carbonate, that the hydroxyl ion resulting from the hydrolysis of the alkali salt of a weak acid cannot be wholly responsible for the observed results.

HOUGHTON, MICHIGAN

THE SURFACE RELATIONS OF THE COMPONENTS OF PINE OIL AND OF POTASSIUM ETHYL XANTHATE. II[1]

BY C. C. DeWITT AND R. F. MAKENS

The object of the work here reported is two-fold: to determine the surface relations of aqueous solutions of various components found in pine oil and to extend the work of DeWitt and Roper[2] on the surface tensions of aqueous potassium ethyl xanthate solutions. The data on surface tension will be used in conjunction with wettability experiments now in progress in this Laboratory. The data on the pine oil components can also be used as a measure of the value of the several constituents as frothers for ore flotation purposes.

All surface-tension determinations were made with a drop-weight apparatus, and all interfacial tension determinations with a drop-volume apparatus. Both sets were constructed by Mr. Richard Kittel of the Kent Chemical Laboratories, the University of Chicago, under the supervision of Dr. Gans.

The drop-weight apparatus was similar to that used by Gans and Harkins[3] except for the method of raising and lowering the supply bottle. Each determination consisted of a run of thirty drops followed by a run of five drops. The difference represented the weight of twenty-five drops. Two determinations were made at each concentration. This procedure is that suggested by Harkins and used in the experiments reported in his latest paper on the subject, except that he made twenty-drop instead of thirty-drop runs. The equation used in the calculation of the surface tension is

$$\gamma = \frac{w\,g\,\phi}{2\,\pi\,r}$$

where γ is the surface tension, w is the weight of one drop, d is the density of the liquid phase, r is the radius of the tip, v is the volume of the drop calculated from the weight and density and ϕ is the reciprocal of a function of $r/v^{1/3}$.

The functions were taken from the work of Harkins and Brown.[4]

[1] These papers were presented at the Spring Meeting of the American Chemical Society at Indianapolis, Division of Physical and Inorganic Chemistry.

[2] DeWitt and Roper, THIS JOURNAL, 54, 444 (1932).

[3] Gans and Harkins, ibid., 52, 2290 (1930).

[4] Harkins and Brown, ibid., 41, 519 (1919).

The interfacial tension apparatus was very similar to that constructed by Harkins and Humphrey.[5] The equation for calculating the interfacial tension is

$$\gamma_{12} = \frac{v\,(d - d)\,g}{2\,\pi\,r}$$

where γ_{12} is the interfacial tension of the liquid–liquid interface, v is the volume of the drop, d is the density of the upper liquid, d' is the density of the lower liquid, r is the radius of the tip, ϕ is a function of the quantity r/v^{1} [?].

The table of correction functions was the same as that applied in the drop weight method.[6] All density determinations were made with ordinary 25-ml. pycnometers. The usual precautions necessary for accurate work were observed. The temperature was maintained at 25.00 ± 0.015° in a water-filled glass thermostat.

The Materials Used.—The benzene for the standardization of the drop-weight and the drop-volume apparatus was a thiophene-free C. P. grade obtained from Eimer and Amend. It was cooled to 0°, and, after it had solidified as much as possible, the mother liquor was poured off. The solid melted at 5.5°, and was then cooled and re-solidified. The mother liquor was poured off, and the benzene crystals were twice distilled in a 76-cm. fractionating column. The boiling point was now constant. The middle fraction was used.

The water for standardization work was purified according to the procedure followed by DeWitt and Roper,[2] and results similar to theirs were obtained. The Harkins drop-weight apparatus showed no detectable difference between the surface tension of the specially purified grade of distilled water and that of the ordinary laboratory grade. However, the specially purified grade was used for all standardization work.

Ordinary steam-distilled Yarmour pine oil was used with no further purification except that it was dried over anhydrous calcium chloride for a month—not an effective method of drying pine oil, as later distillation proved. The densities of two samples from different kegs were d_4^{25} 0.92813 and d_4^{25} 0.92833, respectively, after the drying. That pine oil is by no means constant in composition is indicated by Taggart[7] and by analysis made in this Laboratory.

