to give perfectly satisfactory results from all points of view, on a tip with a diameter of 4.51 millimeters; while, excluding carbon tetrachloride, and possibly a few other similar liquids, characterized by a very small surface tension and a large density, which then form drops of minimum volume, equally satisfactory results are obtained on all tips with diameters between 4.51 and 5.50 mm.; and higher, for many liquids.

In other words, it is shown that when the drop profile is not abnormal to the eye, and the control of the drop is perfect, Tate's first law—the weight of a falling drop is proportional to the diameter of the tip from which it falls—holds rigidly.

4. Surface tensions in dynes, calculated from the benzene constants and the drop weight from the tip employed (*i. e.*, by aid of the proportion $\gamma : w : : K_B : k_B$) are found to agree on all tips from 4.51 to 5.50 mm., independent of the diameter of the tip, as long as the drop profile is normal and the control of the drop is perfect; in other words, for all liquids except carbon tetrachloride, which gives perfectly satisfactory results on tips around 4.5 mm. in diameter only, owing to its exceedingly small drop volume.

Surface tensions in dynes for these liquids are also calculated at 27.8° by aid of the formula $\gamma = w/0.06397 \times (2r)\pi$, which is also found to lead to results independent of the diameter, and which agree with the values calculated from the above proportion.

5. It is to be concluded from this investigation that the Morgan drop weight apparatus will give satisfactory results when the tip diameter lies between 4.51 and 5.50 millimeters, although if such a liquid as carbon tetrachloride is to be used it would be necessary to reduce the tip diameter to 4.51 mm., which will probably give satisfactory results for every known liquid.

LABORATORY OF PHYSICAL CHEMISTRY.

ANHYDROUS HYDRAZINE. I. A CONVENIENT APPARATUS FOR THE PREPARATION OF ANHYDROUS HYDRAZINE.

BY C. F. HALE AND FRED F. SHETTERLY.

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The first compound of hydrazine was prepared in 1875 by E. Fischer[1] by the reduction of a diazonium compound with potassium bisulfite. Curtius[2] obtained the sulfate of hydrazine by digesting an aqueous solution of triazoacetic acid with dilute sulfuric acid. By distilling hydrazine hydrate over barium oxide, Curtius and Schulz[3] attempted to prepare

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[1] *Ber.*, **8**, 589 (1875).

[2] *Ibid.*, 20, 1632 (1887); Curtius and Jay, *J. prakt. Chem.*, [2] 39, 27, 107 (1889).

[3] *J. prakt. Chem.*, [2] **42**, 521–49 (1890).

anhydrous hydrazine but obtained only a mixture of this substance with the hydrate.

Lobry de Bruyn succeeded in isolating hydrazine by either one of two methods: The first[1] of these methods consisted in heating hydrazine monochloride in absolute methyl alcohol with the calculated amount of sodium methoxide and repeatedly distilling the filtered liquid. The last fraction of the distillate, containing 82.6 per cent. of free hydrazine, was further concentrated by freezing out the hydrazine, with the result that a solution containing 92 per cent. of the compound was finally obtained. The second[2] consisted in the dehydration of hydrazine hydrate by means of barium oxide. Small quantities of the hydrate were added to an excess of barium oxide, the resulting mixture was heated to a temperature of from 110° to 120° for several hours in an atmosphere of hydrogen, and finally distilled under a pressure of from 100 to 150 mm. of mercury. The distillate contained from 96 to 97 per cent. of hydrazine. A second distillation over a comparatively small amount of fresh barium oxide yielded pure anhydrous hydrazine. An analysis of this product gave the results, 87.9 per cent. nitrogen and 12.5 per cent. hydrogen (theory, 87.5 per cent. nitrogen and 12.5 per cent. hydrogen).

Dschawachow[3] obtained free hydrazine by heating the dry hydrazine borate, $(N_2H_4)_2(B_2O_3)_5$, to a temperature above 260°.

Stollé and Hofmann[4] suggested the use of hydrazine carboxylic acid ($NH_2NHCOOH$) and of the hydrazine salt of this compound in the preparation of anhydrous hydrazine and recommended the distillation of these compounds over calcium oxide or barium oxide.

