The results, therefore, showed quite conclusively that the reaction proceeds according to the equation given above and that no carbon is lost if the reaction takes place in a current of chlorine. The extraction of tungsten from its ores by the action of chlorine, therefore, should be materially hastened by an intimate contact with carbon. This contact should be possible of accomplishment with a relatively small amount of carbon by keeping the mixture well agitated. In order to test this principle, samples of different tungsten ores including Scheelite, ferberite, wolframite and huebnerite were mixed with relatively small proportions of carbon, the mixtures were then introduced into the reaction chamber arranged so as to admit of constant stirring. In all cases complete extraction of the tungsten was obtained and the rate of reaction was very materially increased by the stirring.

Summary and Conclusion

1. The reaction tungstic oxide–carbon–chlorine has been studied and has been shown to proceed by steps with the production of WO_2Cl_2, $WOCl_4$ and probably WCl_6, oxygen being evolved.

2. The presence of free oxygen among the reaction products was confirmed by first extracting the chlorine by absorption with mercury followed by the usual methods of gas analysis.

3. The role of carbon is that of a catalyst which increases the rate of the reaction.

Reno, Nevada Received April 24, 1934

[Contribution from the Chemical Department, Michigan College of Mining and Technology]

The Surface Relations of the Xanthates

By C. C. De Witt, R. F. Makens and A. W. Helz

The mechanism of flotation of ores is one involving adsorption and other physico-chemical phenomena. Since there are many controversial views regarding various adsorption theories, it follows that the theories of flotation mechanism are equally unsettled.

This paper presents a correlation of the data on the surface relations of the various xanthates with the known performances of these xanthates in actual flotation practice.

Purification of Materials

The laboratory distilled water was redistilled once from an alkaline permanganate solution.

The solvents used, acetone, benzene, ether, were carefully dried and distilled. The carbon disulfide used in preparing the xanthates was redistilled, the middle portion being used.

Potassium hydroxide was recrystallized and made up as a solution containing 46.6% potassium hydroxide.

Metallic potassium was used in the preparation of the higher xanthates. The oxide coating was removed before use.

Thiophene-free benzene used for standardization purposes was distilled, the middle fraction was frozen, the mother liquor was poured off and the crystals were allowed to melt. After three recrystallizations the benzene was kept over fused calcium chloride and redistilled just before use.

The alcohols used in the preparation of the xanthates were obtained from reliable sources and were further purified by fractional distillation with a specially constructed 80-cm. Pyrex glass fractionating column sealed to a two-liter Pyrex flask. The corrected boiling points as obtained were: propyl alcohol, 97.06° (D), 97.2° (S) at 760 mm.; *n*-butyl alcohol, 117.70 ± 0.05° at 760 mm.; *n*-butylcarbinol 137.6 ± 0.3° at 760 mm.; isobutylcarbinol, 130.5 ± 0.05° at 760 mm.; *s*-butylcarbinol, 129.1 ± 0.2° at 760 mm.; methyl-*n*-propylcarbinol, 119.0 ± 0.2° at 760 mm.; diethylcarbinol, 115.8 ± 0.3° at 760 mm.; *n*-hexyl alcohol, 154.1 to 155.0° at 760 mm.; *n*-heptyl alcohol, 173.6 to 175.1° at 760 mm.; *n*-nonyl alcohol, 211.1 to 213.3° at 760 mm.

Preparation and Purification of Xanthates

Foster's[1] method as modified by De Witt and Roper[2] was used in the preparation of the xanthates. The additional precaution of having the solvents dry was found to give better yields of both potassium and sodium xanthates. The sodium ethyl xanthate was prepared by recrystallization of the commercial product. Normal propyl xanthate did not give clear water solutions even after five recrystallizations from acetone–ether solutions. Two samples of propyl alcohol were used: du Pont *n*-propyl alcohol was carefully dried and fractionated, converted to propyl acetate. The acetate was dried and then converted to the alcohol by hydrolysis with 25% sodium hydroxide. The propyl alcohol so obtained was dried with calcium oxide and finally distilled from metallic calcium. Synthetic propyl alcohol was made from ethylmagnesium bromide and formaldehyde.

