

S 47. *The Liquid Dinitrogen Tetroxide Solvent System. Part II. Liquid and Solid Solutions of Nitrosyl Chloride in Dinitrogen Tetroxide.*

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A study of the binary phase system nitrosyl chloride–dinitrogen tetroxide has shown that compound formation between these two components does not occur. The liquidus curves form a simple eutectic system, while the solidus curves indicate that the components are partially miscible in the solid state and that two solid solutions are formed. The miscibility limits in the solid state are discussed in relation to the structure of the pure solids.

THE significance of nitrosyl chloride in the dinitrogen tetroxide acid–base system has been discussed in Part I (preceding paper). Combination of  $\text{NO}_2$  molecules to form  $\text{N}_2\text{O}_4$  occurs readily, and in view of the general similarity between the  $\text{NO}_2$  and the  $\text{NOCl}$  structure, it appeared that compound formation between these molecules might also occur. The presence of any such compound in the liquid state would clearly influence the chemical behaviour, and the effective concentration, of nitrosyl chloride dissolved in liquid dinitrogen tetroxide, and the tetroxide could no longer be regarded simply as a medium for reaction. Thermal analysis of the two-component system nitrosyl chloride–dinitrogen tetroxide has therefore been carried out. The liquidus curves form a simple eutectic system and indicate the absence of compound formation. On cooling liquid mixtures of these two compounds, it was clear that the crystals obtained on either side of the eutectic contained both components and that the system had the typical eutectic form involving two solid solutions, with partial miscibility in the solid state. Since the miscibility limits are related to the structure of solid nitrosyl chloride and dinitrogen tetroxide, the positions of the solidus curves have also been obtained with accuracy.

## EXPERIMENTAL.

*Preparation of Liquid Dinitrogen Tetroxide.*—Powdered lead nitrate, previously dried for 2 hours at  $120^\circ$ , was heated in a steel tube in 250-g. batches. The evolved gas was passed through a  $30 \times 2$  cm. glass tube packed with phosphoric oxide and liquefied in a condenser (Fig. 1a) cooled in solid carbon dioxide–acetone at  $-15^\circ$ ; because of the attack on rubber by the gas, ground-glass joints were used throughout. The liquid tetroxide was purified by distillation through further tubes of phosphoric oxide. Unless the lead nitrate was well dried, blue dinitrogen trioxide condensed with the tetroxide, and could not be removed on subsequent distillation, except in a stream of oxygen. It is still generally considered\* that calcium chloride may be used as a drying agent. This is not permissible, since reaction occurs with dinitrogen tetroxide to form nitrosyl chloride. On cooling, the pure liquid tetroxide supercooled for several degrees, then solidified at  $-9.3^\circ$  from a pale straw-coloured liquid to a colourless solid. With gentle agitation the solid collects as a coherent glassy layer on the sides of the vessel; this layer is only detached by strong agitation, but in the presence of even a small amount of nitrosyl chloride as impurity this is prevented, and the solid separates as a mass of heavy, granular crystals.

*Preparation of Nitrosyl Chloride.*—Nitrosyl chloride was prepared by the method of Whittaker, Lundstrom, and Merz (*Ind. Eng. Chem.*, 1931, **23**, 1410) from dinitrogen tetroxide and moist potassium chloride. The gas evolved from 150 g. of lead nitrate was passed first through a  $60 \times 2$  cm. tube of crystalline potassium chloride containing about 2.5% of moisture, then through a drying tube of similar dimensions containing 10–20 B.S.S. mesh calcium chloride, and the liquid was collected in a condenser similar to that used for the tetroxide, cooled in solid carbon dioxide–acetone at  $-40^\circ$ . The conversion of dinitrogen tetroxide into nitrosyl chloride in the reaction tube is evident by a sharp colour change from brown to greenish-yellow, and the progress of the reaction can be followed by movement of the colour boundary along the tube. Since the reaction  $\text{KCl} + \text{N}_2\text{O}_4 = \text{KNO}_3 + \text{NOCl}$  occurs at the crystal surface (Part I), the potassium chloride becomes exhausted in a single experiment before an equivalent amount of tetroxide has reacted, but reaction is partly restored after some days' standing, owing presumably to the mechanical breakdown of the crystals to expose fresh surface. With fresh potassium chloride the reaction is rapid, and it was not found necessary to re-cycle the gas.

