SOME POINTS IN THE DISTILLATION OF NITRIC ACID.[1]

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IN a previous paper I described a tube condenser for use, among other things, in the condensation of nitric acid. Further experience with this condenser has enabled us to obtain still better results. We can now obtain a distillate very low in nitrogen peroxide. The specific gravities of the distillate are about as follows:

84 pounds.	1st distillate	Sp. gr., 1.527
83 "	2nd "	" 1.526
83 "	3rd "	" 1.523
82 "	4th "	" 1.512
77 "	5th "	" 1.504
77 "	6th "	" 1.493
74 "	7th "	" 1.487
74 "	8th "	" 1.485
47 "	9th "	" 1.474
47 "	10th "	" 1.448
57 "	11th "	" 1.300
785 "		

The amount of fuel necessary is surprisingly low if proper care is taken. For the distillation of 1,000 pounds nitrate, we use regularly but 150 pounds of pea anthracite coal, working day turn only; this is, no doubt, largely due to the short time within which the distillation has been brought by the use of this condenser, the distillation proper occupying but six hours, and the entire time, including charging and discharging, eight hours. During the night the retort and masonry, of course, cool off. I have no doubt that by running two shifts—day and night—the coal necessary could be brought within 125 pounds for the same weight of nitrate.

Source of the Nitrogen Peroxide Produced.—The contrast in color between nitric acid produced on the small scale in glass, and that made on the large scale in iron retorts, is very noticeable and I have been at some pains to look into the cause, since this formation often represents a dead loss to the manufacturer. I shall later on call attention to a period in the ordinary distillation during which, with no increase in the firing, the acid

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[1] Read at the Boston Meeting, Dec. 27, 1894.

comes over very rapidly. It has often been noticed that during this stage, the acid is unusually white. I attribute this to the rapidity with which the gas passes from the retort, and consequent decrease in decomposition caused by the radiated heat. The same thing is noticed by distilling in glass. Certainly, therefore, part of the nitrogen peroxide is due to too long heating of the vapor, and the importance of an efficient condenser and a rapid distillation is evident.

The effect of concentration of the vitriol on the color is very evident. The ease with which concentrated nitric acid is decomposed is well-known and, as might be expected, the strong acid made from distilled vitriol and dry nitrate shows much stronger color than that made from the less concentrated materials. In glass, heating over a Bunsen, such acid may be obtained without difficulty of only a pale straw color, but in the ordinary iron retort the crude aqua fortis will frequently contain as much as three per cent. nitrgen peroxide.

It is the common opinion among acid makers that part of this color, perhaps a large part, is due to action of the acid on the iron. In most cases this is no doubt true, as the retort, as ordinarily set, is but imperfectly heated at the ends. In the retorts which I have been using, however, the retorts are *entirely* surrounded with the fire gases. It is quite possible, however, that even here the iron is notably attacked. Part of the color, no doubt, arises from impurity of the materials—chlorine, organic material, and iron in solution principally—but I suspect that this is responsible for only a part of the trouble. A gentleman who has for years carried on the distillation of nitric acid on the large scale, recently informed me that he had distilled fused nitrate and white vitriol in iron with no perceptible diminution of the color in the product.

As stated in the books, the only reactions occurring are

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3, \text{ or}$$
$$2NaNO_3 + H_2SO_4 = Na_2SO_4 + 2HNO_3.$$

In practice only the first reaction is usually employed, especially where, as in acid for mixed acids, to be used for nitroglycerol, the product must be as concentrated as possible. In this connection, however, one point I think should be noted that seems to have escaped attention, that is, that with weak vitriol the water is largely retained by the cake until the last stage of the operation, and greatly assists the decomposition giving a fair acid and a cake which is practically infusible. If, however, strong vitriol is used, the decomposition is incomplete and the acid exceedingly red.

The Frothing.—This matter of frothing is one that frequently gives great trouble to the nitric acid distiller, especially where weak acid and wet nitrate are used. The frothing begins in such cases after about seven-elevenths of the acid has distilled over.

This is easily demonstrated by conducting a distillation in glass with acid of 1.80 sp. gr., or less. The trouble becomes then plainly apparent, and is evidently due to the decomposition of the $NaHSO_4$ at first produced into $Na_2S_2O_7$ and water: $2NaHSO_4 = Na_2S_2O_7 + H_2O$. That this is the reason may easily be demonstrated by heating in another similar retort a mixture of dry sodium sulphate and sulphuric acid. We then have $NaHSO_4$ formed, and on continuing the heat the same frothing is noticed, although the distillate is, of course, entirely free from nitric acid. Frothing over is prevented by giving sufficient capacity to the retort, and by care and skill in firing. Neither alone is sufficient to prevent it.

