

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<sup>1</sup>

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

<sup>1</sup> In memory of Ira Remsen.

improvements in the original apparatus, necessitated by the use of the organic liquid, are described below. Referring to the diagram of the original apparatus, vessel L was substituted by a cylindrical vessel of 200-cc. capacity, provided with a magnetic stirrer. There was no need for vessel E and trap F; they were therefore eliminated. The bulbs A and B, serving as a means for removing the dissolved air and as a reservoir for the liquid, were substituted by a vessel shown in the accompanying Fig. 1. This proved less troublesome and much more efficient in freeing the liquid from the last traces of air. It was operated by means of a suction interrupter similar to the one designated by O. When the water pump diminishes the pressure over the mercury in the reservoir, the column of mercury, over which the liquid in the lower bulb rests, falls and allows the liquid to fill up the small side bulb; when the suction is broken by the interrupter, the column of mercury rises to its original height, fills the side bulb with mercury and pushes the liquid into the upper bulb filled with glass beads. The spreading of the liquid in such a manner over a large surface facilitates the removal of the dissolved gases. Many repetitions of this procedure, followed by pumping, removed the last traces of air in the course of several days.

This apparatus used for the removal of air is essentially that devised by Dr. R. K. Taylor of this Laboratory in connection with the study of the vapor pressure of alcoholic soap solutions made by Dr. R. D. Drinkard, the results of which are to be published later.

In order to transfer desired amounts of liquid from vessels A and B into vessel L, calibrated bulbs of various sizes were sealed into the apparatus between traps T and H. By opening trap G and cooling one of these calibrated bulbs with an ice-water mixture, a desired volume of toluene was obtained. In closing trap G and opening trap K, the liquid was transferred by evaporation into the solution vessel L.

**Microprojector.**—The capillary was placed in a vertical position and observations were made upon it by means of a microprojector. This optical system consisting of a microscope in a horizontal position, and a low power objective placed between the object and the microscope so as to produce a real image in the focus of the microscope, was a great improvement upon the original method. The whole system was rigidly mounted on a slow motion stand to allow observations of various

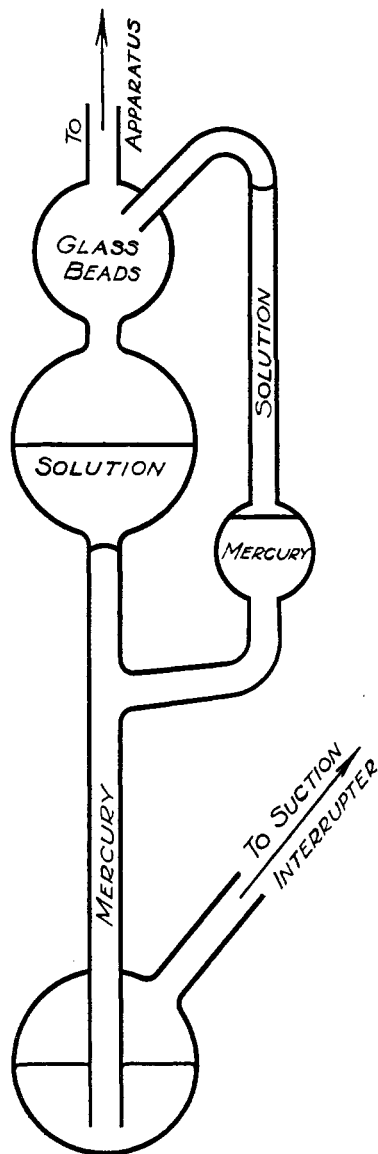


Fig. 1.

points along the length of the capillary. This arrangement has been utilized already in part of the work presented in the first paper, namely, the work on quartz capillaries.

**Thermostat.**—The temperature control was of utmost importance, and to obtain a fairly constant temperature for a considerable time very sensitive regulating devices were used. The thermo-regulator consisted of a coil of 50 feet of  $\frac{3}{8}$ -inch copper tubing filled with toluene. The electrical circuit was so arranged that sparking at the point of contact between the tungsten needle and the mercury was eliminated.<sup>2</sup>

Since the temperature maintained was below that of the room, a device was introduced that controlled the amount of cooling water passing through the cooling coil. This device shut off the cooling water when the heating unit was on and *vice versa*. It consisted of a long piece of heavy wire suspended vertically and fastened at the upper end to the circuit breaker of a strong relay, the coils of which were connected in series with those of the main relay. The lower end of the wire carried a rubber stopper cut to seat securely in the mouth of the cooling water pipe leading to the thermostat. This pipe was mounted in a wide glass tube provided with two side tubes, one near the bottom and above the mouth of the pipe serving as the water inlet, the other near the top as the overflow. By manipulating this device in conjunction with the heating unit, conditions were such that the latter went on and off every fifteen seconds for more than twelve hours.