The corresponding reaction with calcium chloride is much slower; a single passage of the gas through a tube packed with calcium chloride comparable in quantity with the potassium chloride used (at such a rate that reaction with potassium chloride would have been complete) gave about 10% conversion into nitrosyl chloride. Therefore, calcium chloride placed in the gas stream after passage of the gas over potassium chloride serves as a suitable drying agent. The purity of the nitrosyl chloride was confirmed by m. p. and analysis. The m. p., determined as described below for  $\text{N}_2\text{O}_4$ – $\text{NOCl}$  mixtures, was  $-60.8^\circ$ , which compares favourably with the value of  $-61.5^\circ$  reported by Whittaker, Lundstrom, and Merz (*loc. cit.*) and Trautz and Gerwig (*Z. anorg. Chem.*, 1924, **134**, 409).

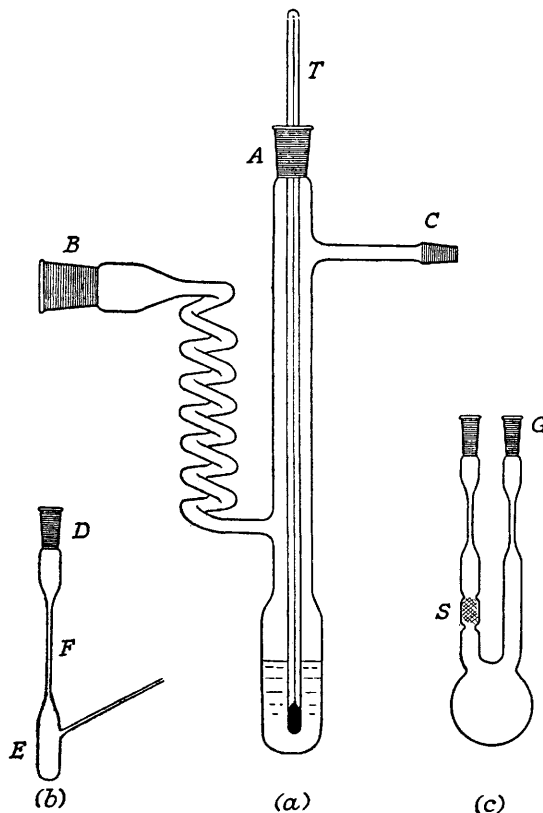
Solid nitrosyl chloride separated from the liquid in the form of thin, feather-like flakes and appeared to differ little in density from the liquid. There is some confusion in the literature concerning the colour of solid nitrosyl chloride; Francesconi and Bresciani (*Atti R. Accad. Lincei*, 1903, **12**, 75) report

\* *E.g.*, Thorpe's "Dictionary of Applied Chemistry", 4th Edn., 1946, p. 524; Partington, "General and Inorganic Chemistry", Macmillan, 1946, p. 582.

the crystals to be lemon-yellow at the temperature of liquid air, and Partington (*op. cit.*, p. 580) states that the liquid freezes to a lemon-yellow solid. In common with Whittaker, Lundstrom, and Merz (*loc. cit.*) and van Heteren (*Z. anorg. Chem.*, 1899, **22**, 277), we find the crystals to be blood-red in colour.

*Preparation of Dinitrogen Tetroxide-Nitrosyl Chloride Mixtures.*—The mixtures were prepared by adding the tetroxide to the nitrosyl chloride in approximately the required proportion, followed by analysis of the mixture. It was found convenient (see below) to adjust the concentration by further additions of tetroxide rather than of nitrosyl chloride, and the order of the determinations was from high to low nitrosyl chloride concentration. On account of the readiness with which both components hydrolyse, the major precaution to be observed in the preparation of the mixtures is to avoid contact with the atmosphere. The condensers used in the preparation of both liquid dinitrogen tetroxide and liquid nitrosyl chloride were as shown in Fig. 1 (a) (without thermometer, but with B 14 ground-glass stopper at A and a guard tube packed with phosphoric oxide at C). The condensers differed only in the ground (B 7) joint C; the cone was attached to the nitrosyl chloride, and the socket to the dinitrogen

FIG. 1.

