297. *Thermal Analysis, and its Application to the Dinitrobenzenes.*

By Frederick E. Pounder and Irvine Masson.

In the course of work described in the preceding paper, we have used a simple procedure for the accurate thermal analysis of ternary mixtures, which is applicable to quite small quantities of material; it avoids the somewhat serious errors which, though simple in their origin, prove to have affected the results of some other workers, and possibly have prevented others from applying the thermal method in cases where it would have been useful. The specific case for which we have tested the method, and by which we here exemplify intrinsic defects in existing modifications of it, is that of mixtures of the three isomeric dinitro-benzenes, particularly those rich in the *m*-compound.

In the thermal analysis of binary and ternary mixtures, the two extremes, as regards quantity of material needed, are (1) the " setting-point " method, where the thermometer or thermocouple is embedded in a stirred mass of material, and arrests during cooling are observed; (2) the " melting-point tube " method, where a few mg. of material are in a thin capillary glass tube in contact with a thermometer, and the last disappearance of solid during heating is observed.

The first method, apart from its disadvantages in needing much material and in being apt to expose the substance to moist air, is defective in that with a given sample in a given apparatus the maximum arrest-point becomes lower as the degree of initial supercooling increases. This was studied by Andrews (*J. Physical Chem.*, 1925, **29**, 914), who overcame the difficulty by making several experiments with each sample, and, by plotting the observed arrest-temperatures against the degrees of supercooling, was able to extrapolate back to zero supercooling, so as to find the highest temperature at which crystals could form in that sample.

The method in which ordinary m. p. tubes are used has the advantage of needing only minute quantities; but it suffers from the serious defect that, as the substance is not stirred during heating, residual solid sinks to the bottom of the small column of liquid, and the last crystals to disappear are not in equilibrium with liquid having the composition of the original mixture. The error, moreover, is capricious, so that it is not covered by the calibration with synthetic mixtures. Again, whether the heating arrangement is a metal block, a liquid bath, or an air envelope, temperature gradients in it can and do produce spurious results if they are not explored and counteracted.

In both methods, poor thermal conductivity, especially of organic substances, is also

apt to cause errors, unless the rate of temperature change is extremely slow, and the substance is directly stirred—not merely shaken—continuously.

These difficulties are very simply met as follows. About 0·2 g. of the dry, powdered mixture is quickly shaken to the closed end of a quill-glass tube about 20 cm. long and of 3 mm. bore, carefully dried with hot, dust-free air just beforehand. A glass stirring rod about 1 mm. in diameter, drawn from a piece of glass rod and twisted at its lower end, is inserted into the tube. A thin and flexible rubber sleeve, the neck of a toy balloon, ensheathes the top of the tube and also the projecting rod which forms the handle of the stirrer; thus the tube is sealed against moisture, while up-and-down stirring is easy. The tube is clipped vertically against a standard thermometer with its mercury thread wholly immersed in the heating bath. The bath (for temperatures up to about 120°) is a tall 2-litre beaker filled either with oil-covered water or with glycerol, and provided with a vigorous mechanical stirrer; hand-regulation of Bunsen burners very readily gives temperatures steady within 0·1° for over 15 minutes if required. The process of melting under constant stirring is watched with a lens, the temperature being raised by 0·1° every 3 minutes or so; and the melt with the last trace of solid is held within 0·1° for 5—10 minutes, with continual stirring, so as to leave no doubt that the true m. p. is being observed. Repetition with the same sample has always given complete agreement with the first reading.

In illustration of the discrepancies which arise through the use of the other methods, we may quote as typical the case of one mixture containing 90·45% of *m*-dinitrobenzene. By our method this gave 84·15°, 84·10°. Its setting point, carried out with ordinary thermal precautions, was 83·3° : a typical discrepancy, noted in 25 other cases. Observed in sealed capillary m. p. tubes heated in a hand-stirred bath of sulphuric acid, with a temperature rise of 1° in 5 minutes, four identical portions of the same sample gave 84·2°, 85·4°, 84·8°, 85·1°. (With the first of these portions, three further determinations gave successively 84·8°, 86·2°, 87·1°; showing by the progressive rise that segregation of one component was occurring at each liquefaction.) Similar results with other mixtures make it plain that the method with capillary m. p. tubes is quite unreliable for the thermal examination of such mixtures; and the setting-point method, as ordinarily conducted, is also incorrect.

