotic-pressure measurements are capable of the greatest refinement, being measurable with an extreme accuracy. Though we possess other accurate means of measurement such as of the freezing point and the vapor pressure, these are very limited, the former being confined to one temperature, the latter applicable over only a limited range of temperature. Osmotic-pressure measurements, on the other hand, can be carried out with equal precision over the range of temperature in which the solvent in question exists in the liquid form and throughout all possible concentration limits.

Despite these desirable conditions and advantages, measurements of osmotic pressures have been limited to a few substances, such as sugar and glucose. Substances of lower atomic weight, and especially electrolytes, have defied measurement and it has usually been assumed in the case of electrolytes that measurement is impossible because of the destructive effect on the semipermeable membrane and the permeability of the latter to such substances. The object of this investigation was so to modify the present mode of measurement as to make it more widely applicable and, if possible, to apply it to the measurement of electrolytes.

The Cells and Membranes

Of primary importance in the experimental determination of osmotic pressure is the character of the clay cell used as the support of the semipermeable membrane. Indeed, the lack of cells of proper texture was the cause of failure by early investigators. The cells used by Morse and Frazer in their work were made with every precaution to obtain a final product having a uniform porosity, a fine structure, and lacking, above all, any "air blisters." Such cells were obtained in the laboratory by carefully elutriating and washing the clays, pressing the obtained mixture, and finally turning to the required form on the lathe, after which the cell was baked and its collar glazed. The microscopic structure of such a cell (Type A) showed that it had a fine and uniform texture.

Since the function of the cell in measurements of osmotic pressure is to secure a support for the membrane to be used, it is perfectly obvious that the fineness of texture of the latter will depend entirely on the size of the pores of the cell itself. If there should happen to be a point where the cell wall is highly porous, the membrane, if deposited at all over this area, must necessarily be held but loosely, and the exertion of any pressure at this point would easily disrupt it.

The failure of early attempts to measure the osmotic pressure of solutions of electrolytes was usually attributed to the destructive effect of the electrolytes on the colloidal nature of the copper ferrocyanide membrane. To be sure, this is an important factor in such determinations, but it appeared likely that the failure of early attempts was due also, in a large measure, to the character of the cell itself. The fact that only substances of high molecular weight could be studied while other materials of molecular weights of a lower magnitude including electrolytes, passed through the semipermeable membrane suggested that cells of a finer structure might support membranes of a finer structure which, though incapable of prolonged existence in the presence of disrupting agencies would, nevertheless, prevent leakage of the solute and thus serve as true semipermeable materials for the period of time required to make a measurement.

To obtain cells with a texture finer than the one described above by the same method is scarcely possible. This cell was subjected during preparation to a pressure of about 3000 kg. per sq. cm. of surface of clay for 15 hours. Moreover, as shown later, cells of any appreciable thickness of finer texture than shown by Type A, although capable of supporting a membrane impervious to the solute would, nevertheless, fail to give accurate osmotic-pressure measurements. It was decided, therefore, to produce in the cells heretofore used some insoluble material which would give a support for the membrane. Microphotographs of cross sections of cells so prepared (Types B, C, D and E) showed darker areas representing the areas where the interior of the cell had been modified by the introduction of these fillings, whose extremely fine structure was indicated by the opacity to light which these sections showed under the microscope.

The Type B cell was filled with magnesium silicate by electrical diffusion. The cell to be treated was placed in an apparatus similar to that used in depositing the membrane, and a current (taken directly from the lighting circuit) passed between a roll of platinum foil placed within the cell, which served as the anode, and a foil (2 cm. wide) which surrounds the cell, dilute solutions of magnesium nitrate and sodium silicate serving as anolyte and catholyte, respectively. In this manner the required filling can be obtained in any thickness required, depending on the period of deposition. The optimum results are obtained with an electrolysis of about 10 hours. The initial amperage, which varies with the porosity of the cell in question, ranged from 0.5 to 1 ampere under the above conditions and drops in 10 hours to 0.02–0.2 amperes. It was found that cells filled in this manner scarcely cracked on baking and gave most efficient results. After all treatments, the cells are baked in a pottery kiln for several days at 1000–1450° and then, after thorough electrolysis with a 0.05% lithium sulfate solution to remove all air from the cell by endosmosis, the cell is electrolyzed with pure water until all electrolytes have been removed. It is then ready for the deposition of the membrane.

