289. *The Liquid Dinitrogen Tetroxide Solvent System. Part VI. Thermal and Conductometric Studies of Solutions of Diethylnitrosamine in Liquid Dinitrogen Tetroxide.*

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Thermal and conductometric measurements carried out over the full concentration range show that liquid dinitrogen tetroxide and diethylnitrosamine undergo compound formation, and that the state of the liquid mixtures may be represented by the equilibria

$$N_2O_4 + nEt_2N{\cdot}NO \rightleftharpoons N_2O_4,nEt_2N{\cdot}NO \rightleftharpoons \text{ionic dissociation products}$$

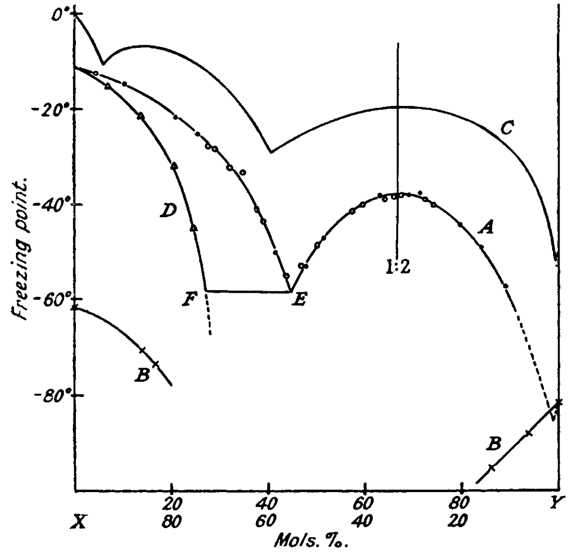
Freezing-point data show that at low temperatures the compound $N_2O_4,2Et_2N{\cdot}NO$ is predominant; the positions of the maxima on the conductivity and heat evolution curves of the mixtures suggest that compounds involving other molecular ratios may exist. The compound (or compounds) formed undergo sufficient ionic dissociation to give rise to a maximum specific conductivity of $3{\cdot}5 \times 10^{-4}$ ohm^{-1} cm.$^{-1}$ (at 0°) at the composition equivalent to $N_2O_4,2Et_2N{\cdot}NO$. Molecular-weight values determined from cryoscopic data are consistent with appreciable ionic dissociation. The cryoscopic constant of liquid dinitrogen tetroxide has been redetermined as 3·64.

In Part V (preceding paper) it was suggested that diethylnitrosamine may have significance as a " free base " in the liquid dinitrogen tetroxide solvent system. Its solutions have been found to possess certain properties which are not inconsistent with this concept (such as reactions with metals to give soluble compounds, discussed in a later paper); for this reason, together with the fact that diethylnitrosamine is produced in solutions of diethylammonium nitrate, it became necessary to determine some of the properties of solutions of diethylnitrosamine in liquid dinitrogen tetroxide. The properties described in this paper are considered in four sections: (1) phase diagram, (2) conductometric analysis of the solutions, (3) molecular-weight determinations, and (4) heats evolved on mixing the two components.

(1) *Freezing Points of Solutions.*—The liquidus curve for solutions of diethylnitrosamine in liquid dinitrogen tetroxide is shown in Fig. 1 (curve *A*). On addition of diethylnitrosamine to

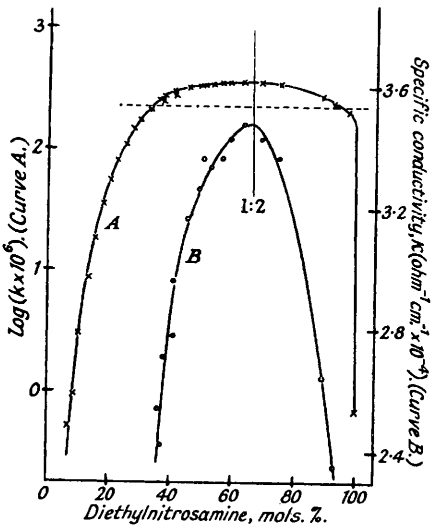
the tetroxide, the freezing points fall smoothly to a eutectic (*E*) at 44·5 mols. % of diethylnitrosamine and −58°. No breaks in the curve which might indicate compound formation were detected in this concentration range. At concentrations above 44·5 mols. %, the freezing-point curve passes through a maximum at −37·5°, and at a dinitrogen tetroxide : diethylnitrosamine ratio of 1 : 2. Thereafter the curve falls towards the freezing point of pure diethylnitrosamine which has been found to be −81°. Although accurate freezing points were not determined for diethylnitrosamine concentrations above 90 mols. %, the shape of the curve is probably as shown by the broken portion of curve *A*, with a second eutectic close to the diethylnitrosamine axis. Curve *A* therefore provides evidence for the formation of a compound of formula $N_2O_4,2Et_2N{\cdot}NO$. The shape of the maximum, and the width of this portion of the curve, suggest that the compound should have an appreciable stability, although the maximum is not sufficiently sharp to exclude the possibility of some dissociation. This curve, together with the conductometric measurements reported below, indicates that there is considerable interaction between the two components in the liquid state. It is probable, therefore, that the maximum in curve *A* (Fig. 1) reflects the formation of a chemical, rather than a lattice, compound.

