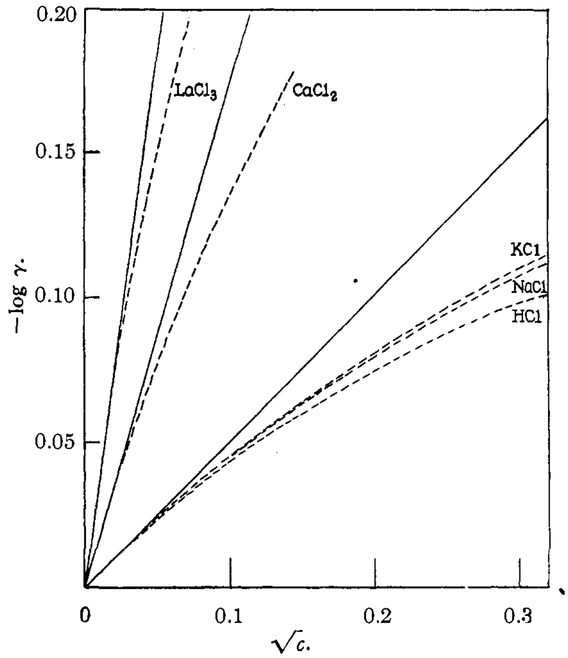

Fig. 1.

In Table IV values of γ, the activity coefficients on the molality (m) basis, which is most commonly used, are listed for the five electrolytes at round concentrations. They are obtained from the appropriate equations resulting from equations 3 and 2. In Fig. 1, the values of ($-\log \gamma$) as a function of $\sqrt{C}$ are shown by the broken curves. The solid lines are the corresponding theoretical slopes, A. It is evident, of course, that the curves for all these electrolytes approach the limiting slopes, in accord with theory. The average ionic diameters ($\mathring{a}$ values) for KCl, NaCl and HCl are 4.6, 4.0 and 4.4 ångströms, respectively, which would indicate that $\mathring{a}$ (Na^+) < $\mathring{a}$ (H_3O^+) < $\mathring{a}$ (K^+). The reason why the deviations of the curves for these chlorides from the limiting slope are not in this sequence is because the higher terms, in C and $C \log C$, which were used empirically to fit the data with equation 3, were different. However, the ion sizes obtained appear to be reasonable.[11]

TABLE IV

ACTIVITY COEFFICIENTS (γ) AT ROUND CONCENTRATIONS (m)

m (moles/ kg. H_2O)	γ				
	HCl	NaCl	KCl	CalC$_2$	LaCl$_3$
0.001	0.9653	0.9651	0.9650	0.8893	0.7902
.002	.9525	.9519	.9516	.8519	.7294
.005	.9287	.9273	.9270	.7888	.6361
.01	.9049	.9022	.9015	.7314	.5597
.02	.8757	.8707	.8694	.6681	.4831
.05	.8301	.8192	.8164	.5825	.3881
.10	.7938	.7744	.7692	.5232	(.3252)

Summary

1. Activity coefficients for $LaCl_3$ in water at 25° obtained from measurements on the e. m. f. of concentration cells with transference are in accord with the Debye–Hückel theory.

2. New values are presented for activity coefficients of HCl, NaCl, KCl, $CaCl_2$ and $LaCl_3$, based on revised fundamental constants.

NEW YORK, N. Y. RECEIVED OCTOBER 13, 1949

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, HOWARD UNIVERSITY]

Liquid-Vapor Equilibrium in Microscopic Capillaries.[1] I. Aqueous System

BY J. L. SHERESHEFSKY AND CLARENCE P. CARTER

The capillary condensation theory of adsorption proposed by Zsigmondy[2] stimulated a number of investigations seeking to establish experimentally the validity of the Kelvin[3] equation, $\ln (P/P_0) = \pm 2\sigma V/RTr$, with respect to convex and concave surfaces of liquid bodies of microscopic size. In this equation σ is the surface tension and V is the molar volume of the liquid, r is the radius of curvature and RT has the usual significance. The positive sign applies to convex surfaces and the negative sign to concave surfaces.

