ON THE DECOMPOSITION OF SODIUM NITRATE BY SULPHURIC ACID AND THE DISTILLATION OF NITRIC ACID.

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When distilling nitric acid from the usual mixture of sodium nitrate and sulphuric acid, it is frequently observed that at certain periods a violent reaction sets in, and that the contents of the retort are carried over in the receivers. The general supposition is that its cause is overheating, and to prevent it, the distillation is carried on at a low temperature, and the retorts are made of such capacity that the foaming may spend itself without reaching the conducting tube and running over.

However, it can be observed that the foaming of the retort contents occurs at certain periods of the continuation of the process, even when only a very moderate heat is applied, and is therefore dependent not merely upon its external application; and as it does appear that the distilling acid has a close connection with the reaction taking place in the retort, in relation to boiling point and constitution, a consideration of the qualities of nitric acid of different concentrations will serve in the explanation of these different reactions, especially during the distillation of the acid from the mixture of sodium nitrate and sulphuric acid.

A. Smith [1] found that a nitric acid of the constant boiling point 81,56°C had a specific gravity of 1.503—1.51, and was the first hydrate, NO_5HO or HNO_3; also that an acid, boiling constantly at 121°, had the specific gravity 1.41 and was the second hydrate, NO_52HO or $N_2O_52H_2O$.

Roscoe [2] states, that by boiling nitric acid of any concentration, a residue of constant specific gravity 1.41 and boiling point 120.5° remains; this seems to correspond with Smith's second hydrate.

The existence of definite hydrates of nitric acid has been questioned frequently, but the corresponding boiling points and specific

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[1] A. Smith, *Phil. Magazine* (3) 31, p. 454.

[2] Roscoe. *Jahresbericht* 1860, p. 65.

gravities, as well as some reactions in the decomposition of nitrates in presence of water, and the fact that not only anhydrous nitric acid, but also the hydrates, when brought in contact with water, develop heat, cannot very well be explained except upon the theory that several chemical combinations with water exist. Discrepancies in boiling points as well as in specific gravities are always likely to exist, also, the first and second hydrate are constantly decomposing, especially under the influence of light, and this cannot therefore be held as a valid objection to the theory of distinct hydrates. In the preparation and manufacture of nitric acid, the processes and reactions can best be explained by the acceptance of the several hydrates of nitric acid, and the following table of observations furnishes a direct proof of it.

I concluded to conduct the experiments with, comparatively speaking, large quantities, and as I had facilities for obtaining strong acid for the preparation of nitro-compounds and organic nitrates, I had occasion to repeat my observations. The table thereof, which I give here, refers to the distillation of the acid from a mixture of 2500grms. sodium nitrate and 2600grms. of commercial sulphuric acid of 1.837 specific gravity at 67° F. The tubulated glass retort had a capacity of about two gallons, was provided with a thermometer in the tubulus and heated in a paraffine bath the temperature of which could also be ascertained by thermometer. The bulb of the inside thermometer did not reach the mixture in the retort and indicated the temperature of the distilling vapors. The condensation was effected by a Liebig's condenser, whereby an exchange of receivers was rendered easy.

I noted, during the distillation, the time, the temperature, as indicated by the in- and outside thermometer, and the quantities of acid received in different periods; the reactions of the contents of the retort were also observed. These notes are contained in the following:

Time.	Temperature — Outside.	Temperature — Inside.	Remarks.	
A. M. 10.10	83°	45°	Reaction commences.	
11.30	85°	47°	Gas forming;	mass caking.
11.45	90°	50°	"	"
	94°	52°	"	"

Time.	Temperature		Remarks.
	Outside.	Inside.	
A. M. 11.45	97°	55°	Gas forming, mass caking.
	102°	58°	“ “
11.53	106°	65°	Red vapors appear.
	110°	70°	The red vapors lessen.
	118°	75°	Disappear; white fumes.
	120°	77°	Salt in retort melts; acid vapors distil over.
Noon. 12.00	122°	80°	Mass is foaming; nitrate dissolves rapidly; nitric acid distils well.
P. M. 12.10	122°	81°	Contents of retort are foaming strongly; acid distils rapidly.
12.15	122°	81°	Foaming ; contents have risen two inches.
12.16	122°	81°	Foaming ; contents have risen two inches.
12.16	122°	81°	The fire lessened to prevent running over.
12.20	120°	80°	Acid distils rapidly and quietly.
	118°	80°	Danger of running over is past.
	115°	81°	Distils well and quietly; I increase fire.
12.30	117°	88°	Distils well; foaming commences again.
12.47	118°	88°	Distils well; foaming commen again.
1.00	120°	90°	Distilling and foaming.
1.10	122°	90°	Distils more slowly; foaming increases.
1.37	125°	90°	Distils less, but foams strongly.
1.45	130°	90°	I increase the fire.
2.00	130°	90°	Foaming; keep up a brisk fire and change the receivers.
2.10	131°	90°	Foaming ; commences to distil again.
2.20	131°	90°	Distillation ceases; foaming.
2.45	130°	94°	“ “ “