FIG. 1.



Curve.	Components : X.	Y.
A	*Dinitrogen tetroxide.*	*Diethylnitrosamine.*
B	*Nitrosyl chloride.*	*Diethylnitrosamine.*
C	*Water.*	*Diethylamine.*

FIG. 2.



(*Curve B represents the portion of Curve A above the broken line, regraphed on a linear scale.*)

On a formal analogy with the aqueous system, the solution of diethylnitrosamine in dinitrogen tetroxide is equivalent to a solution of diethylamine in water. The freezing points of this latter system are reproduced, from Pickering's results (*J.*, 1893, **63**, 141), as curve C, Fig. 1. Various minor fluctuations in the freezing-point values on the left-hand side of the eutectic, which Pickering considered to represent additional compounds, have been omitted in drawing the smooth curve *C*. It is of interest that over the 20—100 mols. % concentration range the curves are closely similar; the major feature in each curve is the occurrence of a maximum at the 1 : 2 mol. ratio.

Diethylnitrosamine and dinitrogen tetroxide form solid solutions. For the purpose of the molecular-weight measurements discussed below, part of the solidus curve has been determined experimentally, and is shown as curve *D* in Fig. 1 (cf. the corresponding nitrosyl chloride–dinitrogen tetroxide phase diagram, Part II, *J.*, 1949, S 218). A somewhat unusual effect was observed on cooling solutions containing about 40 mols. % of diethylnitrosamine (*i.e.*, slightly below the eutectic concentration). When the liquid was cooled, solid crystallised continuously from the liquid phase; on reaching the eutectic temperature (−58°), no thermal arrest occurred in spite of the fact that an appreciable proportion of solid phase was present. The liquid could be cooled through a further 10°; at about $-68°$ the whole mass solidified, and the temperature returned sharply to the eutectic value. In the temperature range $-58°$ to $-68°$ the liquid therefore appears to be supercooled with respect to some solid other than that represented by a saturated solid solution of diethylnitrosamine (or the 1 : 2 compound) in dinitrogen tetroxide (point *F*). A full investigation of the solidus systems involved here was outside the scope of the present work; however, the liquid may be supersaturated below $-58°$, with respect to the second eutectic solid, which would represent (by a point to the right of *E*) a saturated solid solution of dinitrogen tetroxide in the 1 : 2 compound. The phenomenon may then be explained by assuming continued crystallisation along curve *D* and beyond *F*, until the lattice becomes so strained that it breaks down into the two eutectic solids, with an accompanying rise in temperature to the true eutectic value.

For purposes of comparison, an attempt was made to obtain the phase diagram for the system diethylnitrosamine–nitrosyl chloride. At concentration ranges up to about 20 mols. % of either component in the other, the solutions crystallised normally, with little supercooling. Freezing points are represented by curves *B*, Fig. 1. In the concentration range 20—80 mols. %, supercooling occurred, accompanied by a considerable increase in viscosity. These solutions crystallised with difficulty; they were so viscous that efficient stirring was not possible, and accurate freezing points could not be determined. The approximate values obtained indicated that the liquidus curves fall to a simple eutectic at about 55 mols. % of diethylnitrosamine, and a temperature of $-130°$, with no evidence of compound formation.