Rate of Distillation.—One of the most remarkable things in the distillation, especially noticeable in glass and with pure dry materials, is the variation in the rate of distillation and the almost explosive evolution of acid, which takes place, for a short period, after about three-tenths of the acid has distilled over. For example: In distilling in glass 200 grams sodium nitrate and 235 grams distilled sulphuric acid, the proportions required by the equation $NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$, the following results were obtained. It should be understood that the Bunsen, over which the operation was conducted, was allowed to remain untouched, except where noted, and that the apparatus was shielded from air currents. The thermometer bulb was shielded from radiation by placing it within a porcelain crucible in the retort.

Time.	Time interval.	Temperature.	Temperature interval.	Acid distilled.	Remarks.
1 : 46 : 40	.....	108°	...	..	Distillation begun.
2 : 48 : 25	1 : 43	110°	2°	5	
2 : 50 : 20	1 : 57	113°	3°	10	
2 : 52 : 30	2 : 10	117°	4°	15	
2 : 55 : 15	2 : 45	124°	7°	20	
2 : 59 : 00	3 : 50	128°	4°	25	
3 : 02 : 00	3 : 00	133°	5°	30	Froth rises.
3 : 02 : 55	0 : 55	125°	—8°	35	Froth very high.
3 : 03 : 30	0 : 35	125°	0°	40	Froth sinking.
3 : 04 : 00	0 : 30	125°	0°	45	No froth
3 : 04 : 45	0 : 45	126°	1°	50	No froth.
3 : 17 : 40	12 : 55	135°	9°	55	Mushy mass fusing to clear liquid below.
3 : 23 : 30	5 : 40	148°	13°	60	Half fused.
3 : 38 : 30	.....	157°	9°	65	Three-fourths fused.
3 : 45 : 20	.....	152°	—5°	70	Piece of cake dropped into fused mass, lowering temperature.
3 : 52 . 00	.....	158°	Acid not running, clear fusion, lamp turned up.		
3 : 58 : 30	.....	170°	12°	75	No froth.
4 : 03 : 00	.....	178°	8°	80	No froth.
4 : 04 : 45	.....	180°	Lamp turned still higher.		
4 : 06 : 00	.....	194°	14°	85	Slight froth.
4 : 08 : 15	.....	200°	6°	90	Half-inch froth.
4 : 12 : 20	.....	220°	20°	20	Retort full of froth during this interval.
4 : 16 : 00	.....	246°	26	96	Froth gone, lamp turned out.

The drop of the temperature at 133° is, I think, unmistakable, and reminds one of the rise of temperature produced in the crystallization of a supersaturated solution. There we have the change from the fluid to the solid condition—here from the solid to the fluid. This explosive evolution is noticeable also in distilling in iron on the large scale and, perhaps, explains in part the difficulty nitric acid makers have hitherto had in properly condensing their product. By proper firing, and with a properly set retort, this difficulty is lessened.

To decompose strong nitric acid by heat or by its action on iron, and then to drive off the nitrogen peroxide with great pains and loss, is evidently a clumsy and probably unnecessary operation. I shall, therefore, make a determined effort to so arrange the retort that this will be in future unnecessary. There would seem to be no insuperable obstacle in the way of so conducting the distillation that even the first distillate would be of a pale straw color, like that made in glass, and quite fit for the manufacture of dynamite and other nitro compounds with no purification whatever.

The use of nitro compounds has, of late years, become so large that a rational method of conducting the process of nitric acid distillation is imperatively called for.

Berthelot has shown that strong nitric acid is completely decomposed at about 360° into nitrogen peroxide, oxygen, and water. It is certain that with the retorts entirely surrounded by fire gases the temperature of the upper part of the retort exceeds 100°. It is not surprising, therefore, that the first distillate should show a dark red color. A recent distillation in glass, with pieces of cast iron immersed in the mixture of acid and nitrate, gave no additional color to the first distillate.

NEW BOOKS.

COD-LIVER OIL AND CHEMISTRY. BY F. PECKEL MÖLLER, PH.D. London: Peter Möller. New York: Wm. H. Schieffelin & Co. Printed for private distribution.

This book is really two books in one. The first part treats of cod-liver oil, the methods of catching the fish, the preparation of the oil, and an account of its constituents. We learn that cod-liver oil was originally made from fresh cod-livers by the steam process, by Peter Möller, in 1853. The oil so prepared was a great improvement over the older product prepared by the putrefaction of the livers. It still, however, caused disagreeable after-effects when exhibited, and to remedy this an investigation was undertaken by P. M. Hyerdahl, presumably in the employ of Peter Möller. Mr. Hyerdahl finds that the disagreeable after-effects are caused by the presence of hydroxy acids in the oil, and that these may be excluded by rendering the livers in an atmosphere of carbon dioxide. This process is now carried out by Peter Möller, therefore buy your cod-liver oil of this firm. The deduction is not so stated in the book, which is well written and gives a very readable account of the subject, but the advertising purpose is obvious.

It is a pity that Mr. Hyerdahl's work was not made known through the regular channels—the *Berichte* for example. Chemists will be apt to look with suspicion upon statements so obviously interested.