halide ion or the alkali metal ion. This is evident for example in the increasing values of e_1 and e_2 as one goes from lithium iodide to lithium chloride. The exception to this rule in the e_2 value of sodium bromide may possibly be due to experimental error in the sodium series.

III. In the lithium series the relation $E = AT_m + B$ holds quite well. T_m is the melting point in degrees Kelvin and the constants A and B have the values, respectively, 83.6 and -40.8×10^{-3}. In the sodium and potassium series, perhaps due to experimental error in the earlier determinations of E, a linear equation is not adequate.

Summary

The temperature–conductance curves of solid lithium halides have been determined between room temperatures and temperatures near the melting point. Two slopes were found for the lithium halides, a behavior previously observed for the sodium and potassium halide series. This is taken to indicate a similarity in the conduction process in all three series. If this interpretation is correct, the lithium ion alone conducts at lower temperatures and both lithium and halide ions take part in the conduction at higher temperatures.

A comparison of the "heats of liberation" of the conducting ions in the different series, as calculated from the slopes of the conductance curves, has led to three generalizations. In the incomplete lithium series the "heat of liberation" appears to be a linear function of the temperature of the melting point.

URBANA, ILLINOIS

[CONTRIBUTION FROM MELLON INSTITUTE OF INDUSTRIAL RESEARCH]

THE JAMIN EFFECT IN CYLINDRICAL TUBES

BY W. O. SMITH[1] AND MILTON D. CRANE[2]

RECEIVED NOVEMBER 8, 1929 PUBLISHED APRIL 7, 1930

About the middle of the last century Jamin[3] noticed that an ordinary cylindrical capillary tube filled with a chain of alternate air and water bubbles is capable of sustaining a finite pressure. If a series of constrictions is placed in the tube, the pressure sustenance is considerably increased. Each of these two effects, which might be termed the cylindrical and non-cylindrical, respectively, is referred to by Jamin's name. The writers have investigated the former, and conclude from their work that careful cleaning and avoidance of contamination render a cylindrical capillary incapable of sustaining pressure.

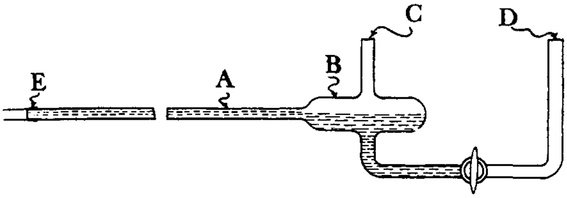
---

[1] Industrial Fellow, Mellon Institute of Industrial Research, Pittsburgh, Pa.

[2] This work was done while the junior author was a senior student in the School of Mines, University of Pittsburgh.

[3] M. J. Jamin, *Compt. rend.*, 50, 172–176, 311–314, 385–389 (1860).

Apparatus.—The device used consisted of a cylindrical capillary about 1 meter long. On one end was fastened a cylindrical glass reservoir 2 cm. in diameter and 10 cm. long. An open water manometer fastened to this reservoir served to measure pressure. A second opening into the reservoir introduced water and fluids. If the reservoir is partly filled and a vacuum is applied to the end of the capillary, a chain can be quickly introduced. The apparatus is shown in Fig. 1.



A, Capillary; C, manometer connection; B, reservoir; D, filling connection; E, ground-glass joint for applying vacuum.

Fig. 1.—Apparatus for producing Jamin chain.

Experimental Procedure.—This apparatus was cleaned with hot chromic acid mixture and was finally washed out by prolonged steaming. Pure water was prepared by distillation from alkaline permanganate solution in a still constructed entirely of hard glass. Its surface tension was found to be 72.2 dynes at 24°. The water was distilled directly into the reservoir described until a quantity sufficient to introduce a chain had been obtained. In general, a chain shorter than the length of the tube was used and placed so as to occupy the portion of the tube adjacent to the reservoir, the remainder of the capillary being open. While the chain was confined within the tube, no pressure could be sustained. However, when a bubble had reached the end of the tube and had formed a meniscus over its plane surface (Fig. 2), small pressures were supported. The pressure p required to overcome this end-resistance is given in order of magnitude by $p = 2\pi r\sigma/\pi r^2 = 2\sigma/r$, where r is the radius of the tube and σ the surface tension of the water. Table I shows the observed and calculated end-pressure for chains of varying lengths. The agreement is well within the limits of error when it is remembered that the end bubble is formed partly exterior to the capillary.