(2) *Conductivity Measurements.*—The specific conductivities of mixtures of diethylnitrosamine and liquid dinitrogen tetroxide have been determined at 0° over the full concentration range, and the values are given in Fig. 2 (curve *A*). On addition of diethylnitrosamine to the liquid tetroxide, the specific conductivity undergoes a considerable increase, from $1{\cdot}3 \times 10^{-12}$ ohm^{-1} cm.$^{-1}$ for the pure liquid tetroxide (Part III) to a maximum of $3{\cdot}5 \times 10^{-4}$ ohm^{-1} cm.$^{-1}$. However, the increase in conductivity occurs much more rapidly on addition of dinitrogen tetroxide to the diethylnitrosamine. The best value for the specific conductivity of pure diethylnitrosamine (achieved by repeated distillation under reduced pressure) was $5{\cdot}4 \times 10^{-7}$ ohm^{-1} cm.$^{-1}$. In order to prepare dilute solutions of the tetroxide in diethylnitrosamine for conductivity measurement, the latter was placed in the conductivity cell (Fig. 4) and the liquid tetroxide poured in by the usual closed-system technique. It was observed that during this process the conductivity of the diethylnitrosamine increased more than 100-fold immediately after contact with the tetroxide vapour, *i.e.*, before any liquid tetroxide was actually added. The quantity of tetroxide required to bring about this considerable increase in conductivity was too small to be measurable with accuracy, and in consequence the specific conductivity of the mixture is shown in Fig. 2 (curve *A*) as rising almost vertically from the diethylnitrosamine value.

It would appear from the logarithmic plot of the specific conductivity (curve *A*) that the conductivity curve possesses a broad, flat maximum extending over the 50—80 mols. % diethylnitrosamine range. However, the conductivity measurements are of sufficient accuracy to enable the values to be plotted on a linear scale over this concentration range (curve *B*). The specific conductivity is then seen to pass through a fairly sharp maximum, at a composition corresponding to that of the compound $N_2O_4,2Et_2N{\cdot}NO$. Although the general chemistry of dinitrogen tetroxide and diethylnitrosamine suggests that neither of these molecules is likely to undergo appreciable ionisation separately, the conductivity measurements indicate that they combine to form a 1 : 2 compound which is capable of considerable ionic dissociation.

The general form of the conductivity curve *A* may be interpreted on the basis of the dielectric constants of the two liquids. Liquid dinitrogen tetroxide has been shown to have a low dielectric constant (2·42; Part IV, *J.*, 1951, 1294). The structure of the dialkylnitrosamines might be expected to give rise to high dielectric-constant values for the pure liquids. The Raman spectra (Barredo and Goubeau, *Z. anorg. Chem.*, 1943, **251**, 2; Wittek, *Anz. Akad. Wiss. Wien, Math.-Naturw. Klasse*, 1943, 5; *Chem. Zentr.*, 1943, ii, 1701) for the dimethyl compound have been interpreted on the basis of the resonance states $Me_2N{-}N{=}O$ and $Me_2N^+{=}N{-}O^-$. If the latter state makes an appreciable contribution to the structure of the diethyl compound also, this liquid should possess dipolar character. The dielectric constant for diethylnitrosamine has therefore been determined experimentally, and found to be 42·5 at 22°; this is of the same order as the value (53·3) obtained for dimethylnitrosamine by Walden (*Z. physikal. Chem.*, 1903, **46**, 103).

The compound formed on the addition of small quantities of diethylnitrosamine to liquid dinitrogen tetroxide will be dissolved in a medium consisting mainly of dinitrogen tetroxide, and therefore of low dielectric constant. The ions produced by dissociation of the compound will, in consequence, exist predominantly in the form of ion-pairs, which make no contribution to the conductivity. The addition of further quantities of diethylnitrosamine will increase the amount of compound present, and will also increase the dielectric constant of the medium, with consequent increase in the proportion of free ions to ion-pairs. On the other hand, the compound when formed by addition of a small quantity of dinitrogen tetroxide to a large excess of diethylnitrosamine is dissolved in a medium of high dielectric constant, in which the compound is able to dissociate into free ions. It was therefore to be expected that the increase in conductivity would be more rapid on the diethylnitrosamine than on the dinitrogen tetroxide side of the conductivity curve (Fig. 2, curve *A* or *B*). A further factor may contribute to the rapid rise in conductivity on adding small quantities of tetroxide to diethylnitrosamine. Goulden and Millen (*J.*, 1950, 2620) have shown, from studies of Raman spectra of the solutions, that in dilute solution in pure nitric acid, dinitrogen tetroxide is almost completely dissociated, and that the dissociation occurs mainly heterolytically into the NO^+ and NO_3^- ions. If similar ionisation occurs in solution in diethylnitrosamine, then this fact may in itself contribute towards the rapid rise in electrical conductivity.

