corrections are included in the values of column two of Table II, in which the changes in observed microvolts are tabulated. The change in the thermocouple correction with change in temperature was also considered in calculating the temperatures, tabulated in column three of Table II. The values lie on a reasonably smooth curve, fitted by the equation

$$C_p = 2.69 + 0.0560\ T - 2.66 \times 10^{-4}\ T^2 + 4.35 \times 10^{-7}\ T^3$$

The values in the last column of Table II have been calculated by the use of the above equation.

Summary

1. The heat capacity of metallic selenium was determined by the Nernst method. The selenium was carefully purified by the Lenher and Kao method.

2. The experimental values for the temperature range from 100 to 300°A. lie between 6.08 and 7.25. Values for this range have not been reported previously. The value calculated for 300°A. is approximately ten per cent. larger than that reported by Bettendorf and Wüllner.

W. LAFAYETTE, INDIANA

NOTES

The Standardization of Weights

BY FRED C. EATON

The method of Richards[1] for calibrating a set of weights has one particularly attractive feature, the procedure used in calculating the corrections from the system of observation equations. The discussion which follows will show that this procedure gives values which are exactly the same as the values defined by the system of equations. In other words, they are identical with the values to be found by substituting in algebraic formulas like those of Kohlrausch.[2]

The Reasoning of Richards.—A study of what Richards has written will explain why some do not appreciate just how accurate the calculation is. His preliminary values are *consistent* by reason of two assumptions. First, there is the assumption that the first centigram weight, called the standard of comparison, has the mass of 0.01 g. Second, it is implicitly assumed that the small differences between the masses of the various combinations of weights have been correctly measured by the rider in terms of grams. These consistent values are then translated into other terms by a method depending upon the properties of small numbers in presence

[1] T. W. Richards, THIS JOURNAL, 22, 144 (1900); Z. physik. Chem.. 33, 605 (1900).

[2] F. Kohlrausch, "Lehrbuch der praktischen Physik," 11th edition, p. 62.

of large ones.[3] This reasoning may well confuse those who study it carefully. Semon,[4] for example, was guided by it in making his analysis.

A Different Interpretation.—That procedure of Richards will now be explained in a different way. Let the symbol (A) denote the actual number of grams in the mass of the weight whose face value is A grams. Moreover, let (0.01) denote the mass of the first centigram weight. Then, if $[A]$ and $[0.01]$ are the corrections for these weights, the relation between their masses is expressed by the equation

$$(A) = [A] + 100\,A\,\{(0.01) - [0.01]\}$$

The first step in calculating the corrections is to find from the equations a preliminary value for each weight. In doing this we shall make no assumption regarding the mass of the first centigram weight. The preliminary values in Table I are *defined* by assigning to (0.01) the value 0.[5] Hence, it follows immediately from the preceding equation that

$$\text{Preliminary value of } (A) = [A] - 100\,A\,[0.01]$$

TABLE I

$(A) = A + [A]$ $(0.01) = 0.01 + [0.01]$ Standard: $(100) = 100.00158$ g.

(A)	Observation equations	Grams	Preliminary values [A] − 100 A [0.01]	Aliquot parts 100 A [0.01]	Corrections [A], milligrams
(0.01)	...	......	0.00000	+0.00007	+0.07
(0.01′) = (0.01)		−0.00006	− .00006	+ .00007	+ .01
(0.01″) = (0.01)		− .00009	− .00009	+ .00007	− .02
(0.02) = (0.01) + (0.01′)		− .00004	− .00010	+ .00014	+ .04
(0.05) = Σ(0.05)[a]		− .00013	− .00038	+ .00035	− .03
(0.1) = Σ(0.1)		− .00013	− .00076	+ .00070	− .06
(0.1′) = (0.1)		+ .00006	− .00070	+ .00070	.00
(0.2) = (0.1) + (0.1′)		+ .00002	− .00144	+ .00141	− .03
(0.5) = Σ(0.5)		+ .00005	− .00348	+ .00352	+ .04
(1) = Σ(1)		− .00008	− .00709	+ .00703	− .06
(1′) = (1)		+ .00013	− .00696	+ .00703	+ .07
(1″) = (1)		+ .00003	− .00706	+ .00703	− .03
(2) = (1) + (1′)		+ .00002	− .01403	+ .01407	+ .04
(5) = Σ(5)		+ .00004	− .03510	+ .03517	+ .07
(10) = Σ(10)		− .00014	− .07038	+ .07035	− .03
(10′) = (10)		+ .00030	− .07008	+ .07035	+ .27
(20) = (10) + (10′)		+ .00043	− .14003	+ .14069	+ .66
(50) = Σ(50)		+ .00024	− .35049	+ .35173	+1.24
(100) = Σ(100)		− .00067	− .70189	+ .70347	+1.58