The quality of the xanthate was judged by the amount of

---

[1] L. S. Foster, "Preparation of Xanthates and Other Organic Thiocarbonates," Utah Engineering Experiment Station, Technical Paper No. 2, 1928.

[2] De Witt and Roper, This Journal, **54**, 445 (1932).

sulfur it contained after repeated recrystallization. The Carius method was used. Table I gives the analyses of the xanthates.

TABLE I

	Sulfur, %	
	Found	Calcd.
Sodium ethyl xanthate	44.34	44.48
Potassium ethyl xanthate	39.98	40.01[a]
Potassium *n*-propyl xanthate	37.22	36.80[b]
Potassium *n*-butyl xanthate	34.10	34.06
Potassium *n*-amyl xanthate	31.72	31.70
Potassium isoamyl xanthate	31.75	31.70
Potassium *s*-butylcarbinyl xanthate	31.74	31.70
Potassium methyl-*n*-propylcarbinyl xanthate	31.80	31.70
Potassium *n*-hexyl xanthate	29.67	29.64
Potassium *n*-heptyl xanthate	27.75	27.84
Potassium *n*-nonyl xanthate	24.85	24.82
Potassium diethylcarbinyl xanthate	32.10	31.70[c]

[a] From data of De Witt and Roper, *loc. cit.;* De Witt and Makens, THIS JOURNAL, 54, 456 (1932). [b] Solutions cloudy with slight yellow precipitate which repeated recrystallization would not remove. [c] Low yield, solutions clear; had a sharp irritating odor. Repeated recrystallization did not remove odor.

Apparatus

Drop Weight Method.—The apparatus used in obtaining part of the data was essentially that of Harkins and Gans.[3] The usual precautions were observed. The tip diameter was 0.7980 ± 0.0005 cm. This tip gave 72.11 ±0.006 dynes as the surface tension of water. Since the previous work[4] the tip had been resurfaced while this work was in progress.

Ferguson Balanced Pressure Method.—The apparatus used by De Witt and Roper[3] had been modified further as shown in Fig. 1. The apparatus is a single unit made entirely of Pyrex glass tubing. The final adjustment of pressure is made when the stopcock is closed by lowering bob C into tube B. The tube connecting B with A is large enough to allow quick adjustment. The pressure is indicated on the manometer M, which contains water. The pressure is adjusted roughly by applying pressure at D. The bob C is lowered or raised by means of a microscope stand in a manner similar to that outlined in the previous method.

Comparator readings gave the capillary radius as 0.02285 cm. Calibration with water using 71.97 dynes at 25° gave a mean radius of 0.022863 cm. The relative value of the radius was used.

The average value of duplicate determinations on two samples of xanthate solutions is reported for each concentration.

All weighing of xanthates was done on a micro balance sensitive to 0.01 mg. Bureau of Standards calibrated volumetric glassware was used in making up solutions. Bureau of Standards calibrated thermometers were used. All data were taken at 25 ± 0.01°. The density determinations were made with a double-walled 10 or 25 cc. pycnometer.

TABLE II

SODIUM ETHYL XANTHATE, DROP WEIGHT METHOD

The tip radius was 0.3985 cm.

Molality	Density$^{25}_{4}$	Average γ	Average deviation
0.0272	0.9986	72.06	±0.01
.0294	.9988	71.95	.02
.0427	.9995	71.74	.03
.1184	1.0037	71.59	.01
.1912	1.0077	71.18	.02
.2061	1.0086	71.22	.03
.3884	1.0182	70.33	.05
.3950	1.0186	70.33	.00
.5652	1.0272	69.65	.01
.8976	1.0433	68.30	.01
.9659	1.0466	68.09	.01
1.1189	1.0537	67.46	.02
1.6838	1.0777	64.98	.02
2.1933	1.0998	62.56	.03
4.1569	1.1573	59.28	.03
8.2127	1.2342	53.08	.03