The two concepts discussed above may be closely complementary. The formation of ionic species may be considered to arise either (*a*) from the formation of a compound $N_2O_4,2Et_2N{\cdot}NO$, which undergoes ionic dissociation in solution in diethylnitrosamine, or (*b*) from ionisation of dinitrogen tetroxide, aided by the ability of one of the ions (*e.g.*, the nitrosonium ion) to form a molecular compound with the diethylnitrosamine.

The broad maximum on the conductivity curve may arise from at least three factors. (*a*) Further addition of diethylnitrosamine to the 1 : 2 compound decreases the concentration of ionisable compound, but the increase in dielectric constant will increase the degree of ionisation, and will thus tend to maintain the high conductivity value. (*b*) With changing concentration there may also be a displacement of the equilibrium between the compound and its constituents. Nitrogen dioxide could be observed in the atmosphere above the liquid mixtures at all concentrations; it is possible to displace the equilibria in the equation given below entirely to the left-hand side, since dinitrogen tetroxide may be removed quantitatively from the system by evaporation under reduced pressure. (*c*) The results in Fig. 2 do not exclude the possibility of association of the two components in the liquid state in other simple ratios, since the conductivity has almost its maximum value at the 1 : 1 ratio. The equilibria concerned in this system may therefore be represented as follows :

$$N_2O_4 + nEt_2N{\cdot}NO \rightleftharpoons N_2O_4,nEt_2N{\cdot}NO \rightleftharpoons \text{ionic dissociation products}$$

Although no quantitative measurements of the temperature coefficient of conductivity have been made, it was observed that the electrical conductivity of these liquid mixtures increased with increasing temperature over the full concentration range.

(3) *Cryoscopic Constant.*—The cryoscopic constant of liquid dinitrogen tetroxide was determined by Ramsay (*J.*, 1890, **57**, 590). In view of the experimental technique involved, the results were only approximate, and it was considered desirable to redetermine this value. The measurements were carried out by using a simple Beckmann method; the solute was added, by means of a weight pipette, through a side arm in the melting-point tube with precautions to avoid contact with the atmosphere. Duplicate values for the cryoscopic constant (K_f), obtained by using three different solutes, are compared with Ramsay's values below :

	K_f (degrees/g.-mol./1000 g. solvent).	
Solute.	Present work.	Ramsay (*loc. cit.*).
$CHCl_3$	3·69, 3·64	4·10
C_6H_5Cl	3·57, 3·53	4·166
CCl_4	3·73, 3·65	—
	Mean value = 3·64.	

The mean value is significantly lower than Ramsay's value. From the relation $K_f = RT_f^2M/1000L$, and with the values $T_f = 261{\cdot}9°$ K., $L = 3502$ cals./g.-mol. (Giauque and Kemp, *J. Chem. Physics*, 1938, **6**, 40), the calculated cryoscopic constant is 3·58, in close agreement with our measured value. Ramsay (*loc. cit.*) made a similar comparison, and observed that the latent heat of fusion measured experimentally (32·6 cals./g.) was close to the value (33·7 cals./g.) calculated by assuming $K_f = 4{\cdot}1$. However, this agreement is coincidental, since the experimental determination of *L* involved the use of values for the specific heats of liquid and solid dinitrogen tetroxide which were incorrect, and which Ramsay considered to be unreliable.

It is of interest that the mean value for the molecular weight of dinitrogen trioxide dissolved in dinitrogen tetroxide, found by Ramsay to be 84·9 on the basis of $K_f = 4{\cdot}10$, becomes 75·4 (*i.e.*, almost the theoretical value for the N_2O_3 molecule) when K_f is adjusted to 3·64.

