normal curvature of the surface so that the vapor pressure of the liquid is reduced. The rates of distillation from solvent to solution under different tensions were measured and these plotted to give the tension corresponding to equilibrium or the osmotic pressure.

This method extends the possibility of direct osmotic pressure measurement to aqueous solutions of electrolytes and possibly colloids, and to solutions in organic liquids. It is particularly applicable to extremely dilute solutions where a knowledge of the properties is desirable from a theoretical standpoint. Moreover, it has the advantage that measurements are made under air-free conditions.

BALTIMORE, MARYLAND

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

# A STUDY OF VAPOR PRESSURES IN SMALL CAPILLARIES. PART I. WATER VAPOR. (A). SOFT GLASS CAPILLARIES[1,2]

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## Introduction

When a liquid bounded by a curved surface is in a state of tension, the pressures on each side of the surface layer are not equal. The pressure on the concave side of the surface is greater than that on the convex. When such a system is in a state of equilibrium we know from the laws of mechanics that the algebraical sum of the work done by these forces when the body undergoes a small displacement is zero. This pressure difference as deduced on the basis of the well-known theory of Laplace, in the case of a sphere of radius $r$, is given by the equation

$$p = \frac{2\sigma}{r} \tag{1}$$

where $\sigma$ is the surface tension.[3]

Suppose we have a capillary dipped into a liquid contained in a large vessel. At the plane surface, since the radius of curvature is infinite, the pressure difference, $p$, is zero. On the other hand, at the concave side of the meniscus

$$p = \frac{2\sigma}{r} \tag{2}$$

$r$ being assumed to be equal to the radius of the capillary. Since the vapor pressure of the liquid in the capillary is lower than the vapor pressure of

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[1] In memory of Ira Remsen.

[2] The substance of this paper was presented by the author to the Board of University Studies of the Johns Hopkins University as part of the requirement for the degree of Doctor of Philosophy.

[3] "Scientific Papers," Vol. II, p. 564, by Clerk Maxwell.

the liquid over the plane surface, we may look upon the surface layer in the capillary as upon a semi-permeable membrane on which it is necessary to impose a pressure, $p$, in order to produce the above lowering of the vapor pressure.

The relationship between the pressure, $p$, and the vapor pressure, $P$, is expressed by the equation of Willard Gibbs

$$-\frac{dP}{dp} = \frac{v}{V} \tag{3}$$

which states that the change of vapor pressure, $P$, with respect to the pressure, $p$, is equal to the ratio of the molar volumes of the substance in the liquid state, $v$, and the gaseous state, $V$.

Assuming that at low pressures the gas laws hold, we obtain by substitution in Equation 3 and subsequent integration

$$\ln P = -\frac{v}{RT}p + C \tag{4}$$

When $p$ is zero, that is, in the case of a plane surface, the vapor pressure is $P_0$, and

$$C = \ln P_0 \tag{5}$$

Substituting in the above, we get

$$\ln P = -\frac{v}{RT}p + \ln P_0 \tag{6}$$

or

$$\ln \frac{P}{P_0} = -\frac{V}{RT}p \tag{7}$$

Combining with Equation 1, we obtain the expression

$$\ln \frac{P}{P_0} = -\frac{V}{RT}\cdot\frac{2\sigma}{r} = -\frac{2\sigma v}{RTr} \tag{8}$$

which is the well-known equation first deduced by Lord Kelvin,[4] where $P_0$ and $P$ are the vapor pressures over the plane and concave surfaces, respectively, at temperature $T$, $R$ is the universal gas constant, $\sigma$ is the surface tension and $v$ and $r$ are as indicated above.

Laplace in his monumental work on capillarity assumes that the forces that give rise to capillary phenomena are "insensible for sensible distances, and sensible for insensible distances," that is, as far as surface tension is concerned, its value would be the same for small drops, or liquids in small capillaries, as for liquids in bulk. Thus surface tension would begin to undergo a change only when the radius of the drop or the capillary would approach the range of influence of molecular forces, which he assumed to be the same for all substances. This led many experimenters to measure the radius of molecular forces.

Plateau[5] observed the thickness of soap bubbles and concluded that the

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[4] Sir W. Thomson, *Phil. Mag.*, [4] **42**, 448 (1871).

[5] Plateau, "Statique experimentale et theorique des liquides."

range is not larger than $0.056\mu$. Drude's[6] observations assign a value of $0.009\mu$, while Reinold and Rucker[7] give about $0.006\mu$.

Quincke,[8] using a different method, measured the range to be about 0.05 and $0.08\mu$.

Here it is noteworthy to mention that Plateau also observed that the viscosity of the surface layer in thin films is different from that of the interior of the liquid, and that this viscosity change varies in sign with different liquids, a fact that would justify us in doubting whether the above values correspond to the magnitude of the range of molecular forces in the interior of the liquid.