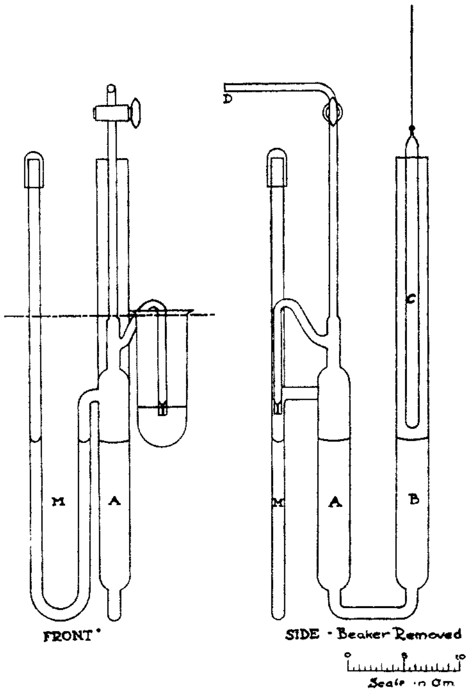

Fig. 1.—Modified Ferguson apparatus.

TABLE III

POTASSIUM *n*-PROPYL XANTHATE, DROP WEIGHT METHOD

The tip radius was −0.3990 cm. D. Propyl xanthate from du Pont *n*-propyl alcohol. S. Propyl xanthate from synthetic propyl alcohol.

	Molality	Density$^{25}_{4}$	Average γ	Average deviation
D	0.0279	0.9985	71.24	±0.05
S	.0626	.9990	71.15	.15
D	.1122	1.0075	69.94	.06
S	.1304	1.0090	69.92	.05
D	.2292	1.0102	68.45	.04
D	.4359	1.0192	65.74	.10
D	.6032	1.0361	63.43	.06
S	.8711	1.0442	59.54	00

---

(3) Harkins and Gans, THIS JOURNAL, **52**, 2287 (1930).

(4) De Witt and Makens, *ibid.*, **54**, 456 (1932).

TABLE IV

POTASSIUM *n*-BUTYL XANTHATE. FERGUSON METHOD

Molality	Density$^{25}_{4}$	Average γ
0	0.9970	71.97
0.0579	1.0003	70.39
.1121	1.0035	68.88
.2121	1.0092	66.42
.3231	1.0152	64.01
.5839	1.0285	59.42
1.1836	1.0557	52.38
2.3851	1.0969	46.50
3.0182	1.1138	45.05
3.60[a]	1.1280	43.90[a]

[a] The molality of this solution was obtained from the density–concentration curve by extrapolation.

TABLE V

POTASSIUM *n*-AMYL XANTHATE. DROP WEIGHT METHOD

The tip radius was 0.3985 cm.

Molality	Density$^{25}_{4}$	Average γ	Average deviation
0.0421	0.9994	69.33	+0.00
.0733	1.0012	67.37	.09
.0979	1.0025	66.00	.02
.1010	1.0027	65.94	.12
.1573	1.0058	62.16	.02
.2772	1.0121	56.41	.04
.3633	1.0167	53.74	.04
.7257	1.0336	44.43	.03

TABLE VI

POTASSIUM *n*-HEXYL XANTHATE. FERGUSON METHOD

Molality	Density$^{25}_{4}$	Average γ
0.0499	1.0006	63.26
.1156	1.0038	54.85
.2315	1.0096	47.90
.3551	1.0160	42.53
.4702	1.0214	38.87

DROP WEIGHT METHOD

The tip radius was 0.3990 cm.

Molality	Density$^{25}_{4}$	Average γ	Average deviation
0.0076	0.9976	70.48	±0.06
.0141	.9979	69.45	.09

TABLE VII

POTASSIUM *n*-HEPTYL XANTHATE, FERGUSON METHOD

Molality	Density$^{25}_{4}$	Average γ
0.0076	0.9976	68.78
.1044	1.0030	47.36
.1641	1.0057	41.07
.3042	1.0117	38.25
.5128	1.0197	37.12

DROP WEIGHT METHOD

The tip radius was 0.3990 cm.

