

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]
**COMPOUND FORMATION IN THE SYSTEM NAPHTHALENE-
META-DINITROBENZENE**

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In a recent article Puschin¹ arrives at the conclusion that the supposed compound between naphthalene and *m*-dinitrobenzene is really only a mechanical mixture of these two substances. He has repeated the work of Kremann² on the binary freezing point diagram of these compounds, which shows a range for compound formation, and he states that the true diagram is of the simple single eutectic type.³ As a further argument against compound formation he presents data on heats of combustion obtained for the supposed compound and for an equimolecular mixture of the two substances in question.

In the course of some freezing point work done three years ago, we had occasion to construct the freezing point diagram for this binary system, making our measurements by two methods either of which would have been adequate. We found by both methods that Kremann's diagram is substantially correct and that the system has the characteristics of one showing compound formation.

Binary Freezing Point Data

Materials.—A sample of Kahlbaum *m*-dinitrobenzene was purified by systematic fractional crystallization from benzene making use of centrifugal filtration tubes.⁴ The pure naphthalene was prepared by successive sublimation of Kahlbaum naphthalene.

Method and Results.—The freezing points were determined by the method and apparatus previously described⁵ and a few pertinent points were determined by the visual method described by Johnston and Jones,⁶ which involves observing the temperature at which the last crystal disappears when the specimen is heated extremely slowly. The data are given in Table I, the temperatures being accurate probably to within 0.25° in all cases.

Discussion of Freezing Point Diagram

Our data are reproduced in Fig. 1, the heavy dots representing the values determined by the freezing point method mentioned, the circles

¹ Puschin, *Z. physik. Chem.*, **124**, 16 (1926).

² Kremann, *Monatsh.*, **25**, 1283 (1904).

³ The freezing point determinations were evidently made by B. E. Kitran and were published separately by him in another paper, *Farmaceutski Vjesnik*, **14**, 777 (1924).

⁴ Skau, *J. Phys. Chem.*, **33**, 951 (1929).

⁵ Skau and Saxton, *THIS JOURNAL*, **50**, 2693 (1928).

⁶ Johnston and Jones, *J. Phys. Chem.*, **32**, 593 (1928).

TABLE I
FREEZING POINTS OF BINARY MIXTURES OF NAPHTHALENE AND *m*-DINITROBENZENE

Mole % of naphthalene	F. p., °C.	Equilib. temp. (visual method), °C.	Eutectic flat, °C.
0.00	90.1		
14.35	80.5		
29.83	68.6		
36.42		62.5	
40.43	58.6		50.8
44.45		54.4	
46.23	50.8		
57.54	50.5		49.7 ^a
56.95	50.4		
55.36	50.7	51.1	
53.68	50.8		
51.27	51.1		
62.53	52.8		49.7 ^a 49.7
62.65		53.3	
68.42		58.6	
81.41	68.7		
100.00	80.0		

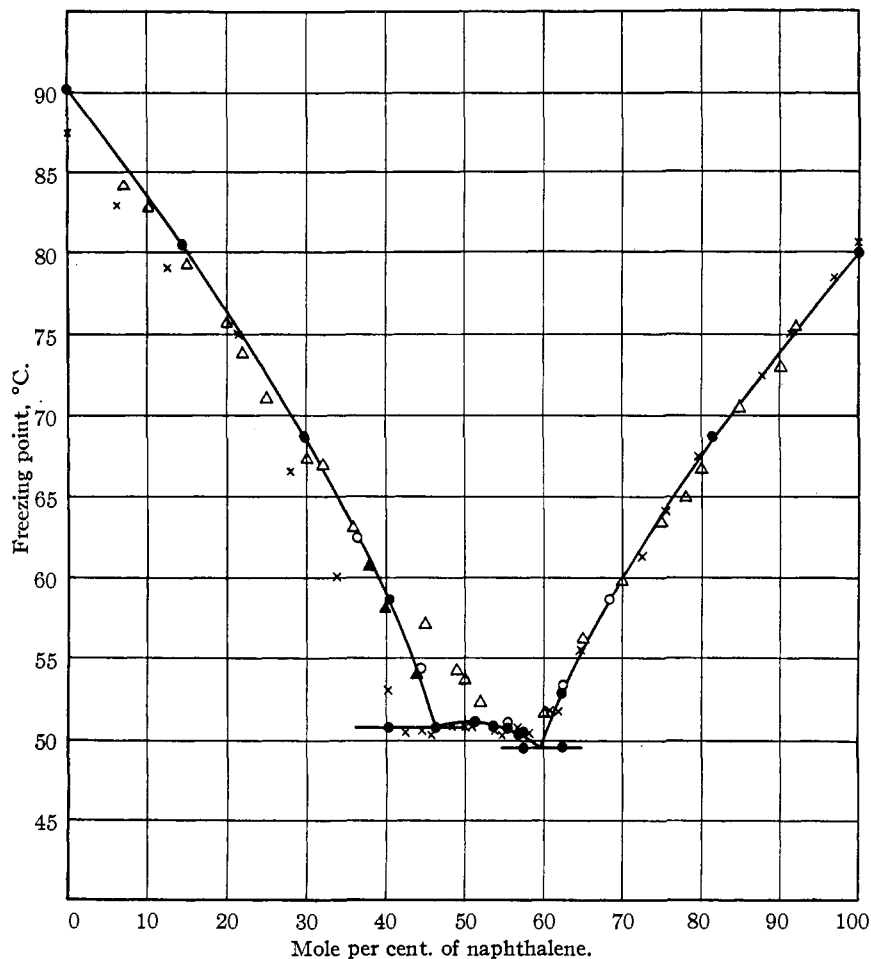
^a By heating curves.