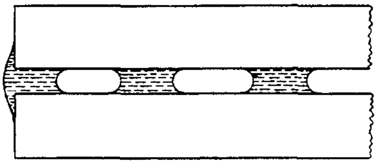


Fig. 2.—Position of bubble at end of capillary.

After drying the inside of the tube by a stream of clean dry air, it was contaminated by being completely filled with a solution of oleic acid in benzene. The filled tube was allowed to stand from thirty minutes to one

TABLE I

END-RESISTANCE FOR UNCONTAMINATED TUBE

Number of bubbles in tube	Length of bubbles		End-press., cm. of water	Computed end-press., cm. of water	Radius of tube, cm.
	Air, mm.	Water, mm.			
118	5–10	2	2.20	2.72	0.054
92	4.5–7	1.5	2.25	2.72	.054
108	4.5–9	1.75	2.22	2.72	.054
120	5–15	1	2.00	2.72	.054
106	4.5–10	1.5	2.20	2.72	.054
110	4.5–10	1	2.05	2.72	.054
117	4.5–10	1	2.05	2.72	.054

hour and was again drained and dried by a stream of clean dry air. The chain of alternate air and water bubbles was then re-introduced, with the result that the column sustained finite pressures ranging from several centimeters to over a meter of water, depending on the concentration of the oleic acid solution used. The data are tabulated in Table II. Relatively small concentrations of oleic acid were found to show a greater sustaining capability than larger ones, but the limits have not been completely investigated. The results reported seem to warrant the conclusion that there is no Jamin effect in cylindrical tubes when perfect wetting liquids are used. However, when there is only partial wetting and hysteretic contact angles are present, there will be a definite effect.

TABLE II

CONTAMINATED TUBE

No. of bubbles in tube	Length of bubble		Press. obs., cm. of water	Press. per bubble, cm. of water	Radius of tube, mm.	Concn. of contamination soln. (oleic acid in benzene), *N*
	Air, mm.	Water, mm.				
185	2	3	161	0.870	0.54	0.001
149	2–4	1	106	.711	.54	.001
175	2–4	1	48.5	.278	.54	.02
69	1–2	1	12.2	.177	.54	.02

Theory.—Let us consider a single tube containing a chain of alternate air and water bubbles. Let one end be exposed to the atmosphere and the other be acted upon by a pressure P. Then, if n is the number of bubbles, each designated by i, r the radius of the tube, σ the surface tension of the contaminated liquid, Θ_1 and Θ_2 the contact angles on the advancing and receding ends of a bubble, respectively, we have the following equilibrium relation for tubes which are so small that gravity effects are negligible

$$\pi r^2 P - \sum_{1}^{n}{}_{i}\; 2\pi r\, \sigma\, (\cos \Theta_2 - \cos \Theta_1)_i = \pi r^2 A$$

from which

$$P = \frac{2}{r} \sum_{1}^{n}{}_{i}\; \sigma\, (\cos \Theta_2 - \cos \Theta_1)_i + A \tag{1}$$

where A is atmospheric pressure.

There are several possibilities. It is apparent that, if $\Theta_1 = \Theta_2$, including $\Theta_1 = \Theta_2 = 0$, we have $P = A$, and no finite pressure can be sustained. On the other hand, when $\Theta_1 \neq \Theta_2$, a finite pressure given by Equation 1 can be supported. The greatest pressure P' which can be sustained is given by

$$P' = \frac{2\sigma n}{r} (\cos \Theta'_2 - \cos \Theta'_1) + A \qquad (2)$$

where Θ'_2 and Θ'_1 are the extreme values which the contact angles assume. This is obviously produced by increasing the pressure P until all bubbles have suffered their maximum distortion.