Stähler[5] investigated the action of calcium oxide upon hydrazine hydrate and utilized this reaction in the preparation of anhydrous hydrazine. He also suggests the possible existence of either a solid solution of hydrazine in calcium oxide or hydroxide or a compound of the formula $Ca(ON_2H_3)_2$, which may be subsequently decomposed into calcium hydroxide and hydrazine.

Ebler and Krause,[6] in connection with their study of metallic hydrazides, prepared 99.7 per cent. hydrazine by distilling the hydrate twice over barium oxide and finally freezing out the pure hydrazine from the distillate.

Raschig[7] made use of sodium hydroxide in effecting the dehydration

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[1] *Rec. trav. chim.*, 13, 433–40 (1894); see also *Ber.*, 28, 976 (1895), Ref.

[2] *Rec. trav. chim.*, 14, 858 (1895); 15, 174–84 (1896); see also *Ber.*, 29, 770 (1896), Ref.

[3] *J. russ. phys.-chem. Soc.*, 34, 227–30 (1902); *Chem. Zentr.*, 1902, I, 1393.

[4] *Ber.*, 37, 4523–4 (1904).

[5] *Ibid.*, 42, 3018–19 (1909).

[6] *Ibid.*, 43, 1690 (1910).

[7] *Ibid.*, 43, 1927 (1910).

of hydrazine hydrate. A mixture of equal parts of the two substances was heated at a temperature of 113° for two hours and the hydrazine was then distilled over into a suitable receiver. Without submitting analytical details, the author states that an almost theoretical yield of absolutely anhydrous hydrazine was obtained.

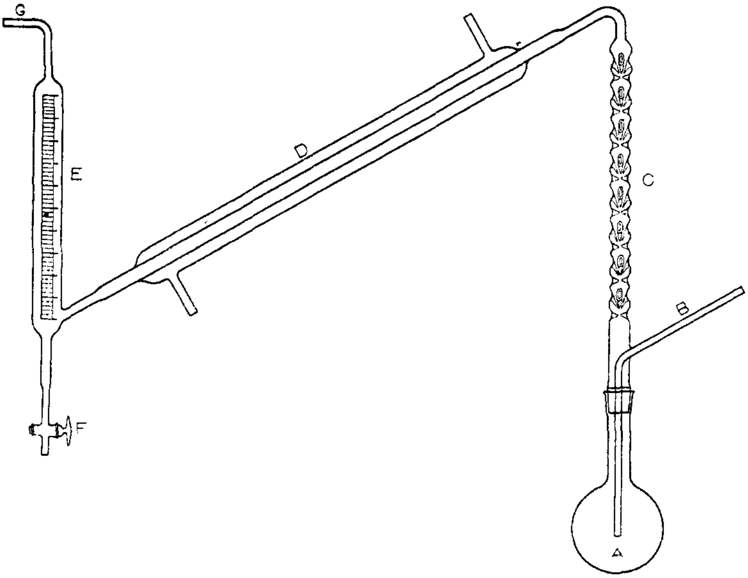
Stollé[1] obtained nearly anhydrous hydrazine by the action of sodium amide upon hydrazine hydrate in excess, which he found to proceed in the manner indicated by the equation

$$N_2H_4.H_2O + NaNH_2 = N_2H_4 + NH_3 + NaOH.$$

When the sodium amide was used in excess he found the reaction to proceed further in concordance with the equation[2]

$$N_2H_4 + NaNH_2 = NaN_2H_3 + NH_3.$$

In preparing the comparatively large amounts of anhydrous hydrazine that have from time to time been required for certain investigations in progress in this laboratory during the past three years, a special form of apparatus has been employed, in the designing of which, the following considerations have been borne in mind: (1) exclusion of all cork and rubber stoppers and connections; (2) provision of a suitable distilling column; (3) provision for distillation in a current of hydrogen and under reduced pressure; and (4) provision of a suitable receiver for the measurement, fractionation, sampling, or storing of the distillate.



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[1] *J. prakt. Chem.*, [2] 83, 200 (1911).

