of the compounds limited the amount which could be reduced at one time to 2 g. per 200 cc. of 95% alcohol. No reaction was obtained in absolute alcohol. The white product was in quantitive yield (in contrast to the poor yield of red product reported[20] for stannous chloride reduction). It sublimed and decomposed over a wide range without melting. *Anal.* Calcd. for $C_9H_9N_3O$: N, 24.00. Found: N, 24.29. The dihydrobromide was formed from absolute alcoholic HBr. *Anal.* Calcd. for $C_9H_9N_3O.2HBr$: Br, 47.4. Found: Br, 47.7, 47.1.

5-Acetamino-4-hydroxy-2-methylquinazoline.—The amine (0.60 g.) was refluxed twenty-four hours with 3 cc. acetic anhydride and 6 cc. dry pyridine. The product was isolated and purified in the same manner as 4-acetaminoquinazoline. The yield was 0.48 g. of white crystals, which sublimed about 180° but did not melt below 300°. *Anal.* Calcd. for $C_{11}H_{11}N_3O_2$: C, 60.82; H, 5.11; N, 19.35. Found: C, 60.84; H, 5.32; N, 19.64.

5-Cyano-4-hydroxy-2-methylquinazoline.—Pure amine (1.75 g.) was dissolved in 13 cc. hot 21% hydrochloric acid and diazotized at 0° by adding during a period of one hour a solution of 0.81 g. of sodium nitrite in 2 cc. of water. The diazonium solution was neutralized with sodium carbonate to *p*H 7, poured into 11 cc. of cold cuprous cyanide solution,[21] warmed, recooled, strongly acidified with concentrated hydrochloric acid and filtered. The precipitate suspended in a little water was neutralized to *p*H 7 and filtered. Extracting this several times with boiling alcohol removed 1.30 g. (70%) of the crude 5-cyano-4-hydroxy-2-methylquinazoline. Recrystallization from alcohol or water yielded rosets of long, very thin, white needles, which sublimed about 200° but did not melt below 300°. The hydrochloride salt had a similar melting behavior. *Anal.* Calcd. for $C_{10}H_7N_3O$: C, 64.86; H, 3.81; N, 22.69. Found: C, 64.57; H, 3.52; N, 22.58.

4-Hydroxy-2-methylquinazoline-5-carboxylic Acid Hydrochloride.—The nitrile was sealed in a tube with concentrated hydrochloric acid and heated at 160° for twenty hours. After cooling, some acid hydrochloride was filtered out as white, frequently triangular plates. *Anal.* Calcd. for $C_{10}H_8N_2O_3.HCl$: C, 49.90; H, 3.77; N, 11.64. Found: C, 49.24, 49.25; H, 3.80, 3.88; N, 11.46.

The free base obtained by neutralization of the liquors, evaporating to dryness, and extracting with absolute alcohol was not free of sodium chloride. It sublimed about 235° but did not melt below 300°.

Summary

1. Evidence is presented that acid, acting catalytically, increased the reactivity of 4-chloro-4-alkoxy- and 4-aminoquinazolines.

2. Experimental support is provided for the mechanism suggested by Banks.

3. Several previously undescribed compounds of the 4-quinazoline amine and ether series are reported; but the use of 4-chloroquinazoline as an intermediate for other derivatives was not successful.

CORVALLIS, OREGON RECEIVED MAY 14, 1945

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[20] Bogert and Chambers, THIS JOURNAL, **28**, 212 (1906).

[21] Clarke and Read, "Organic Syntheses," 2nd ed. Coll. Vol. I, 1941, p. 514.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WASHINGTON]

The Determination of Surface Tension by the Sessile Bubble Method

BY O. L. WHEELER,[1] H. V. TARTAR AND E. C. LINGAFELTER

The surface tensions of solutions of paraffin-chain colloidal electrolytes have become of considerable theoretical interest in the past few years; their determination has, however, been handicapped by the lack of suitable experimental procedures. The more conventional methods are not applicable because the surfaces of these solutions age so slowly that equilibrium values cannot be obtained. It is the purpose of this paper to describe some of the newer procedures that permit unlimited aging of the surfaces so that equilibrium values may be obtained.

