are needed. For 25° we shall use the values 73.52 for the potassium ion and 101.0 for the ferricyanide ion given by MacInnes,[9] based on measurements of the conductance of potassium ferricyanide solutions by Hartley and Donaldson.[10] These measurements were evidently well done and cover a very low range of concentration; N = 0.00004 to 0.0002. The results are supported by the measurement of Hölzl[11] which cover the range from $N = 0.001\ N$ to $0.03\ N$ but when plotted appear to be consistent with those of Hartley and Donaldson. On the other hand, the earlier measurements of Harry C. Jones and C. Watkins[12] are inconsistent with the others by nearly 7%, and deserve no further consideration.

Unfortunately, the available information as to the mobility of the ferricyanide at 0° is far less satisfactory. The only measurements of the conductance of a ferricyanide solution at 0° which we have found in the literature are those of Harry Jones and Watkins which, as explained above, are grossly in error at 25°. There is a strong presumption that an error of this magnitude is due to a wrong choice of the reference standard used in the determination of their cell constants. This is supported by the values for potassium chloride given by Harry C. Jones[13] which are also substantially below the correct values at both 25 and 0°. It is necessary to multiply his values for potassium chloride by a factor 1.067 to obtain the correct values. We have, therefore, applied this factor to his data on potassium ferricyanide and plotted the results against $\sqrt{c}$. Extrapolation gives a value of 94.4 for the limiting conductance at infinite dilution. The values thus obtained are consistent with the values given in the "International Critical Tables" which are stated to be based on Jones and Watkins and, therefore, the process of adjustment described above must have been used in preparing the "International Critical Tables." Subtracting the mobility of the potassium ion at 0°, 40.4, gives 54 for the ferricyanide ion.

TABLE IV

	25°C.	0°C.
T	298.18	278.18
D	78.8	88.0
η	0.008949	0.01792
$l_1(K^+)$	73.52	40.4
$l_2(\mathrm{Fe(CN)_6}^{---})$	101.0	54
A computed	0.0222	0.020
A experimental	.0244	.0211

The other parameters used in the calculation and in the results are shown in Table IV. The agreement between the computed and experimental results is about as close as usual[14] and shows that the formula of Falkenhagen and Vernon correctly evaluates the influence of valence type and of the temperature.

Summary

1. Data are given for the density and viscosity of potassium ferricyanide solutions at 25 and 0° covering the range up to saturation.

2. Equations expressing the density, viscosity and fluidity as functions of the concentration are given.

3. The predictions of the Falkenhagen and Vernon equation are verified for this case.

---

(9) D. A. MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Company, N. Y., 1939, p. 342.

(10) G. H. Hartley and G. W. Donaldson, *Trans. Faraday Soc.*, **33**, 465 (1937).

(11) F. Hölzl, *Monatsh.*, **55**, 137 (1930).

(12) Harry C. Jones and C. Watkins, THIS JOURNAL, **37**, 2631 (1915).

(13) H. C. Jones, Carnegie Institute at Washington, Pub. 130, p. 20.

(14) See H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Company, New York, N. Y., 1943, p. 177, for a tabulation of the available data in other cases.

CAMBRIDGE, MASSACHUSETTS RECEIVED MARCH 18, 1944

[CONTRIBUTION FROM THE DEPARTMENT OF ANATOMY, CORNELL UNIVERSITY MEDICAL COLLEGE]

The Characterization of Capillaries Used for Dropping Mercury Electrodes in Polarographic Studies

BY OTTO H. MÜLLER

The best identifying characteristics of a capillary are its length and internal diameter, provided that it has a truly uniform bore. While some factory made capillaries fulfill this condition, all laboratory made capillaries do not, because they are drawn from wider stock and are consequently more or less tapered. Even if capillaries of uniform bore were used exclusively, the means for measuring with sufficient accuracy diameters varying from 10–50 μ, or for determining the uniformity of the bore are not available to most chemists. The present study was therefore undertaken to find certain characteristics which would (a) be peculiar to *all* kinds of capillaries, (b) be determinable without special apparatus, (c) permit comparison of straight and tapered capillaries and a prediction of their performance, and (d) give enough information for the duplication of any given capillary. It was found that the capillary constant, κ, and the radius of the capillary orifice, ρ, are two factors which meet all of these requirements. Some simple techniques for their precise determination and some incidental observations made during this study will be discussed in this paper. The value of incorporating these factors in the Ilkovič equation will be described in another communication.