[2] See also Scandola, *Boll. soc. med.-chir. Pavia*, 1910; *Chem. Zentr.*, 1910, II, 544, and Ebler and Krause, *loc. cit.*

Description of Apparatus.—After a series of preliminary experiments, the form of apparatus shown in the subjoined sketch was adopted. The 500 cc. flask *A* is connected by means of a ground glass joint with the Vigreux[1] distillation tube *C*. The tube *B*, which serves as an inlet for hydrogen, is fused into the wall of *C* and extends somewhat below the middle of the flask *A*. The distillation tube is fused to an ordinary Liebig condenser *D*, which in turn communicates with the graduated receiver *E*. The tube *G* is connected with a convenient form of vacuum pump provided with a suitable accessory reservoir and absorption tubes, and with a mercury manometer.

General Procedure.—Measured amounts of the hydrazine hydrate and the solid dehydrating agent in excess were brought together in the flask *A* under such conditions as to prevent the loss of hydrazine vapor by too rapid heating of the mixture. This was satisfactorily accomplished either by slowly adding small pieces of the solid to the entire mass of the liquid, or by pouring the hydrate a little at a time upon the solid. In either case, it was found advisable to immerse the flask, from time to time, in cold water to prevent premature distillation of the hydrazine. After the flask had been connected to the Vigreux tube it was heated over a bath containing a concentrated solution of calcium chloride to the boiling point of hydrazine for a period of from half an hour to an hour, the Vigreux tube serving as an efficient reflux condenser. A slow current of hydrogen was then passed through the apparatus and the pressure was, in general, reduced to from 30 to 2 centimeters of mercury. The distillate was drawn off from time to time through the stopcock *F*, after the pressure in the apparatus had been brought up to that of the atmosphere by the admission of hydrogen.

Dehydration of Hydrazine Hydrate with Barium Oxide.—The hydrazine hydrate used in these experiments was obtained from F. Raschig, and the barium oxide (crude, 98 per cent.) from Kahlbaum. By means of a number of experiments it was demonstrated that anhydrous hydrazine could be obtained after a single distillation in the apparatus and by the procedure just described. The details of two typical experiments are as follows:

(1) One hundred and fifty cc. of 100 per cent. hydrazine hydrate were treated with 415 grams of barium oxide which had been previously crushed in a mortar. The entire distillate obtained weighed about 92 grams and was shown by subsequent analysis by the method of Rimini[2] to contain 99.83 per cent. of hydrazine. These figures correspond to a yield of approximately 92.5 per cent. of the theory.

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[1] *Bull. soc. chim.*, [4] 3, 855 (1908).

[2] *Gazz. chim. ital.*, **29**, I, 265–9 (1899); *Atti accad. Lincei Roma*, [5] **15**, II, 320; *Chem. Zentr.*, **1906**, II, 1662.

(2) One hundred cc. of 93.6 per cent. hydrazine hydrate and 530 grams of crushed barium oxide were used in this experiment. The distillate contained 99.9 per cent. of hydrazine and weighed 59.5 grams, which corresponds to a yield of about 96.5 per cent. It is to be noted that a considerable excess of barium oxide above the amount theoretically required for pure hydrate was used in this experiment since the hydrazine hydrate used was not of a high degree of purity. In case 100 per cent. hydrazine hydrate is used, however, an amount slightly in excess of the theoretical quantity of barium oxide will suffice.

Dehydration of Hydrazine Hydrate with Barium Hydroxide.—In connection with the investigation of the interaction of barium oxide and hydrazine hydrate, it may be of interest to record the behavior of barium hydroxide toward hydrazine hydrate. Since, in the experiments, the same apparatus was employed, the results obtained are comparable with those obtained with barium oxide. The barium hydroxide used was shown, by analysis, to contain 80.23 per cent. barium (theory for Ba in $Ba(OH)_2$, 80.16 per cent.). In one experiment a mixture of 97 per cent. hydrazine hydrate and barium hydroxide yielded, on distillation, a product containing 78 per cent. hydrazine (theory for hydrazine in hydrazine hydrate, 64 per cent.). A second distillation over the same material gave a distillate containing 88 per cent. of hydrazine.