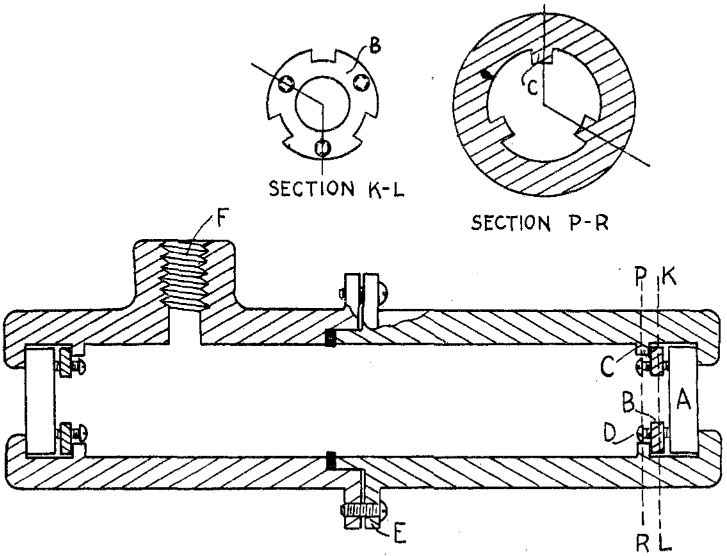

Fig. 2

Type C cell was filled in a similar manner, except that sodium hydroxide was used instead of the silicate and the magnesium hydroxide thus formed was burned in the kiln. The filling was rather narrow and not at the very surface of the cell, but toward the interior.

Type D was filled exactly as was Type E cell but was not baked after filling. This was made evident in the photographs by the greater porosity of the baked cell due to the contracting effect of heat on the filling. The baked cells invariably gave better results, which may be explained by the fact that too dense or too thick a filling does not allow free and easy diffusion of solvent through the cell which, in turn, results in a slow and incomplete attainment of equilibrium, despite the fact that with such cells no leakage or a negligible amount occurs.

Type E cell contained a filling of magnesium silicate produced as follows. The cell was placed in a solution of concentrated magnesium chloride which diffused and thoroughly filled the pores of the cell. After the outer surface had been washed, the cell was transferred to a solution of sodium hydroxide which on diffusion precipitated magnesium hydroxide in the cell. In order to produce a more insoluble filling, this was converted to the silicate by boiling in a 10% solution of sodium silicate. The above process was repeated several times until no more "filling" could be inserted. The "filling" was precipitated at the outer surface of the cell where it was desired, since it is here that the membrane is deposited. The main objection to this method of cell treatment is the fact that the majority of cells so treated crack on drying.

Type F cell was filled by diffusion. A cell filled with magnesium chloride and inserted in a beaker of sodium hydroxide was allowed to stand for several weeks. In this way a fine layer of magnesium hydroxide was precipitated where the solutions met, which was then converted to the silicate. One cell of this type was actually used in quantitative measurements and gave excellent results until finally it cracked from the pressure developed in use.

Deposition of Membrane.—It was found that the optimum and quickest results are obtained if, instead of bringing about the first deposition of the membrane by means of electrolysis as is commonly done, a modified form of the method described by Pfeffer[1] be used.

The cell is filled with a molar solution of cupric sulfate and placed in a beaker of water until the solute has diffused through the cell. The cell is then washed, the water is replaced with a molar solution of potassium ferrocyanide, and the arrangement allowed to stand overnight. Such a cell set up immediately with a 2 M solution of sugar often gives the theoretical pressure which in the case of unfilled cells can only be obtained after from 6 months to a year of constant seasoning.