The potassium ethyl xanthate used was purified by the method used by DeWitt and Roper. A Carius combustion to determine purity gave very satisfactory results.

The compounds found in pine oil vary to some extent with the wood or needles used. The compounds usually found in pine oil in appreciable amounts have been named by O. A. Pickett,[8] as α-terpineol, pinene, dipentene, terpinolene, borneol and fenchyl alcohol. A. Schorger[9] and R. H. Stevens[10] mention small amounts of camphor and other products.

[5] Harkins and Humphrey, THIS JOURNAL, **38**, 237 (1916).

[6] Harkins, "Colloid Chemistry," Alexander, The Chemical Catalog Co., New York, 1926, p. 259.

[7] Taggart, "Manual of Flotation Processes," John Wiley and Sons, New York, p. 41.

[8] O. A. Pickett, in a private communication, Hercules Powder Company, Experimental Station, Kenvil, New Jersey.

[9] A. Schorger, "The Oils of the Coniferae; The Leaf and Twig Oils of Long Leaf Pine and Cone Oils of Long Leaf Pine," *J. Ind. Eng. Chem.*, **6**, 723 (1914).

[10] R. H. Stevens, *Chem. Met. Eng.*, **26**, 37 (1922).

The pinene, dipentene and terpinolene were purified by drying and by from five to eight distillations in a still with a 23-cm. fractionating column.

The physical constants obtained are listed in the table.

Substance	Density$_4^{25}$	n_D^{25}	$(\alpha_s)_D^{25}$	Boiling point, °C.
Pinene	0.85353	1.4671	+0.83	156.1–157.6
Dipentene	.84108	1.4748	+4.38	176.3–177.2
Terpinolene	.85768	1.4823'	+0.20	185–186.7

The symbols have their usual significance; that is, n_D^{25} is the index of refraction at 25° and $(\alpha_s)_D^{25}$ the angle of specific rotation at 25°. Sodium light was used in both measurements.

Borneol was dissolved in a little hot ethyl alcohol and filtered, and then water was added. Then the borneol was removed and the process repeated. The crystals were dissolved in benzene at 70° and were recrystallized when cooled to twenty degrees. They were again filtered, and dried in a vacuum desiccator. The melting point was 207.0–207.5°. It was taken with a sealed tube, since borneol boils at 212°.

α-Terpineol has a decided tendency to supercool when in the liquid state. In a low freezing mixture, however, it crystallizes fairly rapidly. The crystals thus produced were filtered off, dissolved in a small amount of warm alcohol, refiltered and again placed in the freezing mixture. The resulting crystals were dried. The crystals melted at 35° over a one-degree range.

The fenchyl alcohol was similarly treated. Its melting point was 37.8–38.3°.

The camphor was a U. S. P. grade, and no further purification was attempted. It melted at 179.9–180.8°.

The results of the surface and interfacial tension measurements are given in the tables.

TABLE I

THE SURFACE TENSIONS OF AQUEOUS SOLUTIONS OF YARMOUR STEAM DISTILLED PINE OIL AT 25°. MEASURED WITH A HARKINS DROP-WEIGHT APPARATUS

Concn., g. per 1000 g. of H₂O	Wt. of 1 drop, g. a	b	Surface tension γ_a	γ_b	γ_{av}
0.000	0.11034	0.11034	72.13	72.13	72.13
.00353	.11040	.11039	72.16	72.13	72.14
.00911	.11034	.11031	72.13	72.12	72.13
.01265	.11005	.11015	71.92	71.98	71.95
.02083	.10977	.10977	71.93	71.79	71.85
.03795	.10836	.10850	70.82	70.91	70.86
.07495	.10593	.10603	69.25	69.31	69.28
.11458	.10118	.10109	66.14	66.08	66.11
.15359	.10036	.10070	65.71	65.83	65.77
.20313	.09614	.09594	62.79	72.72	62.75
.39982	.08919	.08913	58.26	58.27	58.26
.86327	.07822	.07816	50.91	50.87	50.89

The tip radius of the drop-weight apparatus is 0.3985 cm.

