corresponding to the production of hydrogen of 65, 80, and 99 per cent purity for all ratios of volume of gas space to volume of solution up to 60.

(6) OPERATING DIRECTIONS—The conclusions outlined above may be taken as representative of the information which is to be gained by the method of calculating the momentary variation of conditions during the process. Many minor conclusions have also been drawn which cannot be included in this paper for lack of space.

It was possible from these data to write a complete set of directions for the operation of a generator, and to indicate the means whereby the operator could determine when his methods were faulty. These directions have been made the basis of practice in the United States Navy and it may be said that such large scale tests as could be made without the installation of unjustifiably expensive machinery for quantitative measurement have failed to show that any of the conclusions drawn from the small scale experiments were at fault.

SUMMARY

The work done upon the determination of the best conditions for the operation of a hydrogen generator using ferrosilicon and a solution of sodium hydroxide is presented as an example of a somewhat unusual method of studying a complicated industrial process. The author desires to express his indebtedness to Mr. W. M. Berry and Mr. V. L. Bohnson, who did most of the experimental work involved.

LOSSES INCURRED IN THE PREPARATION OF ACETONE BY THE DISTILLATION OF ACETATE OF LIME

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In the commercial production of acetone by the destructive distillation of calcium acetate, the quantity of crude acetone obtained is very far from that to be expected from the analysis of the acetate. Guttmann[1] states that the acetone yield is only about 75 per cent of the theoretical, e. g., 100 kg. of 80 to 82 per cent calcium acetate should yield theoretically about 30 kg. of acetone, but in practice only about 22.5 kg. of crude acetone are obtained, and on purification this is still further reduced to 20 to 21 kg. acetone of British War Office specification acetone. Yields as high as 25 kg. of raw acetone per 100 kg. acetate of lime are claimed by some manufacturers, but the general average at the time this investigation was started appeared to be 22 to 23 kg., a yield of only 75 per cent of the theoretical.

When discussing the subject with manufacturers it was usually stated that the amount of gases evolved through decomposition was small, but that they carried off an inappreciable amount of acetone, which it did not pay to recover. It became of interest therefore to study this low yield—if not simply due to defects in manufacture—to see how much was lost by decomposition of the acetone through contact with the walls of the heat-

1 "The Manufacture of Explosives," Vol. I.

ing tubes, and to determine the amount of gases evolved as well as the acetone entrained by them.

This investigation was started in 1913 and completed in April 1914. Absence of the senior author at the war made earlier publication impossible.

To attain the object of the investigation it was necessary to employ as small an amount of acetate as possible in order to ensure uniform and rapid heating. Since no difficulty is involved in condensing and accurately weighing the products formed and measuring the gases evolved, amounts of 5 or 10 g. should yield accurate results. The ratio of the surface of the heated tube, compared to the acetate used, was much larger than that obtaining in practice.

DESCRIPTION OF APPARATUS

The apparatus used, as shown in the figure, consisted of a decomposition tube for heating the calcium acetate, a suitable condenser for the collection of the crude acetone, a trap for the retention of the acetone contained in the gases, and a gas holder for collecting them.

Condenser   NaHSO₃
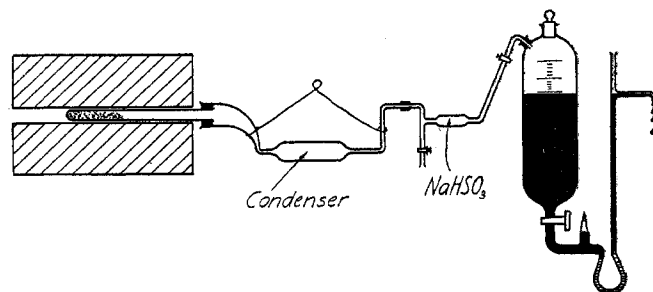
The decomposition tube consisted of a piece of Jena glass tubing of about 16 mm. bore, and 14 in. long, sealed at one end, and heated in a horizontal electric tube furnace wound with nichrome ribbon. The furnace was calibrated by means of a platinum-platinum rhodium thermocouple, and the heating current plotted against the temperature. A constant heating zone of 3 in. was obtained in the middle of the furnace.

The capacity of the condenser employed must be as small as possible compared with the volume of the gases produced. The condenser consisted of a 25 cc. pipette bent as shown in the figure with an adapter fused on to one end. This adapter fitted over a piece of rubber tubing, slipped over the end of the decomposition tube, and made an air-tight joint, exposing a minimum of surface for the absorption of acetone vapors by the rubber.

