tion of phenylacetyl peroxide was decomposed in the presence of oxygen at 18°, had a stable peroxide content of 5.65 mM/l.; the initial concentration was 46.0 mM/l. When a portion of the residual solution (5.65 mM/l.) was shaken with 10% sodium hydroxide, the peroxide content was reduced to 2.32 mM/l. The concentration of the residual solution after standing one more day was 4.88 mM/l. To 3 cc. of the latter solution in 10 cc. of acetic acid was added a solution of lead tetraacetate in acetic acid equivalent to 5.51 cc. of 0.01009 *N* thiosulfate. If all the peroxide were of the type not attacked by lead tetraacetate, the titer should have been 2.90 plus 5.51 cc. Actually the titer was, after letting the solution stand half an hour and treating with sodium acetate–potassium iodide solution, 4.90 cc. This suggests that only about 61% of the peroxide is hydroperoxide, in fair agreement with the proportion destroyed by alkali, 59.5%.

Carbon Dioxide Evolution.—The carbon dioxide was swept through an Ascarite tube by a stream of pure nitrogen until the tube attained a constant weight. Toluene and water vapor were kept out by a Dry Ice and alcohol trap.

Summary

Bis-phenylacetyl peroxide like benzoyl peroxide decomposes with mixed first order and three-halves order kinetics. It is an inefficient initiator of the polymerization of styrene at 0°, at which temperature the peroxide decomposes slightly faster than benzoyl peroxide does at 70°. Despite evidence that free radicals are involved in the decomposition, this reaction is subject to general acid catalysis, the efficiency of an acid catalyst being parallel to its acid strength. It is concluded that bis-phenylacetyl peroxide can decompose according to conditions by both free radical and ionic mechanisms and that a carbon–carbon bond as well as an oxygen–oxygen bond must be broken in the rate-determining step.

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[CONTRIBUTION FROM THE ARGONNE NATIONAL LABORATORY]

The Capillary Rise, Contact Angle and Surface Tension of Potassium

BY LLOYD A. QUARTERMAN AND WILLIAM L. PRIMAK

The surface tension of potassium was first measured by Quincke[1] using a drop weight method in an atmosphere of carbon dioxide. He reported 37 mg./mm. This was recalculated by G. Meyer[2] who obtained the result 411 dynes/cm. The authors recalculated Quincke's results using modern values for the density of potassium[3] and the drop weight corrections given by Harkins and Brown[4] and obtained 500–580 dynes/cm. The Harkins–Brown correction is a little uncertain since Quincke did not completely describe the shape of his drops; but the correction, being always positive, would cause the corrected value to be larger than the value originally reported. If these values are correct, a large capillary rise (or depression) might be expected because the density of potassium is so low. This is not found to be the case.

(a) **The Surface Tension Apparatus.**—A short mercury thread was run down several lengths of Pyrex capillary and observed with a microscope equipped with a micrometer disk eyepiece. From one section whose radius was found constant to 1%, a short piece was selected. The length of a long mercury thread was then measured with a comparator at three positions along this capillary tube, and the mercury weighed. The radius was computed to be 0.0380 cm. with an extreme deviation of 0.5% among the three results. The value agreed with a direct measurement of the cut end of the capillary using a microscope with a micrometer disk eyepiece calibrated against a stage micrometer. The cross section was found to be circular within the precision of the latter measurement (3%). The capillary was sealed to a 35 mm. o. d. tube (about 32 mm. i. d.) to form the apparatus G of Fig. 1, similar to the apparatus described by Richards and Coombs.[5]

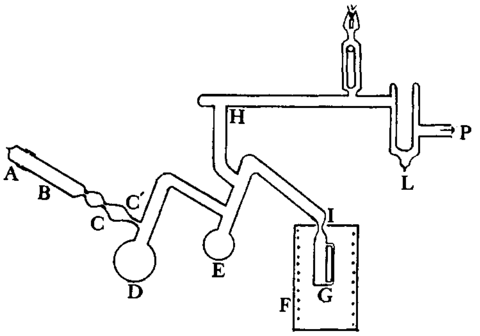

Fig. 1.—Arrangement for filling the surface tension apparatus: L, liquid air trap; P, mercury pump.

