

*Citation:*

A.F. Holleman, The nitration of toluene, in:  
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He also remarks that this formula agrees in character with my theoretical one, viz.

$$\frac{A}{M} = C \frac{\rho}{1 + c'} \cdot \frac{1}{T}$$

because  $1 + c'$  slowly increases with decreasing  $T$ .

This, indeed is the case. For instance when we assume  $\rho = 3.70 \times 10^{13}$  or  $\sigma = 10$ , and consider the spherical function of order 2 we find after SCHUSTER (Phil. Tr. Vol. 180 p. 496):

$\sigma$	$1 + c'$	$\frac{1 + c'}{1.172}$
1	1.019	$0.869 = 0.1^{0.061}$
5	1.093	$0.933 = 0.5^{0.100}$
10	1.172	1.000 —
20	1.278	$1.091 = 2^{0.126}$
30	1.337	$1.141 = 3^{0.120}$
40	1.374	$1.173 = 4^{0.115}$
50	1.399	$1.194 = 5^{0.110}$
100	1.466	$1.251 = 10^{0.097}$

The exponent accordingly changes slowly, and reaches as a maximum 0.126, a value, which approaches the value 0.2 required by the empirical formula.

I think this points to a possibility to bring agreement between the theoretical assumptions and the observed facts for the daily variation of earth-current and magnetic component. However this is not the case for the short oscillations.

I regret that my near return to Europe prevents me from entering now on those questions, or making new experiments.

Batavia, Aug. 1908.

**Chemistry.** — “*The nitration of toluene*”, by Prof. A. F. HOLLEMAN.

(Communicated in the meeting, of September 26 1908).

On account of its great technical importance the nitration of toluene has been studied repeatedly; the determination of the quantity of *o*- and *p*-nitrotoluene contained in the product of the reaction has also been carried out a few times. RAOUL PICTET, (C.R. **116**, 815) states that when toluene is nitrated at  $-55^{\circ}$  5.5 times as much *p*-nitrotoluene is formed as when the nitration is carried out at  $0^{\circ}$ . HOLDERMANN, (B. **39**, 1250) tried to modify the proportions in which

*o*- and *p*-nitrotoluene are formed by adding catalyzers (generally consisting of metallic salts) to the mixture of nitric and sulphuric acid used in the nitration. The amount of *o*-nitrotoluene present in the product of nitration only varied however from 57.16 to 60.85%. In these experiments the temperature was kept between 5 and 10°. When nitrated at 0° with nitric acid (sp. gr. 1.52) 52.7% of nitro-toluene was obtained; on addition of different salts (the proportions are not stated) to this acid the quantity of *o*-compound diminished and when nickel sulphate was added it even got as low as 45.5%.

FRISWELL, (C. Bl. 1908<sup>1</sup>, 2092) nitrated toluene under many various conditions in order to increase the yield of *p*-nitrotoluene. He obtained however, always 60—65% of *ortho*- and 40—35% of *para*-compound.

None of these chemists make any statement as to the method used in these determinations, although HOLDERMANN expresses his results even in two decimals. As will be noticed from the above quotations the figures differ widely. Moreover, NÖLTING (B. 12, 443; 18, 1337) has shown that the nitration product of toluene contains *m*-nitrotoluene the amount of which he estimates at 1—2%. It is, therefore, obvious that there is, as yet, no question of a fairly accurate knowledge as to the composition of the product of nitration of toluene, and, for this reason, I instructed Mr. VAN DEN AREND to determine the composition, with the aid of the more accurate methods, which for that purpose have been worked out in my laboratory. In this particular case the method of the solidifying points was the most practical one.

In order to apply the same, it is necessary to procure, first of all, the three *mononitrotoluenes* in an absolutely pure condition. A preparation of *o*-nitrotoluene of great purity has been obtainable for the last few years from MEISTER, LUCIUS and BRÜNING. A specimen received previously from that firm still contained 0.4% of *p*-nitrotoluene (These Proc. VII, p. 395). At my request they were kind enough to once more purify a sample of this almost pure *o*-nitrotoluene by freezing, and to place two kilos of the purified preparation at my disposal, for which I express to that firm my sincere thanks. This was found to contain only 0.13% of *p*-nitrotoluene and was used by Mr. VAN DEN AREND in his experiments without any further purification, except a single distillation in order to remove the dissolved water; a correction was then applied for the *p*-compound content.