The density of the most concentrated aqueous solution of pine oil used was found to be d_4^{25} 0.99696, while that of pure distilled water at this temperature is d_4^{25} 0.99797.

The amount in solution at the highest concentration given was taken as the weight of pine oil added. At this point two distinct phases were visible.
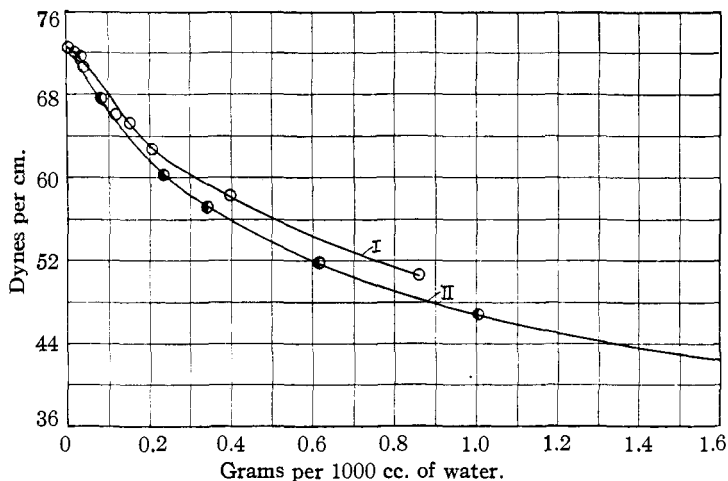
The foregoing data are plotted in Fig. 1.

Fig. 1.—Surface tensions of aqueous solutions of pine oil (I) and α-ter-
pineol (II) at 25° given for purposes of comparison.

TABLE II

THE SURFACE TENSIONS OF SATURATED AQUEOUS SOLUTIONS OF CERTAIN TERPENES AT
25°, MEASURED WITH A HARKINS DROP-WEIGHT APPARATUS

Terpene	Wt. of 1 drop, g. a	b	γ_a	Surface tension γ_b	$\gamma_{av.}$
Pinene	0.11004	0.11009	71.91	71.93	71.92
Dipentene	.10941	.10937	71.53	71.48	71.51
Terpineolene	.10956	.10959	71.62	71.63	71.62

These terpenes are nearly insoluble in water.

TABLE III

THE SURFACE TENSIONS OF AQUEOUS SOLUTIONS OF CAMPHOR AT 25°

Molality	Wt. of 1 drop, g. a	b	γ_a	Surface tension γ_b	$\gamma_{av.}$
0.000000	0.11034	0.11039	72.12	72.14	72.13
.001009	.10309	.10321	67.40	67.47	67.43
.001540	.10009	.00984	65.42	65.27	65.34
.005083	.08759	.08758	57.22	57.21	57.21
.007250	.08297	.08285	54.11	54.03	54.07
.012	.08002	.08005	52.09	52.11	52.10

The density of the concd. solution is d_4^{25} 0.99699.   The tip radius is 0.3985 cm.

The solubility of the saturated solution was taken from the work of Leo
and Rimbach.[11]

The solubility of the saturated solution was determined by extrapolation
of the surface tension–concentration curve.   The density of the concd.
solution was d_4^{25} 0.99701.

[11] Leo and Rimbach, *Biochem. Z.*, **950**, 306 (1919).

TABLE IV

THE SURFACE TENSIONS OF AQUEOUS SOLUTIONS OF FENCHYL ALCOHOL

Molality	Wt. of 1 drop, g.		Surface tension		
	a	b	γ_a	γ_b	$\gamma_{av.}$
0.00000	0.11034	0.11039	72.12	72.14	72.13
.0003061	.10612	.10622	69.50	69.37	69.43
.0006631	.10045	.10052	65.66	65.71	65.68
.0013856	.09820	.09279	60.64	60.64	60.64
.0021076	.08829	.08804	57.53	57.68	67.60
.0024146	.08639	.08632	56.39	56.44	56.42
.0034289	.08240	.08239	53.72	53.72	53.72
.0040092	.07992	.07979	52.05	51.97	52.01
.0067747	.07404	.07409	48.05	48.12	48.07
.0078624	.07178	.07161	46.52	46.42	46.47
.00840	.07115	.07112	46.09	46.07	46.08

The tip radius is 0.3985 cm.