Goodris and Kulikova[4] substantiate the Kelvin equation for water droplets several microns in diameter. Woodland and Mack[5] assume the presence of a halo of vapor about 0.5 to 0.6μ in thickness surrounding the microscopic n-butyl phthalate droplets in order to validate the Kelvin equation. This is substantiated by Shereshefsky and Steckler[6] who studied the evaporation of n-butyl droplets from 1.673 to 0.473 μ in radius, but find that without this assumption the surface tension decreases with increase in curvature.

For concave surfaces the data in the literature are very limited. The early work of one of the authors[7] shows that the lowering of the vapor pressure of water in a uniform capillary of 8.1 microns in diameter is 23 times greater than the Kelvin value. For capillaries of other sizes and

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(1) Based on a thesis submitted by Clarence P. Carter to the Graduate School of Howard University in partial fulfillment of the requirements for the degree of Master of Science.

(2) Zsigmondy, *Z. anorg. Chem.*, **71**, 356 (1911).

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

(4) Goodris and Kulikova, *J. Russ. Phys.-Chem. Soc.*, Phys. Part, **56**, 167 (1924).

(5) Woodland and Mack, THIS JOURNAL, **55**, 3149 (1933).

(6) Shereshefsky and Steckler, *J. Chem. Physics*, **4**, 108 (1936).

(7) Shereshefsky, THIS JOURNAL, **50**, 2966 (1928).

for other liquids, the data are only qualitative. Furthermore, the method employed in this investigation was involved and difficult and not conducive to extensive application. It was therefore considered desirable to devise a more simple apparatus based on the equilibrium principle, and to extend the data on the liquid–vapor equilibrium in capillaries.

Experimental

1. Theory of Experiment.—When a cone-shaped capillary closed at the apex and filled with a pure liquid is enclosed in an air-free vessel containing a solution of a non-volatile solute in a solvent which is identical with the pure liquid in the capillary, equilibrium will be established at a given temperature. When this occurs some of the liquid will have evaporated from the capillary into the solution. After some time has elapsed the vapor pressure of the pure liquid in the capillary is in equilibrium with the vapor pressure of the solution system. The position of the meniscus in the capillary may be used to determine the radius of curvature of the surface when the variation of the radius of the cone with distance from the base is known. This enables one to establish the lowering of the vapor pressure due to capillarity since the concentration of the solution enables one to determine the lowering of the vapor pressure due to the solute. By introducing into this system solutions of different concentration, one should be able to obtain the lowering of the vapor pressure corresponding to the different curvatures in the same capillary.

2. Apparatus.—The apparatus consisted of a vessel which contained the capillaries and solution, a thermostat in which the vessel was placed, a traveling microscope for measuring the distance of the meniscus from the top of the capillary, and a source of light for illuminating the capillaries on the outside of the thermostat.

The vessel containing the capillaries shown in Fig. 1 consists of a bulb, A, 50 cc. in volume sealed to a tube, D, 15 mm. in diameter called the capillary chamber. The constricted tip, B, served to prevent splashing of the solution into the capillary chamber during the process of removing dissolved air from the solution. The capillaries, C, are attached to the wall of the capillary chamber. The bulb, E, approximately 25 cc. in volume served as a condenser and receiver when the solution was distilled in the process of removing dissolved air from the solution. F is a closed monometer used to determine whether the system was air tight during the measurements. G is the point at which the capillary vessel was connected to and detached from the vacuum apparatus.

The capillary chamber and solutions were maintained at constant temperature by a thermostat which was heated by one 125-watt and one 150-watt heater and cooled by running water through copper coils and a mercury–stainless steel thermo-regulator. The stirring was done by an electric turbine type stirrer placed in such a position as to give the best agitation and the least temperature gradient. The temperature was maintained at 20° and could be held constant to 0.002° for seven or eight hours.

The capillaries were made by drawing out 0.5-mm. capillary tubing for a short distance and repeating this operation until the desired size had been attained. The first drawing required an oxygen flame but for all other drawings a universal burner was sufficient. In order to obtain capillaries with a decreasing radius, after the first drawing had been made, the universal burner with wing top was used. The flame was turned very low and the capillary was held so as to cut the flame at right angles. In this position only a small portion of the capillary was heated. This process produced pyrex capillaries in which the radius decreases quite uniformly. For quartz capillaries, an oxygen flame had to be used throughout the entire process.

