



I. Researches on melting-point

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To cite this article: Edmund J. Mills D.Sc. F.R.S. (1882) I. Researches on melting-point , Philosophical Magazine Series 5, 14:85, 1-29, DOI: [10.1080/14786448208628413](https://doi.org/10.1080/14786448208628413)

To link to this article: <http://dx.doi.org/10.1080/14786448208628413>



Published online: 28 Apr 2009.



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THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[FIFTH SERIES.]

JULY 1882.

- I. *Researches on Melting-point.* By EDMUND J. MILLS, D.Sc., F.R.S., "Young" Professor of Technical Chemistry in Anderson's College Glasgow*.

IF we desire to ascertain the purity of a chemical substance—in other words, to establish its species—two lines of investigation are open to us. We may (1) by analytical means determine the composition, or (2) measure by physical methods some natural property of the body. Both modes of research require that what is determined—whether composition or natural property—shall be constant over a fair range of genetic condition. Both modes also involve a considerable amount of inference; but, of the two, far less is demanded by the methods of physical science, which are, as a rule, distinguished by their greater certainty because of their experimental directness. To the property of melting, these characteristics are preeminently applicable.

The accurate ascertainment of melting-point, in terms of the air-thermometer, supplies us with physical constants of considerable importance. While the readings of the mercurial thermometer are subject to grave correction—its zero, in particular, being never stationary,—it is most unlikely that the melting-point of a substance will vary in any ordinary interval of time, under any common change of pressure, or with transition to a distant latitude. Actuated chiefly by these considerations, I undertook the researches of which an account is comprised in the following sections.

* Communicated by the Author.

Phil. Mag. S. 5. Vol. 14. No. 85. July 1882.

B

A. Benzol Derivatives.

1. *Dinitrobenzol*.—The benzol from which specimens A and C were prepared had been purified by myself, first by fractional distillation, then by fractional distillation after treatment with bromine, and, lastly, by freezing and pressure. The preparation of the dinitro-compound was effected with the aid of hydric sulphate. The crude product was washed with water, alkaline water, and water successively, and then submitted to a process of purification repeatedly adopted in these experiments.

[The process in question consists in crystallization from *distinct successive solvents*, followed each time by pressure. It is well known that small quantities of impurity are prone to cling to substances with much tenacity; but the observation has most frequently been made in connexion with some single solvent. One can readily conceive that the tenacity with which a given trace of a foreign body is held may, under such circumstances, be in effect constant. If, however, we now transfer the mixture to a new solvent, then, we may fairly presume, the trace will be in a condition of altered adhesiveness, and may be much more readily separable. It is of course not easy to decide whether this result is always attained, or whether the later solvent makes any impression at all; but it will probably be granted that the method of multiple successive solvents is in general expedient to adopt.

After each crystallization the crystals were in all cases submitted to powerful pressure between folds of carefully cleansed linen or, occasionally, of silk tissue. The surface-tension of the dissolved impurities appears to be for the most part considerable; and this, aided by mechanical compression, greatly economizes the time required in preparing a pure substance.

The pressed crystals were next reduced to a very fine powder, and dried for eleven days over oil of vitriol in the dark. Care was taken never to make determinations with substances previously melted; for it not unfrequently happens that a second melting takes place at an appreciably different temperature.]

Specimens A and C were crystallized twice from naphtha, and thrice &c. (A_3 &c., C_3 &c.) from purified alcohol. Specimen B was given me by Mr. C. E. Groves, who had prepared it from thrice frozen and pressed benzol. It was crystallized once from water, once from naphtha, once &c. (B_1 &c.) from pure alcohol. The results are contained in Table I.

Dinitrobenzol melts with some sharpness after a decided pasty stage. It strongly resists pulverization—a character more especially observable in specimen B.

TABLE I.

	A ₃ .	A ₄ .	B ₁ .	B ₂ .	B ₂ .	C ₃ .	C ₄ .
	89.86	89.71	89.79	89.75	89.64	89.73	89.67
	.75	.71	.82	.78	.71	.62	.59
	.75	.74	.71	.70	.66	.73	.62
	.78	.68	.71	.70	.64	.76	.67
	.73	.84	.66	.70	.66	.73	.64
	.75	.76	.68	.70	.74	.70	.73
	.81	.82	.79	.67	.71	.76	.64
	.78	.79	.66	.80	.69	.73	.62
	.81	.84	.71	.78	.71	.65	.75
	.67	.84	.68	.70	.74	.78	.70
	.75	.79	.79	.70	.71	.76	.62
	.59	.82	.76	.83	.62	.73	.78
	.81	.82	.66	.72	.64	.68	.70
	.83	.71	.74	.7265	.59
Mean	89.76	89.78	89.73	89.73	89.68	89.71	89.67
Probable error012	.010	.010	.008	.007	.008	.010
Thermometer ...	2	2	2	2	3	2	2

2. *Dichlorobenzol*.—For this specimen I was indebted to Dr. Hugo Müller, who prepared it by his well-known process of chlorination, which consists in treating hydrogenated bodies with chlorine in presence of iodine. It was crystallized twice from naphtha, and four times &c. (A₄ &c.) from alcohol. *Dichlorobenzol* melts very suddenly.

TABLE II.

	A ₁ .	A ₂ .	A ₃ .	A ₄ .	A ₅ .	A ₆ .	A ₇ .
	52.61	52.72	52.66	52.74	52.74	52.74	52.83
	.66	.72	.71	.72	.72	.76	.75
	.74	.70	.71	.69	.69	.72	.75
	.71	.67	.74	.69	.74	.66	.75
	.74	.75	.79	.72	.74	.72	.78
	.79	.72	.74	.69	.72	.72	.73
	.74	.75	.76	.69	.69	.64	.73
	.71	.72	.79	.72	.74	.76	.70
	.76	.72	.71	.66	.76	.76	.75
	.71	.75	.71	.69	.69	.76	.73
	.69	.77	.68	.69	.76	.76	.73
	.76	.75	.74	.72	.72	.74	.67
	.74	.72	.74	.69	.74	.72	.75
	.79	.75	.74	.66	.76	.74	.73
Mean	52.72	52.73	52.73	52.70	52.73	52.73	52.74
Probable error008	.004	.006	.004	.004	.006	.006
Thermometer ...	3	3	3	3	3	3	2

3. *Dibromobenzol*.—A was a sample prepared by heating
B 2

benzol (permanently reddened by bromine) for a short time nearly to boiling, washing and rectifying the product. The benzol thus purified was used in preparing benzol by Couper's process*; and from this product, on distillation, a residue of dibromobenzol was obtained. This was crystallized once from spirit, twice from naphtha, and thrice from spirit; at the last crystallization the substance was only partly dissolved; and the crystals obtained from the solution were alone examined. C was prepared from the monobromobenzol above referred to. The product of Couper's process always contains a little dibromobenzol, which cannot be removed in the ordinary way. This was allowed to remain. Traces of another solid impurity were precipitated by exposure to sunlight for some weeks in presence of solid potassic hydrate, followed by filtration and distillation. Finally the purified monobromobenzol was mixed with bromine in the proportion $C_6H_5Br : Br_2$, and left for some weeks in the laboratory, during which it was once heated in the water-bath. The product was washed with aqueous caustic soda, some unaltered monobromobenzol removed by partial distillation with water, and the remainder crystallized once from alcohol, once from naphtha, and once from alcohol in presence of charcoal (C_1): successive fractions (C_2 &c.) from alcohol were then taken. C_{6a} was obtained from a hot liquid which had deposited about half its contents, which I have named $C_{6\beta}$.

Dibromobenzol melts nearly as sharply as dichlorobenzol. It is hardly possible to trace a pasty stage.

TABLE III.