[a] The meaning of this notation is shown by the following example: Σ(5) = (2) + (1″) + (1′) + (1).

[3] When α and β are quite small in comparison with N, then $N\,(N + \alpha)/(N + \beta) \simeq N + \alpha - \beta$.

[4] W. L. Semon, *J. Chem. Ed.*, **2**, 132 (1925).

[5] As we are giving a definition, this value may be chosen arbitrarily. The preliminary values of Richards would result from setting $(0.01) = 0.01000$.

This equation easily explains the rest of the procedure. Let the last term *define* what we mean by the aliquot part for (A). Then it is self-evident that, when the aliquot part for one weight is known, the aliquot parts for all the others can be found. Theoretically, if we know the correction for *any* one weight, we can quickly calculate the corrections for all the others. In practical work, however, the face value of the standard should not be less than that of the largest weight in the set.

This explanation of the procedure of Richards makes no assumption and requires the use of no approximation. Consequently that procedure gives values which are precisely the same as those defined by the system of equations, and the accuracy of those values depends solely on the errors made in measuring the small differences between the masses of the various combinations of weights.

Another convenient method of arranging the computation is shown in Table II. This arrangement has the advantage of using smaller numbers. A few additional remarks will make the procedure clear. In dealing with the first group we know the mass of the weight (100) and we define the preliminary values by assigning to (10) the value 0. When we come to the second group, we know the mass of the weight (10) and we define the preliminary values by assigning to (1) the value 0.

TABLE II

Observation equations		Grams	Preliminary values	Aliquot parts	Corrections, milligrams
(10)	....	....	0.00000	−0.00003	−0.03
(10′)	= (10)	+0.00030	+ .00030	− .00003	+ .27
Σ(10)	= (10)	+ .00014	+ .00014	− .00003	+ .11
(20)	= (10) + (10′)	+ .00043	+ .00073	− .00007	+ .66
(50)	= Σ(50)	+ .00024	+ .00141	− .00017	+1.24
(100)	= Σ(100)	− .00067	+ .00191	− .00033	+1.58
(1)	...	....	0.00000	−0.00006	−0.06
(1′)	= (1)	+0.00013	+ .00013	− .00006	+ .07
(1″)	= (1)	+ .00003	+ .00003	− .00006	− .03
(2)	= (1) + (1′)	+ .00002	+ .00015	− .00011	+ .04
(5)	= Σ(5)	+ .00004	+ .00035	− .00028	+ .07
(10)	= Σ(10)	− .00014	+ .00052	− .00055	− .03[a]

[a] This value has been taken from the corrections for the preceding group of weights.

Summary.—The procedure of Richards for calculating corrections from the system of observation equations has been discussed. It has been shown that this procedure gives values which are identical with those to be found by substituting in algebraic formulas like those of Kohlrausch.

Alkaline Persulfate as an Analytical Reagent

By WILLIAM M. DEHN AND DONALD A. BALLARD

Though persulfate in acid[1] or neutral solutions[2] has frequently been applied as a qualitative reagent, its use in alkaline[3] solution has been limited to the precipitation of cobaltic oxide. Using potassium persulfate in potassium hydroxide solution, instead of ammonium persulfate in sodium hydroxide solution as used by Pozzi-Escot, a more complete precipitation of Co_2O_3 can be made ($1:1,000,000$).