TABLE V

THE SURFACE TENSIONS OF AQUEOUS SOLUTIONS IN BORNEOL

Molality	Weight of 1 drop, g.		Surface tension		
	a	b	γ_a	γ_b	$\gamma_{av.}$
0.00000	0.11034	0.11039	72.12	72.14	72.13
.0000984	.11001	.10994	71.89	71.84	71.86
.0003244	.10705	.10691	69.98	69.89	69.93
.0006354	.09954	.09956	65.07	65.08	65.07
.0009543	.09510	.09526	62.21	62.26	62.23
.0012120	.09326	.09326	60.91	60.78	60.84
.0019256	.08694	.08680	56.79	56.74	56.76
.0031404	.08051	.08041	52.45	52.39	52.42
.00407	.07560	.07566	49.14	49.20	49.17

The density of the concd. solution was d_4^{25} 0.99702.   The tip radius is 0.3985 cm.

The solubility of the saturated solution was taken from the work of S. Mitchell.[12]

TABLE VI

THE SURFACE TENSIONS OF AQUEOUS SOLUTIONS OF α-TERPINEOL

Concn., g. per 1000 g. of H₂O	Molality	Wt. of 1 drop, g.		Surface tension		
		a	b	γ_a	γ_b	$\gamma_{av.}$
0.00000	0.00000	0.11034	0.11039	72.12	72.14	72.13
.08088	.0002245	.10345	.10345	67.63	67.63	67.63
.23118	.001500	.09212	.09200	60.19	60.12	60.15
.34200	.002218	.08736	.08741	57.07	57.10	57.08
.61610	.003995	.07955	.07973	51.92	51.81	51.86
1.0331	.006704	.07250	.07247	47.01	47.03	47.02
1.71102	.011095	.06598	.06590	41.79	41.84	31.82
2.10	.0136	.06004	.05997	38.39	38.36	38.38

The tip radius is 0.3985 cm.   The density of concd. soln. is d_4^{25} 0.99691.

Concentrated solution surface tension was redetermined with another tip. The results were as follows:

[12] S. Mitchell, THIS JOURNAL, **48**, 1333 (1926).

G. per 1000 g. of H₂O	Molality	Wt. of 1 drop, g.		Surface tension γ_a	γ_b	$\gamma_{av.}$
2.10	0.0136	0.06004	0.05997	38.56	38.50	38.53

The tip radius was 0.2702 cm.

The solubility found by Rhode[13] was 1.98 g. or 0.0129 mole per liter at 15–20° for terpineol in aqueous solution.

The concentration given for the saturated solution is slightly larger. It was determined by extrapolation of the surface tension–concentration curve for the data given above.

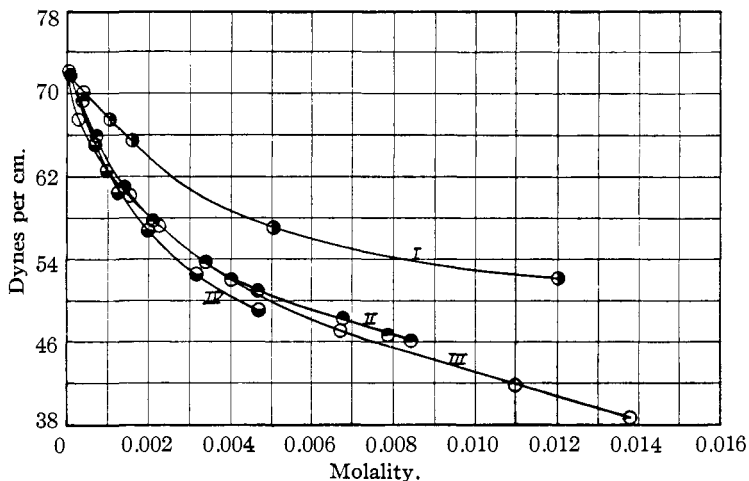The data for the terpene alcohols and camphor are plotted in Fig. 2.