	A.	A.	C_1 .	C_2 .	C_3 .	C_4 .	C_5 .	C_{6a} .	$C_{6\beta}$.
	87.08	87.05	87.10	86.97	87.06	87.10	87.04	87.06	87.10
	87.03	87.07	86.99	87.08	87.01	87.05	87.01	87.06	87.05
	86.87	87.03	87.12	86.97	87.03	87.10	87.01	87.03	86.94
	86.97	87.05	86.99	87.16	87.03	87.10	87.01	86.98	87.07
	87.00	87.01	87.10	87.13	87.11	87.05	87.01	87.09	87.07
	86.97	86.96	87.07	86.99	87.01	87.07	87.01	87.06	87.07
	86.95	87.01	86.97	87.08	87.01	87.04	86.96	87.06	87.05
	87.03	87.01	87.12	87.13	86.98	87.06	87.01	87.06	87.05
	87.03	87.05	86.99	87.05	87.11	87.15	86.99	87.06	87.02
	87.08	87.10	87.02	87.05	87.03	87.07	87.04	87.11	87.02
	87.00	87.01	86.99	87.10	87.01	87.13	86.99	87.03	87.02
	87.03	87.03	87.12	87.08	87.03	87.04	86.99	87.10	87.02
	86.97	87.12							
	87.03	87.09							
Mean	87.00	87.04	87.05	87.06	87.04	87.08	87.01	87.06	87.04
Probable error.	.010	.007	.011	.012	.007	.007	.004	.006	.008
Thermometer ..	2	4	2	2	2	2	2	2	2

* *Ann. Chim. Phys.* [3] lii. p. 309.

4. *Dinitrobromobenzol.*—Benzol purified by bromine distillation, and freezing, was brominated by the Couper process, and freed from dibromobenzol by heating to the boiling-point with a mixture of Nordhausen and common oil of vitriol; this treatment was followed by washing and distillation.

Sample A was prepared from the above bromobenzol by Kekulé's method*. The crude product amounted to 148 per cent., theory requiring 157 per cent.: it contained a small quantity of an oily body. This was crystallized twice from naphtha and five times &c. (A₅ &c.) from alcohol.

The crystals of dinitrobromobenzol are, as observed by Kekulé, remarkably large and well defined. They powder harshly, like rosin. The concentrated alcoholic solution emits sound as it crystallizes.

Dinitrobromobenzol melts with considerable sharpness.

TABLE IV.

	A ₅ .	A ₆ .	A ₇ .	A ₈ .	A ₉ .	A ₁₀ .	A ₁₀ .
	70°53	70°54	70°56	70°68	70°67	70°68	70°56
	53	51	64	55	54	71	59
	50	65	61	55	64	55	53
	53	49	64	55	67	71	53
	48	51	56	57	54	55	56
	53	57	67	68	70	60	66
	61	51	59	57	56	60	66
	58	65	59	68	64	63	56
	66	59	48	57	59	68	46
	53	57	67	68	59	60	69
	64	54	69	63	67	57	71
	48	54	67	65	62	68	
	50	67	64	63	67	57	
	56	62	67	63	67	57	
Mean	70°55	70°57	70°62	70°61	70°62	70°62	70°59
Probable error ...	·010	·010	·010	·009	·009	·010	·015
Thermometer ...	2	2	2	2	2	2	3

5. *Nitrodibromobenzol.*—Sample A, from (D) dibromobenzol (q. v.) which had been crystallized once from alcohol, once from naphtha, and once from alcohol. 25 grm. of substance were gently heated with 250 cub. cent. of "fuming nitric acid," and allowed to cool during a rather longer period. The product, purified by means of water and ammonia, contained a little oily impurity, and weighed 28·5 grm. (= 114 per cent., theory requiring 119·1 per cent.): it was crystallized twice from naphtha, and thrice &c. (A₃ &c.) from alcohol.

* *Ann. Chem. Pharm.* cxxxvii. p. 167.

B was prepared from another portion of (D) dibromobenzol. 25 grm. were gently heated for two hours with 250 cub. cent. nitrate as before, and allowed to cool during twenty-one hours. The pressed product, which had at first contained an oily body, weighed 17 grm. (=68 per cent.): it was crystallized twice from naphtha, and thrice &c. (B₃ &c.) from alcohol.

The melting-point of nitrodibromobenzol is satisfactorily sharp.

TABLE V.

	A ₃ .	A ₁ .	A ₅ .	B ₃ .	B ₁ .	B ₁ .	B ₅ .
	83°49	83°43	83°46	83°46	83°49	83°50	83°32
	·53	·48	·46	·49	·49	·52	·49
	·47	·46	·51	·46	·44	·50	·44
	·55	·54	·43	·43	·54	·45	·47
	·47	·46	·49	·46	·49	·52	·49
	·55	·43	·43	·44	·46	·48	·55
	·53	·48	·51	·39	·57	·52	·57
	·53	·54	·49	·49	·52	·50	·49
	·47	·54	·49	·46	·52	·50	·41
	·49	·48	·46	·52	·52	·60	·52
	·53	·51	·49	·44	·41	·50	·52
	·55	·51	·49	·46	·49	·52	·49
Mean	83·51	83·49	83·48	83·46	83·49	83·51	83·50
Probable error ...	·006	·007	·005	·006	·008	·006	·008
Thermometer ...	2	2	2	2	2	3	2

B. Aniline Derivatives.

1. *Monochloraniline*.—Sample A was prepared from chlorinated acetanilide*, free from toluol. It was purified by solution in aqueous hydric chloride, evaporating thrice to dryness after filtration, precipitating with ammonia, and distilling in a current of steam. The product was crystallized twice from naphtha, and thrice &c. (A₃ &c.) from alcohol.

B was prepared more directly from aniline by the following method:—Half a pound of aniline, purified by cohobation for several hours with one sixteenth of its weight of mercuric chloride, was mixed with a pound of glacial acetate, and chlorine led slowly over its surface. Considerable heat was evolved. When this sign of action ceased to be manifested the mixture was allowed to cool, and the now solid product heated with water and caustic soda: the oily layer thus formed was withdrawn, and cohobated for a few hours with alcoholic potash. Water was next added to this solution and its residue; and the

* For the details of the methods of obtaining aniline derivatives from acetanilide see Proc. Roy. Soc. x. p. 589, and Phil. Mag. 1875, xlix. p. 21.

united amines thereby precipitated were separated by appropriate treatment with aqueous hydric chloride*. B was crystallized twice from naphtha, and thrice &c. (B₃ &c.) from alcohol.

The chlorination of acetanilide yields but little dichloraniline; the chlorination of the acetate still less.

Monochloraniline produces great cold when dissolved in alcohol. On the application of heat to its powder, it melts with great sharpness.

TABLE VI.

	A ₃ .	A ₄ .	A ₅ .	A ₆ .	B ₁ .	B ₇ .	B ₈ .	B ₉ .	B.
	69.66	69.68	69.69	69.66	69.75	69.68	69.69	69.69	69.66
	.74	.76	.69	.63	.64	.63	.66	.66	.56
	.74	.71	.74	.63	.64	.63	.72	.63	.56
	.58	.71	.74	.66	.70	.65	.74	.66	.48
	.74	.65	.66	.79	.64	.65	.72	.71	.51
	.71	.76	.69	.69	.62	.65	.69	.66	.56
	.66	.71	.64	.71	.64	.71	.72	.58	.53
	.66	.65	.64	.66	.70	.71	.66	.61	.53
	.71	.63	.64	.63	.64	.73	.69	.66	.53
	.69	.73	.64	.66	.64	.63	.64	.66	.48
	.69	.68	.74	.71	.64	.73	.66	.63	.48
	.79	.76	.66	.77	.67	.63	.69	.71	.58
	.61	.68	.64	.77					
	.77	.63	.72	.71					
Mean	69.69	69.69	69.68	69.69	69.66	69.67	69.69	69.65	69.54
Probable error.	.010	.008	.007	.009	.007	.008	.006	.007	.010
Thermometer.	2	2	2	2	2	2	2	2	3

2. *Trichloraniline*.—A was obtained by chlorinating a solution of aniline in glacial acetate, as described under *Monochloraniline*. The product was melted under aqueous potash, twice distilled in a current of steam, and crystallized twice from naphtha and thrice &c. (A₃ &c.) from alcohol.

The chlorination of acetanilide suspended in water yields little or no trichloraniline.