In light of the above discussion of the fundamental assumptions of Laplace and the experimental facts concerning thin films, it would appear that the surface tension term in Equation 8 is constant and does not depend on the radius of the capillary, but this conclusion is not in conformity with many experimental facts and certain theoretical considerations that will follow.

Patrick and Eberman[9] in correlating the extensive work of the former and his collaborators on adsorption by silica gel from both liquid and vapor phases, express the internal volume of a gram of gel by the equation

$$V = Kr^{1/n} \tag{9}$$

since adsorption by silica gel is caused by the capillaries in the adsorbent. By combining this equation with Equation 8, they eliminate $r$ and get a relationship between volume adsorbed, $V$ and the equilibrium pressure, $P$. Calculating $r$ from Equation 8 they plot $V$ against the radius for many substances. They state "it is obvious that if we plot radius as found by Equation 8 against ($V$) as measured, we should obtain a parabolic curve which should be the same for all substances adsorbed by the same sample of gel whether from the gas or from solution—regardless of temperature. For, if adsorption consists in capillary condensation, the same volume of internal gel space must hold the same volume of liquid regardless of circumstances."

The curves that they obtain for water, sulfur dioxide at different temperatures and butane are parabolic but do not coincide. After a consideration of such factors as density and molecular weight that figure in Lord Kelvin's equation and also the possibility of polymerization, they come to the conclusion that "the surface tension of a liquid is a function of curvature; that a liquid existing in small drops has a much lower surface tension than ordinarily, and that the liquid has a much greater surface tension if its surface is highly concave. . . ."

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[6] Drude, *Wied. Ann.*, **43**, 158 (1891).

[7] Reinold and Rucker, *Phil. Trans.*, **177**, Part II, 627 (1886).

[8] Quincke, *Pogg. Ann.*, **139**, 1 (1870); **160**, 371 (1877).

[9] Patrick and Eberman, *J. Phys. Chem.*, **29**, 220 (1925).

Patrick, Preston and Owens[10] studied the adsorption of carbon dioxide at several temperatures by silica gel, expressing the adsorption equilibrium by the equation

$$V = K\left(\frac{P\sigma}{P_0}\right)^{1/n} \tag{10}$$

where $V$ is the volume adsorbed, $P_0$ the saturation pressure and $P$ the equilibrium pressure, and $K$ and $n$ are constants dependent upon the sample of gel used. Plotting log $V$ against log $(P\sigma/P_0)^{1/n}$, they get a straight line, where $(1/n)$ is the slope of the curve and $K$ the intercept on the log $(P\sigma/P_0)^{1/n}$ axis. They find that only when the surface tension term $\sigma$ varies are they able to have the curves at the various temperatures coincide, that is, to get the same value for $K$. They also deduce that the change of $\sigma$ with the radius is greater at higher temperatures, that is, $d\sigma/dr$ is also a function of temperature. Further evidence as to the increase of surface tension with the decrease of the radius of the capillary is given by the reported changes in physical properties of liquids such as freezing point, critical temperature and density.

F. W. Parker[11] observed a depression of the freezing point of water, benzene and nitrobenzene when contained in capillary systems. Plotting liquid content against freezing-point depression, he obtained curves showing a gradual increase in depression with decrease in liquid content—in other words, with decrease of capillary radius—in case of the latter two liquids, and a rather steep curve indicating an enormous increase in depression with decrease of liquid content in case of water.

Bouyoucos and McCool[12] ascribe this phenomenon mainly to the dissolved impurities. While this cannot be true of benzene and nitrobenzene, it is surely the case with water; for, if we consider the phase diagram of the system, water and ice, we notice that the equilibrium curve is inclined toward the pressure axis, that is, the temperature increases with decrease in pressure and, inasmuch as the water in a capillary system is under a negative pressure, we should expect a rise in the freezing point.

A. S. Coolidge,[13] similarly, finds that the adsorption isotherm for benzene is continuous when the free liquid is below the freezing point, that is, the adsorbed material is in a liquid state even below the freezing point of the free liquid.

Patrick, Preston and Owens[10] observed no break in the adsorption of carbon dioxide and nitrons oxide between the temperatures 30° and 40°, thus indicating a rise in the critical temperature of the adsorbed substance. The significance of the above phenomena is very well pointed

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[10] Patrick, Preston and Owens, *J. Phys. Chem.*, **29**, 421 (1925).

[11] Parker, THIS JOURNAL, **43**, 1011 (1921).

[12] Bouyoucos and McCool, *Mich. Agr. Expt. Sta. Tech. Bull.*, **1915**, 24; **1917**, 31.

[13] Coolidge, THIS JOURNAL, **46**, 596 (1924).

out by Patrick and Eberman,[9] "if condensation of a gas *does* take place in a capillary above the critical temperature and, in other cases, at pressures always below the saturation pressure; and, if adsorption *does* take place from liquids above the critical solution temperature—it follows that the critical temperature for a fluid in a capillary is higher. If the critical temperature is higher, the surface tension must be correspondingly higher, inasmuch as the temperature–surface tension curve cuts the temperature axis at or near the critical temperature."