The data on the system *m*-, *o*-, *p*-dinitrobenzene which were obtained by Andrews (*loc. cit.*, p. 1041) by his carefully corrected method of setting points, differ from those of Wyler (*Helv. Chim. Acta*, 1932, **15**, 23), who used the capillary m. p. method. Andrews examined binary mixtures only; Wyler examined binary and ternary, spread out at 10% intervals of composition. Andrews concluded that the isomerides behave as ideal solvents and solutes towards one another. Wyler found non-ideal relationships; according to him, *e.g.*, the specific influence of the *o*-compound upon the m. p. of the *m*- differs from that of the *p*-compound, and the m. p. isotherms on his triangular composition diagram are curved or wavy. In using his interpolated results for the analysis of nitration products composed of all three isomerides, Wyler's procedure, accordingly, was first to determine the *m*-content by chemical means and then to measure the m. p.; and he claimed that this gave an unambiguous value for the *o*-content. But if Andrews's conclusions for binary mixtures are true, Wyler's conclusions for ternary mixtures must be improbable and his method unsound. A similar comment was made, soon after our work began, by van der Linden, in a note on Wyler's work (*Helv. Chim. Acta*, 1932, **15**, 591).

We applied our procedure to a series of synthetic mixtures, both binary and ternary, of the carefully purified isomerides, choosing the ranges of composition which most nearly concern those of ordinary nitration products. Our results (Table II) prove that the isomerides do in fact form ideal mixtures in all these cases. Hence, in order to use the m. p.'s for the analysis of a mixture of all three isomerides, a single direct determination will not suffice, even though the percentage of one isomeride may be independently known. For instance, a m. p. of 83·8° corresponds to a *m*-content of 90·0%, but the remaining 10·0% might be wholly *o*-, wholly *p*-, or any mixture of the two. We therefore first fix the *m*-content by measuring the m. p., and then complete the analysis of the sample by a second determination. In this, enough pure *p*-dinitrobenzene is added to a small weighed portion of the original mixture to reduce the ascertained *m*-content to exactly 70%;

i.e., to bring the composition into the region where the solid that separates from a melt is no longer *m*- but *p*-compound, and consequently the rectilinear isotherms in the triangular diagram run at an angle of 60° to those on the other side of the *m*–*p*-eutectic. The measured m. p. of this new mixture then gives unambiguously the *o*/*p* ratio, by reference to the experimental graphs (Table II, data for 70% meta). In principle, this method is, of course, applicable to any ideal ternary system; and it is denoted as Valeton's method by Holleman ("Die Direkte Einführung von Substituenten in den Benzolkern," Leipzig, 1910, p. 503). The experimental error with our procedure may reach 0·1° for a m. p., corresponding with a maximum error of 0·15 in the percentage of *m*-dinitrobenzene and of 0·2 in that of each other isomeride.

For our meta-separating systems, the graph of the logarithm of compositions against the reciprocal of the absolute m. p.'s is quite straight, and follows the equation $1000/T = 2\cdot7510 - 1\cdot1260 \log N$, where N is the molar fraction. For para-separation, the curve is straight so far as can be seen from the four available points. The use of van 't Hoff's isochore accordingly gives the molar heats of fusion (or of mutual solution) as 4·06 kg.-cals. for *m*- and 6·2 kg.-cals. for *p*-dinitrobenzene. Andrews's data (*loc. cit.*) yield 4·11 and 6·6 kg.-cals. respectively. Some direct calorimetric observations by Robertson (J., 1902, **81**, 1242) with dinitrobenzene of m. p. " 90° " gave 4·9 kg.-cals. per mol.

