

Summary.

1. Dilute solutions of dialyzed and undialyzed silicic acid behave towards electrolytes in the same manner as concentrated solution with the exception that proportionally more reagent is needed.

2. The optimum hydrogen ion concentration for the precipitation of the aluminum hydroxide and the removal of silicic acid by aluminum hydroxide is a concentration of 1×10^{-8} .

3. The limiting values of the hydrogen ion concentration, between which the solid aluminum hydroxide phase is present, are 1×10^{-4} and 1×10^{-11} .

4. The presence of silicic acid prevents the formation of a precipitate of aluminum hydroxide, when the sodium hydroxide, equivalent to the aluminum chloride present, is added all at once. The silicic acid probably acts as a protective colloid preventing precipitation of the aluminum hydroxide. The presence of bivalent cations destroys this protective power.

5. The action of electrolytes on clay suspensoids is the same in dilute as in concentrated suspensions.

6. Sodium hydroxide, hydrogen carbonate, carbonate and sulfate stabilize or disperse clay suspensions at one concentration and coagulate at another.

7. The ratio of the coagulating power of calcium and barium hydroxides to aluminum hydroxide is about 1 to 5.

8. Coagulation of clay suspensions is aided by the bivalent and hindered by monovalent cations in the presence of acid carbonate, carbonate, sulfate and hydroxyl anions.

9. Silicic acid retards coagulation of clay suspensoids.

URBANA, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MT. UNION COLLEGE.]

A SURFACE TENSIMETER FOR SMALL QUANTITIES OF LIQUIDS.

BY C. C. KIPLINGER.

Received November 12, 1919.

An instrument for measuring surface tension which requires only a drop or two of the liquid under examination has been developed in our laboratories as an aid in the identification of organic liquids. It comprises a piece of capillary glass tubing 18 cm. long, about 1 mm. internal and 4 mm. external diameter. This is broken very carefully from a long piece by making a minute cut in the glass with a carborundum crystal, then breaking as usual, using all possible precautions to get a clean cut and a right-angled fracture. Several tubes should be broken and the

best one selected for this purpose. A quadrant cut from a celluloid protractor is pierced with two holes and attached to the tube with the device previously described,¹ so that it may be removed with ease or adjusted to tubes of different diameters.

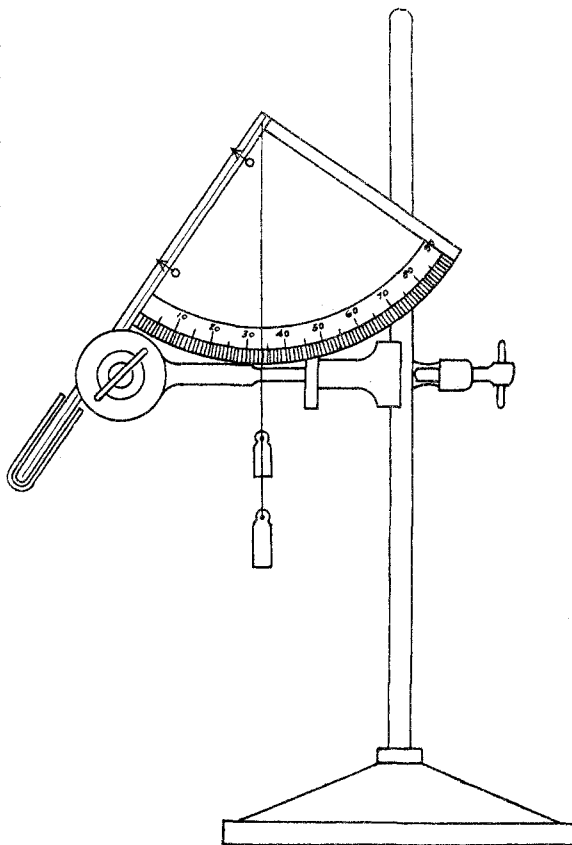
A small notch cut in the apex of the quadrant holds a thread in position which passes over it, the thread carrying a small weight at each end and serving to indicate the angular displacement of the tube. The threads on each side of the protractor eliminate the error of parallax in the readings. A perforated cork supporting a bolt and two grooved cork washers is held by a clamp and stand and carries the tube and its attachments. A glass cap 5 cm. long made from a bit of tubing large enough to pass over the capillary tube without binding, serves to retard evaporation.

The tube is thoroughly cleaned and dried and a short column of liquid, 1 cm. to 3 cm. (the lower the tension and the greater the density, the shorter the column) introduced into the capillary. The tube with its enclosed thread of liquid is then turned

to such an angle that the meniscus at the lower end changes to a plane surface. The point at which this occurs is observed by the use of a pocket magnifier. This adjustment should be made in a good light with a sheet of white paper as a background. The angle A is then read and checked by readjusting 2 or 3 times and the length L of the liquid thread measured to 0.1 mm.

$L \cos A = h$, where h is the height of the vertical column exerting the same downward pressure as the inclined thread of liquid. The tube may

¹ *J. Ind. Eng. Chem.*, 10, 8, 631 (1918).



be calibrated with water and the true diameter of the capillary thus determined, or this diameter may be measured directly with a microscope and micrometer. The latter method was used in this work.

The familiar formula $T = \frac{d \times h \times r \times 980}{2}$ dynes per cm. is used in the calculation of T , the surface tension.

Experimental Results.