(b) **Preparation of Potassium.**—A quantity of commercial C. P. potassium weighing about 150 g. was cleansed of oil by washing in petroleum ether. It was introduced into the tubulation B of the apparatus drawn in Fig. 1, and was dried by passing a stream of purified helium over it while gently warming the glass. The cap A was waxed on, and the apparatus evacuated. The potassium was melted and permitted to flow through the constrictions C and C′ into the 250 ml. flask D, leaving behind a crust of oxide. The tubulation was then sealed off at the constriction C′, and the potassium was refluxed in high vacuum in the flask D. Some potassium was driven into the manifold H to remove volatile impurities and to act as a getter. After refluxing for one hour, about half of the potassium was distilled into the flask E (125 ml.) which had been flamed during the refluxing operation. During the period of refluxing and distillation (some three hours), the surface tension apparatus G was baked out in an oven maintained between 450 and 520°. The glass was colored slightly brown (additive type color centers) as a result of this treatment. About 40 ml. of potassium was now distilled into the surface tension apparatus, and the apparatus sealed off the line at the constriction I. This sample was not analyzed, but another sample prepared in the same way was analyzed. Two assays by the perchlorate method gave the results 99.9_6 and 99.8_2 weight per

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[1] Quincke, *Ann. Physik* (*Poggendorff*), **135**, 621 (1868).

[2] Landolt-Börnstein, "Physikalisch-Chemische Tabellen," 5th ed., p. 200.

[3] "International Critical Tables," Vol. II, p. 463.

[4] Harkins and Brown, THIS JOURNAL, **41**, 519 (1919).

[5] Richards and Coombs, *ibid.*, **37**, 1670 (1915).

cent., respectively,[6] and a study of the melting point curve by the method of White[7] indicated less than 0.014 atomic per cent. impurity. A spectrum analysis was made on this material and the following percentages of impurities reported: Cu 0.05, Ca 0.1, Si 0.01, Na 0.03. These quantities were close to the limit of detection, 0.01%, by the method used.[8]

(c) **Measurements of Capillary Rise.**—The surface tension apparatus was immersed in an oil-bath which could be regulated to several hundredths of a degree, and whose temperature was read on a $^1/_5$ degree mercury thermometer. The capillary was set parallel to a plumb line immersed in the oil-bath. The levels of liquid metal in the capillary and in the tube were observed through a window in the oil-bath and were measured to 0.001 cm. with a cathetometer. After each set of readings, the surface tension apparatus was tipped and potassium poured down the capillary, giving a renewed surface. Most of the results were therefore obtained with a falling meniscus. The results obtained are given in Table I.

The reproducibility of the results on renewing the potassium surface is an indication of its purity. The opacity of the potassium necessitated taking the readings from the top of the meniscus at a point where the potassium did not cling to the glass (see below). To obtain the correct hydrostatic head, a correction must be made to the bottom of the meniscus. The correction for the capillary was observed to be very small. However, the meniscus rose a considerable distance on the wall of the wider tube. This height was not measured; it was judged to be 0.1–0.2 cm. and should be added to the capillary rise reported in Table I.

TABLE I

THE CAPILLARY RISE OF POTASSIUM

Rising temperature			Falling temperature		
Temp., °C.	Capillary rise, cm.	Hydrostatic head, dy./cm.²	Temp. °C.	Capillary rise, cm.	Hydrostatic head, dy./cm.²
64.6	5.667	4600	153.4	5.569	4409
64.5	5.666	4600	145.0	5.618	4458
64.4	5.651	4588	145.0	5.613	4455
73.4	5.655	4579	129.0	5.536	4413
73.4	5.640	4567	129.0	5.534	4412
73.4	5.647	4573	129.0	5.535	4413
85.0	5.613	4532	109.0	5.534	4437
86.1	5.624	4537	109.0	5.542	4443
84.7	5.587	4510	109.0	5.543	4444
83.7	5.679	4586	98.5	5.517	4436
83.0	5.694	4598	98.6	5.518	4437
81.9	5.613	4534	98.8	5.515	4434
97.6	5.554	4467	98.9	5.514	4433
97.8	5.554	4467	75.4	5.462	4420
97.9	5.560	4472	75.4	5.458	4422
108.0	5.602	4493	75.0	5.464	4423
110.0	5.606	4493	75.2	5.459	4418
109.5	5.601	4490	62.0	5.425	4407
110.0	5.590	4481	62.0	5.428	4409
111.8	5.611	4495			
110.8	6.338	4518			
135.0	5.598	4455			
135.0	5.594	4452			
135.0	5.594	4452			
153.4	5.567	4407			
153.4	5.568	4408			
153.4	5.569	4409			