The capillary constant,[1] κ, represents the pressure of mercury necessary to force 1 mg. of mercury through the capillary per second. It is defined by means of the following equation

$$\kappa = \frac{p}{m} = \frac{8\eta l}{d\pi r_c^4} \qquad (1)$$

where p is the pressure (in dynes cm.$^{-2}$) producing a flow per second of m mg. of mercury of viscosity η and density d, through a capillary of length l and with uniform radius r_c. When this pressure is expressed in cm. of mercury and other known values (for 25°) are substituted in this equation, it reduces to

$$\kappa = 2.1567 \times 10^{-10}\ l/r_c^4 \qquad (2)$$

where κ is expressed in cm. sec. mg.$^{-1}$, and l and r_c in cm.

The effect of temperature on this constant is negligible, as may be seen by differentiation of equation (1) with respect to temperature. Using known temperature coefficients of the viscosity and density of mercury, one finds the temperature coefficient of the capillary constant equal to -0.0034 deg.$^{-1}$.

If the radius of the orifice, ρ, is substituted for r_c, the above equations also become applicable to capillaries without uniform bore; l then represents the length of an equivalent hypothetical capillary with a uniform bore of radius ρ. In other words, by means of equation (2) it is possible to calculate the dimensions of a capillary of uniform bore needed to replace a given laboratory made capillary.

Determination of κ.—The value of κ is easily obtained as the ratio of P/m, where P is the pressure (in cm. of mercury) producing a flow of m mg. of mercury per second through the capillary. Even fairly rough measurements of these quantities give practically constant values for κ under a variety of conditions.[1] As will be shown presently, a slight drift in the κ values with changing pressures can be eliminated in more accurate measurements by making appropriate corrections for the applied pressure.

In Tables I and II are given the results of two typical experiments in which the capillary was dropping in air and in a solution of 0.1 N potassium nitrate. The apparent or applied pressure ($P_{\text{app.}}$) was measured accurately to 0.1 cm. from the tip of the capillary to the level in the mercury reservoir. The capillary used was 6.32 cm. long and had an essentially uniform diameter of 54.0 μ. W, t and m were determined as before.[1] Although the drops in air are abnormally large and not as reproducible as drops falling in an electrolyte, the flow of mercury, m, at a given pressure, is constant. Yet, in both experiments, the values for the capillary constant, $\kappa_{\text{app.}}$, calculated from m and the apparent pressure, $P_{\text{app.}}$, show a small drift with changing pressure. This and the small but definite difference between corresponding m values of Tables I and II are caused by the back pressure of the mercury drops.

TABLE I

MEASUREMENTS MADE WITH CAPILLARY NO. 1, DROPPING IN AIR

$P_{\text{app.}}$, cm.	t, sec.	W, mg.	m, mg./sec.	$\kappa_{\text{app.}}$, cm. sec./mg.	$W^{1/3}$, mg.$^{1/3}$	P_{back}, cm.	P, cm.	κ, cm. sec./mg.
70.0	27.2	71.2	2.61	26.8	4.14	0.7	69.3	26.6
70.0	24.1	63.0	2.61	26.8	3.98	.8	69.2	26.5
70.0	26.6	69.5	2.61	26.8	4.11	.8	69.2	26.5
70.0	27.4	71.6	2.61	26.8	4.15	.7	69.3	26.6
60.0	35.2	78.7	2.23	26.9	4.28	.7	59.3	26.6
50.0	42.6	79.0	1.85	27.0	4.29	.7	49.3	26.6
40.0	59.1	87.5	1.48	27.0	4.44	.7	39.3	26.5
30.0	71.8	78.9	1.10	27.3	4.29	.7	29.3	26.6
60.0	44.3	98.6	2.23	26.9	4.62	.7	59.3	26.6
60.0	43.7	96.9	2.22	27.0	4.59	.7	59.3	26.7