Fig. 2.—Surface tensions of aqueous solutions of (I), camphor, (II), fenchyl alcohol, (III), α-terpineol and (IV), borneol at 25°.

TABLE VII

THE SURFACE TENSION RELATIONSHIPS OF AQUEOUS SOLUTIONS OF α-TERPINEOL AND DIPENTENE

	G. of dipentene per 1000 cc. of H₂O	G. of α-terpineol per 1000 cc. of H₂O	Surface tension γ
(1)	0.36848	1.44184	52 01
(2)	.36848	0.00000	71.50
(3)	.00000	1.44184	44.10
(4)	.75306	0.89406	54.21
(5)	.00000	.89406	49.15
(6)	.75306	.00000	71.50

Data for grams of α-terpineol per 1000 cc. of water shown in the horizontal columns (3) and (5) were taken from the surface tension concentration diagrams for aqueous solutions of α-terpineol. Data for grams of dipentene per 1000 cc. of water shown in horizontal columns (2) and (6) were taken from the result for the saturated solution since the solubility is

[13] Rhode, *Biochem. Z.*, **130**, 481–496 (1922).

considerably less than the amounts of dipentene used.   Data in horizontal columns (1) and (4) were measured directly and the surface tensions given are the average of two determinations.

TABLE VIII

THE INTERFACAL TENSION BETWEEN PINENE AND AQUEOUS SOLUTIONS OF α-TERPINEOL

Mole of terpineol solution	Vol. of drops, ml.	Interfacial tension, dynes/cm.
0.00000	0.5737	26.69
.001500	.5717	26.67
.003995	.5700	26.50
.006705	.5710	26.65
.01360	.5716	26.58

The density of the pinene was d_4^{25} 0.85353.   The tip radius is 0.7969.   The density of the satd. terpineol sol. was d_4^{25} 0.99699.

TABLE IX

THE SURFACE TENSIONS OF AQUEOUS SOLUTIONS OF POTASSIUM ETHYL XANTHATE

Molality	Wt. of 1 drop, g.		d_4^{25}	Surface tension		
	a	b		γ_a	γ_b	$\gamma_{av.}$
0.00000	0.11034	0.11039	0.99707	72.12	72.14	72.13
.08392	.10965	.10954	1.0025	71.66	71.59	71.62
.32480	.10858	.10860	1.0146	70.82	70.83	70.82
.63774	.10599	.10597	1.0365	69.26	69.28	69.27
.66189	.10618	.10594	1.0382	69.39	69.24	69.31
.92137	.10429	.10430	1.0507	68.18	68.18	68.18
1.0418	.10341	.10319	1.0562	67.59	67.46	67.52
1.2898	.10146	.10166	1.0670	66.31	66.44	66.37
2.1815	.09770	.09761	1.1104	63.70	63.64	63.67
5.2559	.08920	.08801	1.1994	57.29	57.17	57.23
6.70	.08514	.08509	1.2256	55.08	55.06	55.07

The tip radius is 0.3985 cm.

The foregoing data are plotted in Fig. 3.   The molality of the saturated solution was determined by extrapolation of a density–concentration curve (not shown).

Discussion of Results

The results obtained by DeWitt and Roper[2] through the use of the Ferguson–Dowson method for the measurement of the surface tension of aqueous solutions of potassium ethyl xanthate are in close agreement with those obtained by the drop-weight method in this Laboratory.   Therefore, in the measurement of the surface tensions of aqueous solutions of potassium ethyl xanthate by the Ferguson–Dowson method, there is good reason for assuming that the contact angle is zero or, at least, that it is negligible.