Lesimple† describes a modification of trichloraniline which he prepared from nitrotrichlorobenzol by reduction. It has, he states, a very unpleasant and persistent smell, and melts at 96°.5. On these two points my derivative differs from his: it has a faint but not unpleasant odour, and melts at about 77°. In all the other reactions and characters mentioned by Lesimple the two bodies exhibit a complete agreement. Beilstein (who,

* *Loc. cit.*† *Ann. Chem. Pharm.* cxxxvii. pp. 126, 127.

subsequently to myself, published an account of the derivative having the lower melting-point) confirms my determination. The substance with which I have dealt seems, then, to be isomeric with Lesimple's. Trichloraniline yields a non-electric powder, which, in consequence of the woolliness of this body, is rather difficult to obtain. The powder cakes somewhat on drying. The melting-point is exceedingly sharp.

TABLE VII.

	A ₃ .	A ₁ .	A ₅ .	A ₆ .	A ₇ .	A ₈ .	A ₉ .	A ₉ .
	77°06	77°05	77°08	77°06	77°07	77°03	77°02	77°00
	·03	·05	·05	·03	·07	·03	77°02	·02
	·01	·05	·05	·03	·07	·03	77°05	·02
	·06	·08	·08	·09	·04	·06	77°07	·02
	·06	·05	·08	·06	·07	·06	77°02	·02
	·09	·08	·08	·06	·10	·03	77°02	·05
	·03	·08	·08	·01	·12	·06	76°99	·02
	·03	·02	·05	·06	·10	·03	76°99	·02
	·03	·05	·05	·06	·10	·03	77°07	·05
	·06	·08	·05	·09	·10	·06	77°05	·07
	·11	·08	·05	·03	·07	·03	77°10	·00
	·06	·08	·05	·03	·10	·06	77°02	·02
Mean	77·05	77·06	77·06	77·05	77·08	77·04	77·04	77·03
Probable error ...	·005	·004	·003	·005	·004	·003	·006	·004
Thermometer ...	2	2	2	2	2	2	2	3

3. *Monobromaniline*.—In order to prepare this substance, the best commercial aniline was heated to 100° for three hours with $\frac{1}{32}$ part of mercuric bromide, which gave rise to the formation of a trace of rosaniline. The liquid was for the most part distilled off, cohobated for twelve hours with an equal weight of glacial acetate, and then distilled to 130°. The residue, after treatment with hot water, and pressure, was powdered finely, and rapidly stirred in a large bulk of water; into this, 1·75 part of bromine was gradually introduced. The brominated acetanilides thus produced were decomposed with alcoholic potash, and the resulting bromanilines separated by treatment with aqueous hydric chloride. The principal product was dibromaniline.

Specimens A and B were obtained by partially attacking with alcoholic potash the mixed bromacetanilides; the un-attacked residue yielded no more on renewing the treatment. They were crystallized several times from naphtha and spirit. The remainders of A and B were further crystallized thrice from spirit (A B). The mother-liquids of these preparations

were united, and their bromaniline crystallized four times from naphtha and nine times from alcohol, in the presence, during the last two operations, of animal charcoal (C). Q was obtained by directly treating aniline with bromine. It was purified by crystallization—once from naphtha and thrice from alcohol with the aid of animal charcoal (Q_1), also once more from alcohol (Q_2).

Monobromaniline may be dried over oil of vitriol; but I have preferred to use calcic chloride.

The melting-point of bromaniline is very sharp; A B proved exceptionally sudden in this respect.

TABLE VIII.

	A.	B.	A.B.	C ₁ .	C ₁ .	Q ₁ .	Q ₂ .
	61°78	61°78	61°76	61°82	61°65	61°93	61°94
	78	82	78	86	81	85	78
	74	91	76	76	68	74	97
	89	80	83	80	89	88	97
	84	80	83	80	68	90	97
	85	74	76	82	70	88	94
	91	71	85	75	84	72	83
	80	82	76	82	78	85	81
	84	76	76	78	81	77	83
	87	84	76	78	84	88	83
	87	78	76	76	76	79	81
	84	89	74	82	84	79	81
	78	84	74	84	92	88	78
	84	78	76	84	85	83
	84		
Mean	61·83	61·81	61·78	61·80	61·79	61·84	61·86
Probable error ...	·008	·010	·006	·006	·014	·011	·013
Thermometer ...	4	4	4	4	2	2	2

4. *Dibromaniline* [see *Monobromaniline*].—The substance was dissolved in water containing one tenth vol. of common aqueous hydric chloride, the solution filtered cold, and mixed with sufficient ammonia.

Specimens A and B were obtained by the partial action of alcoholic potash on bromacetanilides. A was crystallized four times from naphtha and five times from alcohol; B three times from naphtha, once from spirit, twice from alcohol. C was similarly obtained; it was separated in an evaporation for monobromaniline, having been held in solution by the hydrochloride of that body: this sample was crystallized three times from naphtha and three times from alcohol, and animal charcoal was used. F and G were a result of the further action of alcoholic potash on bromacetanilides. F was sepa-

rated like C; it was crystallized three times from naphtha, four times from alcohol, and animal charcoal was used. G was treated on five successive occasions with a quantity, insufficient to dissolve it, of the dilute aqueous hydric chloride already named; the cold filtered solution was precipitated with ammonia. Of the successive precipitates (G_1, G_2, G_3, G_4, G_5), G_1, G_3 , and G_5 were used for the determination of melting-point; G_1 and G_3 were crystallized twice from naphtha and thrice from alcohol, animal charcoal being present at the last operation; G_5 was crystallized twice from naphtha, and twice from alcohol in presence of animal charcoal.

The hydrochloric solution of dibromaniline already mentioned sometimes shows supersaturation.

TABLE IX.

	B.	A.	C.	F.	G_5 .	G_1 .	G_3 .	G_5 .
	78·91	78·88	78·74	78·82	78·84	78·68	78·79	78·92
	·94	·91	·85	·85	·73	·73	·79	·85
	·88	·85	·85	·66	·73	·71	·79	·92
	·83	·80	·71	·82	·79	·79	·76	·81
	·88	·91	·93	·79	·76	·76	·82	·81
	·91	·77	·87	·87	·68	·87	·90	·73
	·88	·72	·90	·85	·76	·73	·74	·73
	·80	·88	·87	·69	·76	·81	·82	·83
	·94	·83	·77	·93	·79	·89	·92	·94
	·78	·77	·71	·71	·87	·92	·90	·85
	·91	·69	·85	·71	·71	·84	·82	·79
	·78	·83	·90	·90	·81	·84	·74	·85
	·91	·77	·82	·87	·87	·92	·79
	·78	·91	·77	·90	·81	·82	·92
Mean	78·87	78·82	78·82	78·81	78·78	78·80	78·82	78·84
Probable error ...	·010	·012	·013	·015	·010	·014	·011	·012
Thermometer ...	2	2	2	2	2	2	2	4

5. *Tribromaniline* [see *Monobromaniline*].—Sample A was prepared from brominated phenylacetamide by distilling the crude product of the action of alcoholic potash thereon from strong aqueous hydric chloride, and adding water to the distillate.

Z was precipitated by water from some strongly hydrochloric washings, and crystallized four times from naphtha, four times from alcohol. B was crystallized from a hot mixture of ordinary aqueous hydric chloride diluted with two vols. of water, and washed with the same liquid diluted with six vols. of water. It was crystallized twice from naphtha and twice from alcohol, animal charcoal being present. Q was prepared by directly acting with bromine on aniline dissolved

in a large volume of dilute sulphuric acid. It is the characteristic product of the reaction; but a little bromaniline is also formed, with traces perhaps of dibromaniline. It was purified by extraction with aqueous hydric chloride diluted with nine vols. of water, by distillation, and by crystallization from spirit with the aid of animal charcoal. Q_1 was crystallized thrice from spirit, Q_2 four times. In the preparation of tribromaniline, whether from aniline directly or from phenylacetamide, the product is accompanied with a considerable amount of a black substance, non-volatile, and insoluble even in boiling spirit, which evolves much hydric bromide on distillation, and then carbonizes.