Leslie[14] was the first to show that the rise of a liquid in a capillary was due to the greater pressure in the stratum of liquid adhering to the wall. The direct result of the excess pressure normal to the side of the tube would be to spread the liquid over the surface of the solid. When we plunge a capillary into a liquid, the above pressure would cause the liquid to spread and cover all the surface of the tube were it not for the liquid adhering to the ascending film and balancing the pressure and in this way stopping further wetting of the solid. We may look upon this tendency to spread as a result of a negative pressure or a tension in the film, which is balanced in case of a capillary open at both ends. Were we to prevent by some method some liquid from adhering to the ascending film, the pressure would remain unbalanced, unless the tension in the adhering film increases. This is precisely the condition existing in a capillary closed at one end and partly filled with liquid. It is obvious that the tension would increase with decreasing radius. This theory was expressed by W. A. Patrick[15] as follows, "a film of molecular thickness may have the same surface tension as the liquid in bulk, but when this film is stretched, it is certain that such an operation will cause, according to the principle of Le Chatelier, an increase in the surface tension of the liquid film." Independently and from different considerations Freundlich[16] arrives at the same conclusions.

## Experimental

Let vessel A containing a capillary be in communication with vessel B containing some aqueous solution, and let us assume that the water vapor has wetted the walls of the capillary. If the vapor pressure of the solution is greater than the vapor pressure of pure water in the capillary, the vapor will condense and fill up the capillary. Now, if we concentrate by some method the solution in B until its vapor pressure is lower than the vapor pressure of pure water in the capillary, the process will be reversed and evaporation of the water in the capillary will take place. The condition under which no evaporation from or condensation into the capillary will take place will indicate a state of equilibrium at which the vapor

[14] Leslie, *Phil. Mag.*, **14**, 193 (1802).

[15] Patrick, *Kolloid-Z.*, **36**, 276 (1925).

[16] Freundlich, "Kapillarchemie," Akademische Verlagsges., Leipzig, **1922**, p. 63.

pressure of the pure water in the capillary is equal to the vapor pressure of the solution.

To attain a state of equilibrium by trying solutions of various strengths would be rather tedious and time consuming. Furthermore, it would involve a complication in the temperature control, since the attainment of an equilibrium state would extend over a period of hours beyond the constancy of any temperature regulating device.

This difficulty may be overcome by measuring the rate of condensation or evaporation. If we start with a dilute solution whose vapor pressure is known and which is higher than the vapor pressure of pure water in the capillary, vapor will condense into the capillary with a rate proportional to the vapor pressure difference, $\Delta p = p_1 - p_2$, where $p_1$ is the vapor pressure of the solution and $p_2$ that of water in the capillary. For a given capillary $p_2$ is constant. By concentrating the solution we decrease $p_1$ and simultaneously $\Delta p$, and also the rate of condensation. If we continue to concentrate the solution we may reach values for $p_1$ which will be lower than $p_2$, $\Delta p$ being negative. In such cases we measure the rate of evaporation from the capillaries. Now, if we plot these values of $\Delta p$ against the rate we get a curve that approaches assymptotically the rate axis from two directions. By extrapolation we may evaluate the point of equilibrium when $\Delta p = 0$ and $p_1 = p_2$. Since $p_2$, the vapor pressure of pure water in a given capillary, is constant, we plot $p_1$ against rate and the extrapolated value will be $p_1$ when $\Delta p = 0$, that is, it will give us the value for $p_2$.

In a system completely freed from air the rates of condensation or evaporation are measurable quantities, as it was shown in the course of this experiment. The vapor pressure was not measured directly. It was calculated from the measured concentration as determined by conductivity. For this reason we have used potassium chloride solutions whose vapor pressures for a wide range of concentrations have been very accurately measured in this Laboratory by Frazer, Lovelace and Sease.[17] For calculations of the vapor pressures of very dilute solutions we have also used the freezing point data collected by Noyes and Falk.[18]

## Apparatus

The apparatus as shown in the accompanying Fig. 1 is merely an elaborated form of the simple scheme we have discussed in the previous section.

It is made of soft glass. The two bulbs A and B serve as reservoirs of pure water; their capacity is 500 cc. each. To one of the bulbs is attached a side arm, C, through which the liquid is introduced. The tube connecting the water reservoir with the rest of the apparatus is surrounded by a water jacket, D, to keep the liquid from spreading over the apparatus when it is distilled from one bulb into the other.

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[17] Frazer, Lovelace and Sease, THIS JOURNAL, **43**, 102 (1921).

[18] Noyes and Falk, *ibid.*, **32**, 1020 (1910).

