536. *The Liquid Dinitrogen Tetroxide Solvent System. Part XV.** *Thermal and Conductivity Measurements on Nitromethane–Liquid Dinitrogen Tetroxide Mixtures.*

By C. C. Addison, N. Hodge, and J. Lewis.

Liquidus and solidus curves, and electrical conductivities, have been determined for mixtures of nitromethane and liquid dinitrogen tetroxide over the full concentration range. The liquidus curves form a simple eutectic system (eutectic temperature −56°, at 53 wt.% of nitromethane), and there is no evidence of compound formation. The solidus curves indicate partial miscibility in the solid state. Dinitrogen tetroxide is a very weak electrolyte ($N_2O_4 \rightleftharpoons NO^+ + NO_3^-$) in nitromethane; the specific conductivity values pass through a broad maximum at $9{\cdot}1 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$.

Studies of solution chemistry in liquid dinitrogen tetroxide are limited by the insolubility of many metal salts in the pure liquid. However, nitromethane gives conducting solutions of some anhydrous metal nitrates [*e.g.*, the compounds $UO_2(NO_3)_2,N_2O_4$ and $Zn(NO_3)_2,2N_2O_4$],

---

* Part XIV, *J.*, 1953, 1874.

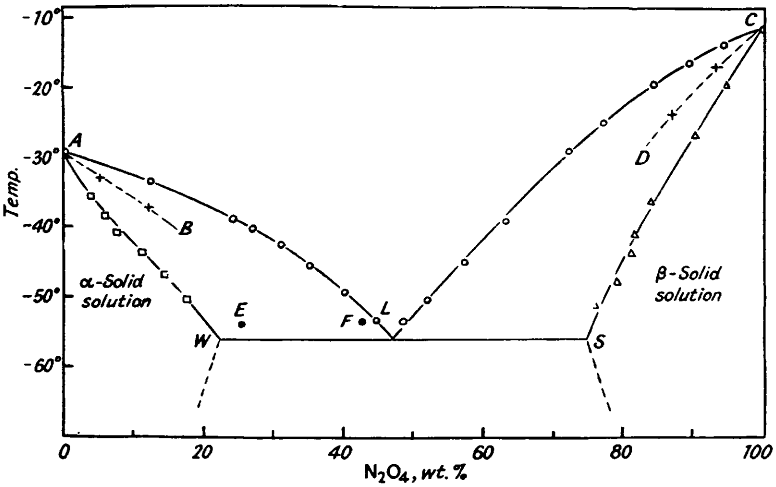
and, since nitromethane and liquid dinitrogen tetroxide are miscible in all proportions, it is of value to determine how far the properties of the tetroxide are influenced by admixture with nitromethane. The nitrosonium ion NO^+ is stable in nitromethane which is known to be a suitable medium for the study of reactions of ionic nitrosonium compounds such as nitrosyl perchlorate (Hantzsch and Berger, *Z. anorg. Chem.*, 1930, **190**, 321) and nitrosyl hydrogen sulphate (Hantzsch, *Z. physikal. Chem.*, 1909. **65**, 41; Angus and Leckie, *Trans. Faraday Soc.*, 1935, **31**, 958).

The very slow rate of reaction between some metals (*e.g.*, uranium) and liquid dinitrogen tetroxide is considerably accelerated by the presence of nitromethane, which has dielectric constant $\varepsilon = 37$ (Lattey and Gatty, *Phil. Mag.*, 1929, **7**, 985). Dinitrogen tetroxide ionises completely into NO^+ and NO_3^- ions in media of very high dielectric constant; and, if the addition of nitromethane to the tetroxide causes an increase in its ionisation by increasing the dielectric constant of the medium rather than by compound formation, then reactions of the mixture with metals may be treated as identical, except in velocity, with reactions of the tetroxide alone. The physical properties reported in this paper were therefore determined in order to ascertain the nature of dinitrogen tetroxide in nitromethane solution.

RESULTS AND DISCUSSION

Thermal Measurements.—The phase diagram is shown in Fig. 1. The liquidus curves form a simple eutectic system indicating the absence of compound formation. The eutectic temperature is —56·0°, at a composition 53·0 wt. % of nitromethane. The crystals formed when a mixture on the tetroxide side of the eutectic was cooled were granular and similar in appearance to crystals of pure dinitrogen tetroxide, and settled rapidly to the bottom of the containing vessel. The crystals formed from liquid mixtures on the nitromethane side of the eutectic were flocculent, colourless plates which settled very slowly. The solidus curves indicate partial miscibility in the solid state. Supercooling was pronounced in mixtures of all compositions; the melting points of the solid which first separated from strongly supercooled mixtures fall on curves *AB* and *CD* (Fig. 1), which are displaced from the true solidus curves (cf. N_2O_4–NOCl mixtures; Part II, *J.*, 1949, S218). The technique employed defined the position of the solidus curves over most of their length with sufficient accuracy, but it was difficult to obtain points on the solidus curves very near to the eutectic temperature. For example, when the minimum quantity of crystals necessary for examination was separated from liquid of composition represented by point *L* the solidus point *E* was obtained. When the crystals were melted and re-