The determinations headed A, Z, and B were made with a thermometer protected by two glass cylinders; in the other cases the thermometer was bare.

The exact observation of the melting-point of tribromaniline is very difficult, inasmuch as the substance becomes transparent only at the edges of a bead which is for the most part dim and pasty.

TABLE X.

	A.	Z.	B.	Q_1 .	Q_2 .	Q_1 .
	116°42	116°07	116°05	116°20	116°14	116°31
	·26	·12	·21	·31	·17	·31
	·28	·26	·24	·23	·28	·24
	·17	·32	·21	·15	·22	·24
	·31	·18	·19	·26	·30	·26
	·23	·23	·16	·31	·22	·19
	·27	·23	·13	·26	·19	·11
	·23	·34	·19	·28	·22	·31
	·28	·23	·13	·31	·36	·31
	·26	·12	·21	·23	·36	·26
	·28	·33	·29
	·28	·28	·24
	·31	·36	
	·31	·30	
	·28	·39	
Mean	116·27	116·21	116·17	116·27	116·27	116·26
Probable error ...	·013	·018	·011	·008	·013	·011
Thermometer ...	2	2	2	2	2	3

C. Toluol Derivatives.

1. *Nitrotoluol*.—Nitrotoluol was prepared from coal-tar toluol, which had been purified by agitation with oil of vitriol and potash successively, and by distillation. According to Beilstein's recommendation, hydric nitrate of spec. grav. 1·48 was dropped into toluol; a stream of air was kept passing through the flask, and a stream of water round it. Through

the washed mixture of liquid and solid nitrotoluol with toluol thus obtained, a current of steam was passed, to remove toluol first; then a mixture of the two nitrotoluols came over; and from this the solid was almost completely extracted by solidification in a freezing-mixture and filtering out suddenly by atmospheric pressure. For the success of this operation, distillation in a current of steam is essential.

Sample A was purified by melting with a little Nordhausen, washing with water, and crystallizing from spirit: the mother-liquids were evaporated for deposits, d_1 , d_2 , d_3 . The results were:—

d_1 .	d_2 .	d_3 .	
51.45	51.18	51.22	} Each result is a mean.
51.11	50.83 (thermometer 2)		
51.12 (recrystallized)			
51.13–51.52 (sublimed)			

It is clear that neither crystallization from spirit (even after Nordhausen) nor sublimation gives a satisfactory result.

Sample B was purified like A, twice crystallized from spirit, once from pure high-boiling-point (132°) naphtha, twice from spirit, once from spirit of wine.

Sample C was similarly purified: four successive extracts (x) were taken in a mixture of 1 spirit, 2 water. Therm. 2. The mean results were:—

x_1 .	x_2 .	x_3 .	x_4 .
44.5	44.9	43.8	50.7

This shows that the method of extracts is also a failure. x_1 , x_2 , x_3 were united as C_a ; x_4 was set aside as C_b ; C_a was twice crystallized from naphtha, once from spirit of wine. Four similar extracts were then made, united, crystallized from naphtha, C_b added, and the mixture was again crystallized, once from naphtha, once from spirit of wine: this product is termed C_c .

Sample D was thrice crystallized from naphtha, once from spirit of wine; twice, thrice, and four times from spirit of wine. Part of the crude substance of D had not been distilled. The fractions are marked D_4 , D_5 , &c., according to the times of crystallization.

M was prepared by dropping purified toluol into twice its bulk of nitrous or "fuming" nitrate of spec. grav. 1.48; 50 cub. cent. of toluol were added to 100 cub. cent. nitrate in each operation, which lasted 1.6 hour. It was crystallized twice from naphtha and thrice from alcohol,

TABLE XI.

	C.	C _α .	C _c .	D ₁ .	D ₅ .	D ₆ .	D ₇ .	B.
	51°43	51°39	51°22	51°22	51°27	51°34	51°34	51°31
	29	39	37	32	10	39	39	34
	40	46	30	35	10	17	24	29
	31	37	40	25	35	32	39	34
	29	34	32	37	37	14	39	21
	31	34	35	37	35	17	34	34
	34	24	37	35	35	19	39	34
	47	24	48	09	27	32	39	37
	31	32	24	35	39	29	30	16
	24	21	25	27	39	17	32	39
	31	26	19	22	27	27	36	29
	21	41	14	35	39	14	30	29
	31	26	26	14	32	22	29
	24	37	31
Mean	51.32	51.33	51.30	51.27	51.27	51.35	51.34	51.30
Probable error011	.013	.017	.016	.016	.016	.010	.010
Thermometer ...	2	3	2	2	3	3	3	2

2. *Dinitrotoluol*.—I have investigated the melting-point of this substance as prepared (1) directly from toluol, (2) from liquid nitrotoluol ("metanitrotoluol"), (3) solid nitrotoluol when the active masses are relatively small, and (4) solid nitrotoluol when the active masses are relatively large.

[Case I.] Dinitrotoluol was prepared from coal-tar toluol, which had been purified by agitation with oil of vitriol and potash successively, and distillation: a mixture of oil of vitriol with hydric nitrate was used. The product was pressed to free it from oily matter, and crystallized from spirit. The portions that fell successively in the act of crystallization were called A, B, C, D, and many experiments were made with them; but the results were not very accordant. The four samples were fractionally crystallized from spirit: the first deposits being called A₁, B₁, &c.; the second, A₂, B₂, &c.

Fractions of F (an old preparation) were also employed.

Melting-points having been taken, C₁, F₄, and F₃ were found to coincide, and mixed together. Four successive fractions of the mixture were taken; and after some further fractionation,

(F₂)₂, (F₁)₁, [(F₃F₄C₁)₂]₂, [(F₃F₄C₁)₃]₂, (F₃F₄C₁)₁
yielded *a*;

A₁, B₁, (F₂)₁, [(F₃F₄C₁)₄]₂, [(F₃F₄C₁)₄]₁, [(F₃F₄C₁)₃]₁,
yielded *b*;

A₂, B₂, C₂, (F₁)₂, [(F₃F₄C₁)₂]₁ yielded *c*;

D yielded *d*.

The following results were then obtained :—

TABLE XII.

	<i>a.</i>	<i>a.</i>	<i>b.</i>	<i>b.</i>	<i>d.</i>	<i>b.</i>	G.	G.	<i>a.</i>
	69°23	69°12	69°22	69°20	69°13	69°23	69°15	69°29	69°33
	·23	·20	·19	·20	·16	·20	·20	·31	·25
	·09	·23	·22	·20	·16	·28	·42	·16	·40
	·33	·20	·22	·20	·18	·25	·29	·09	·22
	·14	·23	·09	·25	·21	·25	·34	·31	·38
	·06	·12	·12	·10	·12	·29	·31	·28
	·23	·16	·12	·15	·06	·33
	·23	·29	·25	·26	·06	·33
	·23	·24	·20	·34	·31	·38
	·27	·21	·29	·29	·17
	·16	·34	·14	·17
	·29	·40
	·31	
	·24	
Mean	69·18	69·18	69·19	69·21	69·18	69·21	69·28	69·23	69·30
Probable error ..	·025	·013	·015	·007	·010	·012	·016	·017	·016
Thermometer ...	3	3	3	3	3	2	2	3	2

[Case II.] The mixture of nitrotoluoIs obtained by nitrating coal-tar toluol was cooled to -17° , and the solid modification (which separated in crystals) removed by sudden application of the filter-pump and subsequent fractional distillation. The product boiled at 219° – 223° . 6·5 cub. cent. of substance dissolved completely in 20 cub. cent. nitrous nitrate, with

TABLE XIII.

	I.	II.
	68°09	69°24
	69°15	·19
	·12	·32
	·23	·24
	·20	·21
	·26	·13
	·23	·21
	·20	·16
	·15	·16
	·23	·00
	·26	·11
	·23	·19
	·15	·03
	·15	·08
	·18	·13
Mean	69·18	69·16
Probable error	·012	·014
Thermometer	2	2

slight evolution of heat; after four hours' contact, 150 cub. cent. water were added. The precipitate, which was solid on the following morning, was washed with warm aqueous sodic carbonate, and then weighed about 8.5 grm., or 112.5 per cent., the theoretical yield being 132.9 per cent. I will call this specimen J dinitrotoluol. It was crystallized four times from naphtha and three times from spirit. (See Table XIII.)