those obtained by the visual method. These two types of measurement, which involve approaching equilibrium from opposite directions, show very good agreement. This proves that the diagram represents real equilibrium conditions and that our method of determining freezing points is valid, even in the neighborhood of the equimolecular mixture where Puschin claims that accurate determinations are impossible owing to a tendency on the part of the liquid to undercool.

The only type of curve which can be drawn through our points is one indicating compound formation with two eutectics, one at 49.7° for about 59.5 mole per cent. of naphthalene and the other at 50.8° for about 46.3 mole per cent. The compound melts at 51.2°. The eutectic temperatures were determined for three mixtures. The higher one, 50.8°, was determined from the second break in the cooling curve. The lower one, 49.7°, was determined from the "flat" on the heating curves for the two mixtures in question and for one of these latter mixtures it was also checked by cooling curves. In the case of the cooling curves, after the first break the mixture cooled to about a degree below the eutectic and the temperature then *rose* to the eutectic "flat," the temperature of the surroundings still remaining below that of the melt. It is not conceivable, therefore, that the temperature reading so obtained could be higher than the true equilibrium value. On the other hand, it is well known that the equilibrium temperature obtained from heating curves is apt to be too high rather than too low.⁷ Thus our data show that there must be two eutec-

⁷ White, *Am. J. Sci.*, 28, 453, 477 (1909).

tics, one certainly not lower than 50.8° , the other certainly not higher than 49.7° . As a matter of fact, these values are probably correct to within a few tenths of a degree, as is shown by the fact that the value obtained for the 49.7° point by the heating curve method was checked by the cooling curve method to within 0.1° .



●, Cooling curve method; ○, visual method; △, Puschin; ×, Kremann; ▲, Kitran.

Fig. 1.—Binary freezing point diagram of the system naphthalene-*m*-dinitrobenzene.

Puschin's results and those of Kremann have been included in Fig. 1, the former by triangles and the latter by crosses. Our results seem to agree in general with those of Kremann except that his values for the *m*-dinitrobenzene side of the diagram are from 2 to 6° low. His two

eutectics are 50.5 and 50.3° and his melting point for the compound is 50.8° Puschin's results seem to agree reasonably well with ours down to within a few per cent. of the compound region and then show marked deviations, his values being considerably higher than ours. He has evidently accepted all of Kitran's³ values except three in this region which he has rejected. These, which have been represented in Fig. 1 by black triangles, show good agreement with our curve.

The diagram which Puschin draws for the binary system does not seem to be justified by his freezing point determinations. In order to make the two branches meet at a single eutectic (at 56% naphthalene and 51.0°) he has distorted the curves considerably and even then the curve, as he has drawn it, does not pass through his experimental points. An examination of his Table I shows that his values for the eutectic temperatures for the various compositions are really not at variance with our diagram showing two eutectics. For percentages of naphthalene less than 50% his eutectic temperature is 51.0°; and for the 56% composition (which he calls the eutectic point) and greater percentages his highest eutectic "flat" comes at 50.0°. These are approximately the values which would be predicted from our Fig. 1.

Unfortunately we have no data for a composition of exactly 56%. The curves for 55.36 and for 56.75%, however, have none of the characteristics of a mixture within 1% of the eutectic composition. On the other hand, our 46.23% mixture gave a typical eutectic cooling curve and the 51.27% mixture gave a curve such as one would expect from a 1:1 compound containing a per cent. or two of one of the constituents in excess.

Puschin presents two reasons for his belief that his simple eutectic diagram represents the facts better than Kremann's diagram. His first is based upon the fact that when the length of the eutectic halt obtained in his freezing point determinations is plotted against the composition, there is a maximum at a composition of 56 mole per cent. of naphthalene. We do not consider the results of this indirect method, a method which at best can be regarded as only approximate, as sufficient evidence to overthrow the actual experimental freezing point results. His second reason is based upon the relative heats of combustion of the supposed compound and of an equimolecular mechanical mixture, but it seems to us that his experimental results do not justify his conclusion. Puschin points to the work of N. N. Nagornow,³ who determined the molecular weight of the compound in benzene, found practically complete dissociation, and then determined the heat of solution of the supposed compound and of the equimolecular mechanical mixture, finding a difference of 2% (actually 165 g. cal. per mole). The difference obtained by Puschin for

³ Nagornow, *J. Russ. Phys.-Chem. Soc.*, **51**, 301 (1919).

the heats of combustion of two such samples is 0.18% (actually 12 g. cal. per gram), which he states is within his experimental accuracy. Due to an oversight, Puschin evidently came to the conclusion that these two results are conflicting. Actually, of course, the absolute difference rather than the percentage difference must be considered, so that his results prove merely that the heat of reaction to form the compound is less than (12×296) or about 3550 g. cal. per mole, which is not at variance with Nagornow's findings.