It was shown that the methods proposed by REVERDIN and LA HARPE (Beilsteins Handbuch II, 91) and by LOESNER, (J. pr Chem. (2) 50, 567) to free *o*-nitrotoluene from any *p*-nitrotoluene present are quite useless. *o*-Nitrotoluene is dimorphous; the melting points of the two modifications were determined by VAN DEN AREND by means of his

preparation and found to be  $-3^{\circ}.7$  and  $-9^{\circ}.4$ . According to his observation the unstable modification with the higher m.p. is formed most readily when the liquid substance is cooled rapidly to about  $-30^{\circ}$ . First, a solid yellowish mass is formed, which, on further lowering of the temperature, begins to show white spots and then turns quite white, with production of a crushing sound; the crystalline mass thus obtained melts at about  $-4^{\circ}$ .

*m*-Nitrotoluene is obtainable from DE HAEN in a very pure condition. It was fractionated a few times when the melting point was found to be  $+16^{\circ}$  and the boiling point  $230-231^{\circ}$  at 756 mm.; it may therefore, be taken as pure.

*p*-Nitrotoluene from KAILBAUM was recrystallised twice from alcohol and then distilled in vacuo; its solidifying point was found to be  $54^{\circ}.4$ .

*Solidifying curve of o- and p-nitrotoluene.*

% <i>para</i> -nitrotoluene	initial solidifying point	end solidifying point
100.0	$+ 54^{\circ}.4$	—
97.5	$50^{\circ}.0$	—
91.6	$46^{\circ}.2$	—
79.0	$38^{\circ}.5$	—
72.9	$33^{\circ}.8$	—
67.5	$30^{\circ}.4$	—
60.5	$24^{\circ}.4$	—
46.6	$11^{\circ}.6$	$- 15^{\circ}.0$
42.3	$5^{\circ}.4$	$15^{\circ}.2$
39.8	$1^{\circ}.8$	$15^{\circ}.7$
% <i>para</i> -nitrotoluene	initial solidifying point	end solidifying point
37.2	$- 1^{\circ}.2$	$14^{\circ}.6$
33.5	$6^{\circ}.8$	—
30.6	$14^{\circ}.8$	—
24.9	$14^{\circ}.4$	$15^{\circ}.6$
16.3	$12^{\circ}.1$	—
11.2	$11^{\circ}.3$	—
0.0	$0^{\circ}.4$	—
		mean $- 15^{\circ}.2$

Fig. 1 represents the solidifying curve constructed with the aid of these figures.

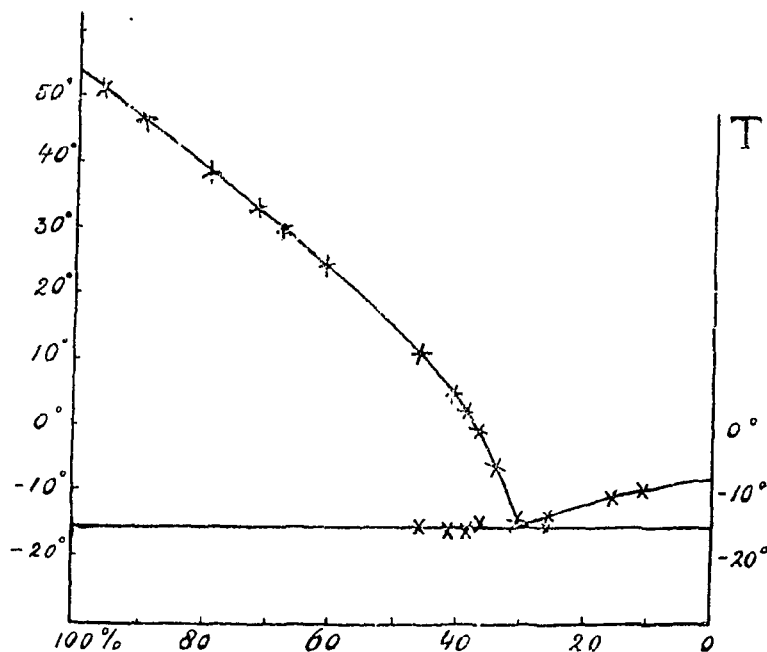


Fig. 1. Melting point curve of *o*- and *p*-nitrotoluene.