Inasmuch as the amount of acetone carried away by the decomposition gases was to be determined, the condenser was cooled in ice and water only, so as to imitate conditions obtaining in practice, where cold water only is used.

The acetone trap consisted of a 5 cc. pipette bent similarly to the condenser. A side tube was fused on near one end to enable the apparatus to be filled initially with nitrogen and to draw off gas samples at the end of a run. The most satisfactory gas-collecting device was found to be that shown in the figure. A cylindrical graduated separating funnel

of one liter capacity was fitted with an overflow tube to allow the mercury in this gas holder to flow out as the gases were collected. The level of this overflow tube was adjustable so that the gases could be kept at atmospheric pressure. An air trap was sealed to the bottom of the gas holder.

EXPERIMENTAL DETAILS

Experiments were first made with pure anhydrous calcium acetate (99.2 per cent, 2 g. distilled with phosphoric acid required 25.18 cc. $N/10$ NaOH). The gray crude acetate subsequently used was anhydrous and 81.8 per cent pure (2 g. required 20.70 cc. $N/10$ NaOH).

In Expts. 1 to 12, 10 g. of the acetate were used for decomposition, but only 5 g. were used in subsequent experiments to ensure more uniform heating.

In Expts. 1 to 13 the acetate was placed in the decomposition tube, the condenser packed in ice and when the whole apparatus had been made tight, the experiment was started. The amounts of acetone and water produced were found by weighing the condenser, and the gases in the gas holder were analyzed.

In Expts. 15 to 21, the apparatus was assembled ready for an experiment, the acetate placed in the decomposition tube and the trap charged with 2 cc. of sodium bisulfite solution (25 per cent) to retain traces of acetone. The side tube of the trap was then connected to a glass Y-tube, one arm of which was connected to a cylinder containing compressed nitrogen, and the other to a vacuum pump and manometer. The glass tap connecting the gas holder with the rest of the apparatus was then closed. The apparatus was then exhausted to about 30 mm. of mercury and nitrogen admitted from the cylinder. This was repeated four or five times, and the rubber tubing on the side tube then closed by a screw pinchcock and glass rod. The gas-holder tap was then opened and after the whole apparatus had been proved air-tight by lowering the discharge tube of the gas holder the heating current was turned on. In Expts. 1 to 19, the gas holder contained water, and in Expts. 20 and 21 mercury.

The experiments were run for 3 or 4 hrs. at a temperature of 620° C. In Runs 15 to 21 the temperature was finally raised to 880° C. for one hour to ensure complete decomposition.

The actual amount of acetone and its homologs in the condensate was not determined, since the composition of this condensate is well known.

The acetone caught by the bisulfite solution was estimated by Messinger's method as follows: The washings from the trap were made alkaline with NaOH and distilled until three-fourths had been condensed in a small wide-mouthed flask. 25 cc. of normal NaOH were added and the mixture allowed to stand 5 min. $N/10$ iodine solution was then run in little by little until the upper portion became clear on standing for one minute, and 25 per cent excess was then added. After standing for 20 min., a slight excess of normal H_2SO_4 was added and the liberated iodine titrated with standard sodium thiosulfate solution, using starch

solution as indicator. 1 cc. $N/10$ iodine solution = 0.96 mg. acetone.

At the end of the experiment the tap leading from the bisulfite trap to the gas holder was closed. A sample of the gases left in the apparatus was then withdrawn through the side tube in the trap into a gas burette filled with mercury. By noting the pressure in the burette and reducing the volume of gas thus withdrawn to normal temperature and pressure, it is possible to calculate the volume of the decomposition and trap part of the apparatus as follows:

$$V = V_1 \frac{(P - d)}{d}$$

Where V = volume of apparatus
V_1 = volume of gas drawn off under atmospheric pressure P
P = atmospheric pressure
d = difference in height of mercury columns in burette and levelling tube

Samples of the gases in the gas holder and of the gas drawn off at the end of the run were analyzed for carbon dioxide, oxygen, carbon monoxide, and ethylene in the usual way. To part of the residue from the ethylene determination an approximately equal volume of oxygen was added and hydrogen estimated by combustion over palladium asbestos. Methane was then determined in the residue by explosion. An Orsat-Lunge apparatus was used.

The following are the data for a typical experiment:

RUN 13

Charge = 5 g. pure calcium acetate (99.2 per cent), giving theoretically 1.835 g. acetone.