Molality	Density$^{25}_{4}$	Average γ	Average deviation
0.0116	0.9977	67.41	±0.06
.0289	.9988	61.48	.08

TABLE VIII

POTASSIUM *n*-NONYL XANTHATE, FERGUSON METHOD

Molality	Density$^{25}_{4}$	Average γ
0.0131	0.9980	54.01
.0273	.9989	38.86
.0414	1.0000	30.90
.0710	1.0018	30.64

DROP WEIGHT METHOD

The tip radius was 0.3990 cm.

Molality	Density$^{25}_{4}$	Average γ	Average deviation
0.0046	0.9974	65.03	±0.04
.0115	.9977	55.33	.10

TABLE IX

POTASSIUM ISOBUTYLCARBINYL XANTHATE, DROP WEIGHT METHOD

The tip radius was 0.3985 cm.

Molality	Density$^{25}_{4}$	Average γ	Average deviation
0.1174	1.0035	63.34	±0.06
.1269	1.0042	62.91	.00
.2453	1.0104	57.36	.2
.3854	1.0176	51.98	.00
.6746	1.0312	46.85	.12

FERGUSON METHOD

Molality	Density$^{25}_{4}$	Average γ
0.0893	1.0020	65.92
.1841	1.0072	60.45

TABLE X

POTASSIUM *s*-BUTYLCARBINYL XANTHATE. FERGUSON METHOD

Molality	Density$^{25}_{4}$	Average γ
0.0	0.9970	71.97
.0598	1.0004	66.96
.1148	1.0034	64.63
.3138	1.0140	58.13
.5346	1.0252	52.41
.6843	1.0321	48.63
.8597	1.0397	47.16

TABLE XI

POTASSIUM METHYL-*n*-PROPYLCARBINYL XANTHATE. FERGUSON METHOD

Molality	Density$^{25}_{4}$	Average γ
0.0	0.9970	71.97
.0783	1.0014	67.63
.1245	1.0040	65.13
.2152	1.0091	61.73
.3718	1.0171	56.93
.5850	1.0276	51.58
1.1614	1.0524	44.54
1.3435	1.0594	43.73
1.9537	1.0789	42.34

Discussion of Experimental Data

Tables II to VIII inclusive and the curves in Fig. 2 show the surface tension of aqueous solutions of the homologous series of normal xanthates. The addition of each CH_2 group in-

TABLE XII

POTASSIUM DIETHYLCARBINYL XANTHATE, FERGUSON METHOD

Molality	Density$^{25}_{4}$	Average γ
0.0	0.9970	71.97
.1009	1.0030	67.13
.2159	1.0095	63.08
.3590	1.0174	59.46
.4614	1.0228	57.14
.7379	1.0365	52.30

creases the surface tension lowering. This is in accord with Traube's rule.

Tables V, and IX to XII inclusive and Fig. 3 show the surface tensions of five of the isomeric amyl xanthates. It is not certain how the xanthates arrange themselves in very dilute solutions, but at higher concentrations the arrangement is definite and in the order: (1) *n*-amyl, (2) isoamyl, (3) *s*-butyl carbinyl, (4) methyl-*n*-propylcarbinyl, (5) diethylcarbinyl. The numbers indicate the order taken if small differences are considered, *e. g.*, the surface activity of potassium *n*-amyl xanthate is greatest, while that of potassium diethylcarbinyl xanthate is least. If it is assumed that the non-polar part of a molecule may in some cases shield or nullify the effect of the polar end, the above order is readily understood. For example, in an extended molecule, such as potassium *n*-amyl xanthate, the shielding effect would be small, while in a bunched molecule, such as the potassium diethylcarbinyl xanthate, the shielding effect would be large.

It is generally agreed that a collector, such as a xanthate, produces a water-repellent coating on the mineral surface. Two things about the collector must therefore be known: first, its tendency to form a coating, and, second, just how strongly water-repellent the resultant coating is. The problem is complicated by the fact that the two functions are not necessarily independent; that is, any increase in the repellent force may decrease the adsorption. The solution of the problem is rendered still more difficult by the fact that the type of adsorption taking place is uncertain.