Recent workers[1a,2] have shown the practicability of the sessile bubble method but they have not developed thoroughly reliable apparatus nor explained some apparent theoretical anomalies. Consequently work was undertaken to perfect the method to give reproducible and accurate experimental results.

Bashforth and Adams[3] have shown that the shape of a drop of liquid, resting on a level surface and acted upon only by static forces, is a surface of revolution about a vertical axis, the shape being determined by the static forces and the surface tension of the liquid. A bubble of gas in a liquid, when resting underneath a horizontal plane, is analogous and subject to the same theoretical treatment. The shape of this sessile bubble can be given in terms of the diameter at a selected horizontal plane, and the vertical distance from this plane to the apex. Therefore the determination of surface tension requires a suitable apparatus to form and maintain the bubble and to measure the appropriate dimensions. When these have been precisely determined, the calculation of the surface tension can best be made by using the tables given by Bashforth and Adams or, for certain bubble shapes where these tables are not applicable, by the equation developed by Porter.[4] When the selected plane coincides with the equatorial plane, the Bashforth and Adams tables cover the range of h^2/r^2 from 0.2 to 1.0, where h is the vertical distance from the apex of the bubble to the equatorial plane and r is the radius of the bubble in this plane.

To permit the calculation of surface tensions of bubbles for all values of h^2/r^2 Porter[4] undertook the task of extending the application of the theory

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[1] Standard Oil Company of California Fellow, 1941-1942.

[1a] Tartar, Sivertz and Reitmeier, THIS JOURNAL **62**, 2375 (1940).

[2] Nutting and Long, *ibid.*, **63**, 84 (1941).

[3] Bashforth and Adams, "An Attempt to Test the Theories of Capillary Action," Cambridge, 1883.

[4] Porter, *Phil. Mag.*, [7] **15**, 163 (1933); [7] **24**, 823 (1937).

to values of h^2/r^2 below 0.2. While the Bashforth and Adams[3] tables are applicable to any selected plane through the bubble, Porter restricted himself to the equatorial plane. Rather than compile a comprehensive table, he calculated a series of values and then fitted an empirical equation to them. He expresses his results in terms of a quantity, Δ, defined as $(^1/_2 h^2/r^2 - \beta^2/r^2)$, where $\beta^2 = \gamma/(D - d)g$, γ is the surface tension, D and d the density of the liquid and gas, respectively, and g is the gravitational constant His empirical equation is $\Delta = 0.3047(h^3/r^3)(1 - 4h^2/r^2)$.

Two suitable procedures are available for measuring the dimensions of sessile bubbles. The bubble may be measured directly by means of a comparator or similar optical instrument, or it may be photographed and the dimensions taken from the photograph. The first will be referred to as the comparator procedure and the latter as the photographic procedure.

Comparator Procedure

Apparatus illumination is provided by a General Electric sodium vapor lamp. Three thicknesses of yellow paper are placed over the lamp window to reduce the intensity. The light is rendered sufficiently unidirectional for the purpose by passing it through a wooden collimating tube, 150 cm. long with rectangular cross section, 2 × 3.3 cm., and painted black on the inside.

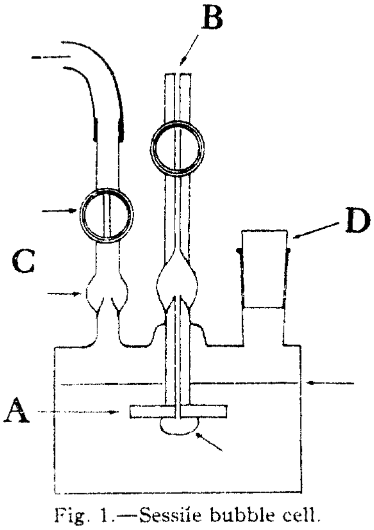

Fig. 1.—Sessile bubble cell.

The cell is made of Pyrex glass and the tubular body is 6 cm. long and 4 cm. in diameter, see Fig. 1. The windows are ground optically plane and carefully sealed to the cell, at the edges, to prevent optical distortion. The plate A beneath which the bubble is formed is 2.5 cm. in diameter and 0.3 cm. thick and ground very slightly concave on the lower surface to prevent the bubble from slipping. A capillary tube B is sealed perpendicular to this plate and coincident with a small hole through the center. The upper end of the tube is equipped with a stopcock. The plate is mounted in the center of the cell. An additional tube C, with a stopcock, is used with suction to facilitate the formation of the bubble. The cell is filled through opening D which is then closed with a rubber stopper. Bubbles are formed by lowering the pressure in the cell and permitting air to flow under the plate, through the capillary opening, until a bubble of the desired size is formed.