In another experiment, 51.5 grams of 78 per cent. hydrazine mixed with 40 grams of 88 per cent. hydrazine were treated with 400 grams of barium hydroxide and were subjected to distillation. The distillate, containing 93.1 per cent. hydrazine, was redistilled over 200 grams of new barium hydroxide with the result that the first fraction contained 96 per cent., and the second 93.5 per cent. of hydrazine. From these results it is apparent that barium hydroxide is, as was to be expected, a much less efficient dehydrating agent than barium oxide.

Dehydration of Hydrazine Hydrate with Sodium Hydroxide.—In order to compare the new method for the preparation of anhydrous hydrazine suggested by Raschig[1] with the older method of de Bruyn, Mr. T. W. B. Welsh, of this laboratory, has subjected 100 per cent. hydrazine hydrate (Raschig) to the action of sodium hydroxide in the apparatus described in a preceding paragraph.

Experiment 1.—Two hundred and fifty grams of hydrazine hydrate were heated to the boiling temperature for two hours with 250 grams of ordinary sodium hydroxide. The mixture was then distilled, and the distillate was caught in four fractions, which weighed 55, 54, 55 and 10 grams, respectively, and which were found to contain 98.6, 97.5, 95.0 and 87.0 per cent. of hydrazine.

Experiment 2.—Two hundred and fifty grams of hydrazine hydrate were heated as before with an equal weight of fused sodium hydroxide. The first three of the six fractions into which the distillate was divided weighed 25, 23 and 21 grams, and contained 99.3, 98.1 and 98.1 per cent. of hydrazine.

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[1] *Loc. cit.*

Fractional Distillation of Hydrazine Hydrate.—As a blank experiment, it was deemed advisable to study the fractional distillation of hydrazine hydrate in the absence of dehydrating agents, in the same apparatus and under conditions similar to those governing the preceding experiments. It has been shown by Scott[1] "that at 100° in a vacuum hydrazine hydrate in vapor is dissociated into hydrazine and water to the extent of 58 per cent., and that at 140° this dissociation is complete." From these facts it is, of course, to be expected that the first fractions obtained by distilling hydrazine hydrate should contain less, and that the middle fractions should contain more than 64.0 per cent., of hydrazine (theory for N_2H_4 in $N_2H_4.H_2O$ = 64.0 per cent.). The results obtained by Mr. Welsh were as follows:

Experiment 1.—Two hundred and fifty grams of hydrazine hydrate (Raschig, 100%) were distilled, in a slow, steady current of hydrogen, in the apparatus already described. The first six 25 cc. fractions were found to contain the following respective percentages of hydrazine: (1) 56.87, (2) 61.50, (3) 62.23, (4) 63.43, (5) 65.03, (6) 65.22.

Experiment 2.—The preceding experiment was duplicated, and the distillate was divided into 10 fractions, the first 9 containing about 25 cc. each, and the tenth somewhat less. Analysis showed the percentages of hydrazine to be respectively as follows: (1) 56.64, (2) 60.19, (3) 61.77, (4) 62.97, (5) 64.36, (6) 65.62, (7) 72.27, (8) 67.22, (9) 68.05, (10) 68.82.

Summary.

In the foregoing paragraphs has been described a convenient form of glass apparatus for the preparation of anhydrous hydrazine by the action of any suitable dehydrating agent upon hydrazine hydrate. The action upon hydrazine hydrate (1) of barium oxide, according to the method of de Bruyn, (2) of barium hydroxide, and (3) of sodium hydroxide, according to the procedure of Raschig, has been studied under comparable conditions. As a blank experiment, pure hydrazine hydrate has been subjected to fractional distillation in the same apparatus and under conditions similar to those prevailing in the other experiments.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN.]

THE STEARATE SEPARATION OF THE RARE EARTHS.

BY C. W. STODDART AND C. W. HILL.[2]

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Introduction.—One of the principles of separating the rare earths by

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[1] *J. Chem. Soc.*, 85, 913–8 (1904).

[2] The investigations covered by these papers were undertaken at the suggestion of Professor Victor Lenher whom the authors wish to thank for his advice and encouragement. They were originally presented as theses for the doctor's degree by their respective authors.

Thanks are also due Mr. H. S. Miner, of the Welsbach Company, for the material employed.