Under these conditions two Beckmann thermometers, one graduated in  $0.002^\circ$  and the other in  $0.001^\circ$ , showed fluctuations not greater than  $0.0015^\circ$ . The temperature of the thermostat was maintained at  $20^\circ$ ; at this temperature the vapor pressure of toluene is 21.60 mm. of mercury. Therefore, the fluctuation in the temperature corresponds to a change of the vapor pressure not greater than 0.0021 mm. of mercury.

In testing various parts of the thermostat by means of a constantan-iron thermopile connected to a galvanometer of 12,400 megohms resistance, a temperature gradient was detected between the part of the thermostat containing the solution vessel and the side compartment holding the capillary. These gradients are established by the currents caused by the stirrer and it was found that changing the direction of stirring reversed the direction of the temperature gradient. Thus, by stirring downward the compartment containing the capillary was colder than the one containing the solution vessel, and by stirring upward the conditions were reversed. Inasmuch as condensation of toluene vapor on the walls of the chamber containing the capillary was to be prevented, the thermostat was stirred upward.

**The Solution.**—The question of finding the proper solute was a perplexing one. Since Raoult's law was to be used in calculating the vapor pressure of toluene solutions, our first requirement was that the compound to be used as the solute should have as close a relation to the solvent as possible, that is, it should form a mixture close to the ideal. The second requirement was that it should have a high boiling point, so that its partial pressure in a saturated solution would be negligible. Third, it should be fairly soluble in toluene and, lastly, the compound should be stable in solution. Although the second and third demands are inversely related, we were inclined to compromise in favor of the second. Usually a compound related to benzene or toluene that satisfies the first and second requirements is unstable and sensitive to light. After a long search and many trials *p*-diphenylbenzene was selected. Its melting point and boiling

<sup>2</sup> A. T. Larson, *THIS JOURNAL*, **44**, 2893 (1922).

point are 212 and 383°, respectively, and, judging from the work of Hildebrand, its solution in toluene would deviate from the ideal very slightly.

However, the low solubility of *p*-diphenylbenzene in toluene imposed limitations upon the possible range of measurements as the vapor pressure of the toluene solution is balanced against the vapor pressure of pure toluene in a capillary.

The toluene used was refluxed over sodium amalgam for twenty-four hours; this was followed by distillation, the middle fraction being retained.

The *p*-diphenylbenzene was obtained from the Eastman Kodak Company.

### Experimental

1. Manipulation of Apparatus (Radius of Capillary =  $1.10\mu$ ;  $n/(N - n) = 0.0038$ ). When vapor from the toluene reservoir was admitted into the capillary chamber, it condensed in the capillary instantaneously, that is, it shot down very rapidly from the mouth of the capillary in the form of a column. The excess liquid on the walls of the vessel (7 mm. Pyrex tubing) and on the outside of the capillary was removed by careful pumping and manipulation of the several mercury traps in the apparatus. The attainment of this condition was ascertained by lowering the mercury trap leading to the capillary so that only a slight amount of liquid near the mouth of the capillary was evaporated. If after some time the capillary did not fill up again, there was no excess liquid present. The trap leading to the solution vessel was lowered, thus bringing into communication the vapor of the solution with the vapor of the pure liquid over the capillary. The latter filled up immediately, indicating that the vapor pressure of the pure liquid over the capillary was less than that of the solution. The trap leading to the solution was then closed and the mercury in the trap leading to the capillary was slightly lowered. The liquid in the capillary began to evaporate, showing the reversibility of the process. The operation was repeated several times and each time the capillary filled completely.

The capillary is completely evacuated; that is, the liquid in it is made to vaporize and then the vessel containing the capillary is closed by means of the trap. By suitable manipulation of the mercury traps in the line leading to the solution vessel, the rest of the apparatus is filled with vapor from the solution. Upon closing off the solution vessel and lowering the mercury in the traps leading to the capillary, this vapor was greatly rarefied; the capillary did not fill up when brought in contact with the rarefied vapor. However, when the capillary was brought into direct contact with the vapor above the solution, it filled rapidly in the same manner as described above.

Similar observations were made on capillaries having radii of  $2.13\mu$ ,  $3.14\mu$ ,  $4.84\mu$  and  $5.33\mu$ . They were subjected to the same treatment as

described above, and in every instance they behaved similarly. In other words, the lowering of the vapor pressure in these capillaries was also greater than in the solution. It is worthy of note that in case of the latter two capillaries the filling was much slower and somewhat different. First, a bright spot appeared slightly below the mouth of the tube. This grew to a column of liquid apparently an inch in length (the magnification was about 1000) which then fell rapidly to the bottom of the capillary. This procedure was repeated until the capillary was not quite full. After it reached this point, the level of the liquid slowly rose until the capillary filled up.