Molecular-weight Determination.—Experiments described above show that the compound which diethylnitrosamine forms with liquid dinitrogen tetroxide appears to be capable of ionic dissociation. In order to elucidate further the nature of these solutions, an attempt has been made to determine the molecular weight of diethylnitrosamine in dilute solution in liquid dinitrogen tetroxide, Beckmann's method of freezing-point depression being used. Fig. 1 shows that diethylnitrosamine has a considerable solubility in solid dinitrogen tetroxide. In view of the assumptions which have, in consequence, to be made, it is not necessary to employ, in the calculation of molecular weights, a treatment more refined than that represented by the equation $M = K_f\,\omega\,(1 - k)/\Delta T$, where ω is the weight of diethylnitrosamine in 1000 g. of the tetroxide, and k represents the ratio of the mol.-fraction of the solute in solid to that in liquid dinitrogen tetroxide. The following results show the ΔT values obtained for three concentrations of diethylnitrosamine.

ω, g.	29·47	44·61	48·76
ΔT	0·88°	1·37°	1·53°

It has been assumed, for the present purpose, that (*a*) when diethylnitrosamine is added to the tetroxide it forms the compound $N_2O_4,2Et_2N{\cdot}NO$ (the weights of added diethylnitrosamine have been adjusted on this basis); (*b*) k represents the ratio of the concentration of this compound in the solid to that in the liquid, irrespective of any dissociation which this compound may undergo in the liquid state.

Expressed as a ratio of the mol.-fraction of compound, k varies with total concentration. However, the position of the liquidus and solidus curves in Fig. 1 show that if k should be expressed as the ratio of the concentration of diethylnitrosamine itself in the solid and the liquid phases, then its value is independent of concentration, within experimental error, over the 0—45 mol. % diethylnitrosamine concentration range.

If the two alternative definitions of k be termed k_1 and k_2, respectively, then the value of k_1 is found to approach the constant value k_2 with decreasing diethylnitrosamine concentration, so that in the dilute solutions used in the cryoscopic measurements a value of k, sufficiently accurate for present purposes, may be obtained from the mean of the values of k_2 read directly from Fig. 1. The following table shows the variation, and constancy, of k_1 and k_2, respectively, with change in concentration.

If k is assigned the value 0·625, the results from ω and ΔT (above) give a value of 59 for the molecular weight of the dissolved compound, compared with the theoretical value of 296 in the absence of dissociation.

$Et_2N{\cdot}NO$, total mol. %	10·7	19·0	25·4	30·4	34·2	37·1	39·7	41·5	44·5
k_1	0·600	0·590	0·570	0·545	0·520	0·515	0·495	0·490	0·465
k_2	0·625	0·630	0·640	0·630	0·620	0·625	0·620	0·620	0·610

In view of the assumptions necessary at this stage, and until further evidence on the nature of the dissociation is available, the molecular weight value of 59 cannot be assumed to have any detailed significance. These results, however, support the belief that a considerable degree of dissociation in solution does occur. Electrolytic and other experiments, designed to determine the precise nature of the ionic species, are in hand.

(4) *Heats of Mixing.*—Although the addition of soluble salts to liquid dinitrogen tetroxide produces no appreciable temperature changes, the addition of diethylnitrosamine produces an immediate increase in temperature which may be as much as 20°. Since this heat evolution is probably due, at least in part, to compound formation, and since the quantities of heat are sufficiently large to permit measurements of some accuracy, this heat evolution (expressed as the heat evolved in the preparation of 10 g. of the mixture) has been measured over the concentration range, and the results are shown in Fig. 3. The curve has a rounded maximum; although freezing-point and conductivity data (Figs. 1 and 2) showed maxima at the composition corresponding to the compound $N_2O_4,2Et_2N{\cdot}NO$, this is not the case with the thermal measurements where the maximum falls between the 1 : 1 and 1 : 2 molecular ratios. This may result from the following factors.

(*a*) The measured heat changes, although they probably arise predominantly from the heat of compound formation, will include other thermal effects, amongst which the heat of ionisation of the compound may be significant. With changing concentration, the compound is produced in media of differing dielectric constant. In consequence, the heat of ionisation will not be a constant factor, and may give rise to a displacement of the maximum.

(*b*) The position of the maximum could arise from the presence, in the mixture, of both the 1 : 1 and the 1 : 2 compound in equilibrium. This is not inconsistent with previous observations. The freezing-point data, at temperatures about −40°, showed the presence of the 1 : 2 compound only. However, the conductivity of a 1 : 1 mixture (determined at 0°) was almost as great as that of the 1 : 2 mixture. These results are all in accord with the postulate that in these liquid mixtures an equilibrium exists between the 1 : 1 and the 1 : 2 compound, and that this equilibrium is displaced towards the 1 : 1 compound with increasing temperature.