Mr. VAN DEN AREND found the following figures for the specific gravities of *o*- and *p*-nitrotoluene and for some of their mixtures, at 80°.0 :

100	%	<i>p</i> -nitrotoluene . . .	1.0981	calculated from
89.4	"	"	1.0993	the sp. gr. of <i>o</i> - and
68.4	"	"	1.1007	of <i>p</i> -nitrotoluene
61.0	"	"	1.1014	1.1006
46.5	"	"	1.1023	1.1015
32.0	"	"	1.1033	
0.0	(100 %	<i>o</i> -nitrotoluene . . .	1.1045 <sup>1)</sup>	

The figures calculated are those which may be deduced from the specific gravities of the isomers without contraction taking place. The graphic representation of these figures gives the subjoined diagram

<sup>1)</sup> Dr S. VAN DORSSSEN has also at my request determined the specific gravities of *o*- and *p*-nitrotoluene by means of an EYKMAN'S pycnometer verified by himself and found as the average result at 80°.0 of four and three determinations respectively: *o*-nitrotoluene 1.1050; *p* nitrotoluene 1.0993, values which are both a little greater than those of VAN DEN AREND. All the values have been corrected for vacuum and the expansion of the glass. I will, however, use v. d. AREND'S figures because he has made all his determinations with the same pycnometer and therefore the results are sure to be mutually comparable.

which plainly shows the contraction which takes place on mixing the isomers, by the higher sp. gr. which the mixtures possess, in comparison with the calculated values (the straight line).

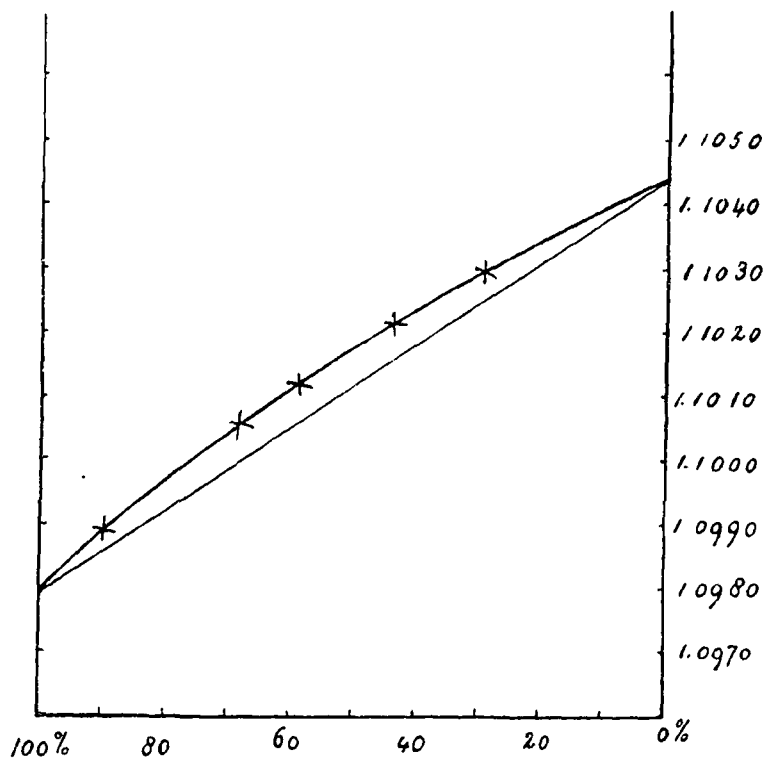


Fig. 2. Line of the specific gravities of *ortho*- and *para*-nitrotoluene.