Comparable precipitations of black Ni_2O_3 can be made from nickelous solutions by treatment with alkaline persulfate. In the absence of cobalt, it is a characteristic test for nickel, since its black will cover up the colors of other metallic hydroxides. Also in the presence of metals whose hydroxides are soluble in fixed alkalies, it can give a separation of either nickel or cobalt or both of these metals. Conversely nickel or cobalt is a qualitative test for persulfate.

Cyanides.—Alkaline persulfate oxidized cyanides, ferricyanides, ferrocyanides, nitroprussides and thioazanates to cyanic acid, as indicated by the following test. To any one of these, add the reagent and heat to boiling. Acidify with hydrochloric acid and again make alkaline. Moist red litmus paper on the convex side of a watch glass covering the beaker turns blue, owing to the liberation of ammonia. Without persulfate, the litmus paper remains unaffected.

Thiosulfate, but not sulfite, or arsenite, is oxidized by the reagent. Sodium peroxide liberates oxygen. These and other reactions will be studied.

[1] Caro, Z. angew. Chem., 845 (1898); Marshall, Chem. News, **83**, 76 (1901).

[2] Merk, Pharm.-Ztg., 1022 (1905); Pozzi-Escot, Compt. rend., 435, 1334 (1907).

[3] Pozzi-Escot, Ann. chim. anal. chim. appl., **13**, 390 (1908); **14**, 207 (1909); Bollenbach, Z. anal. Chem., **47**, 690 (1908).

CHEMICAL LABORATORY
UNIVERSITY OF WASHINGTON
SEATTLE, WASHINGTON

A Lubricant Insoluble in Organic Solvents

By C. C. MELOCHE AND W. G. FREDRICK[1]

In working with organic solvents it is occasionally necessary to lubricate a stopcock or ground-glass joint in such a manner as to maintain a vacuum or a gas-tight seal and at the same time withstand the solvent action of the liquid. Under such conditions lubricants containing petroleum grease or rubber are as a rule useless on account of their solubility in the solvent and inorganic lubricants are often unsuitable due to separation of a constituent, reaction with the solvent, solubility or freezing.

A solution of dextrin in glycerin is occasionally recommended[2] as a lubricant under the special conditions mentioned. The insolubility of this material in many organic solvents, as well as the high viscosity and slightly adhesive quality, renders this mixture suitable where a gas-tight seal is needed but where the frequent turning of a stopcock is unnecessary. The writers have found that the addition of mannitol in proper amount imparts the correct lubricating quality and renders this lubricant practically indispensable in certain types of work. For general use the lubricant may be prepared as follows.

Mix thoroughly 25 g. of anhydrous glycerin, 7 g. of dextrin and 3.5 g. of chemically pure d-mannitol until a thick paste is obtained. Heat carefully with constant stirring until the solid material is dissolved and the solution just begins to boil. A small amount of water is lost. Cool the clear, colorless or sometimes slightly turbid liquid with occasional stirring to room temperature. The liquid becomes highly viscous and finally acquires a lustrous white or opalescent appearance due evidently to the separation of part of the mannitol in a finely divided state. This preparation has excellent lubricating qualities as well as the body and adhesiveness suitable for most purposes. To increase the viscosity add more dextrin. To increase the fluidity add more glycerin. To impart the physical property of a greasy paste add a little more mannitol. Chemically pure d-mannitol is recommended, since commercial mannitol will not always yield the desired result. This lubricant is best stored in an ointment jar or kept in a desiccator, but exposure to laboratory air is not harmful.

The action of a number of solvents on this lubricant was tested as follows. The stopper of a small Erlenmeyer flask was lubricated so as to give a thin uniform film on both ground glass surfaces when the stopper was inserted. The stopper was removed, both lubricated surfaces were drenched with the solvent to be tested, and the excess of the solvent shaken or blown off. The stopper was then replaced in the flask and rotated to test the lubricating action. After repeating the operations of drenching and testing a number of times alternately the relative effects of the various solvents could be easily observed.