The comparator was built by the Gaertner Corporation and gives measurements of vertical distances to an accuracy of ±1.0 micron and horizontal distances to ±2.5 microns. By mounting it on a microscope base it is possible to focus the instrument with the microscope adjusting knobs while holding it in an accurately maintained plane. This mounting is necessary since the periphery and the center of the bubble cannot be brought into focus at the same time.

The cell was mounted in an air thermostat, with fan equipment for circulation and with the temperature held constant to ±0.03° by means of a mercury–toluene regulator. Illumination passed through an opening on one side of the thermostat and the cell was viewed through an opening on the opposite side.

When the bubble is thus illuminated, it appears as a dark silhouette with a bright streak across the center. We had assumed that the quantity h can be determined by measuring the distance from the bright streak to the apex of the bubble. This assumption seemed plausible from a consideration of the apparent optical properties of the gas bubble surrounded by a liquid having a higher index of refraction. The bubble would act as a divergent lens and scatter all light not normally incident to the surface. Since the illuminating beam is horizontal, the light should be normally incident only in the equatorial plane and consequently the bright central slit should also lie in this plane. Reitmeier[5] observed, however, that in order to get reproducible results, it was necessary to use bubbles having radii within a certain range. This requirement should, of course, be unnecessary because the surface tension of the liquid is not a function of bubble diameter. Further investigation has revealed that the h values obtained as described above are apparently not the true values for bubbles with widely varying diameters. Consequently this experimental value obtained with the comparator will henceforth be designated as h_c. The investigation which affords a basis for the use of h_c for the determination of surface tension will now be described.

The Determination of Surface Tension Using h_c.—It has been found convenient to express the experimental results by an empirical equation expressing β^2/r^2 as a function of h_c^2/r^2 rather

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(5) Reitmeier, "A Study of the Properties of Monoethanolamine and its Solutions and The Surface Tension of Paraffin-chain Salts," Thesis, University of Washington, 1939; THIS JOURNAL, **62**, 2375 (1940).

than use a quantity similar to Δ as in Porter's work. Measurements have been made at 40°, therefore, of h_c and r for a series of bubbles covering a wide range of size, using liquids of known capillary constants and surface tensions.

The liquids selected were water (γ = 69.56 ± 0.05 dynes, β = 0.07156) carbon tetrachloride (γ = 24.33 ± 0.2, β = 0.015976) and toluene (γ = 26.15 ± 0.1, β = 0.03145). The conductivity water available was sufficiently pure that no further treatment was necessary. Carbon tetrachloride was pretreated by washing several times with concentrated sulfuric acid and then with water. The final purification was accomplished by distillation in a 35-plate column constructed by H. M. Brooks and R. J. Houston of this Laboratory. The purity was checked by accurate determinations of the refractive index. An identical treatment was given the toluene with the exception that a washing with 40% sodium hydroxide solution followed the washing with sulfuric acid.