[Case III.] The whole of the remainder of D nitrotoluol (p. 12) was treated with nitrous hydric nitrate in the cold; 2.5 grm. of the nitrotoluol being dissolved in 39 grm. of the nitrate, with which it remained in contact $2\frac{1}{2}$ hours. The powder was very electric. I will call this specimen L. It was crystallized four times from naphtha and thrice from spirit.

The following numbers were obtained with Therm. 2:—

TABLE XIII A.

	69°28
	·17
	·20
	·17
	·14
	·12
	·12
	·17
	·22
	·17
	·14
	·03
	·22
	·22
	·22
Mean	69·17
Probable error	·010
Thermometer	2

[Case IV.] When rather larger quantities are taken, though the same proportions between the reagents and time of action be observed, a different result is obtained. Thus Y was prepared from 4.5 grm. M mononitrotoluol; the crude product (122 per cent.) was purified by warming with weak aqueous potash containing ammonia, and was crystallized twice from naphtha, eight times from alcohol. Z was made from 20.5 grm. of a new stock of solid mononitrotoluol (which had been distilled in steam, frozen, pressed, and crystallized twice from naphtha and four times from alcohol); the crude product (120 per cent.) was crystallized twice from naphtha, and eight to nine times (Z_8 , Z_9) from alcohol. Both samples had a faint yellowish tinge.

TABLE XIV.

	Y.	Z _s .	Z _b .
	69°54	69°60	69°43
	57	60	46
	54	57	51
	62	63	51
	57	57	38
	59	55	51
	57	57	51
	57	57	56
	51	65	56
	51	63	62
	51	60	59
	59	57	59
Mean	69°56	69°59	69°52
Probable error ...	007	006	013
Thermometer ...	2	2	2

3. *Trinitrotoluol*.—A. Some crude coal-tar dinitrotoluol was heated with about five times its weight of “fuming” nitrate for more than thirty hours, but not so as to cause ebullition of the liquid. It had lost about 15 per cent. of its weight, but, as shown by its melting-point, had not been converted into trinitrotoluol.—B was lost in the process of crystallization.—C. The deposit from the nitric mother-liquid of the preparation fused at about 59°7. The substance itself fused at about 80°8 when crystallized nine times from spirit; and then, when kept a few days, its melting-point rose to about 181°8. A small residue from the entire preparation, crystallized thrice from spirit, thrice from naphtha, and thrice from spirit of wine, fused at 182°8 nearly. This body is soluble in naphtha, insoluble in cold and very sparingly soluble in hot spirit, insoluble in water or aqueous ammonia. Quantitative experiment seems to indicate that it is a compound of dinitrotoluol with trinitrotoluol. In appearance it closely resembles trinitrotoluol. Subsequent attempts to prepare it, both directly and in the nascent way, did not succeed.—D. The result of A was confirmed.

E. A specimen of coal-tar trinitrotoluol about 3 years old, yellow at the top; the melting-point of the lower and colourless part was taken. (This result will be noticed separately.) The remainder from this first determination (part being yellow) was crystallized twice from naphtha and once from spirit of wine. The results are given under the first E column; the

result of a further crystallization from spirit under the second E column; and so on.

TABLE XV.

	F ₁ .	F ₁ .	F ₁ .	F ₂ .	F ₂ .	E.	E.	E.	E.	K.
	78·88	78·86	78·89	78·78	78·85	78·79	78·83	78·76	78·88	78·87
	·91	·91	·79	·88	·85	·76	·81	·86	·78	·95
	79·05	·81	·87	·80	·83	·81	·86	·73	·80	·95
	78·78	·86	·94	·88	·93	·86	·89	·62	·70	·90
	·81	·73	·89	·88	·80	·83	·83	·78	·88	·90
	·81	·78	·84	·90	·87	·89	·89	·78	·82	·95
	·78	·78	·78	·93	·93	·65	·76	·78	·85	·84
	·81	·84	·84	·93	·93	·83	·81	·88	·80	·90
	·81	·73	·86	·80	·92	·89	·86	·78	·82	·84
	·81	·81	·92	·88	·92	·71	·97	·83	·80	·78
	·78	·81	·83	·93	·83	·86	·73	·78	·90	·84
	79·02	·91	·86	·82	
Mean	78·84	78·81	78·86	78·87	78·88	78·82	78·84	78·78	78·82	78·88
Probable error.	·016	·011	·010	·011	·009	·018	·012	·013	·010	·011
Thermometer...	2	2	3	3	3	2	2	2	2	2

F. Coal-tar toluol boiling at 109°·5–112°·0 was purified with oil of vitriol in the cold; it then boiled at 110°–113°. Equal volumes (300 cub. cent.) of nitrate (sp. gr. 1·48) and this substance were mixed, the latter being run in gradually. 51 cub. cent. of toluol were recovered by distillation; hence benzol was absent. The product was washed, added to 300 cub. cent. “fuming” nitrate (sp. gr. 1·5); washed, added to 4 vols. “fuming” nitrate (the latter), left 24 hours, and 1 vol. Nordhausen poured in—this being done in two operations, on account of the violent action in the cold. The yield was 190·7 per cent.; theory, 246·7 per cent. Half of the yield was crystallized from naphtha and spirit, and termed F₁. The other half was boiled for 6 × 6 hours with “fuming” nitrate, and termed F₂; the product was very dark, contained scarcely any acid bodies, and showed little loss when weighed. The fusion-points of F₁ and F₂ are the same.

K. Prepared from liquid coal-tar nitrotoluol which had been twice distilled, cooled to –17°, filtered, again distilled (under 224°); when cooled as mentioned, only a trace of crystals was deposited. 19 cub. cent. of this liquid, 150 cub. cent. “fuming” nitrate, 100 cub. cent. Nordhausen, yielded 31·5 gm. trinitrotoluol, = 142·6 per cent., theory requiring 165·7 per cent. The product was crystallized four times from

Phil. Mag. S. 5. Vol. 14. No. 85. July 1882.

C

naphtha, five times from spirit; its fusion-point then agreed with that of F_1 and F_2 .

Such trinitrotoluol is found with great ease, an hour's ebullition with a mixture of equal volumes of oil of vitriol and common nitrate sufficing to produce it. Now the presence of oil of vitriol is a great hindrance to making ordinary trinitrotoluol*.

M. M nitrotoluol was treated with Nordhausen and nitrous nitrate, and yielded 157.1 per cent. of product. The melting-point of this preparation having been found not quite regular, the substance was again treated with the nitrating-mixture, and crystallized twice from naphtha, and thrice (M_1), four times (M_2), &c. (&c.) from spirit.

The crystalline form of this modification of trinitrotoluol is distinct from that of F_1 or K_1 , being much more prismatic and less platy.

A small preparation (L) of trinitrotoluol made from L dinittrotoluol (itself made from D nitrotoluol) was treated like M, and the melting-point also determined before complete nitration had been effected. This point was $78^{\circ}91 \pm .008$, after one crystallization from naphtha and two from spirit; and the prismatic character of the crystals was apparent; but the amount of substance was too little to go on with.

TABLE XVI.

	M_1 .	M_2 .	M_3 .	M_4 .	M_5 .
	80.49	80.53	80.50	80.58	80.55
	.36	.56	.47	.53	.52
	.52	.58	.55	.47	.55
	.49	.42	.55	.50	.47
	.52	.56	.50	.53	.60
	.46	.42	.47	.53	.58
	.49	.55	.58	.50	.55
	.49	.53	.55	.50	.55
	.54	.50	.50	.47	.52
	.54	.48	.53	.53	.58
	.49	.61	.61	.53	.58
	.49	.58	.61	.55	.55
	.52	.42	.53	.53	.60
	.54	.42	.50	.53	.58
Mean	80.49	80.51	80.53	80.52	80.55
Probable error008	.012	.008	.005	.006
Thermometer ...	2	2	2	2	2

* *Zeit. Chem.* xiii. p. 539.