Alteration of curvature radii is easily observed, although it cannot be reconciled with the Laplace curvature relation unless hysteresis of contact angles is present. The static problem of capillarity requires the finding of solutions of this equation and adapting them to a given solid boundary for a given angle of contact. If the contact angle is fixed, there is a unique solution, hence a definite curvature.

Discussion.—The results suggest that the hysteresis $(\Theta'_2 - \Theta'_1)$ is determined by the concentration of the contaminating substances present, a slight contamination producing a greater effect than a larger, within a certain range. Another factor, however, is to be considered. One would expect that small concentrations of the contaminating solution contain a sufficient number of molecules to be adsorbed on the glass surface and leave very few to be adsorbed on the water interface after introduction of the chain. Hence, the surface tension of the water is not lowered appreciably. When larger concentrations are used, there is an excess which is adsorbed on the surfaces of the water bubble, lowering its surface tension appreciably. Obviously, from Equation 1, the value of P will be decreased.

In order to verify Equation 2, a detailed study should be made of the manner in which concentration of contaminating solution affects the pressure which can be supported, as well as its relation to contact angles, especially hysteresis. In addition, the variation of σ due to the changed concentrations should be checked.

In conclusion, it must be emphasized that for the case of a non-cylindrical tube, containing a series of constrictions, a definite Jamin action must occur due to the geometrical nature of the boundary, as a simple application of the capillary equation to a completely wetted conical capillary of circular section will demonstrate.

The writers wish to thank Paul D. Foote, Irving Langmuir and W. A. Hamor for advice and suggestions during the progress of this work.

Summary

Two types of Jamin effect are recognized, namely, that occurring in cylindrical tubes, and that in non-cylindrical capillaries. For the cylindri-

cal case, the authors were unable to detect any effect when the tubes were so clean that complete wetting occurred. On contamination of the tubes with solutions of oleic acid in benzene, finite pressures could be supported. Slight contaminations have more effect than larger ones within certain limits. The results suggest that Jamin action arises in cylindrical tubes because of hysteresis of contact angles. The greatest pressure P' which can be sustained is calculated to be

$$P' = \frac{2\sigma n}{r}(\cos \Theta'_2 - \cos \Theta'_1) + A$$

where Θ'_2 and Θ'_1 are the maximum and minimum values which the contact angles assume, n the number of bubbles in the chain, σ the surface tension, r the radius of the tube and A atmospheric pressure.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE ANALYTICAL LABORATORY OF PRINCETON UNIVERSITY]

THE VOLUMETRIC ESTIMATION OF SODIUM

BY EARLE R. CALEY

RECEIVED NOVEMBER 9, 1929 PUBLISHED APRIL 7, 1930

The direct gravimetric magnesium uranyl acetate method for sodium, which is satisfactory when only a few sodium determinations are required, does not readily lend itself to making a series of such determinations rapidly. While it is true that colorimetric modifications of this method are capable of fulfilling this requirement, they suffer from the disadvantage of a limited range. The procedure given below is the result of experiments directed toward devising a rapid volumetric method suitable for making a series of sodium determinations.

The principles underlying this volumetric method are simple. The sodium is separated from the other elements in the same manner as described in a previous paper[1] but, instead of drying and weighing the precipitate of sodium magnesium uranyl tri-acetate, the latter is dissolved in water containing 4–5% of acetic acid and the uranium is titrated with a standard solution of sodium phosphate using potassium ferrocyanide as an outside indicator. Under the proper conditions the uranium is quantitatively precipitated as di-uranyl hydrogen phosphate, while the magnesium remains in solution. Since the uranium and sodium contents of this precipitate have been shown to be in fixed, definite ratio when it is formed under the correct conditions, a measure of the sodium present is thus obtained. While the titration of uranium with phosphate solution using an outside indicator is not an especially accurate procedure, the errors involved are greatly divided by reason of the favorable weight ratio (31.07:1) of uranium to sodium in the triple acetate precipitate. The result is that

---

[1] Caley and Foulk, THIS JOURNAL, **51**, 1664–1674 (1929).