The results obtained for the surface tensions of aqueous pine oil solutions are in accord with those which Fahrenwald[14] secured by the drop-weight

[14] A. W. Fahrenwald, *Trans. Am. Inst. Met. Min. Eng.*, **70**, 647 (1924).

method, but do not agree with those which he obtained with the Jaeger and Fahrenwald methods.

The compounds pinene, dipentene and terpinolene have but little effect on the surface tension of water. Taggart and Guadin[15] found that very slightly soluble substances are not good frothers.
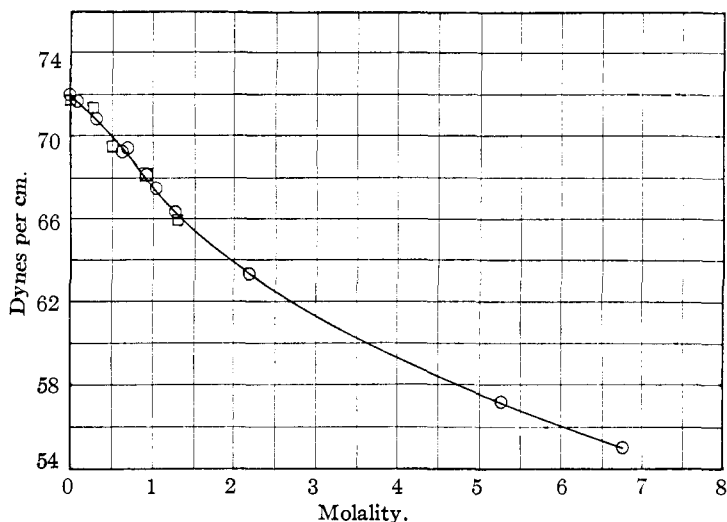

Fig. 3.—The surface tensions of aqueous solutions of potassium ethyl xanthate at 25°. The concentration of the last point was determined by extrapolation of density–concn. curve. Squares represent points determined by DeWitt and Roper using the Ferguson–Dowson method. The circles represent determinations made by the drop-weight method.

Harkins and Cheng[16] state that the highly polar group is necessary to adsorption at the liquid interface. They found that the adhesional energy is greatly increased by the addition of oxygen but is little affected by the presence of the double bond. Since terpineolene, pinene and dipentene all have double bonds but no oxygen, little effect on the surface tension of the water solution would be expected. In spite of the slight effect of these compounds, they appear to act as froth stabilizers by increasing the viscosity of the surface film.[17]

The introduction of the hydroxyl group either into the monocyclic ring, as in fenchyl alcohol or borneol, or in the side chain as in α-terpineol, greatly increases the solubility and surface tension lowering effect. An inspection of the surface tension–concentration curves shows that lowering of surface tension of a dilute aqueous solution is practically the same regardless of the position of the OH radical for the terpene alcohols studied. The effective-

[15] Taggart and Guadin, *Trans. Am. Inst. Met. Min. Eng.*, **68**, 479 (1923).

[16] Harkins and Cheng, THIS JOURNAL, **43**, 35 (1921).

[17] Wilson, "Colloid Chemistry," Alexander, Ref. 6, p. 276

ness, per mole, of camphor is slightly more than half that of borneol and is probably due to the substitution of the O for the OH in the otherwise similar compounds. There is some relation between the position of the hydroxyl group and the solubility, a relation which affects the lowering of surface tension in concentrated solutions.

The work reported here would indicate that terpineol, borneol and fenchyl alcohol are nearly equally effective as frothing agents at the concentrations used in flotation practice. However, according to O. A. Pickett[8] α-terpineol constitutes 40% or more of Yarmour pine oil. The fenchyl alcohol constitutes about 8%, and the borneol 10%.

The presence of dipentene, and presumably of the other terpenes, greatly decreases the effectiveness of α-terpineol as a surface tension lowering agent in water solution. At the concentration at which measurements were made, roughly half the weight of terpineol would have achieved the same surface tension lowering had no dipentene been present.