Thus it is evident that trinitrotoluol prepared from the solid modification of nitrotoluol is distinct both in form and melting-point from the others; it is also more difficult in making.

It deserves to be mentioned that the melting-point of trinitrotoluol appears to undergo a slight change under certain conditions. Thus, a perfectly colourless specimen three years old melted at $78^{\circ}76$ —the number of observations being 13, and the probable error 0.012. A few grammes of the specimen F₂, after exposure to light, with frequent agitation, for 13 days, during which it became mustard-yellow on the surfaces, melted at $78^{\circ}78$; the number of observations being 14, and the probable error 0.013. This result was obtained after two crystallizations from naphtha and two from spirit, when the substance had become brilliantly white.

D. Toluidine Derivatives.

Toluidine.—The modification examined is solid at the ordinary temperature, and obtainable by the reduction of mononitrotoluol.

Sample H was purchased from Messrs. Hopkin and Williams. It was purified by conversion into oxalate, which salt was thrice extracted by ether and then decomposed by potash, distillation in a current of steam, and crystallization thrice from naphtha and four times &c. (H₄ &c.) from alcohol.

S was given me by Mr. Spiller. It was pressed and crystallized twice from naphtha and four to five times (S₄₋₅) from alcohol.

G was purchased from Dr. Schuchardt, of Görlitz. It was pressed, and crystallized twice from naphtha and three to four times from alcohol (G₃₋₄).

The above were ascertained to be all different preparations.

The melting-point of toluidine is difficult to observe. The substance remains for some time in the pasty stage, and then conducts heat very badly; from this cause the melting-point may easily be overestimated. On the other hand, when the solid substance is plunged into a bath which is hotter than the real melting-point, it melts with great readiness and sharpness. Good numbers can only be obtained with finely-powdered material; the capillary tubes must be introduced into the bath at 4° or 5° below the melting-point; and the mercury in the thermometer must rise very slowly towards the last.

TABLE XVII.

	H ₄ .	H ₅ .	H ₆ .	H ₆ .	S ₄ .	S ₅ .	S ₆ .	G ₃ .	G ₄ .
	42°78	42°79	42°78	42°69	42°82	42°81	42°80	42°67	42°83
	·88	·74	·67	·85	·82	·86	·76	·80	·78
	·73	·61	·73	·75	·82	·83	·74	·72	·75
	·76	·77	·76	·73	·82	·76	·76	·83	·80
	·78	·71	·70	·73	·72	·79	·71	·75	·83
	·65	·66	·83	·69	·74	·83	·68	·77	·93
	·83	·69	·70	·75	·87	·76	·86	·85	·78
	·78	·77	·73	·81	·82	·83	·86	·75	·80
	·83	·71	·78	·69	·74	·79	·81		
	·83	·69	·83	·73	·84	·68	·76		
	·70	·63	·65	·79	·74	·71	·78		
	·73	·79	·70	·77	·72	·83	·66		
	·63	·76	·73	·69	·81	·67		
	·77	·62	·81	·82	·79	·76		
Mean	42·77	42·71	42·73	42·76	42·78	42·79	42·76	42·77	42·81
Probable error.	·012	·011	·011	·009	·010	·009	·011	·013	·012
Thermometer ...	2	2	2	4	2	2	2	3	3

E. *Phenol Derivatives.*

1. *α Mononitrophenol.*—By *α* mononitrophenol I mean the more volatile mononitrophenol of the two produced by treating phenol with water and nitrate according to Fritsche's method (*Journ. prak. Chem.* lxxv. p. 257). The crude stock was several times distilled.

A was crystallized from water and dried over oil of vitriol (as the rest were): it had been exposed to light (A₁); it was further and continuously exposed to light (A₂). B₁ was a partial precipitate from spirit by water, dried in the shade; the mother-liquid gave with more water a precipitate which turned brown when dried like B₁, and then melted about 0°·6 below B₁. C₁ was made like B₁, except that scarcely any thing was left in the mother-liquid. E was a total precipitate from a sodic salt which contained, as a mean of two experiments, 14·28 per cent. of sodium (theoretically 14·31): it was dried in the shade. D was twice crystallized, probably from weak spirit, and dried in shade twenty days, *i. e.* very much longer than either of the others.

The powder of *α* mononitrophenol has a tendency to cake together on keeping.

TABLE XVIII.

	D.	B ₁ .	C ₁ .	E.	A ₁ .	A ₂ .
	44°31	44°29	44°29	44°22	44°28	44°31
	·29	·29	·24	·25	·25	·31
	·24	·24	·18	·25	·31	·23
	·33	·18	·10	·22	·28	·17
	·24	·32	·29	·27	·28	·25
	·29	·26	·29	·27	·23	·39
	·37	·29	·29	·30	·28	·31
	·33	·32	·21	·22	·31	
	·24	·21	·29	·27	·31	
	·33	·32	·29	·25	·28	
	·21	·29	·28	
Mean	44·30	44·27	44·25	44·25	44·28	44·28
Probable error ...	·009	·010	·012	·005	·005	·017
Thermometer ...	2	3	3	2	3	3

2. *β Mononitrophenol.*—*β* mononitrophenol is the less volatile mononitrophenol of the two produced by Fritsche's process (*Journ. prak. Chem.* lxxv. p. 257). The crude stock was converted into sodic salt, washed with aqueous sodic hydrate, dissolved in water, and precipitated by hydric chloride: a sodic salt prepared from this contained 14·17 instead of 14·31 per cent. of sodium, the preparation being effected with but very little loss.

A₁ was crystallized thrice from naphtha and once from water; A₂ was the same, twice crystallized from water; B₁, B₂, B₃ were all crystallized together thrice from naphtha, in one quantity; and this was crystallized thrice from water. All the specimens were dried over oil of vitriol in the dark for about two months.

β mononitrophenol becomes pale dirty yellow on exposure to light for a day, especially if a part of it has been melted. As the coloured product probably melts below the temperature at which the uncoloured substance does; and as a broad gas-flame must tend somewhat to produce the same effect as daylight, the long stage of incipient fusion and the uncertainty of the limit are accounted for.

TABLE XIX.

	A ₁ .	A ₂ .	B ₁ .	B ₂ .	B ₃ .
	111°29	111°50	111°37	111°53	111°40
	29	34	60	41	35
	35	53	51	32	40
	40	50	41	34	40
	38	53	41	39	47
	45	50	48	46	51
	40	27	37	41	51
	31	42	51	41	51
	26	42	58	44	49
	24	45	46	37	38
	51	31
	32
Mean	111°34	111°45	111°46	111°41	111°43
Probable error ...	014	017	016	012	014
Thermometer ...	3	2	3	3	3

3. *α* Dinitrophenol.—*α* dinitrophenol appears to have been first observed by Armstrong, who, however, did not obtain it in a state of purity; the exacter definition of the substance is due to Hübner and Schneider (*Zeit. Chem.* xiv. p. 524). In preparing it, I followed the method recommended by the last-named chemists, depending more especially on the insolubility of the baric derivative in boiling spirit of 90 per cent. When the baric derivative was dissolved in water and treated with aqueous hydric chloride, the hydric salt was precipitated: this was afterwards dissolved and crystallized.

α dinitrophenol has an extremely pale yellow colour when crystallized from naphtha or spirit; the powder has a deeper shade; and the solution imparts a dark-orange tint to a tissue on which it has been dried.

A, B, C, D, E were distinct preparations. A and B had been crystallized thrice from naphtha and thrice from spirit; C had been crystallized from water, aqueous potassic chloride, and twice from spirit; D had been made from a baric salt twice extracted with spirit, after which it was crystallized once from naphtha and four times from spirit*; E was formed by uniting the remainders of A, B, and C, extracting the baric salt thrice with alcohol, and crystallizing the resulting *α* dinitrophenol once from naphtha and once from spirit.

* The hot alcoholic solution was poured off from a red, quite insoluble foreign substance.

α dinitrophenol melts sharply, the pasty stage being short. According to Hübner and Schneider its melting-point is 63–64°.