TABLE II

MEASUREMENTS MADE WITH CAPILLARY NO. 1, DROPPING IN 0.1 N POTASSIUM NITRATE SOLUTION

$P_{\text{app.}}$, cm.	t, sec.	W, mg.	m, mg./sec.	$\kappa_{\text{app.}}$, cm. sec./mg.	$W^{1/3}$, mg.$^{1/3}$	$P_{\text{back}}{}^{a}$, cm.	P, cm.	κ, cm. sec./mg.
70.0	2.64	6.77	2.56	27.3	1.89	1.7	68.3	26.6
70.0	2.64	6.77	2.56	27.3	1.89	1.7	68.3	26.6
70.0	2.65	6.77	2.55	27.4	1.89	1.7	68.3	26.7
70.0	2.64	6.76	2.56	27.3	1.89	1.7	68.3	26.6
60.0	3.04	6.66	2.19	27.4	1.88	1.7	58.3	26.6
50.0	3.66	6.66	1.82	27.5	1.88	1.7	48.3	26.5
40.0	4.63	6.66	1.44	27.8	1.88	1.7	38.3	26.6
30.0	6.27	6.62	1.06	28.3	1.87	1.8	28.2	26.6

[a] P_{back} includes a correction of 0.1 cm. for loss in hydrostatic pressure, because the capillary was immersed into the solution to a depth of 1.3 cm.

It should be remembered that not all of the pressure measured is effective in forcing mercury through the capillary. A small fraction of it has to be expended in overcoming the back pressure caused by the surface tension of the expanding drop of mercury. The back pressure is greatest before the drop forms and may amount to tens of centimeters, depending on the capillary bore (see, *e. g.*, the critical pressure values given in Table III). Unless the total pressure exceeds this maximum value of the back pressure, the capillary stops dropping. As soon as a drop is formed, the back pressure diminishes; it becomes minimal as the drop reaches its maximum size before falling off.

According to Kučera,[2] the back pressure is equal to $2\sigma/r_d$, where σ is the surface tension of mercury and r_d is the radius of the mercury drop. Kolthoff and Lingane[3] have evaluated this equation in terms of m and t (the drop time) for the *average* size of the drop and for a surface tension of 400 dynes cm.$^{-1}$ and found

$$\text{Average } P_{\text{back}} = 3.1/m^{1/3}t^{1/3} \qquad (3)$$

Assuming, as a first approximation, the same surface tension, the data of Tables I and II were

---

(1) O. H. Müller, *J. Chem. Education*, **18**, 172 (1941).

(2) G. Kučera, *Ann. Physik*, **11**, 529 (1903).

(3) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers Inc., New York, N. Y., 1941.

corrected. In column 6 is given $W^{1/3}$ (equal to $m^{1/3}t^{1/3}$), and in column 8, P, the pressure corrected for back pressure and any loss in hydrostatic pressure. The new value of κ (Column 9) is now constant within the experimental error and identical for the two media.

To test the validity of the corrected κ value, a further experiment was performed which involved no back pressure. For a carefully measured length of time the capillary was immersed into a pool of mercury contained in a small beaker which was weighed before and after the experiment. The increase in weight represented the quantity of mercury flowing through the capillary in the elapsed time under a pressure equal to the difference between the mercury levels in the reservoir and the beaker. In two experiments the following results were obtained

Pressure, cm.	Weight, g.	Time, sec.	Rate of flow, mg./sec.	κ, cm. sec./mg.
38.6	1.0432	720	1.45	26.6
67.1	2.4261	960	2.53	26.5

Upon substitution of the corrected κ and the known l values in equation (2), r_c was found to be 26.7 μ in good agreement with the direct measurement.

The Attachment of Mercury to Glass.—If the pressure is expressed in cm. of mercury, Kučera's equation becomes

$$P_{\text{back}} = 2\sigma/gdr_{\text{d}} \quad (4)$$

where d is the density of mercury and g the acceleration of gravity. For the present study it was desirable to evaluate this equation in terms of ρ. By combining the two well-known equations relating W, the drop weight, to r_{d}, the radius of the drop, and to ρ, the radius of the capillary orifice

$$W = 4/3\pi r_{\text{d}}^3 d \quad (5)$$

and

$$W = 2\sigma\pi\rho/g \quad (6)$$

one gets r_{d} expressed in terms of ρ

$$r_{\text{d}} = \sqrt[3]{3\sigma\rho/2dg} \quad (7)$$

Substituting this in equation (4), which is multiplied by 4/3 to represent the *average* back pressure[3] in cm. of mercury, we get

$$\text{Average } P_{\text{back}} = 4.1576 \times 10^{-3}\sigma^{2/3}\rho^{-1/3} \text{ cm.} \quad (8)$$