The rest of the apparatus consists of three branches. One branch connects (through the mercury trap F) the water reservoir with the conductivity cell E, designed for the purpose of measuring the change in conductivity of the pure water from time to time during the course of the experiment. The second branch connects the water reservoir, through the mercury traps, G, H and K, with the conductivity cell L, containing the potassium chloride solution. This cell is in communication with the mercury reservoir N, and the mechanical stirrer, O, designed to stir the solution. The third branch connects through the mercury traps, G, H and R, the water reservoir with the vessel, S, containing the capillaries. The capillaries may be brought in contact with the solution by closing trap H and opening the traps, K and R. The trap T connects or disconnects the whole apparatus, or each branch individually, with or from the mercury diffusion pump, J, and the auxiliary Cenco high vacuum pump (not shown on the diagram).

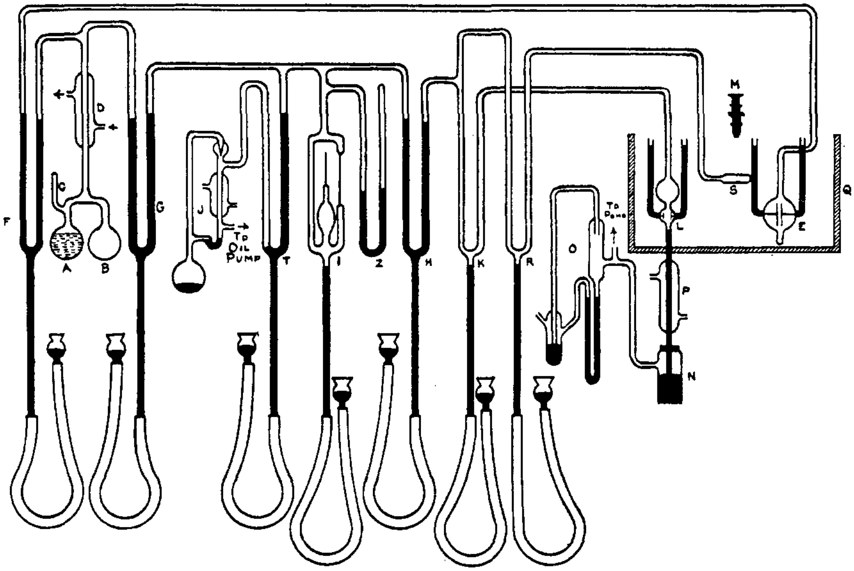

Fig. 1.

I and Z are a McLeod gage and a closed manometer, respectively. The vessels, L, S, and E are immersed in an accurately regulated thermostat, Q. The filling or the emptying of the capillaries is observed through the microscope, M, whose objective is an inch and a half below the surface of the water in the thermostat. The field is illuminated by a 150-watt lamp whose rays are made to pass through a vessel filled with water to absorb the heat rays, and then brought to a focus at a point on the capillary under observation by a system of lenses.

## Capillaries

If we calculate from Equation 8, deduced by Lord Kelvin, the percentage lowering of the vapor pressure of water due to capillarity, we notice that the lowering is inappreciable until we approach the magnitude of $1 \times 10^{-4}$ cm. for the radius of the capillary. As seen from Table I the percentage lowering increases very rapidly with decrease of radius.

TABLE I

CHANGE IN PERCENTAGE LOWERING

| $r$, cm. | $1 \times 10^{-4}$ | $0.8 \times 10^{-4}$ | $0.6 \times 10^{-4}$ | $0.4 \times 10^{-4}$ | $0.2 \times 10^{-4}$ | $0.1 \times 10^{-4}$ |
|---|---|---|---|---|---|---|
| $100\Delta p/p_0$ | 0.01 | 0.14 | 0.18 | 0.27 | 0.53 | 1.06 |

Although a more pronounced effect in the lowering of the vapor pressure was expected, we were certain to have to work in about the same region of magnitudes. Furthermore, the capillaries had to be uniform in bore for a considerable length.

The method devised for producing such capillaries proved to be very successful. It consists of a string supported by two pulleys attached to the ceiling; on one end of the string a weight is hung and the other end is fastened to the top of a short length of capillary tubing of about 0.5mm. diameter. This tubing is clamped to the table top.

When a small area of the tube is heated up to a bright red heat the weight is allowed to fall, thus drawing out the heated portion of the tube to 4 meters—the distance between the table top and the ceiling.

The burner used in heating the tube consisted of a terra cotta cylinder with six evenly distributed perforations normal to the walls. Glass tubes with fine jets at one end are placed in these perforations in such a manner that the jets point toward the center of the cylinder. The ends that protrude outside the cylinder are connected by means of T-tubes, producing the effect of a wheel. A mixture of gas and air introduced into these jets produces a very intense and fine circular flame. The smallest capillary we have been able to draw by this method had a radius of $0.25\mu$.

## Microscopic Measurements

The bore of the capillaries was measured microscopically. For capillaries ranging between 1 and $4\mu$ in radius a combination of lenses giving a magnitude of about 900 is sufficient. Such a magnification was obtained by using a fluorite objective of focal length 2.6 mm. and initial magnification of 70 in combination with a filar screw micrometer eyepiece of a magnification of 12.5, giving a total magnification of 875 times.