Discussion of the Cells.—The results already obtained by the use of filled cells in the case of phenol solutions[2] and qualitative measurements made, show that the above method of cell treatment accomplishes its purpose. Regardless of the magnitude of the molecular species under consideration, the leakage in any case is but minimal. However, it cannot be too strongly emphasized that non-leakage is not to be taken as a criterion of a successful measurement, as has been done by some investigators. The only criteria for a good measurement are the attainment of a pressure which remains constant for some time, non-leakage of solute and, above all, the ability to duplicate all results with other cells and measuring apparatus, in so far as the limit of accuracy of the method permits. Data based on measurements not fulfilling these requirements are to be considered worthless.

[1] Pfeffer, "Osmotische Untersuchungen," **1877**.

[2] Grollman and Frazer, THIS JOURNAL, **45**, 1705 (1923).

Another point of superiority of the filled cells is the speed with which they attain equilibrium, which far exceeds the time required with unfilled cells. Indeed, measurements of 50 atmospheres' pressure have been attained with sugar solutions, using air manometers, within 20 minutes after setting up, and the fact that in such measurements a considerable diffusion of solvent must take place to produce the pressure, shows the potency of the force with which we are dealing.

A New Interferometer Cell for Use as a Pressure Gage

Besides the question of cells, whose improvement has been discussed above, the mode of measuring the pressure exerted is of fundamental importance. Nitrogen-filled manometers which have been used in the past have the great disadvantage that the time for equilibrium is rather long, since for its attainment, considerable solvent must pass through the cell. With electrolytes it is essential to make rapid determinations, since long contact with the solutions has a detrimental effect on the membranes. Hence, a more rapidly registering pressure gage was desired. Van Doren, Parker and Lotz[3] have devised a method of measurement in which the change of refractive index with pressure as measured by the Zeiss water-interferometer serves as a pressure gage. By the use of this instrument rapid determinations can be made. As developed by these investigators the instrument has, however, several defects. It is rather difficult to assemble, leakage at the glass windows being especially hard to avoid. Moreover, due to the manner in which the windows are held in place, the length of the pressure chamber is necessarily made small, which means a corresponding diminution in the sensitivity of the instrument, the sensitivity being directly proportional to the length of the column of liquid compressed.

The two objections mentioned above have been satisfactorily overcome by the modified instrument shown in Fig 1. This new form combines ease of assemblage and high sensitivity, the latter being twice that of the original instrument. As it is generally applicable wherever pressure measurements are to be quickly and accurately made, it will be briefly described.

It consists essentially of a brass tube, with optical glass windows inserted at its ends, which is held in place by means of a square block of brass through which are drilled 2 holes. One of these serves to hold the pressure chamber in place, while the other, which is contiguous to the first, holds the other window which, dipping into the water-bath of the interferometer, serves as the non-pressure or comparison chamber. By this arrangement only the pressure tube requires especial care in construction to avoid leakage, and it is this simplification which gives the instrument both ease in assemblage and greater accuracy. A plate screwed on the end blocks serves as a support of the chambers in the bath. Since the parts on being assembled assume the same relative position, no diffi-

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[3] Van Doren, Parker and Lotz, THIS JOURNAL, **43**, 2497 (1921).

culty is experienced by a change in the zero reading of the instrument such as would occur were the arrangement not exactly reproducible.

In order to introduce the glass windows into the ends of the pressure chambers from the inside, thus giving a tighter joint between glass and metal with increasing pressure, the pressure tube must be made in two parts. These are joined by the flange arrangement E, leakage being prevented by insertion of a washer made of steam packing where the two ends meet within the tube. Such washers do not flow under pressure as ordinary rubber does. The tube, which is otherwise of uniform bore throughout its length, has 3 points of projection, C, which serve to support the washer B. The glass windows, A, are circular, but have 3 notches corresponding to the 3 projections from the tube, in order that the windows may be slipped past these projections. After the windows are introduced as shown in the figure, a circular brass washer, B, having notches similar to those of the glass plate, is slipped beyond the projections, turned so that it is now supported by the projections, C, and the glass windows are held tightly against their supports by means of the screws, D. The windows are made air-tight by the use of a rubber solution which, after assemblage, is vulcanized by slow heating. The tube is joined by F to a mercury trap which in turn is connected to the pressure cell or to the source of the pressure to be measured.