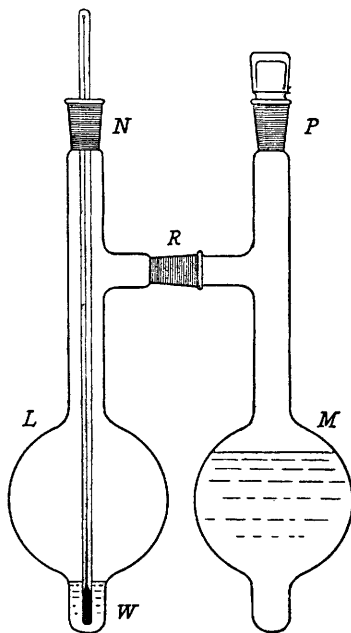


tetroxide condenser. After condensation of suitable quantities of the two liquids, the condensers were disconnected from the remainder of the apparatus at ground-glass joint B and immediately stoppered. In order to add liquid tetroxide to the nitrosyl chloride, the two condensers were then connected at joint C and the combined apparatus tilted to allow the tetroxide to pour through joint C into the nitrosyl chloride condenser. Since it was necessary to carry out this tilting operation in the air, the condensers were given preliminary cooling by immersion in a bath of solid carbon dioxide-acetone and little evaporation took place during the transfer of the liquid tetroxide. However, considerable evaporation of nitrosyl chloride (b. p.  $-5.5^{\circ}$ ) occurred in the tube carrying joint C if attempts were made to pour this liquid into the tetroxide condenser. The two condensers were then separated, stoppered at C, and m. p. determinations and analyses of the liquid mixtures were carried out as described below. During the course of opening and closing joints A, B, and C, there are short intervals of time in which the gaseous contents of the condensers are in contact with the atmosphere; it was arranged that during these intervals the temperature of the liquid was rising slowly, so that a gentle stream of gas issued from the open joint, preventing ingress of moist air.

*Sampling and Analysis of Dinitrogen Tetroxide-Nitrosyl Chloride Mixtures.*—In taking a sample of the liquid from the condenser (Fig. 1a), it is again imperative that any contact with the atmosphere should be avoided. A "Pyrex" tube ( $5 \times 0.8$  cm.) carrying a B 7 socket was drawn out (Fig. 1b) to an overall length of about 10 cm., and a fine tail drawn from the bulb E. The phial was weighed, and joint D attached to the condenser at C. The liquid was then poured into the phial (which was previously cooled to a temperature only slightly above that of the liquid) by tilting the condenser. On

removal, the phial was immediately sealed in the flame at the tail and position *F*, and re-weighed. The weights of sample taken varied within the range 0.25—1.25 g., depending on the nitrosyl chloride content. The phial was then transferred to a stout, stoppered glass bottle containing 100 ml. of *n*-potassium hydroxide solution, and the bottle shaken vigorously in order to break the phial. The excess of hydroxide was neutralised with nitric acid, the solution rendered slightly acid, and hydrazine sulphate added to destroy the nitrite produced during hydrolysis. The chloride content was determined gravimetrically. Whittaker, Lundstrom, and Merz (*loc. cit.*) have shown that analyses of nitrosyl chloride prepared by the method described above, based on either chlorine or nitrogen content, agree to within 0.1%; in these experiments the nitrosyl chloride content of the mixtures was deduced from the chloride analysis. In their analyses, those authors carried out hydrolysis on the gaseous nitrosyl chloride, and owing to the presence of traces of air were unable to obtain a purity greater than 97.4%. The technique described above, in which the liquid is hydrolysed directly, overcomes this difficulty and when applied to the analysis of nitrosyl chloride alone gave a purity of 99.7%.

FIG. 2.