The nitration of toluene was carried out by the method of BENLSTEIN and KUHLEBERG, (A. 158, 348), i.e. the nitric acid being added to the toluene and not reversedly, because, by their method, the formation of dinitro-products is entirely avoided. The toluene employed had a constant boiling point ( $110^{\circ}.8$  at 760 mm.) and had been purified by being boiled with sodium wire in a reflex apparatus.

The nitration of the purified toluene took place at the temperature of  $-30^{\circ}$ ;  $0^{\circ}$ ;  $+30^{\circ}$  and  $+60^{\circ}$  and was carried out as follows:

75 grams of the toluene were placed in a small flask and brought to the required temperature. 200 c.c. of nitric acid (sp.gr. 1.475) were slowly dropped into the toluene, the mixture being stirred mechanically. Immediately after the addition of the first drops of the acid the liquid turned intensely brownish-red; so that it was not possible to see whether two liquid layers or one homogeneous mixture was formed. The heat evolved during the nitration was but trifling, at

least at 0°. After some time, the mixture was shaken repeatedly in a large separation funnel with water until no more acid reaction could be observed.

Being dried over sodium sulphate, the product was distilled in vacuo. The temperature was first kept for some time at 40°, to remove any unattacked toluene; at a pressure of 1 to 2 m.m. and a temperature of 90°—100° the whole distilled over leaving but a very small residue. Towards the end of the distillation much of the *p*-nitrotoluene passed over, which deposited in the exit tube as a yellow crystalline mass.

The distillate consisted of a clear pale yellow liquid.

After the solidifying point and the sp.gr. of such a nitration-mixture had been determined the distillation in vacuo was once more repeated and the solidifying point and the sp. gr. determined again. These did not differ perceptibly from the first ones.

The end solidifying points could also be determined pretty sharply; the subjoined table shows the results obtained:

Nitration at:		Spec. Gr.
- 30°	initial solidifying point + 4°.1	1.1026
	end " " - 16°.6	
0°	initial " " + 2°.8	1.1026
	end " " - 16°.8	
+ 30°	initial " " + 1°.4	1.1027
	end " " - 16°.9	
+ 60°	initial " " - 0°.8	1.1028
	end " " - 17°.4	

The specific gravities were again determined at the temperature of boiling benzene and reduced to 80°.0. They have been corrected for vacuum and expansion of the glass.

I have had these observations repeated in part by Messrs CALAND, VAN DORSSSEN and DE LEEUW who have themselves purified toluene in the manner described, nitrated the same, and determined the initial and end solidifying point, also the sp. gr. of their nitration product. They found:

Nitration at:		Sp. Gr.
0°	initial solidifying point: + 1°.0; + 2°.7	1.1026
	end " " : - 18°.1; - 18°.4; - 18°.2	
60°	initial " " : + 3°.1	1.1023
	end " " : - 18°.5	

The end solidifying points were found to be a little lower; as regards the initial solidifying point of  $+3^{\circ}.1$  in the nitration at  $60^{\circ}$  it should be observed that the mixture of toluene and nitric acid had been left over night and separated into two layers which was not the case in VAN DER AREND'S experiment. With an initial solidifying point of  $-0^{\circ}.8$  corresponds 37.5% of *p*-nitrotoluene; with that of  $+3^{\circ}.1$ , 40.7%, disregarding, for the moment, the small quantity of *m*-nitrotoluene present in the nitration product. As a content of 40.7% of *p*-nitrotoluene corresponds with a sp. gr. of 1.1026 it seems that no higher nitration products are formed, even at  $+60^{\circ}$ , when the nitration is carried out in the manner indicated. This is also shown by the position of the end solidifying point which is but little lower than that found with the nitration products obtained at lower temperatures.

In order to determine the *o*-, *m*- and *p*-nitrotoluene content of the nitration product it must be regarded as a ternary mixture, and the lowering which the initial and end solidifying points undergo, on adding a small quantity of *m*-nitrotoluene, should be determined, as NOLTING'S investigation had shown that the latter is present only to the extent of a few %.

A mixture of pure *o*- and *p*-nitrotoluene weighing 2.8319 grams, composed of 35.5% *para*- and 64.5% *ortho*-nitrotoluene, had an initial solidifying point  $-3^{\circ}.8$  and an end solidifying point  $-14^{\circ}.9$ .