The average back pressure calculated by means of this equation for the capillary used in the above experiments is 1.6 cm. Since this agrees with the data of Table II only, the value of ρ must undergo some change when the capillary is dropping in air, because the surface tension of mercury cannot differ much from 400 dynes cm.$^{-1}$. Substituting in equation (8) the value of P_{back} from Table I, one finds that ρ must be about 320 μ instead of the known 27.0 μ.

This difference became understandable upon microscopic examination of the drops. As long as the mercury was dropping in a solution of 0.1 N potassium nitrate, it was suspended only from the thin column of mercury in the capillary bore. However, mercury dropping in air was attached mainly to the glass of the capillary. These observations are represented schematically in Fig. 1. It could be estimated that the attachment to the glass was over an area with a diameter about ten times that of the capillary orifice.

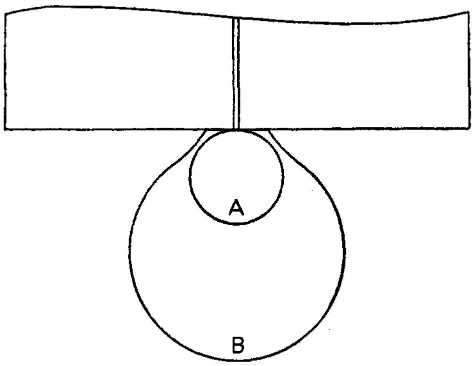

Fig. 1.—Schematic representation of mercury drops formed at a capillary whose orifice is 54 μ in diameter: A, in 0.1 N potassium nitrate—the drop is suspended from the mercury column only; B, in air—the drop is attached to the glass of the capillary.

Kolthoff and Kahan[4] have observed a similar attachment of mercury to the capillary glass when electrically disconnected mercury was dropping in oxygen-containing water. This they explained on the basis of interaction between the negatively charged glass/water double layer and the water/mercury double layer which is charged positively by the adsorption of oxygen from the water. They believe that an aqueous film exists between the attached mercury and the glass. This is probably not the case when the electrode is dropping in air, because the abnormalities are much greater than when it is dropping in water. Hence, a gaseous layer between mercury and glass must be assumed.

Since mercury does not wet glass, it is probable that neutralization of the electrostatic forces acting between mercury and glass cannot take place by direct transfer of the charges but must be effected by means of a conductor, such as an electrolyte. Only partial neutralization of these charges is possible in the presence of the poor conductor, water. Thus we have the paradox: under suitable conditions mercury is attracted to glass because it does not wet glass. Not much can be said without further study about the cause for the opposite charges. Experiments in this Laboratory have shown that the abnormalities persist when the mercury is dropping in an atmosphere of hydrogen gas instead of air; on the other hand, no abnormalities were found in benzene or in absolute ethyl alcohol, although the latter is known to contain much dissolved oxygen and is a poor conductor.

---

[4] I. M. Kolthoff and G. J. Kahan, THIS JOURNAL, 64, 2553 (1942).

TABLE III

DETERMINATION OF THE RADIUS OF THE CAPILLARY ORIFICE

		Capillaries								
		No. 1			No. 2			No. 3		
Methods	Factor	P_c, cm.	W, mg.	ρ, μ	P_c, cm.	W, mg.	ρ, μ	P_c, cm.	W, mg.	ρ, μ
Direct measurement with microscope				27.0			14.1			8.1
Critical pressure method[a] (equation (9); *factor*/P_c)	$\frac{2\sigma}{dg}$									
Capillary dropping in										
Air	0.0695	25.1		27.7	47.7		14.6	81.5		8.5
		25.0		*27.8*	*40.5*		*17.2*	*74.5*		*9.3*
Water, in equilibrium with air	.0564	21.6		26.1	41.7		13.5	74.5		7.6
		20.3		*27.8*	*23.5*		*24.0*	*71.5*		*7.9*
Water, deaerated with tank nitrogen	.0644				42.0		15.3	73.0		8.8
		22.4		*28.8*	*37.0*		*17.4*	*65.0*		*9.9*
0.1 N potassium chloride	.0573	21.1		27.2	40.0		14.3	74.0		7.7
		21.1		*27.2*	*39.8*		*14.4*	*70.5*		*8.1*
Drop weight method (equation (6a); *factor* × W)	$\frac{g}{2\pi\sigma}$									
Capillary dropping in 0.1 N potassium chloride	4.11		6.66	27.4		3.52	14.5		1.95	8.0

[a] Values in italics were obtained by lowering the mercury reservoir, the other values by raising it.