*Liquidus Curves.*—When a liquid mixture of nitrosyl chloride and dinitrogen tetroxide is cooled, the degree of supercooling varies with the proportions of the components, and over a large part of the concentration range supercooling is considerable. The crystallisation temperature could not therefore be determined accurately from cooling curves, but was determined with an accuracy of  $\pm 0.1^\circ$  from the corresponding warming curves. The stopper at *A* of the condenser (Fig. 1*a*) was removed, and a toluene thermometer *T* (calibrated at the m. p. s of ice and of pure chloroform) inserted as shown, the bulb being immersed in about 10 g. of the liquid. This quantity was maintained for all m. p. determinations. Stirring of the liquid was effected by means of the thermometer, the socket *A* being packed with asbestos to give a plug which, while excluding air, permitted free movement of the thermometer and was not attacked by the vapours. The lower tube of the condenser was immersed, with continual stirring of the liquid, in acetone–solid carbon dioxide until about one-third of the liquid had crystallised. It was then transferred to an air-bath surrounded by cold acetone at a temperature slightly above that at which it was anticipated that all crystals would have disappeared. Temperature–time warming curves were plotted, and showed a clear break at a point corresponding to the disappearance of crystals. Temperatures corresponding to these breaks were plotted against composition to give the liquidus curves in Fig. 3.

*Solidus Curves.*—Preliminary experiments had shown that crystals separating from the  $\text{NOCl-N}_2\text{O}_4$  mixtures on either side of the eutectic composition *E* (Fig. 3) were solid solutions of the two components. Determination of solidus curves from the second break in the cooling or warming curves is inaccurate because of the difficulty in ensuring a uniform temperature throughout the unstirred solid. The following techniques have been found to be accurate, and to give identical curves.

(a) *Chemical analysis of the crystals.* After determination of the liquidus temperature of the mixture, the weighed phial (Fig. 1*c*) was attached to the condenser (Fig. 1*a*) by the joints *C* and *G*. The contents of the condenser were poured into the bulb of the phial, which was then stoppered and cooled until approximately 1 g. of the crystals separated in the bulb. The mother-liquor was poured away through the glass-wool plug *S* by inverting the phial, which was then allowed to warm gradually until about 0.3 g. of the crystals remained. The liquid produced washed the remaining crystal free from mother-liquor, and drained away through the plug. Traces of liquid remaining were removed under slightly reduced pressure, and the limbs of the phial sealed in the flame. The phial was re-weighed,

broken in a stoppered bottle containing potassium hydroxide, and the chloride content determined as described above. However, separation and chemical analysis of the crystals is tedious, and the following alternative technique was found to be rapid and to give equally satisfactory results.

(b) *Thermal analysis.* When a mixture of composition  $X$  is cooled along  $XA$  (Fig. 3) the crystals which first separate as the liquidus curve is reached have composition  $B$ . If these crystals are separated from the mother-liquor and warmed, their composition may be determined accurately from the temperature  $C$  at which the last crystals disappear, by reference to the established liquidus curve. This technique is only ideal if a very small proportion of the original mixture is separated as crystals, or if a larger quantity of the crystals is allowed to come to equilibrium with the liquid. Under the conditions of continuous cooling employed, this equilibrium cannot be realised and the composition of the crystals separating at temperatures below  $AB$  moves along  $BD$  on the solidus curve. The following technique was therefore employed to separate the smallest proportion of crystals consistent with accurate m. p. determination. About 125 g. of the liquid mixture were collected in a condenser similar to that shown in Fig. 1a but having a larger bulb, and transferred to vessel  $L$  (Fig. 2, but without thermometer)