FIG. 3.

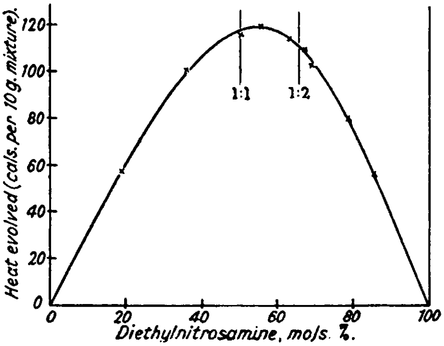


FIG. 4.

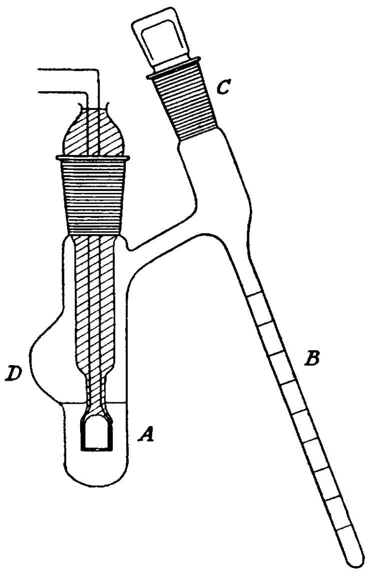
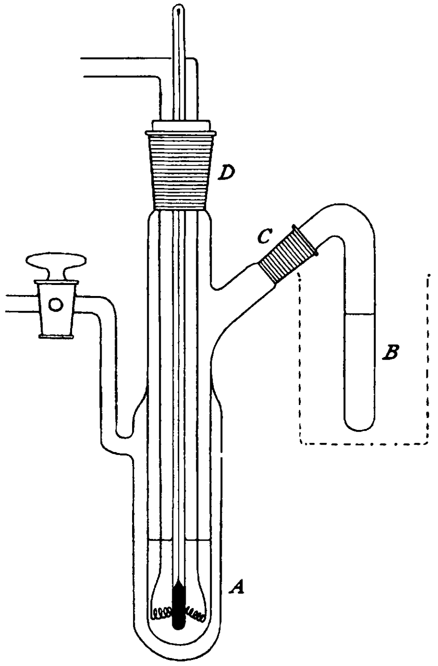


FIG. 5.



During the course of the calorimetric measurements, opportunity was taken to determine the specific heats of the mixtures, and of pure diethylnitrosamine. The values given below were determined over the range 0—15°, with an accuracy of ±0·005 cal./g.

Diethylnitrosamine, mols. %	19·0	35·3	50·2	55·4	60·1	62·8	67·3	68·7	78·6
Specific heat (cals./g.)	0·410	0·450	0·450	0·460	0·470	0·470	0·465	0·465	0·455

The value determined for pure liquid dinitrogen tetroxide was close to the value (0·362 cal./g. at 7°) reported by Giauque and Kemp (*loc. cit.*). The specific heat of pure diethylnitrosamine was found to be 0·452 cal./g. (mean of four determinations 0·448, 0·457, 0·454, 0·449). The specific-heat values of the mixtures pass through a maximum at a concentration close to that at which the maximum heat evolution occurs.

Further Reaction between Diethylnitrosamine and Liquid Dinitrogen Tetroxide.—Over periods of time up to about 12 hours there is no detectable reaction between the two liquids other than the reversible reactions discussed above. However, over periods of days a further and apparently irreversible reaction occurs. When liquid mixtures containing about 30—50 mols. % of diethylnitrosamine were sealed into stout glass tubes, the liquid changed in colour through brown-green to a clear olive green within 1—2 days, and to a deep green-black within 3—4 days. A pressure of gas was generated inside the tube, sufficient in some cases to burst the tube after 2—3 weeks' standing at room temperature. Preliminary analyses of the contents of the tube after 6—7 days indicate that the extent of the reaction is slight, since at least 95% of the original reactants could be recovered. When the tube contents were fractionally distilled, the dinitrogen tetroxide was first removed, leaving a red liquid. On further heating, the red colour faded to the pale yellow colour of diethylnitrosamine, and a trace of a colourless liquid boiling slightly below 100° distilled off. The distillation temperature then rose rapidly to the boiling point of diethylnitrosamine. The reaction probably involves oxidative degradation, with the liberation of nitric oxide. The reaction was not investigated further, since it has so significance in freshly prepared solutions, and does not interfere in any way with the measurements reported in this paper.