TABLE I

DATA ON CARBON TETRACHLORIDE, TOLUENE AND WATER WITH VARYING BUBBLE SIZE AT 40°

Ratio h_c^2/r^2	Hypothetical surface tension dynes/cm.	$\Delta' \times 10^3$	Ratio, β^2/r^2
	Carbon Tetrachloride		
0.02343	23.85	0.77	0.01094
.02405	23.83	0.79	.01123
.02481	23.81	0.82	.01158
.03130	24.12	1.36	.01429
.03434	24.26	1.63	.01554
.03686	24.28	1.80	.01662
.04808	24.65	2.87	.02117
.07721	24.95	5.37	.03324
.08336	25.02	5.90	.03578
.09532	25.01	6.70	.04097
.1002	25.10	7.14	.04294
.1106	25.12	7.79	.04753
.1189	25.16	8.30	.05117
.1264	25.15	8.61	.05459
.1320	25.17	8.87	.05712
.1420	25.18	9.20	.06182
.1523	25.18	9.40	.06674
.1564	25.23	9.60	.06861
.1570	25.18	9.47	.06904
.1663	25.24	9.67	.07346
.1716	25.18	9.46	.07635
.1745	25.24	9.59	.07767
.1747	25.24	9.60	.07774
.1796	25.15	9.26	.08052
.1872	25.25	9.39	.08418
.1946	25.18	8.89	.08839
.1966	25.20	8.87	.08944
.1976	25.12	8.55	.09025
.2099	25.15	7.96	.09701
.2141	25.17	7.75	.09929
.2333	25.20	6.24	.1104
.2393	25.14	5.31	.1143
.2519	25.17	4.59	.1214
.2579	25.25	3.11	.1258
.2814	25.25	−1.31	.1420
	Toluene		
0.04880	26.35	2.83	0.02158
.06186	26.64	4.05	.02688
.08293	26.70	5.65	.03582
.1001	26.85	6.98	.04308
.1508	27.06	9.43	.06598
.1582	26.92	9.16	.06996
.1661	27.08	9.60	.07344
.1894	26.97	8.84	.08587
.1920	27.07	9.08	.08693
.1929	27.10	9.12	.08731
.2062	26.92	7.88	.09519
.2214	26.96	6.94	.1038
.2310	27.03	6.34	.1092
.2414	27.01	5.12	.1156
.2429	27.02	5.00	.1165
.2476	27.00	4.36	.1195
.2613	27.07	2.28	.1284
.2708	27.09	0.70	.1347
.2858	27.12	−2.24	.1451
	Water		
0.1023	71.19	6.93	0.04423
.1295	72.16	8.93	.05583
.1496	71.79	9.19	.06561
.1757	72.14	9.58	.07829
.1961	72.49	9.33	.08870
.2277	72.85	7.97	.1059
.2568	72.14	3.18	.1252

From the measurements at 40° on air bubbles of varying radii in each of these liquids, a hypothetical surface tension was calculated using h_c/r as h/r and employing Porter's[4] empirical equation for values of h_c^2/r^2 less than 0.25 and the Bashforth and Adams[3] tables for greater values. The data are given in Table I and the hypothetical surface tensions of carbon tetrachloride and of toluene as functions of h_c^2/r^2 are presented in Fig. 2. The similarity of the two curves is striking.

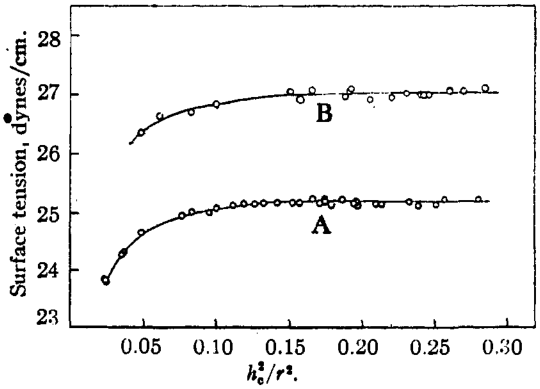

Fig. 2.—Calculated values of "hypothetical" surface tension as a function of bubble shape: curve A, carbon tetrachloride; curve B, toluene.

Not only are they parallel but the true surface tension falls in each case at the same value for h_c^2/r^2.

In order to correlate further the experimental data obtained with the various liquids use was made of a quantity Δ' calculated by Porter's defining equation using h_c/r for h/r. These results are also given in Table I and Δ' is plotted as a function of h_c^2/r^2 in Fig. 3. For comparison, a theoretical curve is given of values of Δ against h^2/r^2 calculated by the method of Porter and of Bashforth and Adams. It will be noted that in the region where these overlap there is some discrepancy between the two sets of data. The deviations are not large, however, for this region of values of h/r and fall within the limits of error specified by Porter.