The radii of the capillaries were measured microscopically. For these measurements we used an objective with a magnification of 40 times and a screw micrometer eyepiece which had a magnification of six times. The micrometer was calibrated by use of an objective micrometer which had a millimeter divided into one hundred divisions. Having determined the number of divisions on the eyepiece micrometer which corresponds to one division on the objective micrometer, the latter was replaced with a capillary and the size of the bore of the capillary determined.

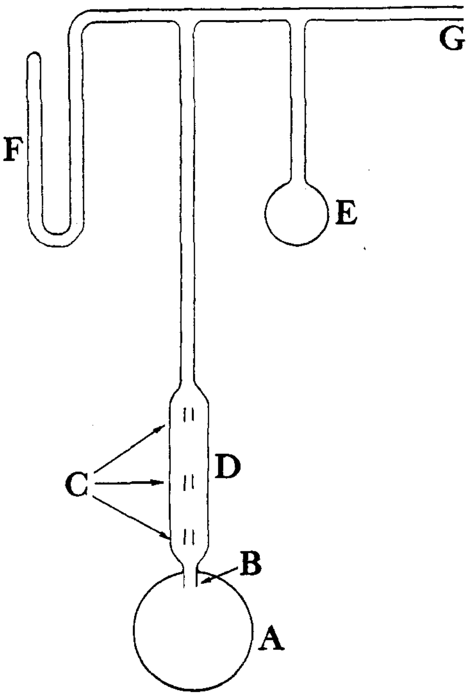

Fig. 1.—Apparatus for measuring liquid–vapor equilibrium in microscopic capillaries.

The walls of the capillary also produced magnification, and for this reason, the radius, when determined as described above, was larger than the true radius of the capillary and had to be corrected. If the outer radius of the capillary is large in comparison with the radius of the bore, this correction is simply the apparent radius divided by the index of refraction of the glass.[7] We have used this simplified correction because all capillaries used in this investigation had outer radii which were 50 to 100 times as large as the inner radii. The index of refraction of the glass or quartz was determined with an accuracy better than 0.7% by mixing acetone and carbon disulfide in such a proportion that when a piece of ordinary capillary tubing was immersed in the mixture, and an object, say a pencil, held in an inclined position was observed through it, there was no break in the object. The index of refraction of this solution was taken as the index of refraction of the glass.

Each capillary which was put into the system was measured at various points along the length of the capillary. These data allowed the construction of a curve showing the relation of the radius of the capillary to the distance from the large end. These curves are shown in Fig. 2.

The capillaries were sealed to the inner wall of the capillary chamber by use of a pin-point oxygen flame. The flame was directed at a point on the wall of the vessel just below the end of the capillary until the tip of the capillary fused slightly.

The solutions used in these experiments were prepared from specially purified potassium chloride which had been dried in the oven at 200° for two hours and triple distilled water. After introducing the solution through H and freezing it with a mixture of solid carbon dioxide and ether, the system is evacuated. At this temperature the