(d) **Contact Angle.**—The potassium, when distilled into the surface tension apparatus, wet the glass immediately and exhibited a capillary rise. When the apparatus was immersed in the oil-bath, the potassium was found to cling to the walls of the larger tube in places, and the surface of the main body of metal showed a uniform, well-formed meniscus. From the observed convex shape of the meniscus, it was apparent that the contact angle was small. Unfortunately, no quantitative measurements of contact angle were made at that time. The apparatus was stored with the potassium solidified in the lower part of it. A year after the capillary rise measurements were made, the apparatus was re-examined. The vacuum was still good, as evidenced by the sharp report obtained when the potassium was melted and poured down the capillary by tilting the vessel. No gas bubble could be observed in the capillary in this operation. The parts of the glass which were covered with potassium during the storage period (the lower glass) behaved quite differently from the rest, in contrast to the uniform behavior exhibited by the glass when the vessel was first filled. Wetting of the parts of the glass which had not been covered (upper glass) was now very poor, and the potassium no longer seemed to cling even to the lower glass as well as it had to all parts of the glass when the apparatus was first prepared. It was concluded that the contact angle had changed on standing.

Quantitative measurements of the contact angle between the potassium and the glass of this apparatus which had been stored for a year were made at 80° by two methods. The first was a modification of the method used by Adam and Jessup.[9] The cylindrical vessel was tipped until the point of farthest advance of the liquid showed no curvature toward or away from the glass. The angle between the tube and a level was measured with a protractor to obtain the contact angle. By solidifying some of the potassium on the upper glass, measurements could be made on the lower glass; and by inverting the apparatus, measurements could be made on the upper glass. A series of measurements on various parts of the lower glass gave the values 25, 26, 30, 25, 26.5 and 26.5°, respectively. On the upper glass, values from 35 to 55° were obtained. The extreme variability in the values for the upper glass was caused in part by the difficulty in observing the curvature at those angles, and in part by the variation in contact angle from point to point on the upper glass. The latter was confirmed by the irregularity in the shape of the meniscus on the upper glass, in marked contrast to its uniformity on the lower glass.

The second method was a quantitative modification of the method described by Richards and Carver.[10] A straight filament lamp was focused on a cylindrical element of the inner wall of the large tube. The reflections from the wall and the uppermost part of the meniscus were observed with a sighting arrangement, and the angle between the beams measured with a protractor.[11] The normals to these surfaces at the highest point on the meniscus were therefore determined, and hence the contact angle. No reflection could be found for the meniscus on the upper glass, confirming a large contact angle. The method was used to determine the contact angle at several points on the lower glass and the values 22 and 26° were obtained with the incident beam grazing the level surface of the potassium at 15°. A value of 24° was obtained with the incident beam grazing the level surface of the potassium at 7°.

In both methods a large part of the potassium vessel was above the surface of the oil-bath, and evaporation was taking place as proved by the film of potassium which condensed on the part of the glass above the oil. Since evaporation has been found to increase the contact angle mark-

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(6) We are indebted to K. Jensen of this Laboratory for these analyses.

(7) White, *J. Phys. Chem.*, **24**, 396 (1920).

(8) We are indebted to J. A. Goleb of this Laboratory for this analysis.

(9) N. K. Adam, "Physics and Chemistry of Surfaces," 3rd ed., Oxford University Press, New York, N. Y., p. 185.