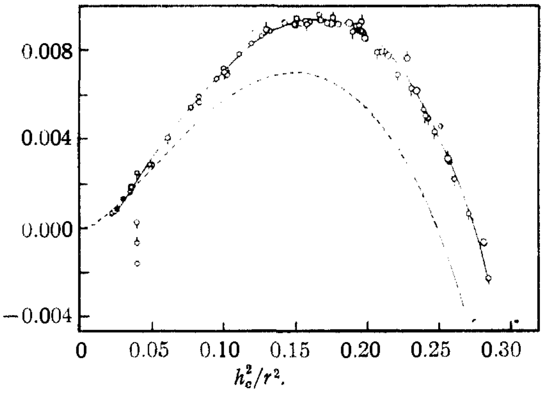

Fig. 3.—Δ' *vs.* h_c^2/r^2: ♀, toluene; ȯ, water; O, carbon tetrachloride; ————, Bashforth and Adams[3]; - - - - ⊥, Porter.[4]

The general trend of the Δ' curve is for the experimental values obtained with toluene to lie below, and those with water to lie above, the values obtained with carbon tetrachloride. This might be due to the fact that the values for the capillary constants are slightly inaccurate. Only a few points were determined with water because this liquid readily evidences contamination and consequently extreme precautions and considerable time was required for each point obtained.

The deviations of the hypothetical surface tensions and of Δ' from the true values as shown in Figs. 2 and 3 are considerable. Whatever the cause of these deviations from theory, they are evidently a function of bubble shape, that is, of h_c^2/r^2; it was accordingly deemed justifiable to use these experimental data for the determination of the surface tension of a liquid.

The simplest procedure is to find β^2/r^2 as a function of h_c^2/r^2; and since $\beta^2 = \gamma/(D - d)g$, the value of γ can be calculated. This can be accomplished by using either a large-scale plot, similar to Fig. 4 using the data obtained with toluene and carbon tetrachloride or empirical equations obtained from the plot giving β^2/r^2 as a function of h_c^2/r^2. Since the curve has a point of inflection, two equations were derived, by the method of least squares; one (a) for the region below, $(0 < h_c^2/r^2 < 0.065)$ and one (b) for the region above $(0.065 < h_c^2/r^2 < 0.300)$ the point of inflection.

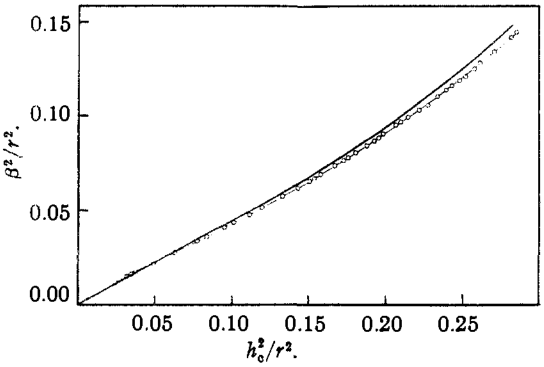

Fig. 4.—β^2/r^2 *vs.* h_c^2/r^2: -o-o-o-, experiment; ————, theory.

$$\text{(a)}\quad \beta^2/r^2 = 0.4543\ h_c^2/r^2 - 0.860\ h_c^4/r^4$$

$$\text{(b)}\quad \beta^2/r^2 = 0.4353\ h_c^2/r^2 - 0.233\ h_c^4/r^4 + 1.675\ h_c^6/r^6$$

Using these data, the surface tension of a liquid can be determined by the sessile bubble method with a precision of ±0.2% or better. The method is independent of the use of Porter's equation or of the Bashforth and Adams tables.

Photographic Procedure

In this procedure the illuminating system and the location of the cell was similar to that of the comparator procedure. However, the comparator was replaced by a magnifying camera which was part of an apparatus for the pendent–drop method.

It was necessary to devise some way of obtaining a reference dimension on the photograph of each bubble. This was accomplished by mounting a black, Pyrex glass rod in a vertical position directly below the center of the bubble-forming plate of the cell. The tip of the rod was of accurately known diameter and arranged so that it appeared on the photograph just below the apex of the bubble.

Using the photograph with its accompanying reference dimension, two procedures may be followed in making the calculations. In the first, a plane mirror is placed so that its surface is perpendicular to the photograph and to the axis of revolution of the bubble. The mirror is then moved slowly over the photograph, while carefully maintaining its alignment, until both edges of the bubble appear to be continuous with their images. When these conditions are fulfilled, the edge of the mirror will lie on the equatorial plane of the bubble. Once the equatorial plane is located, the quantities h and r are measured on the photograph and converted to actual dimensions by comparison with the known diameter of the rod. The calculations from this point on are done by the theoretical methods outlined in the discussion of the comparator procedure.