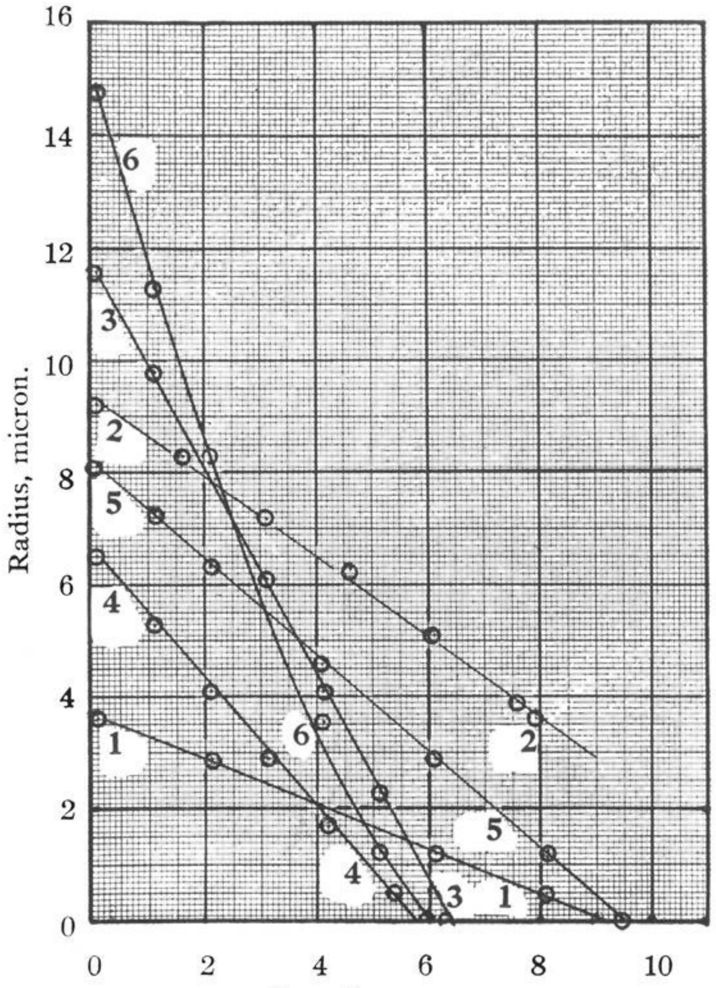

Fig. 2.—The variation of bore of capillaries: nos. 1 and 2 are of quartz; the others of Pyrex.

vapor pressure of the frozen solution was of the order of 10^{-4} mm., and any vapor lost in freeing the system of air was negligible.

When a good vacuum was obtained, the capillary vessel was closed to the vacuum system. The solution in bulb A was allowed to thaw and bulb E was cooled by the freezing mixture to cause distillation and release of dissolved gases. The distillation was reversed and the solution in bulb A was frozen. The released gases were pumped out by opening the capillary vessel to the vacuum system. This was repeated several times until all dissolved gases had been removed. The capillary vessel was then sealed under vacuum at G, placed in the thermostat, and time allowed to reach equilibrium. A piece of ice was then placed against the capillary chamber at the area where the capillaries were attached for a few seconds to fill the capillaries with pure solvent. By means of a traveling microscope the position of the menisci were observed until no further evaporation of the liquid from the capillaries took place. The capillary radii at the level of the meniscus were obtained from the curves in Fig. 2.

Results and Discussion

Determinations of vapor pressure lowering were made with solutions of ten different concentrations ranging from 0.025 to 0.80 molal. In the beginning, that is, when observations were made with 0.1 to 0.6 molal, four capillaries were in the system. Capillaries 1 and 2 were quartz, and 3 and 4 were pyrex. The observations at frequent time intervals with a 0.1 molal solution are shown in Table I.

TABLE I

EQUILIBRATION OF LIQUID IN CAPILLARIES

Time, hr.		0	0.5	1.0	1.5	2.0	2.5	3.0	3.5
Capillary radii at levels of meniscus, microns	Capil. 2	..	9.1	9.0	8.9	8.9	8.85	8.9	8.9
	Capil. 3	..	10.3	8.25	8.2	7.2	7.5	7.5	7.5

The next five determinations were made with 0.20, 0.30, 0.40, 0.50 and 0.60 molal solutions, respectively. The last four determinations were made with 0.80, 0.075, 0.05 and 0.025 molal solutions in the order given. No change in the condition was made with the exception that the pyrex capillaries 5 and 6 were added. Time-interval observations of the last nine determinations are not given but the final equilibrium values of r are shown in Table II. The vapor pressures of the solutions were obtained from a ΔP–concentration curve constructed from the data of Frazer, Lovelace and Sease.[8]

As shown in Fig. 3 the vapor pressure lowering decreases approximately linearly with an increase in the radius until a value of 7.5 or 8.0 microns is reached. For larger values the vapor pressure lowering decreases very slowly. The observed radii are from 7 to 80 times larger than those calculated from the Kelvin equation, as shown in the last column of this table.