(10) Richards and Carver, THIS JOURNAL, **43**, 827 (1921).

(11) Some care was needed to sort the multiple reflections from the direct ones.

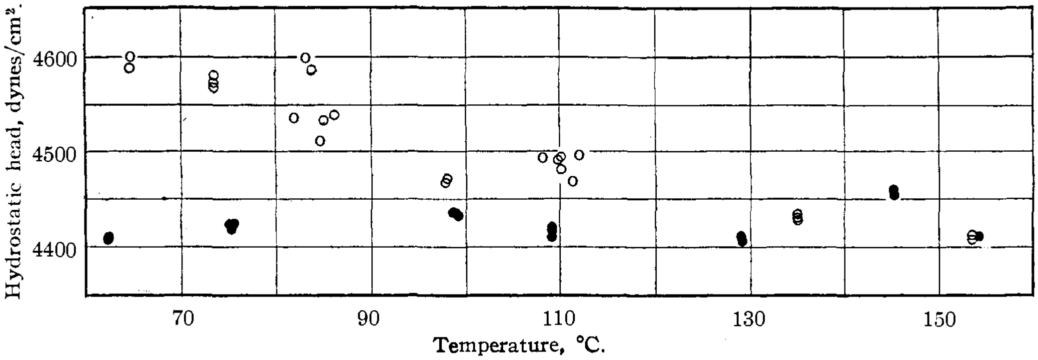

Fig. 2.—Capillary rise of potassium: ○, rising temperature; ●, falling temperature.

edly,[9,10] and since, in this work, the contact angle was found to have increased on standing, it is concluded that the contact angle in the original measurements was much less than 26°.

It is believed that the low contact angle originally observed is to be attributed to the manner of treating the glass: *i. e.*, baking out in high vacuum and in potassium vapor. Similar wetting effects have been reported for other metals.[9] It was not considered worthwhile to measure the contact angles more precisely with the cell employed; and, hence, the contact angle was not measured over a range of temperatures. It is doubtful whether the dependence of the contact angle on temperature would affect the surface tension markedly since only the cosine of the angle is involved in the formula and in a range where the cosine is not very sensitive to changes in angle. Since the high reflectance of the liquid metal surface makes it possible to obtain measurements of high precision, future workers might well consider building an optically suitable cell and using a telescope with a Gaussian eyepiece.

(e) **The Surface Tension of Potassium.**—If the contact angle is assumed to be zero, the surface tension calculated from the corrected hydrostatic head in Table I is 86 dynes/cm. Even a contact angle as large as that measured, 24–26°, would increase the above value by only 11%, and give the result 95 dynes/cm. The uncertainty of the correction in hydrostatic head because the measurements were made from the top of the meniscus is estimated as 2%.

(f) **The Temperature Coefficient of the Surface Tension.**—The results given in Table I are plotted in Fig. 2. The measurements were made over a period of several days, first with rising temperatures, and then with falling temperatures. It is seen that the hydrostatic head of the capillary rise decreased slightly with increasing temperature and remained constant with decreasing temperature. This behavior is believed to be further evidence of an increase of the contact angle on standing. The change in capillary rise during the time of measurements was a little under 4%. For original contact angles of 0, 5, 10 and 15°, the change in contact angle required to produce a 4% change in capillary rise would be 16, 14, 9 and 7°, respectively. If such a change were taking place, the surface tension plotted as a function of temperature would be less steep than the values obtained from the rising temperature curve of Fig. 2, but more steep than the values obtained from the falling temperature curve.

Summary

A sample of pure potassium was prepared and distilled into a Pyrex glass surface tension apparatus that was baked out in high vacuum and potassium vapor. It was found that the potassium wetted the glass with a small contact angle and exhibited a capillary rise which would have required a surface tension of 86 dynes/cm. if the contact angle were zero. It was indicated that on standing the glass surface altered, causing the contact angle to increase. Contact angles were measured by two methods. It was shown that the contact angle must have been less than 26° at the time of the original measurements. Hence, the contact angle correction to the above result must be less than 11%.

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