Tested in the manner described, the following solvents had no detectable effect, or at most a very slight and negligible effect: acetic anhydride, acetophenone, benzaldehyde, benzene, bromobenzene, carbon bisulfide, carbon tetrachloride, chlorobenzene, tetrachloroethane, cyclohexane, ethyl acetate, ethyl acetoacetate, ethyl bromide, ethyl carbonate, ethylene dichloride, methyl acetate, methylaniline, nitrobenzene, nitromethane, petroleum ether, diphenyl ether, toluene, o-toluidine, turpentine, o-xylene.

The following solvents had a slight effect, not, however, sufficient to prevent the use of the lubricant provided the latter is renewed when

[2] Iredale, *Phil. Mag.*, **45**, 1097 (1923).

necessary: acetaldehyde, acetone, acetyl chloride, amyl acetate, amyl nitrate, benzoyl chloride, n-butyl ether, diethyl ether, methylene chloride.

The solvent or disintegrating action of the following was sufficient to prevent or greatly hinder the use of the lubricant: aniline, acetic acid, tertiary amyl alcohol, benzyl alcohol, n-butyl alcohol, tertiary butyl alcohol, ethyl alcohol, methyl alcohol, diethylamine, ethylene chlorohydrin, ethylene glycol, formic acid, propionic acid, pyridine, quinoline, water and solvents containing water. In general, therefore, water, alcohols, aliphatic acids and to a lesser extent certain amines and nitrogen containing heterocyclic compounds prevent the use of the lubricant.

Before lubricating a stopcock with this preparation, petroleum and rubber grease should be entirely removed by means of benzene or acetone and the stopcock should be thoroughly dried. After applying a thin film of the lubricant, a stopcock will remain gas tight even when frequently turned in the presence of solvents of the first group mentioned above. With a liquid-air trap in the line to remove any water vapor evolved, a stopcock lubricated as described will hold a good vacuum. In gas analytical operations where the presence of petroleum grease was thought to cause error by absorbing constituents such as ether vapor, the glycerin–dextrin–mannitol lubricant has been used with success. Water dissolves the lubricant readily and may therefore be used to remove it when desired.

The Probable Non-Existence of Normal Tribasic Aluminum Soaps Such as Aluminum Tripalmitate

BY JAMES W. MCBAIN AND WINIFRED L. MCCLATCHIE

Aluminum soaps are articles of commerce used in several industries; they are even listed in most catalogs of pure reagents, and they have frequently been employed in scientific work.[1] Nevertheless. after repeated purchases and attempts to prepare aluminum tripalmitate and other tribasic aluminum soaps, we have come to the conclusion that the product is a mechanical mixture from which an appreciable proportion of free fatty acid is at once dissolved by ether, leaving behind a monobasic or at most a dibasic soap such as a dipalmitate, even when prepared and extracted in the complete absence of moisture. For example, Kahlbaum's aluminum tripalmitate yielded 50% of its fatty acid content to ether dried over sodium. A sample of aluminum palmitate obtained from Eimer and Amend contained only one equivalent of fatty acid to three equivalents of aluminum.

Aluminum soaps are usually prepared from aqueous solution by pre-

[1] For example, in emulsions of water with other solvents, in studies of swelling, etc.

cipitating a soluble soap with aluminum salt. The precipitate is then taken to be the tribasic aluminum soap. Consideration of the elementary theory of aqueous solutions (compare, for example, aluminum sulfide) would lead one to expect a doubtful or negative result on account of the extensive hydrolysis of a salt of a weak fatty acid with a base at once so weak and insoluble as aluminum hydroxide.

Preparations of Oleates, Stearates, and Palmitates from Aqueous Solutions.—When aluminum sulfate solution was added in excess to an aqueous solution of a sodium or potassium soap, the P_H of the soap solution changed during precipitation from about 8.5 to about 4.5. The precipitates were washed with water, alcohol and ether or with acetone, and aluminum was determined by ignition as Al_2O_3. They contained from 5.5 to 6.7% aluminum for palmitates and from 5.0 to 6.2% for stearates and oleates. This indicates a gross composition slightly nearer to dibasic rather than monobasic soap, which was confirmed by a determination of fatty acid present. Preparations made when the P_H was kept equal to 8.5 with sodium bicarbonate gave similar results. With P_H between 3 and 4.5 the product contained little more palmitic acid than corresponded to monopalmitate.