The instrument as described above has a range of 30 atmospheres. This can be increased as described by Van Doren, Parker and Lotz[3] by the use of thin glass plates inserted in the path of the beam passing through the non-pressure side.

Since the range of 30 atmospheres corresponds to 3000 divisions on the interferometer and since readings on the latter are capable of duplication within 10 divisions, the pressure readings are accurate to 0.1 of an atmosphere. The accuracy can be further increased by using a more compressible liquid than water in the instrument and interferometer bath and by the use of a longer pressure chamber and wider windows. The length of the pressure chamber of the instrument as described above was 80 mm. By arranging the mirrors and prisms of the interferometer so that there is a greater distance between the two beams, larger windows can be used in the pressure gage, which insures more accurate readings.

For a complete description of the use of the interferometer, the reader is referred to the papers[4] by Adams, Cohen and Bruins, Löwe, and Haber and Löwe.

Owing to the difficulties inherent in most methods of pressure measurements, their limited applicability and accuracy, the use of the water interferometer should prove itself a most desirable substitute for certain methods heretofore employed.

Conclusion

It is hoped that with the modifications above described, the road is paved for the measurement of the osmotic pressure of electrolytes and other substances whose behavior in solution, as shown by the osmotic pressures

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[4] Adams, This Journal, **37,** 1181 (1915). Cohen and Bruins, *Z. physik. Chem.*, **103,** 337 (1923). Löwe, *Chem.-Ztg.*, **51,** 405 (1921). Haber and Löwe, *Z. angew. Chem.*, **23,** 1393 (1910).

which they exert, may throw light on the important questions of solutions. Qualitative results obtained with lithium chloride, sodium nitrate, sodium acetate, cupric chloride, sodium chloride, ethyl alcohol and acetic acid are promising and though no successful quantitative results with concentrated solutions have as yet been obtained, experiments on the more dilute solutions are now in progress, the results with phenol having already been published.

Summary

1. The method of experimentally determining osmotic pressures has been improved by filling with various silicates the cells on which the membrane is precipitated.

2. Such cells are efficient supporters of the membrane, allow but a minimal leakage, a rapid attainment of equilibrium, and do not require long seasoning.

3. An interferometer cell has been devised which is capable of acting as an accurate and rapid pressure gage.

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ELECTROMOTIVE-FORCE MEASUREMENTS WITH A SATURATED POTASSIUM CHLORIDE BRIDGE OR WITH CONCENTRATION CELLS WITH A LIQUID JUNCTION

By George Scatchard

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The determination of the activities of individual ion species is a very interesting and important problem of physical chemistry. The measurement of hydrogen-ion activity, often under the name of hydrogen-ion concentration or P_H, is being applied to so many varied problems that a consideration of all the possible evidence as to the validity of the procedure becomes important. The applications themselves present a considerable body of evidence.

The electromotive force of a cell of the type, Pt, $H_2 | HCl, AgCl | Ag$, can be derived rigorously from thermodynamics alone. At constant temperature and pressure it is $E_1 = E'_1 - RT/F \, ln(a_H \times a_{Cl})$, where E'_1 is the corresponding electromotive force when the activities are unity, and the other symbols have their usual significance. This electromotive force is divided between the two electrodes; we will assume that it is so divided that the electromotive force at the hydrogen electrode is $E_2 = E'_2 - RT/F \, ln \, a_H$ and that at the silver-silver chloride electrode is $E_3 = E'_3 - RT/F \, ln \, a_{Cl}$. Although this generally accepted assumption is apparently incapable of direct proof there seems little reason to question it, for it is difficult to imagine a mechanism of the reaction in which the chloride ion