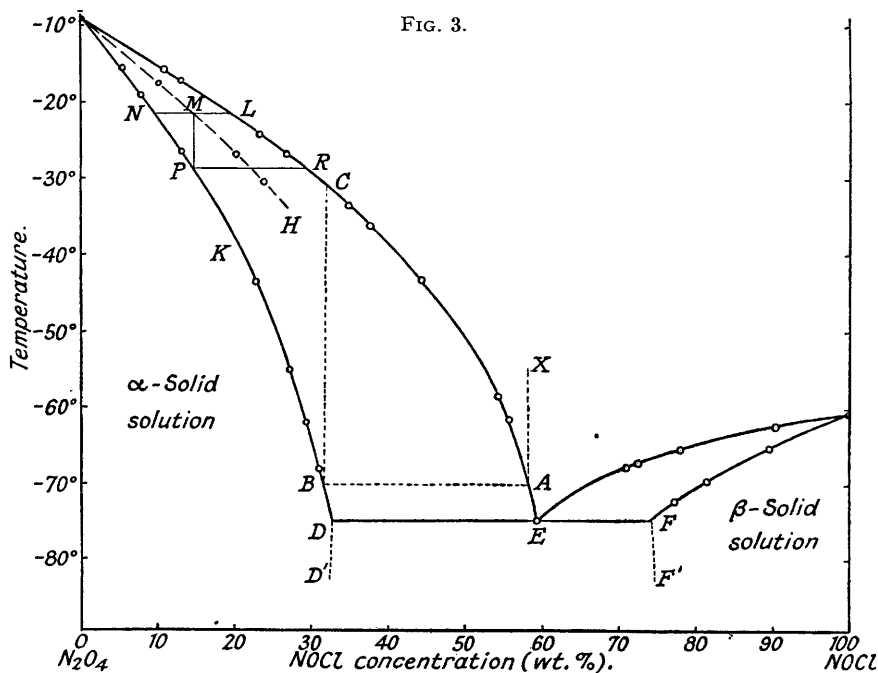


FIG. 3.

by attaching joints  $C$  (Fig. 1a) and  $N$  (Fig. 2) through a B 7-B 14 adapter. With the thermometer in position and joint  $P$  stoppered, point  $A$  (Fig. 3) on the liquidus curve was determined. The thermometer was removed, and the liquid cooled until about 10 g. of crystals separated in the well  $W$ . By careful inversion of vessel  $L$ , the mother-liquor was then poured through joint  $R$  into the vessel  $M$ , which was made identical with  $L$  so that by appropriate adjustments in concentration, the whole series of determinations could be carried out using the same apparatus. This inverted position being maintained, vessel  $L$  was then allowed to warm until about 4 g. of the crystals remained. The liquid produced drained away, and washed the remaining crystals free from mother-liquor. Again, during this melting process the crystals which melt will be those farthest removed in composition from point  $B$ . In this system a 3% variation in composition on the liquidus is equivalent to about 2% variation on the solidus curve. The crystals remaining (3% of the total mixture) will therefore have a composition varying uniformly over the range  $B$  to  $(B + 2)\%$  (Fig. 3). Since solidus curves can be considered to be straight over short ranges, the composition of the homogeneous liquid obtained by melting these crystals will have the composition  $(B + 1)\%$ . Vessel  $L$  was restored to the vertical position and warmed to obtain this liquid, which when collected in the well  $W$  was more than sufficient to cover the bulb of the thermometer. From warming curves on this liquid, point  $C$  on the liquidus curve was obtained. The intersection of  $AB$  and  $BC$  gives a point on the solidus curve which has the correct temperature value, but is 1% too high in concentration. Similar considerations apply on the nitrosyl chloride side of the eutectic, and also to the results of chemical analysis of the crystals; these corrections have been applied in drawing the solidus curves in Fig. 3.

#### Results and Discussion.

The full phase diagram is shown in Fig. 3. The liquidus curves fall smoothly from the melting points of the pure components to a simple eutectic point  $E$  at  $-74.8^\circ$ . On the tetroxide side of the eutectic the granular crystals obtained on cooling the liquid varied in colour, with increasing nitrosyl chloride concentration, from colourless to deep orange. The hexagonal