In regard to the first factor it might be expected that Freundlich's[5] conclusion would furnish a reliable answer: "The absolute amounts adsorbed from solution are of the same order as those condensed by capillary active substances upon the interface liquid–gas." In general, Freundlich shows that the interface solid–liquid is exactly analogous to the liquid–gas interface. It is notable that in all examples which Freundlich gives to substantiate this hypothesis, the adsorbents are various forms of charcoal. From various studies of the effect of carbon on reaction rates, it appears that carbon is non-polar with respect to water. It seems, therefore, that the condition that the adsorbent be non-polar[6] might be included in the above quotation. If the adsorbent is polar, an analogy with the above might not be expected. Recent theories of adsorption, however, consider a solid surface too complicated and specific in nature to permit such a generalization.

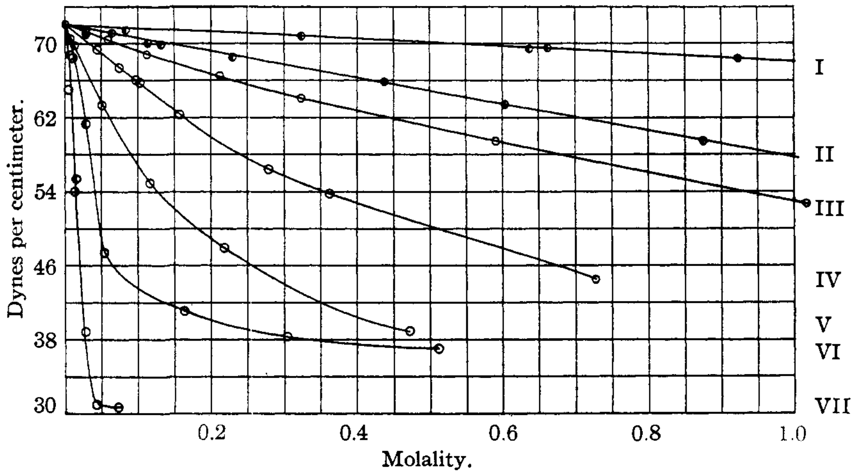

Fig. 2.—Surface tensions of aqueous solutions of xanthates: ○, indicates a point determined by the Ferguson method; ◐, indicates a point determined by the drop weight method; I, potassium *n*-ethyl xanthate; II, potassium *n*-propyl xanthate; III, potassium *n*-butyl xanthate; IV, potassium *n*-amyl xanthate; V, potassium *n*-hexyl xanthate; VI, potassium *n*-heptyl xanthate; VII, potassium *n*-nonyl xanthate.

If Freundlich's statement were applicable to flotation problems, surface tension data should prove useful in predicting the amount of adsorption. However, if as Gaudin[7] points out "The mineral particle is polar," we may not have a case analogous to the experiments substantiating Freundlich's statement. Freundlich[5] has shown that Traube's rule holds for the fatty acids and

(5) Freundlich, "Colloid and Capillary Chemistry," E. P. Dutton and Company, New York, 1922.

(6) Kruyt and van Klooster, "Colloids," John Wiley and Sons, Inc., 1930, p. 25.

(7) Gaudin, *Eng. Min. J.*, **125**, 1045 (1927).

the urethans at both interfaces, liquid–gas and liquid–solid. The data reported for the various xanthates show that Traube's rule may also be expected to hold for these compounds.

If the concentration of the xanthate molecules in the solid–liquid interface is greater than the concentration in the main body of the liquid—a condition which certainly exists in the liquid–gas interface—the xanthate possessing the largest negative value of $d\gamma/dc$ should have the greatest number of molecules in the interface liquid–solid, and therefore should be adsorbed more completely to form the water-repellent coating necessary to float the solid.