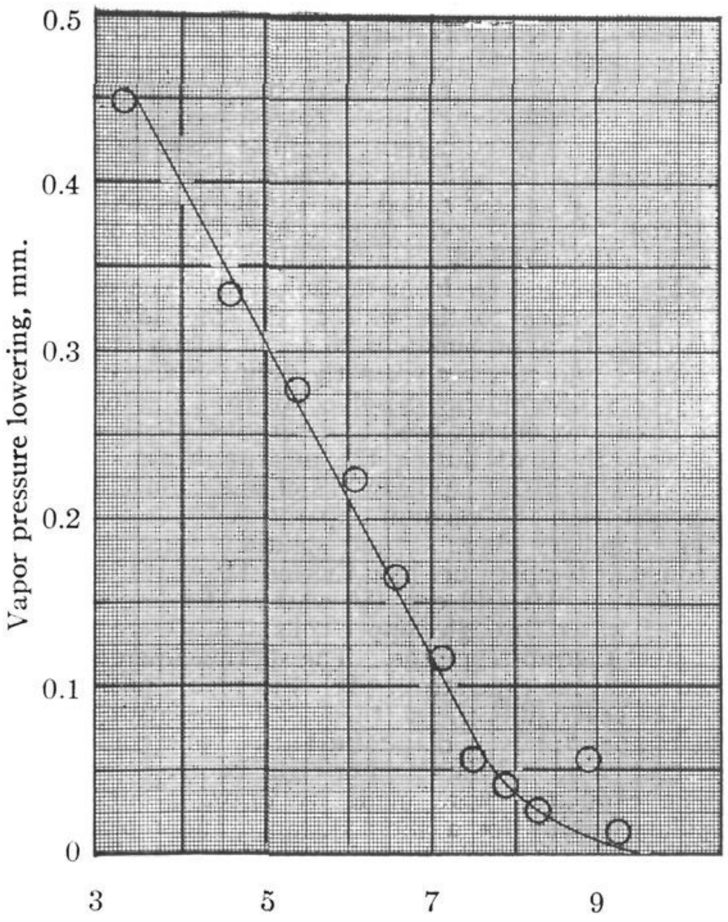

Fig. 3.—Vapor pressure lowering in capillaries: each circle includes all experimental points for a given vapor pressure.

Good agreement is observed between the values of r in the different capillaries. This fact together with the wide variation of the angle of the cone-shaped capillaries shown in Fig. 2, indicate that the length of the capillaries had no notice-

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

TABLE II

LIQUID–VAPOR EQUILIBRIUM IN MICROSCOPIC CAPILLARIES

KCl solution, molal	Vapor pressure lowering, mm.	No. and dimensions of capillaries, microns						Radius calcd. from Kelvin equation	Ratio $\frac{r\text{ (obs.)}}{r\text{ (calcd.)}}$
		1	2	3	4	4	6		
		3.6–0	9.2–3.6	11.5–2.2	6.5–0.4	8.1–0	14.7–0		
		Capillary radii at level of meniscus at equilibrium, microns							
0.025	0.0150	F[a]	9.2	9.3	F	F	9.3	1.34	6.9
.050	.0300	F	8.2	8.3	F	F	8.3	0.64	13.0
.075	.0424	F	7.9	7.8	F	7.9	7.8	.43	17.4
.100	.0575	F	8.9	7.5	F	...	...	.33	23.0
.200	.1175	F	7.2	7.1	F	...	...	.16	44.4
.300	.1680	F	6.7	6.5	6.5	...	...	.11	58.0
.400	.2250	F	6.15	6.1	6.05	...	...	.08	67.5
.500	.2800	F	5.5	5.4	5.3	...	...	.07	77.1
.600	.3352	F	4.7	4.6	4.5	...	...	.056	82.1
.800	.4470	3.30	E[a]	3.5	3.2	3.4	3.4	.04	80.0

[a] Capillaries completely filled are designated by F, and when empty by E.

able effect on the equilibrium. Furthermore, the good agreement between the quartz and pyrex capillaries leads us to believe that the probable solution effect in the capillaries due to the high ratio of glass surface to volume of solvent was either absent or negligible. Only in one instance was the observed radius for a quartz capillary larger than for the pyrex. In the measurements with 0.1 molal solution 8.9 microns was obtained for the quartz and 7.5 microns for the pyrex capillaries. At the other 9 concentrations, the agreement between the observed values for the quartz and pyrex capillaries is very good.