FIG. 1.



frozen, and the melting point again determined, point *F* was obtained. The original crystal crop was therefore not homogeneous (resulting from crystallisation on both sides of the eutectic composition) but such observations were of value in confirming the existence of two distinct solid solutions. On slow crystallisation of a mixture of any composition, the stage at which the liquid passed the eutectic proportions was visually evident by a sharp change in crystal form. The miscibility limit of the β-solid solution, represented by point *S*, occurs at a molecular ratio $MeNO_2 : N_2O_4$ of 1 : 2; the unit cube of solid dinitrogen tetroxide contains twelve NO_2 units (Vegard, *Z. Physik*, 1931, **68**, 184). This ratio is therefore consistent with one-in-three replacement of N_2O_4 by $MeNO_2$ molecules. The corresponding ratio for the α-solid solution (point *W*) is about 5 : 1.

Electrical Conductivities.—Fig. 2 shows the electrical conductivity of nitromethane–dinitrogen tetroxide mixtures at −10°. On contact with dinitrogen tetroxide vapour the specific conductivity of nitromethane increased almost immediately from 1×10^{-7} (for the pure liquid) to $2{\cdot}2 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$, although the quantity of tetroxide absorbed was minute. On addition of liquid tetroxide, the conductivity continued to rise slightly to a broad maximum at about 20 wt. % of dinitrogen tetroxide and $\kappa = 9{\cdot}1 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$ (cf. $3{\cdot}5 \times 10^{-4}$ ohm^{-1} cm.$^{-1}$ for mixtures of the tetroxide with diethylnitrosamine, which has a similar pure liquid conductivity and dielectric constant, but forms an addition compound with the tetroxide). Thereafter, the conductivity falls gradually to the value for pure dinitrogen tetroxide (10^{-12} ohm^{-1} cm.$^{-1}$). There is therefore no feature in this curve to suggest compound formation in the liquid state. The initial rise in conductivity is considered to arise only from enhancement of the ionic dissociation $N_2O_4 \rightleftharpoons NO^+ + NO_3^-$ in a medium of high dielectric constant; the subsequent change in conductivity reflects the gradual decrease in dielectric constant of the mixture.

The change in conductivity of a 43 wt. % solution of dinitrogen tetroxide in nitromethane with temperature is shown in the following Table :

Temp.	11·2°	1·0°	−10·0°	−12·0°	−13·0°	−14·0°	−19·2°	−31·4°	−40·0°	−50·0°
Specific conductivity ($10^6\kappa$, ohm^{-1} cm.$^{-1}$)	7·03	6·45	5·25	5·07	4·95	4·86	4·45	3·54	2·81	2·05

Over this temperature range, the conductivity changes linearly with temperature. The value (8×10^{-8} ohm^{-1} cm.$^{-1}$/degree) and the sign of the temperature coefficient confirm that the ions present in the liquid are thermally stable.

Values for the equivalent conductivity Λ, extended to very low concentrations of dinitrogen tetroxide in nitromethane, are :

Λ (ohm^{-1})	1·29	1·17	0·703	0·347	0·190	0·093	0·063	0·047	0·031
Concn. of N_2O_4 (molar)	0·00026	0·00045	0·00084	0·0022	0·0045	0·012	0·025	0·051	0·12

The magnitude of the Λ values, and their variation with concentration, indicate that even in dilute solution dinitrogen tetroxide behaves as a very weak electrolyte. Since the specific conductivity does not exceed 10^{-5} ohm^{-1} cm.$^{-1}$, the degree of electrolytic dissociation is clearly very small, but it is considerable in comparison with that occurring in pure liquid dinitrogen tetroxide (*J.*, 1951, 1294). Because of the high electrical resistance of these mixtures, attempts to identify the ionic species were not made, but there is now no reason to suppose that the dissociation of dinitrogen tetroxide in nitromethane differs in any way (other than degree) from that in the pure tetroxide.

EXPERIMENTAL

Materials.—Liquid dinitrogen tetroxide was prepared and purified as described in Part III (*J.*, 1951, 1289). The nitromethane was dried over calcium chloride for a week, refluxed for 12 hr. in a current of dry air to remove volatile impurities and fractionated twice through a 4-ft. column. The purity of the product was followed by incorporating a conductivity cell in the receiver at the top of the column. The receiver was fitted with a syphon so that the distillate could be collected, and its conductivity measured, in 13-ml. batches. The results below show the variation in conductivity of alternate batches during the second fractionation :

$10^7\kappa$ (ohm^{-1} cm.$^{-1}$)	44·5	19·0	4·45	1·55	1·49	1·08
Distillation temp.	100·5—110·7°	100·7—100·8°	100·9°	101·0°	101·0°	101·0°

The conductivity of the nitromethane used for Figs. 1 and 2 was near 1×10^{-7} ohm^{-1} cm.$^{-1}$, but the best sample had $\kappa = 0{\cdot}45 \times 10^{-7}$ ohm^{-1} cm.$^{-1}$. These values were increased somewhat even on pouring from one " dry " vessel into another in a closed system, so that samples were normally taken directly from the receiver syphon. Weight percentages were calculated by assuming densities 1·131 for nitromethane (Wright, Murray-Rust, and Hartley, *J.*, 1931, 199) and 1·49 for dinitrogen tetroxide.