Further evidence of the loss in effectiveness of the α-terpineol is shown by a comparison of the surface tension–concentration curves of aqueous solutions of pine oil and α-terpineol. The terpineol curve is steeper.

Guadin, Glover, Hansen and Orr[18] have measured the surface tensions of terpineol solutions by the du Nouy method. Their results are not in agreement with the results obtained in this Laboratory. The discrepancy in values is probably due to the difference in results found by Harkins, Young and Cheng,[19] who compared the du Nouy and drop-weight methods.

The interfacial tension of aqueous solutions of α-terpineol against pinene did not change with concentration. Since the α-terpineol is very soluble in pinene, however, most of it is probably in the pinene phase. The interfacial tension of pinene–aqueous solutions of α-terpineol is high, a fact which indicates very little mutual attraction of the water and pinene molecules.

Summary

1. The surface tension–concentration curves of potassium ethyl xanthate have been extended. Good agreement has been found to exist between the measurements given by the drop-weight method and those obtained by Roper and DeWitt through the use of the Ferguson–Dowson method.

2. The addition of the compounds α-pinene, terpinolene, and dipentene affects but slightly the surface tensions of the water solutions.

3. The lowering of surface tension in dilute aqueous solutions of the terpene alcohols, borneol, α-terpineol, and fenchyl alcohol is nearly the same. The variation becomes greater in concentrated solutions, since not all are of the same solubility.

[18] Guadin, Glover, Hansen and Orr, University of Utah Technical Paper No. 1, p. 7

[19] Harkins, Young and Cheng, *Science*, **64**, 333 (1926).

4. The surface tensions of aqueous camphor solutions change much less rapidly with concentration than do those of the aqueous solutions of borneol.

5. The presence of the dipentene and presumably of the other terpenes lowers the effectiveness of α-terpineol as a frothing agent in so far as that property can be determined by surface and interfacial tension methods.

HOUGHTON, MICHIGAN

THE CATALYTIC EFFECT OF ALKALI AND ALKALINE EARTH SULFIDES ON THE REACTION BETWEEN PHOSPHORUS TRICHLORIDE AND SULFUR

BY WILLARD H. WOODSTOCK AND HOWARD ADLER

In connection with work in this Laboratory on the preparation of phosphorus thiochloride, the reaction between phosphorus trichloride and sulfur as first reported by L. Henry[1] was investigated. A repetition of his experiment disclosed almost complete absence of reaction at 150° at the end of two hours and only partial reaction after eight hours' time.

Since such a reaction afforded a direct as well as simple means of preparing phosphorus thiochloride, it was hoped that further investigation would reveal a method of obtaining more complete reaction in shorter experimental periods.

Experimental

Sulfur.—C. P. flowers of sulfur were used.

Phosphorus Trichloride.—The phosphorus trichloride was made by the direct combination of yellow phosphorus and dry chlorine gas. The crude product was redistilled over fresh yellow phosphorus to remove any pentachloride. The boiling point of the final product was 76°.

Sodium Polysulfide.—Technical sodium monosulfide, $Na_2S \cdot 9H_2O$, was dehydrated by fusion. By heating together calculated quantities of anhydrous sodium monosulfide and sulfur, anhydrous sodium polysulfide was obtained. It was stored in a desiccator.

Other Sulfides.—The potassium, calcium and barium sulfides were of technical grade. They were dried before using.

Procedure.—The experiments at atmospheric pressure were carried out in an all-glass refluxing apparatus. The theoretical quantities of the reactants were placed in a 250-cc. round-bottomed flask attached to a reflux condenser by a ground-glass joint. At the top of the condenser was mounted a drying tube of phosphorus pentoxide to prevent moisture from entering the apparatus. At the end of the experiment the liquid in the flask was distilled from any residue into a distilling flask preparatory to determining its boiling range and gravimetric analysis.

When experimenting at elevated temperatures, sealed Pyrex tubes were used. The

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[1] L. Henry, Ber., 2, 638 (1869).