The filar screw micrometer has been calibrated against an objective micrometer divided into 0.01 mm. Knowing the number of divisions on the eyepiece micrometer that correspond to one division on the objective micrometer, we may replace the latter by a capillary and determine its size.

The hollow of a capillary tube when observed under a microscope appears black at the sides of the wall and shades off into a gray toward the center of the capillary when the hollow is filled with a gas or a vapor. In case the capillary is filled with a liquid, the hollow appears bright and bounded by very thin black lines at the interface of the liquid and the glass.

## Thermostat

The thermostat as shown in Fig. 1 contained the two cells and the capillary vessel. The former were in the main body of the thermostat; the latter was placed in a chamber projecting out at the side and in full communication with the rest of the thermostat. The projecting side chamber had a window through which the capillaries were illuminated.

The water in the thermostat was agitated by two stirrers symmetrically placed. The heating device was made up of two 150-watt Westinghouse heating lamps, and water running through a copper coil was used for cooling the thermostat.

The thermo-regulator was of the toluene–mercury type. It consisted of twenty feet of half-inch copper tubing coiled into a helix nine inches in diameter, filled with toluene and sealed to a glass head. The temperature of the thermostat was kept at 18° as read from Bureau of Standards thermometer No. 31091.

The constancy of the temperature was read from two Beckmann thermometers graduated in 0.001°. One was placed near the solution cell and the other near the capillary vessel. The thermometers indicated a temperature lower by 0.003° at the solution cell. This was probably due to the fact that the solution cell was nearer to the cooling coil than the capillary vessel. For any one portion of the thermostat the temperature remained constant to 0.002° for over ten hours.

## Observations

It was noted quite early in the course of the experiment that the condition of freeing the system of air was essential. Air present in the system clogged the capillaries and interfered with the formation of a uniform unbroken column of liquid. A capillary column formed under such conditions was invariably made up of a chain of intermittent air and water layers. As the system was made more air-free, this effect was minimized but even a slight trace of air remaining in the system was sufficient to cause the formation of broken columns of water.

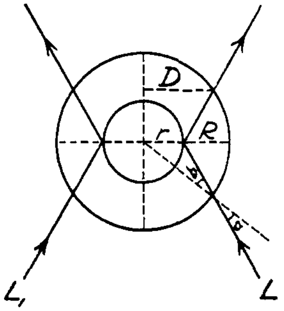

Fig. 2.

Although the above phenomenon prevented the measuring of the rate of condensation or evaporation, it did not interfere with the process of condensation *per se*.

**Experiment I.**—The capillary chamber was filled with water vapor by bringing it into communication with the water reservoir for a moment. The chamber was closed and allowed to stand for several hours until the capillaries were filled. The chamber was opened to the potassium chloride solution by closing trap H and opening traps K and R. The five capillaries were observed for several hours; no evaporation from any one occurred.

The chamber and the concentration cell were discommunicated, and the conductivity of the solution determined after the solution in the cell was thoroughly stirred. To verify the observation the process was reversed. The capillary chamber was evacuated and brought into communication with the solution cell by adjusting the traps as above. The capillaries seemed to fill up slowly. They were left in this condition for several hours until they filled up completely. Then they were discommunicated and the conductivity of the solution measured again.

TABLE II

MEASUREMENTS

$X = 30.2$; $(\Lambda_0 - \Lambda) = 17.5$; Concn. $= 0.11$; $(P_0 - P_1)_X = 0.055$

| Capillary | I | II | III | IV | V |
|---|---|---|---|---|---|
| $r$ ($\mu$) | 1.076 | 2.284 | 2.443 | 3.019 | 4.052 |
| $(P_0 - P_1)_K$ | 0.015 | 0.007 | 0.007 | 0.0056 | 0.004 |

Table II gives the observed measurements of the radii, $r$, of the capillaries; $X$, the resistance of the solution, $(P_0 - P_1)$ the vapor pressure lowering corresponding to the measured resistance, $X$, and $(P_0 - P_1)_K$ the vapor pressure lowering as calculated from the equation of Lord Kelvin.

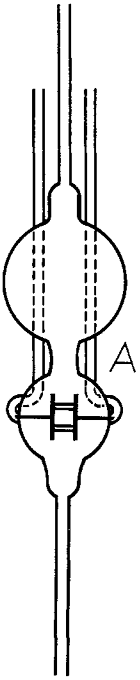

Fig. 3A.

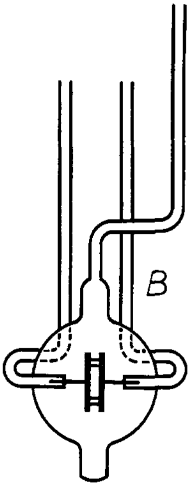

Fig. 3B.

**Experiment II.**—The solution in the cell was concentrated by bringing the latter into communication with the reservoir which was subjected to an ice-bath. When the resistance indicated a concentration of about 0.13–0.14 $N$, the concentrating process was stopped.