In the second procedure, a horizontal metal wire is mounted so that its silhouette appears just beneath the apex of the bubble. A parallel horizontal line can then be drawn through any selected plane of the bubble. The mirror is held perpendicular to the photograph and rotated about the point where the horizontal line intersects one edge of the bubble. When a position is found where the edge of the bubble is continuous with its image, the mirror is held firmly in position and a line drawn along its edge on the photograph. The process is repeated on the opposite side of the bubble in order to obtain a check. The line drawn along the mirror is the normal to the bubble edge at this point. The angle between the normal and the selected plane is measured on both sides by a protractor and the two results averaged. This angle is, then, the complement of the angle ϕ (see Fig. 5), which is the angle between the normal to the surface of the bubble at any point and the axis of revolution. In the case of the equatorial plane, $\phi = 90°$. The appropriate dimensions are measured, as in the first procedure, but the calculations are confined to the use of the Bashforth and Adams[3] tables which can be used, by interpolation, for all values of ϕ.

Neither of these procedures has the accuracy obtained with the comparator. This is due not only to the increased number of measurements necessary but, also, to the inaccuracies in mounting the reference glass rod directly below the center of the bubble. The fact of greatest significance, however, is that, when the first procedure was used, it was found that the equatorial plane does not coincide with the center of the illuminated slit of light, although it does pass through near one edge. This observation may be accounted for by a study of the properties of bubbles. With small and medium sized bubbles the bright central line is relatively broad and short. With larger bubbles, however, it becomes long and so narrow that it may be covered by the crosshairs of the comparator. In Fig. 5, which was taken from a photograph, one can observe that the bubble is flattened by contact with the glass plate and hence is asymmetrical with respect to the equatorial plane. As a consequence of this asymmetry, the illuminated slit or band does not fall symmetrically about the equatorial plane. Since the crosshairs of the comparator are always focused on the center of the slit, considerable error is experienced when dealing with small or medium sized bubbles having broad illuminated slits. With larger bubbles, however, experiment and theory should more closely agree as the asymmetry of the bubble would have less effect.

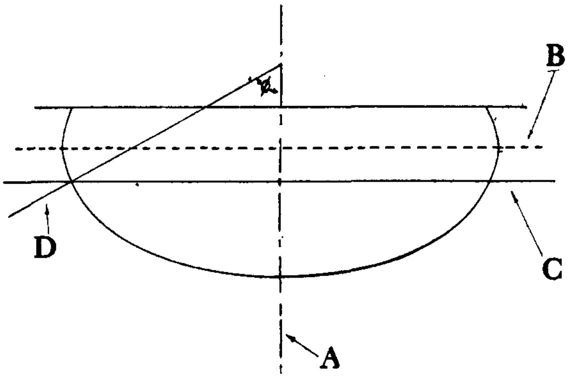

Fig. 5.—Geometry of the sessile bubble: A, axis of revolution; B, equatorial plane; C, selected plane; D, normal to bubble surface at selected plane.

To a certain extent, this prediction is realized. An examination of Figs. 3 and 4 shows that, as h^2/r^2 is decreased, the experimental curve approaches the theoretical and actually crosses below $h^2/r^2 = 0.04$. Below this point the curves again approach each other and presumably meet at $h^2/r^2 = 0$. The crossing of these two curves might well be due to small inaccuracies in Porter's equation.[4]

Summary

1. An improved apparatus for the determination of surface tension with sessile bubbles has been devised in which the dimensions of the bubbles are measured with a comparator. Certain anomalies in the calculated values were observed which proved to be a function of bubble shape. These deviations from theory have been quantitatively determined over a wide range of bubble shapes using liquids of known surface tensions, and empirical equations have been derived which permit the determination of surface tension with good precision.

2. A photographic procedure has also been developed for use with sessile bubbles. Its use has revealed that the anomalies encountered with the comparator are due to the inaccurate definition of the equatorial plane by the horizontal slit of light transmitted by the bubbles.

SEATTLE, WASHINGTON RECEIVED[6] SEPT. 18, 1945

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(6) Original manuscript received October 8, 1943.