Started 2 P.M., current 2 amps. = 620° C. } Total time 5½ hrs.
Stopped 7.30 P.M., current 2 amps.

Gas collected in gas holder 100 cc. first 2 hrs., total of 340 cc.

Acetone and water condensed = 40.50 — 38.77 = 1.73 g.

Acetone collected in trap required a net amount of 27.12 cc. iodine solution ($N/10$) = 26 mg. acetone.

Total acetone = 1.756 g. = 96.2 per cent yield.

The combined results of experiments with pure and with crude calcium acetate are given in Table I.

TABLE I—YIELD OF ACETONE

Run No.	Quality	Time Hrs.	Max. Temp. ° C.	Vol. of Gas Evolved Cc.	Acetate Used G.	Theoretical Yield of Acetone G.	Acetone in Condenser G.	Acetone in Trap G.	Yield Per cent
11	Pure	4.5	620	500	10	3.67	3.55	0.025[1]	97.4
12	Pure	4	620	750	10	3.67	3.42	0.025[1]	93.8
13	Pure	5.5	620	340	5	1.83	1.73	0.026	96.2
15	Pure	5.75	880	325	5	1.83	1.79	0.025	99.0
18	Pure	4.5	880	500	5	1.83	1.73	0.026	96.0
20	Pure	4.5	880	225	5	1.83	1.72	0.024	95.3
								AVERAGE	96.3
8[2]	Crude	4	620	350	10	3.009	2.52	0.090	86.8
9[2]	Crude	4	620	600	10	3.009	2.94	0.020	98.3
16	Crude	5	880	540	5	1.504	1.44	0.013	96.5
17	Crude	5	880	680	5	1.504	1.28	0.070	89.8
19	Crude	5	880	670	5	1.504	1.48	0.030	98.5
								AVERAGE	94.0

[1] Estimated.

[2] In Expts. 8 and 9 a less suitable condenser of 125 cc. capacity had been used.

From these figures it is evident that the **volume** of gas evolved is roughly proportional to the amount of acetate decomposed, and little influenced by the

final temperature in the tube. The final heating for $1/2$ to 1 hr. at 880° can naturally only decompose traces of acetone still left in the tube.

The average yield of raw acetone and water is 96.3 per cent for pure acetate, against 94.0 for crude, the amount of gases formed through decomposition being approximately twice as much for the crude acetate as for the pure.

Table II shows the amount of acetone carried off by the decomposition gases in the various experiments and also the degree to which the gases were saturated with acetone vapor.

TABLE II—ACETONE IN DECOMPOSITION GASES

Run No.	Acetone in Trap Mg.	Per cent of Total Recovered in Bisulfite Solution	Vol. of Gases Produced Cc.	Mg. of Acetone when Saturated	Saturation of Gas Per cent	Acetate Used
13	26	1.5	340	73	36	Pure
15	25	1.4	325	70	36	Pure
16	13	0.86	540	116	11	Crude
17	69	5.1	680	146	47	Crude
18	26	1.5	500	107	24	Pure
19	34	2.3	670	144	24	Crude
20	24	1.4	225	43	56	Pure
AVERAGE		2.0			33	

The percentage saturation of the gases with acetone was calculated from the vapor pressure of acetone at 0° C. This value, calculated by applying Ramsay and Young's formula to similar liquids whose vapor pressure is known down to 0°, was found to be 63 mm. of mercury.

1 cc. acetone vapor at 0°, 760 mm. weighs 2.589 mg.
100 cc. gas can carry at 0° C. and 760 mm. pressure

$$2.589 \times 100 \times \frac{63}{760} = 21.47 \text{ mg. of acetone}$$

It is therefore concluded that under conditions simulating practice, the average saturation of the gases is 33 per cent, and that about 2 per cent of the acetone is lost with the gases formed during distillation, and can be recovered by means of absorption in sodium bisulfite solution. This has been done for many years in the case of the vapors issuing from cordite drying stoves, and in celluloid manufacture, and could well be applied to acetone manufacture.

A sample calculation to a nitrogen-oxygen-free basis is given below.

RUN 15

Volume of gas in holder 325 cc., 5.8 per cent CO_2, 1.8 per cent O_2, 16.0 per cent CO, 12.4 per cent H_2, 10.7 per cent CH_4, 53.3 per cent N_2.

Volume of residual gas in apparatus 157 cc., 0.4 per cent CO_2, 0 per cent O_2, 42.6 per cent CO, 5.1 per cent H_2, 33.5 per cent CH_4, 12.7 per cent C_2H_4, 5.7 per cent N_2.