It is also desirable to consider the possible effects of temperature gradients in the thermostat. To ascribe the observed lowering of the vapor pressure in the capillaries to differences in the temperatures of the solutions and the area of the locations of the capillaries, one would have to assume a temperature difference of approximately 0.015° for the most dilute and about 0.44° for the most concentrated solution used in these experiments. This—under the conditions of the thermostatic control—was highly improbable. Furthermore, to detect any appreciable temperature gradient, the capillaries were arranged in groups of two along the length of the capillary chamber. The first two were 6 cm. from the surface of the solution, the next group 12, and the third group 16 cm. The agreement in the r-values of the capillaries in these different locations indicates no noticeable temperature gradient.

In explanation of the observed abnormal lowering of the vapor pressure one of the authors[7] suggested the possible variation of density and surface tension of the liquid. This explanation was later advanced in connection with adsorption studies[9,10] of water, benzene, ether and chloropicrin on charcoal. Other investigators of capillary phenomena observed abnormal freezing points[11] of water and non-polar liquids, abnormal thickness[12] and form elasticity[13] of water films. On the other hand, measurements[14] of the density and surface tension of water in open capillaries of microscopic size show no appreciable difference from the normal values. It is worth noting that the phenomena of Kubelka, Parker, Chmutov and Deryagin refer to capillaries less than 1 micron, while the observations of Cohan and Meyer were made on capillaries of 4 to 29 microns in diameter. Furthermore, the latter observations were made on capillaries open at both ends, while the abnormal pressures observed in the present experiments were in capillaries closed at one end. Professor Patrick[15] ascribes special significance to this difference, as he bases upon it the presence of an unbalanced negative pressure in the surface film coating the glass.

Microscopic examination of similar capillaries partially filled with water, observed under atmospheric conditions and at a magnification of about 250, showed no noticeable deformation of the menisci in the direction of high curvature. The radii of the menisci appeared normal and equal to those of the capillaries at these levels. There is no reason to suppose that under reduced pressure, which prevailed under the experimental conditions, the menisci would possess higher curvatures, which in turn could account for the increased vapor-pressure lowering observed.

It is obvious that the Kelvin equation does not take into account the influence of the capillary wall. The question of the range of such influence was the subject of a number of investigations by Drude,[16] Reinold and Rucker,[17] and Quincke[18] and recently by Deryagin.[13] According to the latter the influence of glass upon a water film placed between two glass plates extends over a distance less than 0.75 μ. This value, although the largest ever given, is still from 4 to 10 times

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(9) Kubelka, *Z. Elektrochem.*, **37**, 637 (1931).

(10) Kubelka, *Kolloid. Z.*, **55**, 129 (1931); **58**, 189 (1932).

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

(12) Chmutov, *J. Phys. Chem.* (*U. S. S. R.*), **9**, 345 (1937).

(13) Deryagin, *Z. Physik.*, **84**, 657 (1933).

(14) Cohan and Meyer, THIS JOURNAL, **62**, 2715 (1940).

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

(16) Drude, *Wied. Ann.*, **43**, 158 (1891).

(17) Reinold and Rucker, *Phil. Trans.*, **177**, Part II, 627 (1886).

(18) Quincke, *Pogg. Ann.*, **139**, 1 (1870); **160**, 371 (1877).

smaller than one would have to assume in order to explain the abnormal vapor pressures on the basis of perturbation of the liquid in the capillaries by the glass.

The abnormal lowering of the vapor pressure may perhaps be explained on the basis of a wall effect on the vapor. Under the conditions of the present experiments, the mean free path of the water vapor is of the same order of magnitude as the capillary radii. Due to this a fraction of the molecules escaping from the liquid surface collide directly with the walls, from which they evaporate in all directions after a time-delay. This time-delay may be considered as equivalent to a decrease in the rate of change of momentum or pressure.