Water, benzene, toluene, carbon tetrachloride, and ethylene dibromide were purified according to directions given in part by Richards and Coombs,¹ and the temperature coefficients were taken from a paper by Harkins,² which also gives the surface-tension constants for more than 300 substances.

The water used was redistilled from potassium permanganate and sulfuric acid, boiled in a quartz vessel just before using and the capillary filled with the hot liquid, then allowed to stand until coming to room temperature.

TABLE I.—RESULTS OBTAINED BY USING A POCKET MAGNIFIER.

Angle of inclination measured from horizontal, therefore $A = 90 - \text{angle}$.			
Expt.	Water, degrees.	T_{20° . Dynes, cm.	Correct value.
1.....	56.5	71.1	
2.....	65.5	70.7	
3.....	58	71.8	
		Av., 71.2	72.7
Benzene.			
1.....	53.5	25.9	
2.....	56.5	26.4	
3.....	42.5	27.4	
		Av., 26.6	28.9
Carbon Tetrachloride.			
1.....	28.5	23.9	
2.....	58	23.8	
3.....	61.5	23.7	
4.....	44.5	24.7	
		Av., 24.0	26.7

From the above results it is apparent that this method will serve to distinguish between liquids, the surface tensions of which show a difference of 2 or 3 units. The experimental results are generally low, the above figures being typical. The variations in readings are due in part to the difficulty experienced in determining the exact position in which the meniscus changes to a plane surface. Moreover, it is a hard matter to adjust and read the instrument for angles greater than 70° , hence

¹ THIS JOURNAL, 37, 1656-76 (1915).

² *Ibid.*, 39, 556-69 (1917).

the used angles lie chiefly between 50° and 70° , However, there seems to be little change in accuracy for different angular readings.

The results are very much improved by attaching the tensimeter to the stage of a compound microscope and obtaining the angles by tilting the body of the microscope. The cap of the tensimeter was taped to a rather thick glass slide and proved an adequate support for the capillary tube and quadrant, allowing it to be easily removed. The stage springs

TABLE II.—RESULTS OBTAINED BY USING A MICROSCOPE.

Expt.	Angle, degrees. $A = 90 - \text{angle.}$	T_{20° . Dynes, cm. Water.	Correct value.	Error, %
1.....	59	71.6		
2.....	62.5	72.2		
3.....	64.5	71.2		
4.....	68.5	71.8		
5.....	54	71.1		
		Average, 71.6	72.7	-1.5
Benzene.				
1.....	58	27.7		
2.....	65	28.5		
3.....	49	26.8		
4.....	65.5	27.3		
5.....	53.5	27.4		
		Average, 27.5	28.9	-4.8
Carbon Tetrachloride.				
1.....	63	25.2		
2.....	71	24.3		
3.....	50	25.7		
4.....	58	26.8		
5.....	50.5	25.4		
		Average, 25.5	26.7	-4.5
Toluene.				
1.....	65.5	26.5		
2.....	51.25	27.1		
3.....	55.75	27.4		
4.....	69.5	27.6		
5.....	55	27.6		
		Average, 27.2	28.58	-4.8
Ethylene Dibromide.				
1.....	40.25	37.7		
2.....	50	37.2		
3.....	52.75	37.5		
4.....	58.5	37.7		
5.....	45	37.7		
		Average, 37.6	38.73	-2.9

held the slide firmly enough to prevent movement of the assembled apparatus. The results given above were obtained with a 10× micrometer eyepiece and a $\frac{2}{3}$ in. objective. The microscope was first focussed on the upper edge of the tube, the position of which was read on the micrometer scale, then focussed down to the bottom of the meniscus, which should be so illuminated as to show as a bright line, and the body inclined until the upper edge of the bright line broadened and touched the scale mark, which from the first reading indicated the position of the upper edge of the tube. If a micrometer eyepiece is not available, one with cross-hairs will serve to locate the edge of the tube, although the difficulty of adjustment is somewhat increased. It is obvious that tubes with their ends ground accurately at right angles and polished would give better results than those used in this work. The determinations can be made very rapidly.

The fact that these results are uniformly low is striking. This may be due in part to a slight change in the length of the column arising from the flattening of the meniscus, the actual length being slightly greater than the distance as measured between the bottoms of the two menisci. A correction factor is indicated.

The writer is indebted to Dr. W. B. Harkins for his kind suggestions relative to the testing of this instrument.

Summary.

A device is described, by means of which the surface tension of a liquid may be determined when only a drop or two is available, and which may be used as an aid in identifying organic liquids.

ALLIANCE, OHIO.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY. No. 120.]

A THERMODYNAMIC INVESTIGATION OF REACTIONS INVOLVING SILVER SULFIDE AND SILVER IODIDE.

BY ARTHUR A. NOYES AND E. STANLEY FREED.

Received November 29, 1919.

CONTENTS.—1. Outline of the Investigation. 2. Description of the Equilibrium Experiments. 3. The Data of the Equilibrium Measurements and the Activity-Coefficients Calculated from Them. 4. Discussion of the Activity Coefficients Derived from the Equilibrium Measurements. 5. The Electromotive Force of Hydrogen Silver-Sulfide Cells. 6. The Electromotive Force of Hydrogen Silver-Iodide Cells. 7. Free-Energy Changes Attending the Reactions. 8. Summary of the Free-Energy Values.

1. Outline of the Investigation.

This research consists on the experimental side primarily in a determination of the equilibrium at 25° of the reaction

