able, differing with the nature of the solvent and the character of the linoleate.

2. Each metallic soap affords a maximum percentage of solubility in some special hydrocarbon and, therefore, no one hydrocarbon solvent can be commended for all metals.

3. The time at which the maximum separation takes place is also variable, differing with the metal employed.

It is, therefore, evident that a knowledge of the behavior of each soap with the different solvents is essential to the general analysis of driers and it is with the hope of contributing to this knowledge that the present paper is submitted.

ON THE DECOMPOSITION OF SODIUM NITRATE BY SULPHURIC ACID. PART III.

By C. W. Volney.

Received November 11, 1901.

FROM results of previously reported work, the author concluded[1] that the action of sulphuric acid on sodium nitrate takes place in two distinct phases, expressed by :

$$2NaNO_3 + 2H_2SO_4 = NaNO_3 + NaH_32SO_4 + HNO_3 \cdots\cdots \text{I}$$
$$NaH_32SO_4 + NaNO_3 = 2NaHSO_4 + HNO_3 \cdots\cdots\cdots\cdots \text{II}$$

and that these two phases of the process are marked by distinctly different temperatures.

To obtain direct evidence for these conclusions, I have extended the experimental part of the investigation by producing in the retorts for distillation the exact condition for each phase, by using the materials, as represented therein.

For the first phase, 85 grams of dry sodium nitrate with 200 grams of concentrated sulphuric acid were subjected to distillation, according to I. The distillation was carried out in the manner and apparatus already described, which gave observations for the temperatures of applied heat, the retort contents and distilling acid.

In the following are given the results of this distillation, as they were observed :

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[1] This Journal, **23**, 490.

Time. A.M.	Outside. °C.	Retort content. °C.	Distilled acid. °C.	Remarks.
8	23	23	23	No rise in temperature; heat applied at 8:30; contents of retort dissolve to a clear liquid.
9	90	25	..	
10	90	25	..	
10:12	118	74	..	
10:15	123	81	50	Gas bubbles show in liquid.
10:25	125.5	98	63	The liquid commences to boil; gases condense.
10:35	122	104	70	
10:40	135	105	83	Foaming; distillation commences.
10:47	144	107	86	Distils well; foaming; lessen fire.
11:25	125	107	85	
	113	109	85	
	112	107	60	Increase fire.
11:30	147	109	82	Distils well.
	135	106	83	Liquid in retort boiling quietly; distils well.
12:15	142	127	72	
12:50	162	130	82	Sulphates separate in liquid in retort; salts collect on surface.
P.M.				
1	171	128	81	
1:30	176	128	81.5	Distils well.
2	180	130	81.5	
3	178	132	81.5	Liquid quiet.
3:40	180	136	80	No more gas escaping.
4	180	131	72	Distillation ceases.

The acid collected was of 1.517 sp. gr. at 18°–19°; it was almost colorless and weighed 64.2 grams.

The residue in the retort solidified, on cooling, to elongated prismatic crystals with rhombic base. It weighed 219 grams.

The loss in the observation amounted therefore to 2.8 grams, and is evidently caused by escape of nitrous gases.

An observation of the temperatures shows that the acid distils under these conditions, *i. e.*, when 2 molecules of sulphuric acid to 1 of nitrate are used, in the following manner:

The minimum of applied heat was 123°, the maximum 180°; 160° may be considered an average; the temperatures of the salt in the retort are expressed by 81° and 140°, and may be given as 100° in average, and the temperatures of the distilling acid vapors vary between 80° and 90°, so that the boiling-point of the nitric acid produced is about 81.5°.

Under the conditions given, that is, by using two molecules of sulphuric acid to one molecule of nitrate, the decomposition of the latter can, therefore, be effected at about 100° and the acid distilled at 82°.

The residue in the retorts corresponds with the trisulphate described before. It shows the same crystallization and composition. But it can also be prepared by adding to dry sodium disulphate two molecules of concentrated sulphuric acid and melting it at 80°–90°, whereby a clear liquid is obtained which, on cooling, furnishes the crystals. The same crystals are produced when dry sodium disulphate or monosulphate is dissolved in an excess of concentrated sulphuric acid at a temperature of 90°, when, on cooling, the formed trisulphate crystallizes from the liquid and may be obtained free from adhering sulphuric acid by filtration *in vacuo* or a current of dry air. On a platinum filter they can be repeatedly washed with sulphuric acid without losing their crystalline shape or luster, as long as access of moisture is prevented; these observations may be readily performed in the apparatus already described.[1]

To preserve this salt, perfectly dry bottles must be used and the air excluded. This trisulphate gives 60.51 per cent. of normal sodium sulphate, and the salts from the residues in the retorts above described, gave an average from determinations of 58 per cent., which compares with the theoretical percentage of 60.56 sufficiently to agree with the theory of decomposition assumed by me.