Phase Diagram.—The mixtures used to obtain points on the liquidus curve were prepared by direct weighing in closed tubes, with suitable cooling. The m. p.s were determined from breaks in the warming curves. The mother-liquor was readily decanted from the granular crystals of β-solid solution; for the β-solidus curve the procedure described in Part II (*loc. cit.*) was therefore followed. Because of the flocculent nature of crystals of α-solid solution, adequate separation was not possible by decantation, and the filter-plate modification (Fig. 3) was therefore used. The minimum necessary quantity of crystals was formed by cooling about 100 ml. of liquid in vessel *A*. With very gentle suction applied through a phosphoric oxide guard tube at *B*, the assembly was tilted and the liquid filtered through a sintered-glass filter-plate *C* (size 2) into vessel *D*, which was identical with *A*. If the slight vacuum was released suddenly, the mat of crystals was displaced from plate *C*, and could be shaken into *A* for m. p. determination. The composition of the liquid in *D* was then adjusted, *A* and *D* were disconnected and joined through joints *B* and *E*, the composition in *D* was determined from the position of the m. p. on the known liquidus curve, and the process repeated. When points on the solidus curves which approach the eutectic temperature were being obtained, the m. p. of the solid was taken immediately after isolation, and again after refreezing; agreement confirmed the absence of contamination due to the solid solution of the opposite side of the eutectic point. The thermometer used was calibrated against the m. p. of pure mercury, chloroform, carbon tetrachloride, nitromethane, chlorobenzene, and dinitrogen tetroxide.

FIG. 2.

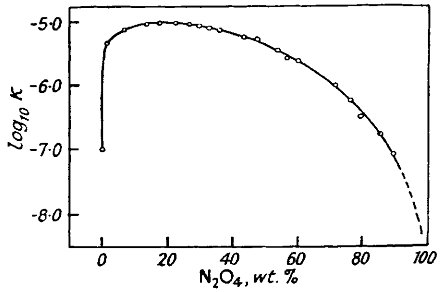
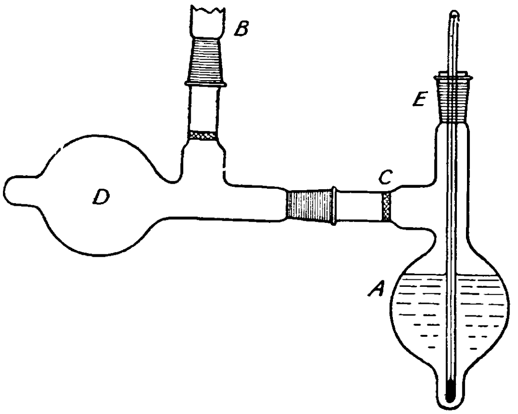


FIG. 3.



Conductivity Measurements.—A Mullard cell G.M.4221 (cell constant 2·25) was assembled as described in Part VI (*J.*, 1951, 1303, Fig. 4) and used in conjunction with a Mullard Measuring Bridge type G.M. 4140/1. Nitromethane (12 ml.) was introduced directly into the cell (capacity 19 ml.) from the top of the fractionating column. The whole cell assembly was immersed in a solid carbon dioxide–alcohol bath at −10°, and the conductivity measured. The graduated side-limb was filled with dinitrogen tetroxide (7 ml.), and the change in conductivity of the nitromethane observed as the tetroxide vapour diffused into the cell. The concentration range 0—43% of tetroxide was covered by small (0·5 ml.) additions of tetroxide from the side-limb. The range 73—100% of tetroxide was covered in a similar experiment by adding nitromethane to a cell containing dinitrogen tetroxide. Intermediate mixtures were obtained by adding nitromethane from the side-limb to a 7 : 5 (vol.) mixture of tetroxide and nitromethane in the cell.

For conductivity measurements on very dilute solutions of tetroxide, the cell consisted of a B24 glass tube into which a microburette (the tap of which was protected by silicone grease) was sealed as a side arm. The cell was fitted with a capillary tube through which liquid could be withdrawn, and a vent-tube guarded by phosphoric oxide; 12 ml. of a 2M-solution of dinitrogen tetroxide were added to the cell. By successively adding nitromethane from the microburette, and withdrawing liquid from the cell, the conductivity of a series of concentrations down to 0·00026M was measured. Stirring after each addition was effected by rotating the electrode assembly.

THE UNIVERSITY, NOTTINGHAM.

[*Received, April 2nd,* 1953.]