EXPERIMENTAL.

Preparation of Materials.—Dinitrogen tetroxide and nitrosyl chloride were prepared as described in Part II (*loc. cit.*). Diethylnitrosamine was prepared from diethylammonium chloride and sodium nitrite (Vogel, "Textbook of Practical Organic Chemistry," Longmans, 1948, p. 417), and was redistilled immediately before use.

Freezing Points.—The f. p.s shown on curve *A* (Fig. 1) as black circles were obtained by the thaw-melt method. Weighed quantities of the two liquids were sealed into a glass phial; the phial was attached to a calibrated thermometer, and immersed in a bath of alcohol. The bath was cooled by solid carbon dioxide until crystals appeared, and then allowed to warm slowly, with stirring, to determine the temperature at which the crystals disappeared. F. p.s shown as open circles on curve *A* (Fig. 1) were obtained by the normal warming-curve technique, and agree closely with the others. To determine the f. p.s of nitrosyl chloride–diethylnitrosamine mixtures, the tube containing the liquid was surrounded by an air-jacket immersed in liquid oxygen, and the f. p.s again determined from warming curves. The solidus curve *D* was determined precisely as described for nitrosyl chloride [method (*b*), p. S 221, Part II].

Electrical Conductivity.—The cell used is shown in Fig. 4. A Mullard Cell Type G.M. 4221 was adapted for the purpose by removing the glass shield surrounding the electrodes (to facilitate the mixing of the liquids); a B 24 ground-glass cone was attached as shown to enable the limb *A* to be closed on insertion of the electrode assembly. The electrodes were platinised to increase the sensitivity with which the null point could be detected, and gave a cell constant of 2·43. Under these conditions there appeared to be little polarisation effect, since the measurements were not affected by a frequency change from 50 to 1000 c./s. The conductivity values were determined by using a Mullard Measuring Bridge Type G.M. 4140/1. A known quantity of pure diethylnitrosamine (about 10 g.) was distilled into limb *A* of the cell, and its conductivity measured in the absence of dinitrogen tetroxide vapour. The cell was then tilted to enable liquid dinitrogen tetroxide to be poured (in a closed system) *via* B 19 joint *C* into the limb *B* of the cell, which carried 0·1-ml. graduation marks. Liquid tetroxide was then poured, by tilting, from limb *B* into *A*, and the angle of limb *B* was so chosen with respect to limb *A* that, on tilting, the liquid surrounding the electrodes was held in the bulb *D* formed on the side of limb *A*. The temperature was kept at 0° by immersing the cell, to a level above the arm connecting limbs *A* and *B*, in a bath of melting ice. At this temperature no difficulties were encountered arising from the distillation of dinitrogen tetroxide from limb *B* into *A*, although at higher temperatures the possibility of errors from this source does arise. The 60—100 mols. % diethylnitrosamine range was covered by the above technique. Conductivities for the remainder of the concentration range were determined by pouring diethylnitrosoamine into either a known quantity of liquid dinitrogen tetroxide or a mixture of known composition.

Purification of Diethylnitrosamine.—The electrical conductivity of diethylnitrosamine is sensitive to traces of moisture, or impurity produced during distillation at atmospheric pressure. Some typical conductivity values obtained by different methods of purification are given below.

Expt.	Treatment.	κ (ohm^{-1} cm.$^{-1}$).
A	Successive distillation at 176°/760 mm.	(1) $1{\cdot}1 \times 10^{-5}$ (2) $6{\cdot}3 \times 10^{-6}$ (3) $4{\cdot}5 \times 10^{-6}$
B	Original product dried (Na_2SO_4) and distilled at 176°/760 mm.; redistilled at 176°/760 mm.; redistilled at 74°/24 mm.	(1) $1{\cdot}2 \times 10^{-5}$ (2) $5{\cdot}6 \times 10^{-6}$ (3) $1{\cdot}4 \times 10^{-6}$
C	Two distillations at 176°/760 mm. followed by one distillation at 36°/3 mm.; redistilled at 36°/3 mm.	(1) $2{\cdot}7 \times 10^{-6}$ (2) $5{\cdot}4 \times 10^{-7}$

The conductivity values quoted were determined in all cases on the middle distillation fraction. Drying agents were found to be of little use in effecting ultimate drying of the diethylnitrosamine; sodium sulphate caused some decomposition. The material used throughout the conductivity measurements was purified by low-pressure distillation (expt. C). The electrical conductivity of dimethylnitrosamine is given by Walden (*loc. cit.*) as $2{\cdot}95 \times 10^{-5}$ ohm^{-1} cm.$^{-1}$ at 25°. It appears possible from the above that this value could be lowered appreciably by low-pressure distillation.