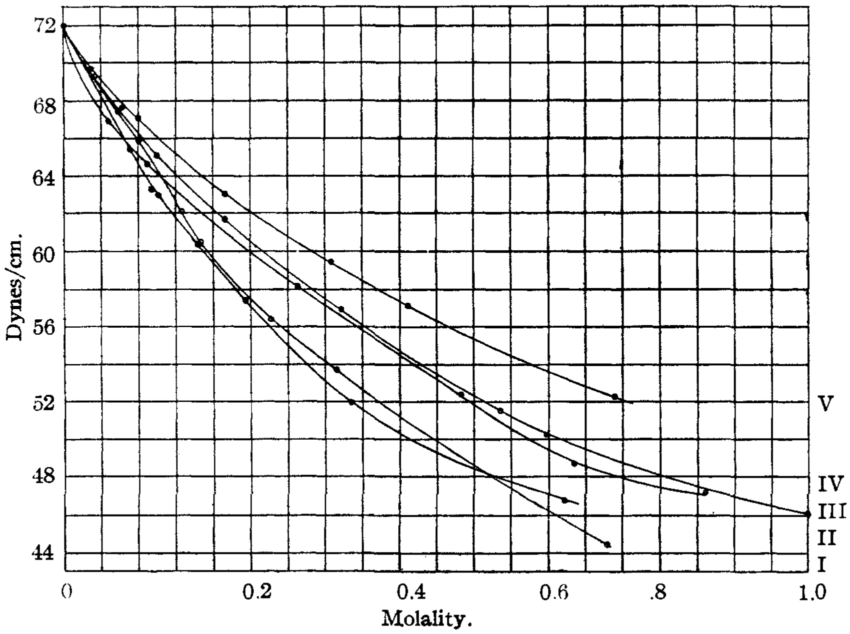

Fig. 3.—Surface tension of aqueous solutions of the potassium xanthates of the amyl alcohols: I, ○, *n*-butylcarbinol; II, ●, isobutylcarbinol; III, ◒, *s*-butylcarbinol: IV, ◓, methyl-*n*-propylcarbinol; V, ◑, diethylcarbinol.

This viewpoint implies that the total adsorption is of two kinds. The first of these is concerned with that portion of the xanthate which adsorbs on or reacts with the surface of the ore particles. This part of the adsorption we choose to designate the promoter activity, because it involves that part of the xanthate which supplies the mineral with a water-repellent coating. The second portion of the adsorption is concerned with the xanthate adsorbed in the liquid–air interface. An additional quantity of xanthate may also be dissolved in the main body of the liquid.

If a chemical reaction takes place between the xanthate molecules and the surface of the mineral particles and forms a firmly adherent film, the xanthate presenting the largest number of molecules at the interface liquid–solid should react more completely. If adsorption of the xanthate molecule takes place at the liquid–solid interface, an equilibrium would be expected to exist at any initial xanthate concentration between xanthate molecules adsorbed on the mineral and those present both in the main body of the liquid and also in the liquid–air interface. The amount adsorbed at the solid–liquid interface would, according to Freundlich, be of the same order of magnitude as at the gas–liquid interface.

In either case any excess of xanthate that may be present in the solution because of equilibrium or other conditions is available for adsorption at the liquid–air interface and should, finally, be carried over in the froth with the ore values, provided the xanthate of itself possesses frothing properties.

Gaudin[8] working with chalcocite concludes "it can be stated as a rule, within the limits of the present experimental facts, that the activity of a collector from a homologous series increases as the non-polar part of the reagent molecule increases." This is in accord with Traube's rule and with surface tension–concentration data of the various xanthates reported in this paper.

Gaudin and Martin[9] show that the maximum promoter activity is reached with malachite–calcite mixtures when the non-polar part of the xanthate molecule contains five carbon atoms. However, they report their results on the basis of pounds of xanthate used per ton of ore. When the data are recomputed on the basis of moles of xanthate used per ton, the promoter activity of the xanthates increases regularly up to heptyl xanthate with no maximum apparent in

---

[8] Gaudin, University of Utah, Research Technical Paper No. 4, Part 2, p. 7.

[9] Gaudin and Martin, "Flotation Fundamentals," Part III, Utah Eng. Expt. Station Pub. No. 5, p. 15 *et seq.* (1928).

the range of concentration used in flotation practice.