TABLE XX.

	A.	A.	B.	B.	C.	D.	E.
	61°89	61°79	61°85	61°82	61°78	61°82	61°79
	·80	·79	·77	·77	·75	·85	·74
	·82	·84	·77	·78	·70	·87	·77
	·80	·82	·80	·75	·73	·74	·75
	·74	·74	·82	·67	·67	·77	·72
	·89	·87	·80	·78	·81	·71	·83
	·87	·87	·77	·80	·70	·74	·85
	·74	·84	·74	·77	·75	·79	·79
	·74	·87	·82	·82	·75	·85	·77
	·73	·92	·74	·78	·75	·74	·77
	·70	·74	·85	·71	·78	·74	·75
	·73	·79	·80	·65	·70	·85	·75
	·74	·78	·78	·82	·70
	·77	·80	·81	·82	·77
Mean	61·79	61·82	61·79	61·76	61·75	61·79	61·77
Probable error ...	·013	·010	·006	·009	·007	·009	·007
Thermometer ...	4	2	2	4	2	2	4

4. β Dinitrophenol.—Z. The crude compound was prepared by Grüner's method, from crystalline phenol. A considerable amount of its baric salt was crystallized repeatedly from a large volume of water, and the cooled and filtered mother-liquid precipitated with hydric chloride.

Z₆ was the tenth precipitate; it was crystallized thrice from water.

Z₇ was the eleventh precipitate; it was crystallized once from water.

Z₇ was the twelfth precipitate; it was crystallized once from water.

Preliminary determinations of melting-point were made with the nine preceding fractions; but the numbers were not sufficiently satisfactory to warrant proceeding with purification.

Y was made by Dr. Armstrong from trinitrophenol, by way of amido-dinitrophenol; it was crystallized thrice from water.

T. For this also I am indebted to Dr. Armstrong: he had prepared it by acting with ordinary hydric nitrate on phenol. It was crystallized once from naphtha, once from alcohol, and four times from water.

In determining the melting-points of Z_η , Z_ζ , and Y, the thermometers were protected by two glass cylinders; in the other three cases the cylinders were not used.

Crystallization, powdering, desiccation, and filling of capillary tubes had to be effected either in total darkness or in a deep shade. β dinitrophenol is very nearly white; but by two hours' exposure to a somewhat gloomy atmosphere it becomes deep turmeric yellow.

β dinitrophenol melts with moderate sharpness.

TABLE XXI.

	Z_η .	Z_ζ .	Y.	T.	Z_e .	Z_c .
	116° 60	111° 63	111° 46	111° 57	111° 66	111° 65
	·60	·63	·57	·57	·64	·55
	·46	·49	·63	·49	·61	·65
	·52	·58	·68	·60	·61	·58
	·55	·63	·82	·57	·64	·53
	·63	·60	·60	·60	·80	·63
	·46	·58	·49	·57	·61	·60
	·43	·68	·57	·52	·66	·58
	·52	·52	·60	·54	·53	·53
	·63	·55	·57	·54	·66	·65
Mean	111° 54	111° 59	111° 60	111° 56	111° 64	111° 59
Probable error ...	·015	·012	·020	·007	·014	·010
Thermometer ...	2	2	2	2	2	3

5. *Trinitrophenol*.—Sample A was a commercial specimen. It was crystallized twice from water, once from alcohol, and again from water.

Z was prepared from dinitrophenol made by Grüner's process (*v. supra*); the material employed was very pure, having been precipitated from a 12th (Z_η) cold aqueous extract of the crude basic salt. This was evaporated to dryness on the water-bath with a very large excess of hydric nitrate, and crystallized once from naphtha, once from ethylic alcohol, and twice from water.

O was made from phenol, containing minute amounts of the two modifications of dinitrophenol, by evaporation, as with Z. It was crystallized thrice from water, once from alcohol, and a first (O_1), second (O_2), and third (O_3) time from water.

M was similarly prepared from sodic α nitrophenate (E under α nitrophenol), and was crystallized thrice from water.

F was derived from sodic β nitrophenate (the analysis is

given under β mononitrophenol); it was crystallized once from water, once from alcohol, and again from water.

N was prepared from some α (Hübner's) dinitrophenol, for which I am indebted to Prof. Armstrong. This was purified by Hübner's two processes, and can have contained at most mere traces of its isomer. The trinitro-compound was crystallized thrice from water.

Trinitrophenol is a nearly white substance when in crystals; if very finely divided by any means, it appears a pale yellow. The powdered crystals, if exposed for two hours to indirect light on a dull morning, acquire a deep mustard-yellow colour. The crystals of the substance termed N were almost perfectly white.

The melting-point of trinitrophenol is, on the whole, not difficult to observe.

TABLE XXII.

	A.	Z.	O ₁ .	O ₂ .	O ₃ .	M.	F.	N.	N.
	121°·11	120°·95	121°·04	121°·14	121°·03	120°·99	121°·20	121°·20	121°·09
	·06	120°·92	·07	121°·11	120°·98	121°·13	121°·17	120°·98	120°·89
	·08	121°·03	·01	120°·97	120°·98	·16	120°·98	121°·09	121°·09
	·11	120°·95	·15	121°·14	121°·08	·18	121°·14	·12	120°·94
	·03	121°·06	·18	120°·97	·00	·10	·09	·12	121°·11
	·06	121°·00	·12	121°·06	·08	·16	·01	·15	121°·11
	·03	120°·98	·23	·14	·06	·19	·12	·12	121°·14
	·06	121°·20	·09	·09	·14	·07	·04	·12	120°·94
	·24	121°·00	·12	·09	·11	·19	·14	·15	120°·99
	120°·97	121°·00	·09	·11	·06	·16	120°·98	·17	121°·07
Mean	121°·07	121°·01	121°·11	121°·08	121°·05	121°·13	121°·09	121°·12	121°·04
Probable error.	·014	·016	·013	·013	·011	·013	·016	·012	·018
Thermometer...	2	2	2	2	2	2	2	2	3

F. Naphthalin Derivatives.

Naphthalin.—Commercial pure naphthalin, which had been twice sublimed, was digested for a few hours with strong oil of vitriol in the water-bath. After washing with water, it was distilled from caustic soda in a current of steam. The first portion of the distillate is termed A, the second B. These portions were crystallized twice from naphtha and thrice (A₃ &c.) from alcohol. Before naphthalin melts it exhibits a decided pasty stage; yet the melting-point is sufficiently sharp.

The powdered substance is highly electric.

TABLE XXIII.

	A ₃ .	A ₄ .	A ₅	A ₆ .	B ₄ .	B ₅ .	B ₆ .
	80·06	80·03	80·01	80·03	80·05	80·05	80·06
	79·98	·06	·06	·08	·05	·08	·14
	80·01	·08	·09	·00	·05	·05	·09
	79·95	·00	·06	·08	·05	·02	·09
	80·03	·00	·09	·08	·05	·08	·09
	80·06	·00	·06	·08	·07	·05	·09
	80·09	·08	·12	·08	·07	·08	·03
	80·06	·06	·12	·11	·05	·08	·09
	80·03	·11	·06	·11	·07	·05	·09
	79·98	·03	·09	·06	·07	·05	·09
	80·06	·11	·06	·06	·07	·10	·11
	80·03	·00	·01	·08	·07	·05	·03
Mean	80·03	80·05	80·07	80·07	80·06	80·06	80·08
Probable error ...	·008	·008	·007	·006	·002	·004	·006
Thermometer ...	2	2	2	2	2	2	2

Nitronaphthalin.—A was a sample which had been in my collection for some years, and the details of its preparation are unknown. It was distilled in steam, and crystallized twice from naphtha and thrice &c. (A₃ &c.) from alcohol.

B was a similar sample from the same source. It was purified and fractionated exactly in the same way as A.

Nitronaphthalin becomes sensibly yellowed by continued exposure to light. It melts with considerable sharpness.

TABLE XXIV.