Dielectric Constant of Diethylnitrosamine.—The condenser and containing cell used were similar to those described in Part IV (*loc. cit.*). Because of the lower electrical resistance of diethylnitrosamine, and in order to adjust the capacity of the condenser to within the capacity range of the standard condenser, the annular distance between the concentric nickel cylinders was increased from 1 mm. to 3 mm. The measurement of capacity was carried out essentially as described in Part IV except that in place of the Mullard Capacity Bridge, the Marconi circuit magnification meter (*Q*-meter) was used as the detecting instrument in conjunction with a Muirhead standard variable air condenser. The sensitivity of the *Q*-meter falls considerably with decreasing resistance of the liquid between the condenser plates. With diethylnitrosamine purified as in Expt. C(2) (above), the resistance of the liquid between the plates was about 10,000 Ω. The *Q* value obtained at this resistance was about one-third of that obtained with infinite resistance (*i.e.*, air), but was sufficiently great to permit accurate detection of resonance in the circuit, over the frequency range 800 Kc./s. to 1·3 Mc./s. To calibrate the cell, pure nitrobenzene (redistilled at 48°/1·2 mm.) was used. Dielectric-constant measurements were carried out at 22°, and an ε value of 34·8 (interpolated from Lattey and Gatty's data, *Phil. Mag.*, 1929, **7**, 985) assumed for nitrobenzene at this temperature.

The total capacity of the cell was $16{\cdot}8 \pm 0{\cdot}3$ $\mu\mu$F. in air, $258{\cdot}7 \pm 2{\cdot}1$ $\mu\mu$F. in nitrobenzene, and $313{\cdot}5 \pm 1{\cdot}4$ $\mu\mu$F. in diethylnitrosamine, each result being derived from ten determinations. These results, together with the assumed ε value for nitrobenzene, give the dielectric constant of diethylnitrosamine as 42·5 at 22°; this value is considered to be accurate to ±0·7 unit, which is adequate for the present purpose.

Heats of Mixing.—The heats of mixing, and specific heats, were determined by using the apparatus shown in Fig. 5. A weighed quantity of one of the components was placed in the main glass calorimeter tube *A*, and a weighed quantity of the second component in tube *B*. The liquid in both tubes was cooled to 0° in baths of melting ice. Preliminary experiments showed that the increase in temperature on mixing the liquids under these conditions was about 15°; tube *A* was therefore surrounded by a bath kept constant at about 7° and jacket *A* was evacuated to assist thermal insulation. Under these conditions the heat which the liquid in *A* gained from, or lost to, the surroundings was negligible during the short periods (not exceeding 1 minute) required for each measurement. With both liquids at 0°, tube *B* was rotated in the ground joint *C*, the liquid in *B* poured into *A*, and the increase in temperature observed with an accuracy of ±0·05°. The thermometer was used as stirrer, and was held in joint *D* by a flexible silicone rubber plug, which also carried the leads to the heating coil. (Silicone rubber is not attacked by dinitrogen tetroxide vapour except after prolonged contact.)

The vacuum in the jacket *A* was released to enable the contents of tube *A* to be cooled rapidly to 0°. The vacuum was then restored, the tube replaced in the constant-temperature bath, and the quantity of electrical energy required to heat the liquid through the same temperature range was measured by using a simple battery–voltmeter–ammeter assembly in conjunction with the heating coil. In measuring the fall in potential across the heating coil, allowance was made for the resistance of the leads. The coil and leads were of Nichrome wire, thickness 30 and 18 S.W.G., respectively.

The specific heats of the mixtures were obtained from the electrical heating data, with allowance for the water equivalent of the apparatus. Because of the low thermal conductivity of glass, the water equivalent was found to vary with the volume of liquid in tube *A*, from 2·21 g. (for 10 ml. of mixture) to 3·80 g. (for 25 ml.). The water equivalent of the apparatus was therefore determined for a series of volumes between these limits using pure acetone.

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