It should also be pointed out that the possibility of compound formation would not be definitely eliminated on theoretical grounds by a zero heat of reaction, for it would still be possible to have a negative free energy change.

Further Evidence of Compound Formation.—Several other investigators who have studied this system have come to the conclusion that it exhibits compound formation. Hepp, who originally discovered the supposed compound, claims that he isolated it in a distinct crystalline form⁹ from an equimolecular solution of the two compounds in benzene. Buehler and Heap¹⁰ report its isolation by recrystallization from absolute alcohol.

Olivari¹¹ confirmed Kremann's freezing point diagram, as we have on the basis of actual freezing point determinations. He found two eutectics, one at 49.5° for a composition of 59 mole per cent. of naphthalene and the other at 50.3° for 42.5 per cent. He gives the freezing point of the compound as 50.5°. Furthermore, he reports that he was able to verify the existence of two eutectics by plotting the length of the eutectic halt against the composition. Viscosity data for the system also points to compound formation. Kurnakow¹² determined the binary viscosity-composition diagram for the system and found that, though the liquid gave normal results at 90°, there was distinct evidence of a compound present in the liquid state at 52°.¹³

⁹ Hepp, *Ann.*, **215**, 379 (1882): "dicke prismatische Nadeln, welche eine Länge von 5 cm. und mehr erreichen. Sie sind glashell, hart und sehr brüchig, werden aber an der Luft sehr bald trübe, in Folge von Abdunstung von Naphthalin, und schmelzen bei 52 bis 53°. Die durch die Analyse ermittelte procentische Zusammensetzung passt für die Formel $C_{10}H_8(NO_2)_2 \cdot C_{10}H_8$."

¹⁰ Buehler and Heap, *THIS JOURNAL*, **48**, 3168 (1926).

¹¹ Olivari, *Rend. soc. chim. ital.*, [2] **3**, 90 (1911). Olivari represents his freezing point data graphically only, giving no numerical results except for the two eutectic points and for the equimolecular mixture. The graphical representation of his data is plotted on such a small scale that it is impossible to read off the values with any accuracy. They have therefore been omitted from Fig. 1. His curve would, however, if reproduced fall between ours and that of Kremann.

¹² Kurnakow, *Z. anorg. allgem. Chem.*, **135**, 81 (1924).

¹³ The density data for the system published in the same paper did not indicate compound formation, but this cannot be regarded as positive evidence, judging from the data of other systems mentioned where compound formation is unquestioned.

Summary

The freezing point-composition diagram of the system naphthalene-*m*-dinitrobenzene has been redetermined, the freezing points being measured by two methods which involve approaching the equilibrium from opposite sides. The resulting diagram is of the compound formation type and thus corroborates substantially the diagrams of Kremann² and of Olivari,¹¹ and disagrees with that of Puschin.¹ Exception is taken to the arguments of Puschin against compound formation in this system, and viscosity data are cited as further evidence showing that the system is not of the simple eutectic type as Puschin claims.

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CONCENTRATION OF HYDROGEN PEROXIDE SOLUTIONS

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Numerous methods have been described for the concentration of hydrogen peroxide solutions to 60–90% strength, but apparently it is impossible to exceed 90–91% by evaporation or distillation methods. An efficient plan for such a process is that of Maass and Hatcher,¹ but in spite of its efficiency this method is made rather cumbersome by requiring an all-glass apparatus with ground-glass joints and also a sulfuric acid pump. Such special equipment detracts materially from the general usefulness of this process.

The method described in the present paper also is capable of concentrating hydrogen peroxide solutions rapidly to 90% strength, and the apparatus required is merely the simple equipment for distillation and for vacuum distillation. The essence of the method is to add an immiscible volatile liquid such as a hydrocarbon and to distil the mixture. This modified steam-distillation leaves a residue of concentrated hydrogen peroxide after the water and hydrocarbon have distilled away. The method is simple and by controlling the conditions one may obtain nearly any degree of concentration up to 90–91%. It is necessary only to mix about one volume of peroxide solution with two volumes of hydrocarbon. By ordinary distillation with xylene a 3% solution may be concentrated to about 30% strength, and by using *p*-cymene and distilling in a vacuum, a 30% solution may be concentrated to about 90%. A similar method was found to be very satisfactory for the concentration of hydrazine hydrate² solutions.

¹ Maass and Hatcher, *THIS JOURNAL*, **42**, 2552 (1920).

² Hurd and Bennett, *ibid.*, **51**, 265 (1929).