	A ₃ .	A ₄ .	A ₅ .	A ₆ .	A ₇ .	B ₄ .	B ₅ .	B ₆ .
	56·17	56·16	56·17	56·21	56·15	56·24	56·17	56·10
	·20	·13	·14	·21	·15	·24	·17	·20
	·14	·21	·12	·16	·18	·19	·20	·15
	·20	·16	·17	·16	·20	·19	·12	·12
	·17	·16	·22	·18	·07	·11	·14	·00
	·20	·21	·22	·26	·15	·16	·09	·15
	·17	·16	·17	·21	·12	·19	·14	·12
	·17	·16	·17	·16	·26	·16	·09	·10
	·17	·16	·14	·13	·14	·19	·09	·10
	·20	·16	·14	·16	·10	·21	·14	·18
	·22	·21	·16	·24	·18	·24	·12	·05
	·21	·21	·22	·16	·23	·16	·20	·15
	·20	·25	·25	·16	·18	·24	·14	·15
	·20	·21	·22	·18	·20	·16	·12	·02
Mean	56·19	56·18	56·18	56·18	56·16	56·19	56·14	56·11
Probable error ...	·004	·006	·007	·006	·009	·007	·006	·010
Thermometer ...	2	2	2	2	2	2	2	3

TABLE XXV.
Summary of Results.

Substance.	Weighted mean.	Probable error.	After Poggendorff's correction.	Air-thermometer.
Toluidine	42.765	.004	42.700	42.890
Nitrophenol (a).....	44.270	.003	44.205	44.392
Nitrotoluol	51.305	.005	51.239	51.407
Dichlorobenzol	52.723	.002	52.657	52.821
Nitronaphthalin	56.175	.002	56.110	56.261
Dinitrophenol (a).....	61.778	.003	61.714	61.843
Monobromaniline	61.806	.003	61.742	61.871
Dinitrotoluol (a)	69.211	.004	69.154	69.252
" " (b)	69.571	.004	69.514	69.610
Monochloraniline	69.667	.003	69.610	69.706
Dinitrobromobenzol ...	70.598	.004	70.542	70.634
Trichloraniline	77.052	.001	77.004	77.068
Dibromaniline	78.821	.004	78.776	78.833
Trinitrotoluol	78.841	.004	78.796	78.853
Naphthalin	80.061	.002	80.018	80.070
Trinitrotoluol (M) ...	80.524	.003	80.481	80.532
Nitrodibromobenzol ...	83.490	.002	83.452	83.492
Dibromobenzol	87.037	.002	87.007	87.035
Dinitrobenzol	89.718	.003	89.693	89.712
Nitrophenol	111.413	.006	111.448	111.455
Dinitrophenol	111.579	.004	111.614	111.621
Tribromaniline	116.247	.005	116.298	116.319
Trinitrophenol	121.082	.005	121.151	121.194

DISCUSSION.

The determinations of melting-point which have been recorded in the preceding tables, and the results of which are summarized in Table XXV., show a very small probable error in connexion with their weighted means. The probable error of a weighted mean has ranged from $0^{\circ}001$ to $0^{\circ}006$, its average value being less than $0^{\circ}004$. So far, then, as regards the actual process of ascertaining melting-point, considerable accuracy has doubtless been attained.

The preliminary operation of calibrating the thermometers was so conducted as not to have introduced material error, as indeed is obvious from a comparison of the results obtained with different thermometers on melting the same substance*. Regnault was of opinion that the height of the barometer cannot be ascertained with a less error than about 0.1 millim. Such an error would correspond to about $0^{\circ}0037$ on 100° ; and the error would be still less on the mean, as in the present case, of several readings. The small errors in the determination of the exposure-corrections could not sensibly affect the

* See, for instance, Table VII.

final results. It is to comparison with the air-thermometer that we have to look for any important source of error. All observers who have made an extended range of such comparisons have found noteworthy errors, though they have in no case stated probable error. The probable error of the result of my own comparisons of thermometer 2 with the air-thermometer is $0^{\circ}085$ for a single set of comparisons, or $0^{\circ}085 \div \sqrt{33} = 0^{\circ}015$ for the results of the thirty-three sets. This number is the measure of probable error of the equation employed in the final reductions. Compounding, then, the mean probable error of the melting-point ($\cdot004$) with that of the comparison ($\cdot015$) with the air-thermometer, we may consider the melting-points in Table XXV. ascertained, in terms of the air-thermometer, with a probable error of

$$\sqrt{(\cdot004)^2 + (\cdot015)^2} = 0\cdot015.$$

The relation of the chemical symbol to the physical properties of a substance is a matter of such great interest that I have sought for it in melting-point, although other investigators of the general subject, working with less definite data, have not arrived at very encouraging results.

It is very easy to show that, in some cases, there is a very simple connexion between the formula and the melting-point of a substance in the centigrade scale. Thus, dichlorobenzol, bromaniline, and trinitrotoluol form a group in which melting-point $= \phi \times$ numerical value of formula.

Substance.	Formula.	Melting-point.	ϕ .
Dichlorobenzol .	$C_6H_4Cl_2 = 147$	$52^{\circ}821$	$\cdot35933$
Bromaniline .	$C_6H_5BrN = 172$	$61^{\circ}742$	$\cdot35971$
Trinitrotoluol .	$C_7H_5N_3O_6 = 227$	$80^{\circ}532$	$\cdot35477$

In the first of these two instances the values of ϕ are almost exactly the same ; in the last, however, the limits of probable error are exceeded, though a close approximation is very evident.

The following comparison furnishes another practical identity:—

Melting-point.	Melting-point.
Trinitrotoluol . $78^{\circ}853$ —	Dinitrotoluol . $69^{\circ}252 = 9\cdot601$ }
Trinitrophenol. $121^{\circ}194$ —	Dinitrophenol. $111^{\circ}621 = 9\cdot573$ }

In the next instance there is an approximation:—

Melting-point.	Melting-point.
Dinitrotoluol . $69^{\circ}252$ —	Nitrotoluol . $51^{\circ}407 = 17\cdot845$ }
Dinitrophenol. $61^{\circ}843$ —	Nitrophenol. $44^{\circ}392 = 17\cdot451$ }

Such illustrations may be of service in enabling us to detect, with more or less probability, the parallelism of chemical series, and to enable us to decide whether a function—nitration, for example—has or has not the same value in different parts of a series. Other groups in which a similar but less intimate relation prevails, might be adduced from the list; and a glance at Table XXV. will show that, on the whole, melting-point and formula grow together. It may not improbably prove to be the case that, when the whole subject of melting-point has been successfully investigated, this simple relation is the limiting condition of the real law. The data, however, hitherto adduced are far from adequate to a discussion of numerical relations among melting-points: for such an object it would be a fruitless task to examine them further.

Some negative results of this investigation are worthy of attention. Thus α and β nitrophenol have the same additive formula, and yet differ by $67^{\circ}063$ in their melting-point. It is clear then, as already well known, that melting-point may, in cases of isomerism, be related to something else than formula. The melting-point of naphthalin is actually lowered in the first stage of nitration. Considerations such as these may perhaps serve as suggestions for future work.

An accurate method of determining melting-point places it within our power to detect far more delicate shades of isomeric differences than have hitherto been regarded as possible. Thus strong presumptive evidence has been adduced (p. 14) that dinitrotoluol, when prepared directly from toluol or from liquid (meta-) nitrotoluol, or from solid (para-) nitrotoluol by gentle nitration, melts at $69^{\circ}252$; but that when paranitrotoluol is energetically nitrated, the product melts at $69^{\circ}610$. There are consequently two modifications of dinitrotoluol obtainable very directly from toluol—the melting-point of these substances differing by $0^{\circ}358$, a quantity far beyond the range of error of the method. In like manner, it can be shown that two parallel modifications of trinitrotoluol exist—one of which melts at $78^{\circ}853$, the other at $80^{\circ}532$ *.

[For a complete account of the thermometers referred to in this memoir the reader is referred to the Transactions of the Royal Society of Edinburgh, 1881, p. 567; for the method of determining melting-point, to the Proceedings of the Royal Society, vol. xxxiii. p. 203.]

* Compare Phil. Mag. 1875, l. p. 17.