The capillaries were allowed to fill up in a manner similar to Experiment I. When they were brought in contact with the solution, no signs of evaporation were observed. When the reverse process was carried out the capillaries filled up. Table III records the measurements of this experiment.

**Experiment III.**—The solution was still further concentrated, and the experiment carried out as before. The data of this experiment are given in Table IV.

**Experiment IV.**—When the solution was concentrated still further and the full capillaries were opened to the solution, Capillary V began to vaporize. The others did not show any change. When the procedure was reversed, Capillaries, I, II, III and IV filled up, but Capillary V remained empty. This observation was reproduced twice. Table V gives the data of this observation.

TABLE III

MEASUREMENTS

$X = 26.9$; $(\Lambda_0 - \Lambda) = 18.45$; Concn. $= 0.12$; $(P_0 - P_1)_X = 0.060$

| Capillary | I | II | III | IV | V |
|---|---|---|---|---|---|
| $r$ ($\mu$) | 1.076 | 2.284 | 2.443 | 3.019 | 4.052 |
| $(P_0 - P_1)_K$ | 0.015 | 0.007 | 0.007 | 0.0056 | 0.004 |

TABLE IV

OBSERVATIONS

$X = 23.4$; $(\Lambda_0 - \Lambda) = 19.35$; Concn. $= 0.148$; $(P_0 - P_1)_X = 0.074$

| Capillary | I | II | III | IV | V |
|---|---|---|---|---|---|
| $r$ ($\mu$) | 1.076 | 2.284 | 2.443 | 3.019 | 4.052 |
| $(P_0 - P_1)_K$ | 0.015 | 0.007 | 0.007 | 0.0056 | 0.004 |

TABLE V

OBSERVATIONS

$X = 18.1$; $(\Lambda_0 - \Lambda) = 20.95$; Concn. = 0.183; $(P_0 - P_1)_X = 0.092$

| Capillary | I | II | III | IV | V |
|---|---|---|---|---|---|
| $r$ ($\mu$) | 1.076 | 2.284 | 2.443 | 3.019 | 4.052 |
| $(P_0-P_1)_K$ | 0.015 | 0.007 | 0.007 | 0.0056 | 0.004 |

Further concentrating of the solution was not advisable since the higher limit of the range of the conductivity cell had been exceeded already.

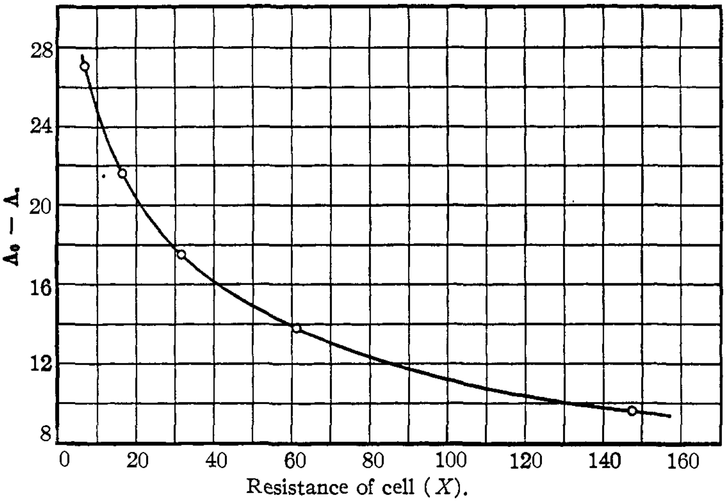

Fig. 4.

The values in Tables II, III, IV and V were obtained in the following manner. Knowing $X$ and $\Lambda_0$ which is 129.5, the value for $\Lambda$ was read from Fig. 4. Substituting these values, and also the relative viscosity read from Fig. 5, in the equation of Bates, the concentration was obtained. $(P_0 - P_1)_X$ was read from Fig. 6. The value for $(P_0 - P_1)_K$ was calculated from Lord Kelvin's equation.[19]

Since $V = M/D$, where $M$ = mol. wt. and $D$ = density

$$\log \frac{P_1}{P_0} = -\frac{0.4343 \times 2\sigma M}{RT\,\mathrm{d}\,r} = \frac{-0.4343 \times 2 \times 73 \times 18.016}{8.32 \times 10^7 \times 291 \times 0.99862 \times 1.076 \times 10^{-4}} = 0.00044$$

$$\log P_1 = \log (P_0) - 0.00044 = \log (15.477) - 0.00044 = 1.18925$$

$$P_0 - P = 0.015 \text{ mm. of mercury.}$$

Although we have not as yet been able to determine quantitatively the vapor pressure lowerings corresponding to each capillary, we have definitely established that the lowering is enormously greater than can be accounted for by Lord Kelvin's equation.

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[19] Calculation: $\ln \frac{P_1}{P_0} = -\frac{2\sigma V}{RTr}$, or $\log \frac{P_1}{P_0} = -\frac{(0.4343)(2\sigma V)}{RTr}$.