2. **Observations (Radius of Capillary = 6.12  $\mu$ ;  $n/(N - n) = 0.0038$ ).**—The capillary was filled in the usual manner, that is, by allowing vapor from the toluene vessel to condense into it. Care was taken to remove all the excess liquid, and then it was brought into communication with the solution by opening trap K. The liquid in the capillary began to evaporate; after a few seconds the rate of evaporation was obtained by determining the time required for a desired length of the liquid, as read on the scale in the ocular, to evaporate. The operation was repeated several times, each time beginning the measurement from the same point on the capillary.

Each division in the table below corresponds approximately to about 0.0005 cm. The volume of liquid evaporated in the measured time is about  $2.4 \times 10^{-8}$  cc.

Divisions	40	40	40
Time	1 min. 20 sec.	1 min. 15 sec.	1 min. 18 sec.

This capillary was also subjected to measurements when the thermostat was stirred downward, the thermopile indicating that the compartment holding the capillary was colder than the one containing the solution. Each time it was found that the capillary was filling up at a very slow rate, requiring about a minute longer for the same volume in case of evaporation.

TABLE I  
TABULATION OF RESULTS

Solute, *p*-diphenylbenzene; solvent, toluene; temperature, 20°; vapor pressure, 21.60 mm. of Hg; density, 0.866 at 20°; surface tension, 28.56 dynes/cm.<sup>2</sup>

Expt.	Radius of capillary, 0.0001 cm.	$P/k$ in mm. Hg	$n$ moles of solute	$N$ moles of solvent	$P$ in mm. Hg	Observations
1	1.10	0.049	0.00159	0.41711	0.082	Condensation
2	2.13	.025	.00159	.41711	.082	Condensation
3	3.14	.015	.00159	.41711	.082	Condensation
4	4.84	.011	.00159	.41711	.082	Condensation
5	5.33	.010	.00159	.41711	.082	Condensation
6	6.12	.009	.00159	.41711	.082	Evaporation

In conclusion, the author wishes to express his profound gratitude to Professors W. A. Patrick and J. C. W. Frazer for their assistance in this work.

### Discussion and Summary

These results may be best summarized by a consideration of the behavior of Expt. 5. In this experiment a capillary of  $5.33\mu$  radius was exposed to a toluene solution whose vapor pressure was lowered to 0.082 mm. by the addition of a solute. It was found that liquid toluene condensed in this capillary, which would indicate that the vapor pressure of the toluene in the capillary was less than  $(21.60 - 0.082)$ . The classical theory of capillarity, however, tells us that the vapor pressure lowering of toluene at  $20^\circ$  in a tube of this radius should be only 0.009 mm. of mercury. It is therefore obvious that either our experimental work is in error or the classical theory as applied to vapor pressure in capillaries is not correct.

We believe the latter to be true and are convinced that this work has been done with sufficient care to warrant such a conclusion. At this point it may be well to add that such a view does not necessarily conflict with the thermodynamic treatment of this question. Thermodynamically the problem is simply the action of a negative pressure upon the vapor pressure of a liquid. This question is rigorously handled by the well-known relationship of Gibbs. What we have shown here is that the negative pressure in the case of small capillaries may be greater than has been assumed to be the case.

BALTIMORE, MARYLAND

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[CONTRIBUTION FROM THE CHEMICAL ENGINEERING DEPARTMENT, THE OHIO STATE UNIVERSITY]

## ZIRCONIUM. II. DETECTION OF POTASSIUM BY ZIRCONIUM SULFATE IN THE PRESENCE OF AMMONIUM IONS<sup>1</sup>

BY RUFUS D. REED AND JAMES R. WITHROW

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We have shown that zirconium sulfate can be used to detect potassium and that the test can be applied in the presence of sodium.<sup>2</sup> Ammonium ions must be eliminated prior to testing for potassium with other reagents such as sodium cobaltic nitrite, chloroplatinic acid or perchloric acid. The sensitivity of zirconium sulfate for potassium in the presence of ammonium ions was therefore investigated.

The results indicated that zirconium sulfate solution will detect 0.48 mg. of potassium in 2 cc. of reaction mixture in the presence of large amounts of ammonium sulfate. This was practically the same sensitivity of this reagent for potassium in the absence of ammonium as in the previous work.

<sup>1</sup> In memory of Ira Remsen.

<sup>2</sup> Reed and Withrow, *THIS JOURNAL*, 50, 1515 (1928).