Determination of ρ.—In equation (2), the capillary radius—or the radius of the capillary orifice—appears raised to the fourth power. It is therefore essential that this radius be determined as accurately as possible. Besides direct measurement under the microscope, there are available two indirect methods involving well-known equations relating to surface tension.

The *critical pressure method* is based on the equation

$$\rho = 2\sigma/gdP_c \qquad (9)$$

in which σ is the surface tension and P_c is that critical pressure (in cm. of mercury), which is necessary to stop the flow of mercury and which leaves the meniscus of the mercury just at the capillary orifice.

The *drop weight method* is based on equation (6), rewritten as follows

$$\rho = Wg/2\pi\sigma \qquad (6a)$$

Both of these methods have been tried with different capillaries and in different media. Because of the attachment of mercury to glass, irregularities were found unless the medium was a satisfactory electrolyte such as 0.1 N potassium chloride.[4] Some typical examples are presented in Table III and compared with the directly determined radius (accurate to ±0.5 μ). Capillary no. 1 was factory made, while the other two were drawn in this Laboratory from 0.5 mm. capillary tubing. Nos. 1 and 2 represent capillaries suitable for general polarographic work, while capillary no. 3 should be used for special studies only because its orifice is too narrow and the bore is too tapered. In the calculations, the following values were assumed for the surface tension, σ: in water,[5] in equilibrium with air, 374 dynes cm.$^{-1}$; in water,[6] free from air, 427 dynes cm.$^{-1}$; in air,[7] 461 dynes cm.$^{-1}$; in 0.1 N potassium chloride,[8] 380 dynes cm.$^{-1}$.

In view of the sensitivity of these measurements to slight vibrations and the uncertainty of some of the surface tension values, the results show a satisfactory agreement as long as the critical pressure is attained by gradually *raising* the mercury reservoir. When the critical pressure was determined by *lowering* the reservoir, erroneous results were often obtained because, in this case, the drops did not "break clean" from the mercury column, but left some residual mercury outside the capillary orifice attached to the glass (see also Kučera[2]). When the pressure was lowered sufficiently that the dropping finally did stop, it was found that the mercury column receded into the capillary for a considerable distance. Gradual increase in the mercury pressure forced the mercury column nearer the capillary orifice until the critical pressure was exceeded and the capillary began to drop. In the potassium chloride solution, such complications were minimal.

Position of the Capillary.—That the capillary should be vertical and the cut surface perfectly horizontal is a foregone assumption in all polarographic work. Yet no clear-cut test has heretofore been described to safeguard against errors from this source. Actually, photographs of capillaries with hanging mercury drops, published by several investigators,[4,9] indicate that this prerequisite was not fully appreciated.

If the capillary is cut off at an angle or tilted, the drops cannot fall freely and become deformed. Under such conditions equation (6a) no longer

(5) H. Brown, THIS JOURNAL, **56**, 2564 (1934).

(6) D. C. Henry and J. Jackson, *Nature*, **142**, 616 (1938).

(7) T. R. Hogness, THIS JOURNAL, **43**, 1621 (1921).

(8) Determined in this Laboratory as the most probable value.

(9) W. M. MacNevin and E. W. Balis, THIS JOURNAL, **65**, 660 (1943).

holds and should give a value for ρ different from that obtained by means of equation (9). However, if the capillary is so adjusted that the plane of the cut surface is horizontal, the value for ρ obtained by both equations should be identical. This phenomenon has been actually observed and is represented diagrammatically in Fig. 2.