Experiment IV also indicates an approximate value for the lowering of the vapor pressure in a capillary of about $4 \times 10^{-4}$ cm. in radius.

According to the classical equation, the vapor pressure lowering for a capillary of $4.052\mu$ in radius is 0.004 mm. of mercury. The value we have obtained is approximately 0.092 mm. of mercury, 23 times as great.

Now, if we consider for a moment Equation 8 we see that its right-hand member contains two terms, $\sigma$ and $V$, surface tension and molal volume, respectively, properties of liquids that would be different in a capillary from liquid in bulk. Which term must be changed in order to account for the enormous increase in the term $\ln (P_1/P_0)$? While it is possible that the molal volume $V$ would be increased due to the decrease in density, it is highly improbable that the decrease in density would assume such magnitudes. The increase in the left-hand term must therefore be due *mainly* to the increase in the surface tension term, $\sigma$.

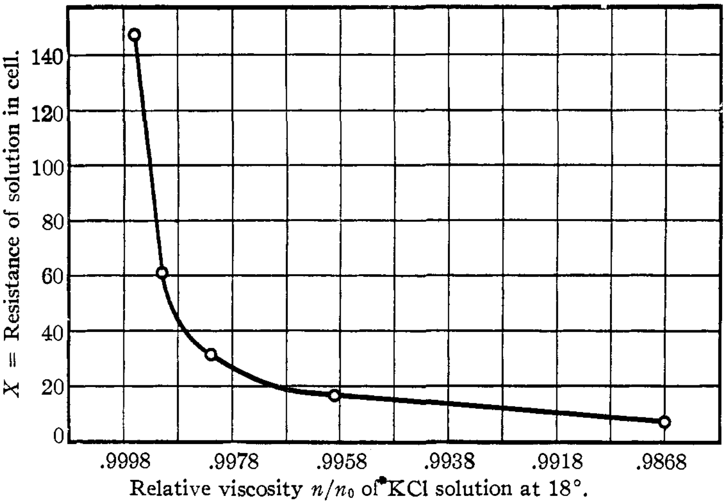

Fig. 5.

## (B). Quartz Capillaries

If the depression of the vapor pressure in a given capillary is due to capillarity alone, then the rate of evaporation into a solution of a given concentration should stay constant irrespective of time. It was found, however, that in case of capillaries made of soft glass the rate of evaporation into a solution of a given concentration became smaller and smaller with time, the measurements being taken at one hour intervals. This indicated that the pressure became less and less. Since the solution was kept at the same concentration, the vapor pressure of the water in the capillary must have become lower. The latter could be due only to the solubility of the glass. In order to eliminate the effect of solubility mentioned above, it was decided to make similar studies in which the glass capillaries should be replaced by capillaries made of pure quartz.

## Method

The apparatus was essentially the same as described in the foregoing work with the exception of the observing instrument, which consisted of a microprojector with a scale in the eyepiece instead of a microscope.

The procedure was to open a full capillary to the vapor of a concentrated solution of potassium chloride and observe the time required for a definite length of the water column in the capillary, as read on the scale in the eyepiece, to evaporate.

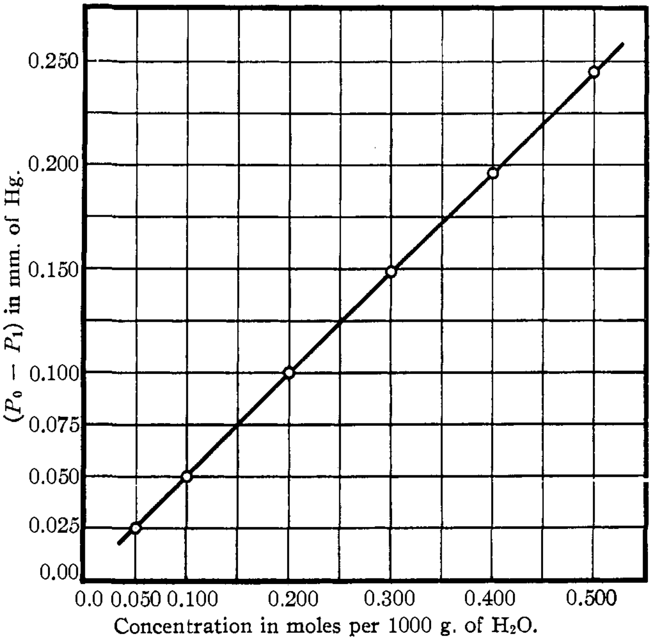

Fig. 6.

For a given capillary the rate of evaporation is proportional to $\Delta p$, the pressure difference between that of water in the capillary and the potassium chloride solution. Having obtained various rates corresponding to different concentrations of the solution, a curve was plotted of rate against $\Delta p$. The intercept on the $\Delta p$-axis will be the depression of the vapor pressure in the capillary.

## Quartz Capillaries

These capillaries were drawn by the same method as described previously for the production of soft glass capillaries. Their size had been measured by means of a microscope supplied with a filar screw micrometer, and the true size calculated by using the approximate formula $r = D/n$, where $D$ is the apparent radius and $n$ the refractive index of the quartz.