Time.	Temperature.		Remarks.
	Outside.	Inside.	
P. M. 2.50	130°	97°	No distillation.
3.00	135°	100°	
3.10	138°	100°	Commences to distil.
3.20	138°	100°	“ “
3.25	138°	101°	Increase firing.
3.30	138°	101°	Little distillation.
3.36	139°	103°	Distilling.
	141°	104°	“
3.40	142°	105°	“
3.45	142°	105°	Liquid in retort is boiling and foaming
	143°	106°	and distilling.
	144°	108°	Distils slowly; the condenser is cooling; increase the fire.
3.53	144°	108½°	It distils again.
4.05	146°	107°	Keep up fire well.
4.15	146°	108°	Foaming and distilling well.
	146°	109°	Liquid is boiling and distilling well.
	147°	109°	It lessens and red vapors appear.
4.20	148°	109°	Distillation lessens; increase the fire again.
4.25	150°	110°	Distillation ceases entirely; condensing tube cools down; change receivers and increase the fire still more.
4.30	151°	110°	No distillation.
4.35	153°	112°	No distillation; foaming a little.
4.40	155°	113°	“ “
4.50	160°	115°	Liquid in retort shows signs of boiling.
5.00	163°	117°	Foaming and distilling a little.
5.10	163°	118°	“ “ “
5.15	164°	119°	Liquid boils and distils.
5.20	165°	119°	“ “ “
5.25	164°	120°	Distils well.

Time.	—Temperature—		Remarks.
	Outside.	Inside.	
P. M. 5.30	165°	121°	Distils well.
5.35	166°	122°	" " Red vapors appear; distillation lessens; increase fire.
5.45	166°	121°	Little distillation; red vapors lessen; condensing tube cools.
5.55	167°	122°	No distillation; tube cools; extinguish fire.

It will be seen that as the periods of this distillation changed, I changed the receivers, and thus obtained three different products, which were weighed and examined.

The first fraction received between 77°–90°, 960g. of 1.5193 sp. gr. at 60° F., almost white. The second fraction, 565grms. of 1.505 sp. gr. and received between 94° and 109°, was nearly white and but slightly yellow. The third portion, which had distilled between 117° and 122°, was light yellow, weighed 316grms., and had a sp. gr. of 1.42.

The first two portions mixed gave 1525grms. of 1.510 sp. gr., which corresponds with the first hydrate usually produced. I have not succeeded in obtaining an acid of over 1.52, and even this had always more or less NO_2 absorbed. I considered this product, therefore, as the yield of first hydrate. As shown in the foregoing notes, this whole product is received between 84° and 109°; it marks at the latter temperature the point where the greatest portion of the acid of the lower boiling point has distilled at the moment of being set free by the decomposition of the nitrate in the retort. This acid should all have gone over at 84°, but below the 109° there are always portions of the sodium nitrate still left undecomposed, and whenever such portions are becoming heated to the point of dissociation they dissolve in the contents of the retort, the foaming spoken of appears and a portion of first hydrate sets in, whereas acid containing more water and of a higher boiling point remains in the retort and only small portions of which of it are carried over with the vapors of the first hydrate. This may explain the occurrence of the second fraction, which ceased to go over at 109°. At this temperature, all sodium nitrate in the retort is decomposed and the retort contents now consist only of sodium bisulphate and trisulphate and nitric acid of the second hydrate, or of acid which boils at 120°–121° and can be distilled over at this temperature. After this, there is still left always a little nitric acid in the retort, which can be distilled only at a higher temperature and is thereby very considerably decomposed. The acids which may now be obtained contain a weaker nitric acid which has absorbed sometimes considerable dioxyde, coloring it red and giving it a high specific gravity.

From the foregoing observations, I conclude that sodium nitrate is not fully decomposed by sulphuric acid at a low temperature, but only under application of heat; that the first hydrate distils always shortly after being set free, and that the temperature of the mixture remains stationary as long as only this acid is formed. Whenever the decomposing temperature of the nitrate is reached, the first hydrate is suddenly liberated and thereby causes the foaming in the retort. At the same time the nitric acid which, in the retort, has occasion to form the second hydrate, remains until the sodium nitrate is entirely decomposed, from which period on a second hydrate and weaker acid of a higher boiling point distils, there being now in the retort only the different sulphates of sodium and nitric acid.

The foregoing also tends to explain why it takes so long to effect the apparently simple decomposition and distillation and why a strong fire is useless and even injurious to quality and yield of acid. A strong fire will invariably overheat the retort and decompose large quantities of nitric acid, especially the first hydrate. On the other hand, the nitrates could not be decomposed by mixing with sulphuric acid nor the first hydrate be produced therefrom by a simple distillation, because at the temperature at which the nitrate is decomposed the first hydrate boils and thus keeps the temperature of the retort nearly stationary until it is distilled off and the acids of a higher boiling point appear.