The capillary used here had been cut off improperly so that the cut surface formed an angle of 70° instead of 90° with the longitudinal axis of the capillary. The capillary radius was found equal to 13.4 μ by direct measurement of the smallest diameter of the oval orifice. In all subsequent calculations, this orifice was considered round and with a radius equal to the one measured. The critical pressure in water and the drop weight in a 0.1 N potassium chloride solution were then determined, first, when the capillary was vertical and the plane of the cut surface slanted, and, second, when the capillary was slanted to bring the orifice on a horizontal plane. The results and the calculated values were

Position of capillary	P_c, cm.	ρ, μ	W, mg.	ρ, μ
Straight	42.0	13.6	2.37	9.7
Slanted	39.5	14.5	3.32	13.7

From this, one must conclude that the ρ values obtained by the drop weight and critical pressure methods should certainly agree within 1μ to insure proper functioning of the capillary. It should be mentioned here that even this type of capillary can be used for some special polarographic work and will give good results as long as its position is rigidly fixed. Because of its extreme sensitivity to slight changes in position, it cannot be recommended for general use.

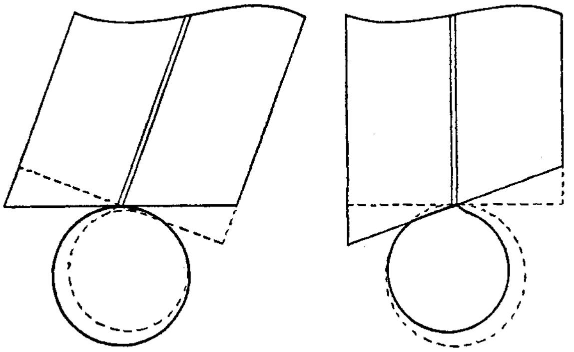

Fig. 2.—Graphical demonstration of the effect of position and improper cutting of the capillary on the drop size. Note that normal drops are obtained whenever the cut surface is perfectly horizontal.

Acknowledgment.—The author wishes to thank Mr. Howard Phipps and Dr. John Staige Davis, Jr., for financial support of this investigation.

Summary

Two factors have been proposed to serve as simple means for the complete characterization of all kinds of capillaries used for dropping mercury electrodes. These are the radius of the capillary orifice, ρ, and the capillary constant, κ, which is the pressure of mercury (in cm.) necessary to force 1 mg. of mercury through the capillary per second.

Various methods for their determination have been described which serve as checks for the proper behavior of the capillary.

Some abnormalities in the behavior of capillaries have been discussed.

NEW YORK, N. Y. RECEIVED MARCH 31, 1944

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

Molecular Compounds of the Quinhydrone Type in Solution

BY LEONOR MICHAELIS AND S. GRANICK

The intensely colored molecular compounds of the quinhydrone type are best known in the crystalline state.[1] In solution all of them dissociate to a very high degree, although not completely. Such compounds usually consist of two components of which one is on a higher oxidation level than the other. One component may be a quinone, or an aromatic nitro compound; the other a phenol, an amine, or even a hydrocarbon such as hexamethylbenzene. Most of the studies here reported were carried out with compounds of a quinone with some phenolic compound. Crystalline compounds of this kind have the following characteristics:

1. When quinone combines with hydroquinone, the stoichiometrical composition of the compound is Q_1B_1, where Q stands for the quinoid and B for the benzenoid component.
2. When quinone combines with a phenolic compound having only one unsubstituted OH group, the molecular compound is Q_1B_2. Examples are the quinone compound of phenol and of *p*-methoxyphenol.
3. Some quinhydrone-like compounds of "anomalous composition" have been described.[2] Their compositions were inferred, not from a straight-forward analysis of the solid, but by indirect methods involving dubious interpretations. Among all such compounds which can be prepared in the crystalline state, and which are of

---

[1] P. Pfeiffer, "Organische Molekülverbindungen," Stuttgart, 1927. Some references to more recent papers are: I. Palacios and O. R. Foz, *Anales soc. españ. fís. quím.*, **34**, 799 (1936); G. Weiss, *J. Chem. Soc.*, **245** (1942) and **462** (1943); H. M. Powell, G. Huse and P. M. Cooke, *ibid.*, **153** (1943) and **435** (1943).

[2] R. Kremann, S. Sutter, F. Sitte, H. Strezelba and A. Dobotzky, *Monatsh.*, **43**, 269 (1922).