	Cc. in 325 Cc. Holder Gas	Cc. in 157 Cc. Residual Gas	Total Cc.	Per cent Reckoned on Pure Gases
CO_2	18.8	0.6	19.4	6.5
CO	52	68	120	40.5
C_2H_4	...	20.3	20.3	6.9
CH_4	34.8	53.5	88.3	29.6
H_2	40	8.2	48.2	16.3
O_2	5.8	..	(5.8)	..
N_2	173	9.1	(182.1)	..
			TOTAL	99.8

Nitrogen found = 173 + 9.1 = 182.1 cc.
Nitrogen calculated = 157 + 5.8 × 4 = 180 cc.

Assuming a condenser temperature in practice of 10°, 33 per cent saturation, and a vapor pressure for acetone of 115 mm. at 10°, the amount of acetone

carried away by the decomposition gases amounts to 0.8 kg. per 100 kg. of acetate distilled, a not inconsiderable loss.

In Table III the composition of the gases evolved has been calculated to an oxygen-nitrogen-free basis. In nearly all cases the total volume of nitrogen agreed closely with the sum of the volume originally present in the apparatus and that due to leakage, as calculated from the amount of oxygen present by multiplying by 79/21. In one or two experiments no oxygen was found, but an excess of nitrogen, and in these cases the oxygen seems to have been used up by the preferential combustion of some of the gases evolved, chiefly the methane.

The average composition of the gases evolved compares fairly well with that found by Barbier and Roux[1] on passing the vapor of acetone through a red-hot copper tube.

TABLE III—COMPOSITION OF GASES

Run No.	Quality	Acetate Used G.	Net Vol. Gas Evolved Cc.	CO_2 Per cent	CO Per cent	H_2 Per cent	CH_4 Per cent	C_2H_4 Per cent
15	Pure	5	296	6.5	40.5	16.3	29.6	6.9
18	Pure	5	409	10.4	50.4	20.4	17.2	1.8
20	Pure	5	142	9.9	35.1	17.7[1]	34.3[1]	4.1
21	Pure	5	176	8.4	38.5	27.6	21.7	4.0
AVERAGE			265	8.8	41.1	20.5	25.7	4.2
16	Crude	5	540	11.2	57.8	25.0	2.2	3.8
17	Crude	5	622	17.0	61.0	16.4	5.1	0.2
19	Crude	5	549	19.3	62.5	17.1	0.5	0.5
AVERAGE			577	15.8	60.4	19.5	2.6	1.5
Barbier and Roux		...	..	39.2	17.5	37.5	5.6

[1] Estimated.

Some tarry products were formed even with pure acetate, but no attempt was made to determine their amount or composition. With crude calcium acetate the amount of tar was considerably greater and a much larger average volume of gas was evolved.

The composition of the gases formed from the crude acetate differs considerably from those evolved on decomposing the pure acetate, but this is probably due to the organic impurities in the crude salt. CO_2 and CO are present in larger quantities, while the percentage of methane and ethylene is much reduced.

CONCLUSIONS

As was to be expected, the decomposition of calcium acetate by heat into acetone and calcium carbonate is almost quantitative, any gases formed arising through the decomposition of acetone in contact with the heated walls of the containers, or in the case of commercial calcium acetate through decomposition caused by the tarry impurities.

The poor yields obtained in practice are therefore due to defective apparatus, and it is known that since this investigation was completed, considerably higher yields are being obtained. It should still be considered whether it would not be worth while to recover the acetone vapors carried away by the decomposition gases, since they may possibly carry away 0.8 kg. of acetone out of a total yield of 22 to 24 kg.

[1] *Compt. rend.*, **102**, 1859.

SUMMARY

1—An investigation was undertaken to elucidate the low yield obtained in practice in the manufacture of acetone by the distillation of gray acetate of lime. An apparatus of small volume was designed to be reasonably air-tight, and the distillation carried out in an atmosphere of nitrogen.

2—The gases formed were measured and analyzed, and reduced to a nitrogen-oxygen-free basis. Their composition was approximately the same as the gases formed by passing acetone through heated tubes.

3—The yield of acetone was determined, and the amount of acetone carried away by the decomposition gases ascertained.

4—The decomposition of calcium acetate, as was to be expected, was found to be nearly quantitative, any losses in practice being therefore due to defective apparatus.