Preparation of Palmitates in Non-Aqueous Media.—Preparations made in 95% alcohol and in absolute methyl and ethyl alcohols gave results no nearer the tripalmitate. Diamyl ether, a good solvent for aluminum soap, was used with palmitic acid and freshly prepared aluminum hydroxide washed with alcohol and ether. The soap from this solution was no better. Similar procedures with chloroform left as much as 14% of aluminum in the soap even when the solution had become clear.

Finally, we turned to the reaction between aluminum ethoxide and palmitic acid and benzene which had been dried over sodium. Of 2.6 g. of Kahlbaum's ethoxide, 2.0 g. dissolved on refluxing with benzene. When the theoretical amount of Kahlbaum's best palmitic acid was added, the resulting solution was clear and fluid, but after evaporation to dryness a large amount of fatty acid or fatty anhydride was extracted at 40° by dry ether, yielding palmitic acid 92.2 and 93.5% and aluminum 5.10 and 5.15%. This corresponds closely to an anhydride or ethoxide of aluminum dipalmitate (there was no water present at any time for formation of $AlPal_2OH$).

Further experiments in the same direction have been made in the Department of Chemistry, University of Nevada, Reno, by S. Allan Lough and E. L. J. Randall. The Kahlbaum palmitic acid used was found to be 99.9% pure as determined by titration with standard alkali. The ethoxide by ignition indicated a content of 45.28% although only 40% was extracted with benzene, leaving the alumina behind. Another sample of benzene extract contained 88% of material removed from the

crude ethoxide after filtering through surgical absorbent cotton. After reaction with more than the theoretical amount of palmitic acid and extracting the dried (at 45°) product with ether, the aluminum content was 4.8% as compared with the 5.1% already quoted. In a final experiment with dried benzene which had dissolved 77% of the crude ethoxide the product was dried in four portions at 25, 45, 55 and 75°. The crude material contained between 2.85 and 3.00% of aluminum and after hydrolysis with sulfuric acid yielded fatty acid determined by titration in alcoholic potash corresponding to from 78.96 to 94.84% of palmitic acid. These four products after extraction with sodium-dried ether contained, respectively, 5.38 and 4.43, 5.36 and 5.34, 5.29 and 5.20, 5.24 and 5.33% of aluminum, whereas aluminum tripalmitate would contain only 3.400% of aluminum. These results again indicate that not more than the dibasic palmitate is attained even under these unusually favorable conditions.

Our conclusion is that aluminum soaps are commonly a mixture of uncombined free fatty acid with either a monobasic or a mixture of mono- and dibasic soaps. Normal tribasic aluminum soaps have never been prepared even in completely anhydrous media.

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY
STANFORD UNIVERSITY, CALIFORNIA

THE DETERMINATION OF IODINE IN BUTTERFAT

BY H. A. A. AITKEN

The estimation of iodine in carbonaceous materials such as oil or butter is generally regarded as the most difficult of all estimations of minute amounts of iodine in natural products. The most recent method that has been described is that of McClendon, Remington, von Kolnitz and Rufe,[1] in which melted butter (as much as 500 g. in one sample) was sprayed from an atomizer into a silica tube and burnt with a current of oxygen in the presence of a catalyst. This process obviates the difficulty inherent in the much simpler method of combustion with alkali, namely, that the low iodine content of the material necessitates so large a sample being taken for analysis that the use of an excess of potash is out of the question. This leads to loss of iodine, and in addition there is a pronounced tendency for the products of saponification of the butter to froth up during combustion in an uncontrollable fashion.

However, in the micro-titration method devised by the author for the

[1] J. F. McClendon, Roe E. Remington, Harry von Kolnitz and Redding Rufe, THIS JOURNAL, **52**, 541 (1930).