If now 0.0860 grams of 2.9% of *meta*-nitrotoluene were added, the initial solidifying point fell to  $-6^{\circ}.0$ , the end solidifying point to  $-16^{\circ}.7$ .

The percentage of *o*- and *p*-nitrotoluene in the mixed nitration product at  $0^{\circ}$ , with an initial solidifying point  $+2^{\circ}.8$  and an end solidifying point  $-16^{\circ}.8$  could now be determined in the following manner, keeping account of the *meta*-compound formed.

On addition of 2.9% of *meta* the end solidifying point falls from  $-14^{\circ}.9$  to  $-16^{\circ}.7 = 1^{\circ}.8$ . Owing to the presence of *meta*-nitrotoluene, the end solidifying point of the mixed nitration product has been found to be  $-16^{\circ}.8$  instead of  $-14^{\circ}.9$  (the eutectic point of the mixture *ortho* + *para*), therefore  $1^{\circ}.9$  lower. From this it follows that in the mixture at  $0^{\circ}$  there is present  $\frac{1.9 \times 2.9}{1.8} = 3.1\%$  of *meta*.

Owing to the presence of those 2.9% of *meta*-compound, the initial solidifying point of the artificial mixture has fallen from  $-3^{\circ}.8$  to  $-6^{\circ}.0$ , therefore  $2^{\circ}.2$ . For 3.1% of *meta* the fall must amount to  $2^{\circ}.4$ . If for the mixed nitration product is found an initial



solidifying point of  $+2^{\circ}.8$ , this would have been  $5^{\circ}.2$  if no *meta*-compound were present, from which it follows that 42.2% of *para*- and 57.8% of *ortho*-nitrotoluene must have formed.

Applying this manner of calculation to the other mixed nitration products we found them to possess the following composition:

Nitration at	initial solidifying point	°	% <i>para</i>	% <i>ortho</i>	% <i>meta</i>
— 30°	initial	$+ 4^{\circ}.1$	41.7	55.6	2.7
	end	$- 16^{\circ}.6$			
0°	initial	$+ 2^{\circ}.8$	40.9	56.0	3.1
	end	$- 16^{\circ}.8$			
+ 30°	initial	$+ 1^{\circ}.4$	39.9	56.9	3.2
	end	$- 16^{\circ}.9$			
+ 60°	initial	$- 0^{\circ}.8$	38.5	57.5	4.0
	end	$- 17^{\circ}.4$			

If the end solidifying point of the nitration product prepared at 0° is taken as  $18^{\circ}.1$ , namely, the mean of the figures found afterwards, the *meta* content increases and amounts to 5.3%. There remains, therefore a doubt of about 1% in regard to the quantity of *meta* compound present in the nitration product, if on the one hand we accept the mean of VAN DEN AREND's values as the true solidifying points, and on the other hand the average values of the other investigations. But also for another reason the quantity of the *m*-compound cannot be determined more accurately.

In the above calculation various surmises have been made. It is for instance, supposed that, at least over the first course, the line which connects the binary eutecticum of *ortho*- and *para*-nitrotoluene with the ternary eutecticum is a straight line. It has also been taken for granted that the fall of the initial solidifying point is proportional to the addition of small quantities of a third isomer. An exact determination would be possible only when the entire ternary melting figure were constructed; yet the method as applied here gives a satisfactory approximation as will be seen from a survey of Fig. 3.

In the plane OPO'P' is situated the melting point curve of *o*- and *p*-nitrotoluene. If, however, a small quantity of *m*-nitrotoluene is present we do not determine a point of the melting point curve O'E<sub>1</sub>P', but a point of a curve situated on a line O'E<sub>1</sub>P'', which is obtained by carrying through the prism a plane parallel to the OP plane, and this at a distance from the OP plane corresponding with the amount of *meta* present. If an arbitrary mixture M consisting of *o*-, *p*- and *m*-nitrotoluene is cooled a separation of solid *ortho* or *para* will take place at a definite temperature; all depends on whether the mixture has the composition indicated by the right or the left melting