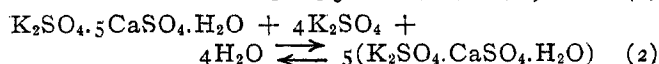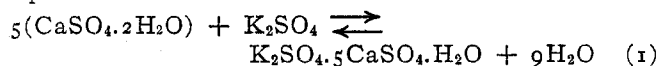# THE FORMATION OF THE DOUBLE SALTS OF CALCIUM AND POTASSIUM SULFATES AT 100° C.

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In a recent paper[1] on "The Double Salts of Calcium and Potassium and Their Occurrence in Leaching of Cement Mill Flue Dust," some of the hitherto published data on the conditions necessary for the formation and stability of these double salts were discussed. It was also stated that since there had apparently been no equilibrium determinations made for the commercially important temperature of 100° C., some tests were being made at the laboratories of this company to determine, if possible, the equilibrium concentration of potassium sulfate, for the formation both of syngenite and potassium penta-calcium sulfate. In the present paper the results of these tests are described.

The object was to determine the equilibrium concentration of K_2SO_4 in solution at 100° C. for the two equations:

$$5(CaSO_4.2H_2O) + K_2SO_4 \rightleftarrows$$
$$K_2SO_4.5CaSO_4.H_2O + 9H_2O \quad (1)$$
$$K_2SO_4.5CaSO_4.H_2O + 4K_2SO_4 +$$
$$4H_2O \rightleftarrows 5(K_2SO_4.CaSO_4.H_2O) \quad (2)$$

METHOD

The method used was similar to the one employed by Cameron and Brezeale[2] for experiments at lower temperatures.

In the first part of the present tests, known weights of water, K_2SO_4, and $CaSO_4.2H_2O$ were agitated in stoppered bottles in a bath of boiling water for several days, and the final solution rapidly sampled and analyzed for K_2O, CaO, and SO_3. In the last part previously prepared syngenite and potassium penta-calcium sulfate were used in place of the gypsum.

The flasks were of the ordinary round-bottom form of 250 cc. capacity, and were rotated in the water bath

[1] THIS JOURNAL, 11 (1919), 327.
[2] *J. Phys. Chem.*, 8 (1904).

in the manner usually employed for thermostatic work. As only 150 cc. of water were used in each flask, good agitation was obtained.

The temperature of the water was that of slowly boiling tapwater at the altitude of Los Angeles (about 250 ft. above sea level). Any error introduced by assuming this temperature to be 100° C. is slight compared with the ordinary errors of the chemical analysis of the solution.

The time of agitation varied from 7 to 23 days. It is probable, however, that the reactions had gone to completion or reached equilibrium in less than 7 days in each case.

In starting a run, 150 cc. of distilled water, together with the determined weight of "Baker's Analyzed" potassium sulfate and calcium sulfate, were put in the flask. The flasks were then carefully heated over the Bunsen burner until the air in the water and space above had been driven out, then closed with rubber stoppers, placed in the agitation frame in the water bath, and agitated continuously until the end of the run.

At the completion of the run the solutions were quickly withdrawn from the flasks, filtered, and later analyzed. In certain tests the solids were also washed and their composition determined. In some cases the potash only was determined by the cobaltinitrite method, and the potassium sulfate content calculated from this determination, while some solutions were also analyzed for lime and sulfates, and the potassium sulfate content calculated by difference.

In making the tests for the determination of the equilibrium concentration of potassium sulfate for the formation of potassium penta-calcium sulfate according to Equation 1, the amounts of potassium sulfate and gypsum added were such that the initial potassium sulfate concentration would be well above the probable equilibrium point, while the final concentration that would result if all of the gypsum added were converted to the penta-salt would be less than this equilibrium concentration. The probable equilibrium concentration was found by extrapolation from D'Ans' diagrams given in the previous paper.[1]

If the proportion of potassium sulfate and gypsum were correctly chosen part of the gypsum would combine with potassium sulfate to form potassium penta-calcium sulfate, thereby lowering the potassium sulfate concentration to the equilibrium point. The final products would then be a mixture of gypsum and potassium penta-calcium sulfate in equilibrium with the potassium sulfate solution. If, on the other hand, the initial potassium sulfate concentration were equal to or less than the equilibrium concentration no combination would take place and the final solution would be the same as the initial one; while if the initial concentration were so high that all the gypsum could combine as the penta-salt without lowering the concentration to the equilibrium point, the difference between the initial and final concentration of potassium sulfate would correspond to the amount

[1] *Loc. cit.*