Gaudin[9] has shown that the cleanest concentrates are obtained with xanthates containing up to five carbon atoms in the hydrocarbon chain. His experiments on zinc ores indicate that octyl xanthate of itself causes frothing. It is, therefore, probable that part of the longer carbon chain xanthates are removed in the froth without reaction at the mineral surface. Preliminary experiments in this Laboratory with normal hexyl and normal nonyl xanthates indicate that normal hexyl froths much less than does normal nonyl xanthate. Quantitative experiments are under way.

It seems quite probable that if an actual maximum activity calculated on a molar basis occurs, this maximum will be caused by the carrying over of the unreacted collecting agent in the froth. Further, from the data cited, it is believed that such a collector will contain more than seven carbon atoms in the hydrocarbon chain.

The data cited would lead one to surmise that the order of the efficiency of xanthates as collectors for both chalcocite and malachite could have been predicted from the surface tension–concentration data of the several xanthates. However, in arriving at such a generalization it may be necessary to make allowance for the frothing properties of the higher xanthates.

Summary

1. A surface tension apparatus is described which involves Ferguson's principle. The novel features of the apparatus are the pressure adjusting part and the unified arrangement which readily lends itself to immersion in a thermostat.

2. The surface tension of aqueous solutions of a number of xanthates is reported. A qualitative statement of the results is as follows. (a) The molal lowering of the surface tension is approximately the same for both sodium and potassium ethyl xanthates within the limits of equal solubility. (b) The lowering of surface tension increases in accordance with Traube's rule, as the homologous series of xanthates is ascended from the ethyl group up to and including the nonyl group. (c) Isomeric forms of potassium amyl xanthate differ considerably in their effect upon the surface tension of water. The lowering sequence of the xanthates is as follows in fairly concentrated solutions: (1) *n*-amyl, (2) isoamyl, (3) *s*-butylcarbinyl, (4) methyl-*n*-propylcarbinyl, (5) diethylcarbinyl. (d) In the dilute range the slopes of the surface tension–concentration curves of the isomeric amyl xanthates are in accord with the findings of Swainson and Anderson[10] as to the promoter activity of the isomeric amyl xanthates —secondary, iso, normal.

3. The efficiency of the normal xanthates, ethyl to heptyl inclusive, as collectors for both chalcocite and malachite has been correlated with the surface tension–concentration data of these xanthates.

[10] Swainson and Anderson, *Am. Electrochem.* Preprint, 1931.

HOUGHTON, MICH. RECEIVED AUGUST 16, 1934

[CONTRIBUTION FROM THE INSTITUTE OF ANALYTICAL CHEMISTRY OF CHARLES UNIVERSITY]

Volumetric Determinations in Strongly Alkaline Solutions. I. The Titration of Cobalt with Ferricyanide

BY O. TOMÍČEK AND F. FREIBERGER

A number of metals have been determined oxidimetrically with ferricyanide,[1] and we wish to present in this communication the direct oxidimetric titration of cobaltous salts by potassium ferricyanide.

Materials

Potassium ferricyanide solutions were made up 0.1 molar by weight from C. P. salt containing a trace of ferrocyanide and the normality determined both potentiometrically[2] and iodimetrically.[3] The solutions were stored in brown bottles and the titer was found to be constant during a week and to lose 0.005 *N* in some three months. The 0.05 and 0.01 *N* solutions were prepared by dilution and analysis.

Potassium iodide, sodium thiosulfate, potassium permanganate, and other solutions were prepared from average pure salts and standardized by the usual methods.

Cobalt Salts and Solutions.—Cobalt sulfate heptahydrate (Kahlbaum–Schering) was used in preliminary

---

[1] Tomíček, *Rec. trav. chim.*, **44**, 410 (1925); Furman and Evans, THIS JOURNAL, **51**, 1128 (1929); Hahn, *Z. angew. Chem.*, **40**, 349 (1927); del Fresno and Valdés, *Z. anorg. allgem. Chem.*, **183**, 251 (1929).

[2] E. Müller and O. Diefenthäler, *Z. anorg. allgem. Chem.*, **135**, 265 (1924).

[3] I. M. Kolthoff, *Pharm. Weekblad*, **59**, 66 (1922).