The present investigation is being extended to non-aqueous systems in order to eliminate beyond doubt the solubility factor and to study the role of polarity of the solvent, and also to other temperatures to study the factor of the ratio of mean-free-path to capillary radius.

Summary

1. The validity of the Kelvin equation is discussed in light of available experimental studies.

2. An apparatus for measuring the vapor pressure of liquids in microscopic capillaries is described.

3. The lowering of vapor pressure of water in cone-shaped capillaries of 3 to 10 microns in radius is found to be greater from 7 to 80 times than the values calculated from the Kelvin equation.

WASHINGTON, D. C. RECEIVED DECEMBER 10, 1949

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

Studies in the Theory of the Polarographic Diffusion Current. I. The Effects of Gelatin on the Diffusion Current Constants of Cadmium and Bismuth

BY LOUIS MEITES AND THELMA MEITES

The most careful test yet made of the $i_d = km^{2/3}t^{1/6}$ prediction of the Ilkovič equation[1-4] was that initiated by Lingane and Loveridge[5,6] and continued by Loveridge.[7] Plotting the diffusion current constant[8] against the drop time, they obtained for lead in slightly acidic *M* potassium chloride and zinc in *M* ammonia–*M* ammonium chloride, both in the presence of 0.01% gelatin, a curve which was essentially flat at drop times above 6 seconds, fell about 5% to a minimum at about 1.6 seconds, and then rose very sharply and apparently without limit as the drop time was still further decreased.

Almost simultaneously there appeared a paper by Buckley and Taylor[9] which cast doubt not only on the conclusions of Lingane and Loveridge on the dependence of the diffusion current on the capillary characteristics, but also on the conclusion reached by many observers that, under otherwise identical conditions, the diffusion current is directly proportional to the concentration of the reducible species. With respect to the first point, they found that, in general, solutions containing as much as 0.01% gelatin gave "constant values of *I* over the entire drop-time range of 1 to 6 seconds," while such constancy was only rarely encountered in the absence of gelatin. With respect to the second, they mention a large "decrease of *I* with extreme dilution of reducible ion."

Although Buckley and Taylor state that their experimental error is of the order of 2–3%, while Loveridge claims an accuracy ten times as great, their conclusions cannot be reconciled on this ground alone. Hence, in view of the importance of the dispute to the theory and practice of quantitative polarographic analysis, we have repeated some of Buckley and Taylor's measurements in a search for the cause of the discrepancy.

Experimental

The stock bismuth(III) solution was prepared from pure bismuth metal. Cadmium(II) solutions were prepared from the reagent grade chloride and standardized by electrodeposition. Other chemicals were ordinary reagent grade.

Diffusion currents were measured with the manual polarograph diagrammed in Fig. 1. A few of the residual current measurements were made with the resistance–potentiometer circuit, but most of the measurements were made with the Type HS galvanometer. All measurements were made in duplicate at from three to six potentials: the mean and extreme differences in any such pair were 0.11 and 0.38%, respectively. Galvanometer calibrations were made in duplicate or triplicate every half-hour or so during use at the Ayrton-type shunt setting being employed.

Drop times were secured by timing sets of 5 to 50 drops each, depending on the drop time, with an electric stopclock: these data were gathered concurrently with the diffusion current measurements. The mean difference between pairs of *t* values was 0.12%. The rate of flow of mercury through the capillary was determined for each

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(1) D. Ilkovič, *Collection Czechoslov. Chem. Communs.*, **6**, 498 (1934).

(2) D. Ilkovič, *J. chim. phys.*, **35**, 129 (1938).

(3) D. MacGillavry and E. K. Rideal, *Rec. trav. chim.*, **56**, 1013 (1937).

(4) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, pp. 30–39, 60–62.

(5) J. J. Lingane and B. A. Loveridge, THIS JOURNAL, **66**, 1425 (1944).

(6) J. J. Lingane and B. A. Loveridge, *ibid.*, **68**, 395 (1946).

(7) B. A. Loveridge, Ph.D. Thesis, Harvard University, 1947.

(8) J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **15**, 583 (1943).

(9) F. Buckley and J. K. Taylor, *J. Res. National Bur. Standards*, **34**, 87 (1945).