shape of these crystals appeared to be unchanged throughout the full (*i.e.*, 0—32%) nitrosyl chloride concentration range available in the  $\alpha$ -solid solution. On progressive addition of the tetroxide to nitrosyl chloride the crystals of  $\beta$ -solid solution varied in colour from blood-red to pale red, and resembled in shape the feather-like flakes of pure solid nitrosyl chloride throughout the full (0—26%) tetroxide concentration range. Crystallisation of a liquid of eutectic composition (59.3% of nitrosyl chloride) gave a tangerine-coloured mixture of the  $\alpha$ - and the  $\beta$ -solid solutions. On cooling mixtures having nitrosyl chloride content greater than the eutectic value, little supercooling occurred, and the solidus curve fell smoothly to the limiting value  $F$ . However, over a nitrosyl chloride concentration range of approximately 5—25%, considerable supercooling occurred unless the liquid was strongly agitated. The full solidus curve  $K$  was obtained by cooling the liquid slowly with violent shaking, supercooling then not exceeding about 2°. If the liquid was allowed to supercool considerably, the composition of the crystals which ultimately separated differed from the equilibrium values (curve  $K$ ), and the solidus curve under these supercooled conditions is shown in Fig. 3 as the broken line  $H$ . These values are not random, but appear to represent the equilibrium values (on solidus  $K$ ) corresponding to the lowest temperature reached on supercooling. Thus in Fig. 3, a liquid mixture of composition  $L$  deposits crystals of composition  $N$  in the absence of appreciable supercooling. If the liquid supercools to a temperature corresponding to  $PR$ , the crystals which deposit have the composition  $P$  (*i.e.*, the equilibrium value equivalent to a liquid of composition  $R$  rather than  $L$ ). Since the extent of supercooling may be as much as 15°, the nitrosyl chloride concentration  $P$  differs appreciably from the true value  $N$ , and the broken line  $H$  traces the values of point  $M$  for the concentration range over which supercooling is significant.

Stockdale (*Trans. Faraday Soc.*, 1936, **32**, 1365) has suggested that in binary eutectic mixtures a simple ratio may exist between the molecular proportions of the two components at the eutectic composition. It is of interest that in this system the eutectic ratio  $N_2O_4 : NOCl$  is almost exactly 1 : 2. It is probably of greater significance that the molecular ratios of the two components at points  $D$  and  $F$  are also simple. In so far as the positions of points  $D$  and  $F$  on the curve of solid miscibility are determined by the eutectic temperature, the composition of the solid solutions at these points may be regarded as somewhat accidental values. However, only those portions of the miscibility curve which lie below the eutectic temperature (represented in approximate position in Fig. 3 by the lines  $DD'$  and  $FF'$ ) are attainable under ordinary conditions. The solid immiscibility range in systems of this type normally narrows with increase in temperature; therefore point  $D$ , for example, represents the maximum amount of nitrosyl chloride which can enter into solid solution with dinitrogen tetroxide under all normal conditions, and the miscibility limits  $D$  and  $F$  should be capable of interpretation in terms of molecular ratios. In alloy systems of this type, where solid solution involves replacement of discrete atoms, the limiting atomic ratios need not be very simple; but Vegard (*Z. Physik*, 1931, **68**, 184) has shown from  $X$ -ray crystallographic data that solid dinitrogen tetroxide has a cubic structure, and that the unit cube contains only twelve  $NO_2$  units. Although the difference between the atomic volumes of chlorine and oxygen is sufficient to prevent the formation of a continuous series of solid solutions, the  $NO_2$  and  $NOCl$  molecules have similar structure; it is therefore to be anticipated (*a*) that several of the  $NO_2$  units in the unit cube should be capable of replacement by  $NOCl$  without undue distortion of the crystal lattice, and (*b*) that the molecular ratio of the components at point  $D$  should total 12 or a factor of 12. The actual  $NO_2 : NOCl$  ratio at  $D$  is 3 : 1, indicating that maximum miscibility in the  $\alpha$ -solid solution is reached when three of the twelve  $NO_2$  units in the unit cube are replaced by  $NOCl$ . It is of interest that Vegard represents the twelve  $NO_2$  units in the unit cube as arranged in three mutually perpendicular groups parallel to the sides of the cube. Whether the  $NO_2$  units are discrete in the solid state, or in the form of  $N_2O_4$  molecules as postulated by Hendricks (*ibid.*, 1931, **70**, 699), need not be considered here.

The molecular arrangement of nitrosyl chloride molecules in the solid state is not known, but it is noteworthy that the  $NO_2 : NOCl$  ratio at point  $F$  is 1 : 2. Since the crystal form of the  $\beta$ -solid solution resembles that of the pure solid nitrosyl chloride and appears to be independent of composition, the molecular arrangement of the  $\beta$ -solid solution is probably that of solid nitrosyl chloride, which is stable provided that not more than one in every three  $NOCl$  units is replaced by  $NO_2$ .

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