Table VII gives the rates of evaporation from a capillary 5.51$\mu$ in radius, the corresponding concentrations of the potassium chloride solution and the lowering of the vapor pressure $P_0 - P_1$ where $P_0$ is the vapor pressure of water and $P_1$ is that of the solution.

TABLE VI

DATA WITH QUARTZ CAPILLARY

$r = 5.51\mu$ $t = 18°$

| Expt. | Rate, mean value | Soln., $N$ | $\Delta p = P_0 - P_1$, mm. Hg | Date of expt. |
|---|---|---|---|---|
| 1 | 562 | 0.4105 | 0.205 | Jan. 10 3 P.M. |
| 2 | 284 | .2154 | .109 | Jan. 6 4 P.M. |
| 3 | 276 | .2154 | .109 | Jan. 7 2 P.M. |
| 4 | 235 | .1815 | .092 | Jan. 8 11 A.M. |
| 5 | 181 | .1440 | .074 | Jan. 7 8 P.M. |
| 6 | 179 | .1345 | .068 | Jan. 11 3 P.M. |
| 7 | 155 | .1090 | .056 | Jan. 12 11 A.M. |
| 8 | 127 | .0930 | .048 | Jan. 11 8 P.M. |
| 9 | 97 | .0785 | .041 | Jan. 12 2 P.M. |
| 10 | 93 | .0690 | .036 | Jan. 13 11 A.M. |

In the above table we observe that although there is a lapse of time of twenty-two hours between Measurements 2 and 3, there is a very slight change in the rate, showing that the solubility of the quartz is insignificant. When we plot the rate against $\Delta p$, a straight line is obtained which cuts the $\Delta p$-axis at 0.05 mm. of mercury. This means that at zero rate, when no evaporation takes place, that is, when the vapor pressure of the solution is equal to the vapor pressure of the water in the capillary, the depression is equal to 0.005 mm. of mercury.

The value calculated by means of Lord Kelvin's equation

$$\ln \frac{P_1}{P_0} = -\frac{2\sigma M}{RT\,\mathrm{d}r}$$

is equal to 0.004 mm. of mercury.

TABLE VII

OBSERVATIONS

$r = 2.07\mu$; $t = 18°$

| Expt. | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| Rate, mean value | 471 | 340 | 288 | 270 | 213 | 144 | 78 |
| Soln., $N$ | 0.4285 | 0.3508 | 0.3585 | 0.2982 | 0.2780 | 0.2304 | 0.1890 |
| $\Delta p = P_0 - P_1$, mm. Hg | 0.216 | 0.175 | 0.179 | 0.154 | 0.140 | 0.116 | 0.096 |

The curve derived from the data given in Table VII cuts the $\Delta p$-axis at 0.068 mm. of mercury, thus indicating that the depression of the vapor pressure in a capillary 2.07$\mu$ in radius is 0.068 mm. of Hg.

The straight line does not run parallel to the one for the larger capillary considered above but recedes from the rate axis with time, showing a slight solubility effect increasing with age of the capillary, that is, with the time the capillary is in contact with water. The value calculated by means of Lord Kelvin's equation for this capillary is 0.08 mm. of mercury.

In conclusion, the author wishes to express his appreciation to Dr. W. A. Patrick, who suggested this research and under whose supervision it was performed. He is also indebted to Dr. J. C. W. Frazer for his interest and advice rendered during this investigation.

## Summary

1. A method is described for measuring vapor pressures of liquids in small capillaries.

2. By means of this method it has been established that the vapor pressure lowering of water in small capillaries is much greater than can be accounted for by Lord Kelvin's equation.

3. It is shown that the greater lowering of the vapor pressure is due to the increase in surface tension.

BALTIMORE, MARYLAND

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

# A STUDY OF VAPOR PRESSURES IN SMALL CAPILLARIES. PART II[1]

BY J. L. SHERESHEFSKY

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Paper I dealt with the direct measurement of vapor pressures of water in glass and quartz capillaries. It was found that in case of capillaries made of thermometer glass the lowering of the vapor pressure was abnormally great. It was first suspected and afterward shown that a great fraction of this lowering was due to the solubility of the glass. From this point the work proceeded with quartz capillaries. The quartz from which the capillaries were drawn was obtained from the General Electric Company and was of the highest purity. The lowerings of vapor pressure in this case were smaller than before, but still abnormally greater than can be accounted for by the Lord Kelvin equation.

There may or may not be any solubility effect in the case of quartz, but when the ratio of the surface to the volume in the capillaries we were dealing with is considered, any negligible solubility may assume considerable importance. Therefore, a non-polar liquid was employed, such that a solubility effect cannot reasonably be involved.

## Apparatus

The method of measuring the depression of the vapor pressure and the underlying theoretical considerations are fully discussed in the first paper. Certain changes and

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[1] In memory of Ira Remsen.