The eutectic of *m*- and *p*- occurs at 84·5% of *m*-, and 79·9°.

<div align="center">EXPERIMENTAL.</div>

Pure Materials.—The *m*-dinitrobenzene had originally been made in this laboratory by a two-stage nitration of pure thiophen-free " A.R." benzene, and had been recrystallised and dried. It was then refluxed with a solution of sodium methoxide in anhydrous methyl alcohol (which removes the other isomerides and any traces of trinitrobenzene, in the form of nitrophenoxides), recrystallised several times from absolute alcohol, and dried on a hot plate and finally in a vacuum over phosphoric oxide. This gave the stock used for synthetic mixtures, and had m. p. 90·2° with softening about 0·2° lower.

A special sample of *m*-dinitrobenzene was prepared from this material by treating it with a suitable nitrating acid (to dinitrate any traces of mononitrobenzene) at 35° for 30 hours, after which the whole was diluted and made alkaline, and the dinitrobenzene extracted with chloroform. It was then recrystallised from alcohol, dried on a hot plate, and kept for 3 weeks in a vacuum over sulphuric acid. Even this sample, m. p. 90·4°, showed signs of softening 0·2—0·3° lower. The existence of a second form of the compound has been reported (for references, see Andrews, *loc. cit.*). The possibility that this might account for the above melting range in the carefully purified material has, however, not been examined by us, and it seems more likely that even our purest specimen (and *a fortiori* those of most of the other workers cited below) was not yet absolutely pure.

The *o*- and the *p*-compound had been purchased as such; each was recrystallised from acetone and dried as before.

The m. p.'s, determined as described, are thermometrically correct by N.P.L. standards; they are given in Table I with the values recorded to the nearest 0·1° by some other workers.

<div align="center">TABLE I.</div>

<div align="center">*Melting points of dinitrobenzenes.*</div>

Meta.	Ortho.	Para.	Authority.
90·4°	—	—	Present authors
90·2	117·4°	174·2°	„ „
89·9	117·1	174·0	Wyler, 1932
89·8*	116·9	173·5	Andrews, 1925
89·8	—	—	Pushin, 1924
91·0	—	—	Steinmetz, 1915
89·8	117·9	172	Körner, 1874

<div align="center">* After 60 fractional crystallisations, 90·05°.</div>

Mixtures.—In making a synthetic mixture, the dry powdered ingredients (0·2—0·3 g. in all) were weighed in a little cup of polished nickel; this was then very carefully heated under cover, the molten contents stirred with a platinum wire, left in a desiccator to solidify, and the solid

finely ground in an agate mortar; after further desiccation, all was transferred into the m. p. tube.

TABLE II.

Melting points of mixtures of the dinitrobenzenes.

Solid phase : meta.

m, %	95					90				
p, %	5·00	3·75	2·5	1·25	—	10·00	7·50	5·00	2·50	—
o, %	—	1·25	2·5	3·75	5·00	—	2·50	5·00	7·50	10·00
M. p.	87·2°	87·15°	87·15°	87·15°	87·2°	83·75°	83·8°	83·8°	83·8°	83·75°

Solid phase : meta.

m, %	88					85				
p, %	12·00	8·99	6·00	3·00	—	14·99	11·22	7·50	3·73	—
o, %	—	3·01	5·99	9·00	11·99	—	3·77	7·51	11·28	15·01
M. p.	82·3°	82·3°	82·4°	82·4°	82·4°	80·2°	80·3°	80·3°	80·3°	80·3°

Solid phase : para.

m, %	83·19	81·95	80·99	80·02	70					
p, %	16·81	18·05	19·01	19·98	30·0	27·5	25·0	22·5	20·0	17·52
o, %	—	—	—	—	—	2·5	5·0	7·5	10·0	12·50
M. p.	83·0°	86·1°	(87·0°)	90·0°	110·3°	105·5°	101·2°	96·75°	91·7°	86·2°

UNIVERSITY OF DURHAM (DURHAM DIVISION).