I have prepared larger quantities of this polysulphate to be used in my investigation of the second phase of the process:

$$NaH_3.2SO_4 + NaNO_3 = 2(NaH.SO_4) + HNO_3.$$

Accordingly, 218 grams of the trisulphate and 85 grams of sodium nitrate were treated in the retort in the manner already described, and the following table shows the results of distillation. When the two dry salts are brought in contact, no reaction takes place and no change of temperature is observed.

On heating, no decomposition can be noticed until the thermometer in the retort indicates 155°, when some yellow vapors make their appearance.

A distinct reaction is perceptible when the contents of the retort show 167°.

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[1] This Journal, **23**, 490.

Time A.M	Outside. °C.	Retort content. °C.	Distilled acid. °C.	Remarks.
11	22	22	..	No reaction.
12	22	22	..	No reaction.
12:30	..	..	..	Heat applied to retort.
P.M.				
1	155	96	40	Slight yellow vapors.
1:35	167	110	60	Reaction shows boiling.
	178	112	..	Red vapors.
	185	118	70	Contents of retort liquid, red vapors condensing.
	200	120	80	Commences to distil.
2	210	121	85	Yellow acid distilling.
	225	122	85	Yellow acid distilling.
	230	127	90	Yellow acid distilling.
2:30	240	125	95	Yellow acid distilling.
	260	127	98	Yellow acid distilling.
	265	140	109	Distilling rapidly.
3	270	160	122	Distilling rapidly.
3:30	270	167	120	Distilling rapidly.
4	270	167	120	Distilling rapidly.
4:10	280	168	119	Distillation lessens.
4:30	280	168	107	Distillation lessens.
5	280	167	69	Distillation ceases.
6	278	168	60	Stop heating.

The acid, resulting from this process, was yellow to red, showed a specific gravity of 1.526 at 21.10°, and weighed 52 grams. The residue in the retort solidified, on cooling, to a white crystalline mass and weighed 242.5 grams.

By calcining 1.3 grams of this salt, 0.74 gram sodium sulphate was obtained; loss, 0.56 gram. Considering this residual salt as $NaHSO_4$ (the disulphate), theory would require the neutral salt to be 0.77 gram, and the loss as suphuric acid to weigh 0.53 gram.

It is safe to assume that at the temperature under which the distillation took place, the residue is $NaHSO_4$, and that the reaction of sodium trisulphate on sodium nitrate is correctly expressed by

$$NaH_3.2SO_4 + NaNO_3 = 2NaH_7SO_4 + HNO_3.$$

The loss of 0.56 gram, representing 6 per cent., is caused by decomposed acid and is probably greater in acid, than it does appear, as the weight of the residue is, by 2.5 grams, greater than it should be. The observed temperatures show that the decomposition during the second phase of the process takes place under the application of outside heat indicated by 167°–280°;

that the acid distils at 104°–122° from the contents of the retort having a temperature of 165°; and that the nitric acid, which is received during this phase, has been partly decomposed and forms the yellow- or red-colored acid.

The conclusions drawn from the foregoing experimental work, may be expressed as follows:

(1) At the common temperature, or below 20, neither concentrated sulphuric acid nor the polysulphate act on sodium nitrate; the reaction is, at least, so very slow, that during a contact of three to four days, only traces of free nitric acid can be observed.

(2) At a higher temperature the nitrate is decomposed by sulphuric acid and the reaction is finished at temperatures below 100°, free nitric acid and $NaH_3.2SO_4$ resulting.

(3) The trisulphate acts on the nitrate at temperatures over 165°, products of the reaction being again free nitric acid and sodium bisulphate.

(4) The nitric acid, resulting during this phase at the corresponding high temperature, is always decomposed; its vapors, in distilling over, show a temperature of about 120°–123°, and this acid was formerly considered the second hydrate of nitric acid, $(H_2O)_2N_2O_5$ (the $(HO)_2NO_5$ of old).

Under the conditions of the described experimental work, the water can be the result of decomposition only of nitric acid, and I have also shown that this can take place only during the second phase of the process.

NEW YORK, September 29, 1901.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY. No. 60.]

ON THE FERROCYANIDES OF CADMIUM.

BY EDMUND H. MILLER.

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IT has already been shown[1] that the results obtained in titrating cadmium by potassium ferrocyanide in a neutral or slightly acid solution do not agree with any of the formulas given for the precipitate, while the values obtained in an ammoniacal solution agree very closely with the formula $K_2CdFe(CN)_6$.

The present work was undertaken to study the variation in composition under different conditions and, if possible, to assign

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[1] Miller and Fisher: This Journal, Sept., 1900.