933. Dinitrogen Trioxide. Part II.* Freezing-point Data in the System Nitrogen Dioxide–Dinitrogen Trioxide. The Freezing Point of Pure Dinitrogen Trioxide.

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The freezing points of mixtures of nitrogen dioxide and dinitrogen trioxide, as well as those of the pure components, have been accurately determined. Although the phase diagram has the appearance of a simple binary mixture with one eutectic it seems probable that, on the nitrogen dioxide-rich side of the composition range, solid solutions crystallise rather than the pure component. A possible misinterpretation of previous results in the region of the eutectic composition would account for the discrepancy between the eutectic temperature and composition found in this work compared with previously accepted values. Dinitrogen trioxide behaves as a pure compound at its freezing point. The following data are recorded: f. p. of nitrogen dioxide, $-11{\cdot}29°$; eutectic composition, 33·7 weight % of nitric oxide; eutectic temperature, $-106{\cdot}2°$; f. p. of dinitrogen trioxide, $-100{\cdot}7°$.

ALTHOUGH Gray and Yoffe [1] state that complete freezing-point data are available for mixtures of dinitrogen trioxide with nitrogen dioxide, the experimental results are in some doubt where x is less than 1·76, and become fragmentary towards $x = 1{\cdot}5$.† The accurate results of Whittaker and his co-workers [2] unfortunately cover only the range near to nitrogen dioxide. In this region agreement with Baume and Robert's results [3] is good, although Wittorf's results [4] appear to be consistently a few degrees above those of the other workers. Insufficient data are available from the work of Baume and Robert [3] to determine the eutectic composition, or the freezing point of dinitrogen trioxide, to any acceptable degree of accuracy. As a precise knowledge of the phase diagram, particularly in the region of dinitrogen trioxide, was considered to be an essential preliminary to any study of the reactions of dinitrogen trioxide, we reinvestigated the system.

In Fig. 1 the results of our investigations are compared with those of other workers. The average freezing-point value we obtained for three samples of nitrogen dioxide was $-11{\cdot}29°$. The value found by Whittaker *et al.*[2] was $-11{\cdot}30°$, which can be compared with the usually accepted value [5] of $-11{\cdot}23°$. Whittaker *et al.*[2] pointed out that the heat of fusion of nitrogen dioxide obtained from the phase diagram is higher than the calorimetric value given by Giauque and Kemp.[5] We studied the effect of adding very small quantities of nitric oxide to nitrogen dioxide. An approximately linear relation was obtained between $\log_{10}$ (mole-fraction of dinitrogen tetroxide) and the reciprocal of the absolute temperature (at the freezing point) whether we regarded nitric oxide or dinitrogen trioxide as the solute in the dinitrogen tetroxide solvent. However, in either case the calculated heat of fusion was too high by about 0·8 kcal. mole^{-1} in 3·5 kcal. mole^{-1}. This suggests that the substance crystallising from solution is a solid solution rather than pure dinitrogen tetroxide.[5a] Wittorf [4] has indeed described the solid crystallising from solutions rich in nitrogen dioxide as being of a similar colour (light blue) to that of the solution. Further,

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* Part I, Beattie and Bell, *J.*, 1957, 1681.

† To define the composition of mixtures of nitric oxide and nitrogen dioxide, without the necessity of making assumptions regarding the species present, we have used the notation NO_x. Thus, for an equimolar mixture of nitrogen dioxide and nitric oxide $x = 1{\cdot}5$, while for pure nitrogen dioxide $x = 2{\cdot}0$.

[1] Gray and Yoffe, *Quart. Rev.*, 1955, **9**, 362.

[2] Whittaker, Sprague, Skolnik, and Smith, *J. Amer. Chem. Soc.*, 1952, **74**, 4794.

[3] Baume and Robert, *Compt. rend.*, 1919, **169**, 968.

[4] Wittorf, *Z. anorg. Chem.*, 1905, **41**, 85.

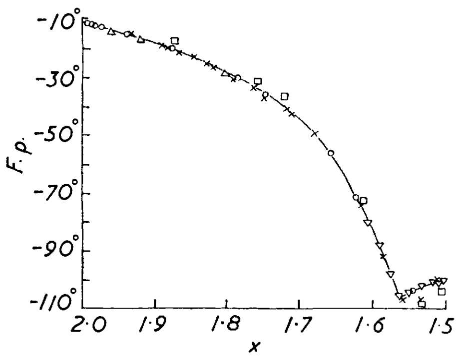
[5] Giauque and Kemp, *J. Chem. Phys.*, 1938, **6**, 40.

[5a] See Glasstone, "Textbook of Physical Chemistry," Macmillan & Co. Ltd., 2nd edn., London, 1953, pp. 649—651.

Addison and Thompson [6] found solid solutions in the system nitrogen dioxide–nitrosyl chloride.

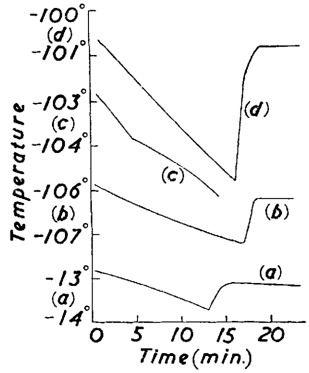
Freezing points in the nitrogen dioxide-rich region of the phase diagram are closely defined and there is no ambiguity in interpretation. Fig. 2(*a*) gives a typical cooling curve for $x = 1{\cdot}774$. In the section of the phase diagram from the last of the results of Whittaker *et al.*[2] ($x = 1{\cdot}763$) to our eutectic composition ($x = 1{\cdot}560$) our results are in good agreement with those of Baume and Robert.[3] However, our eutectic temperature of —106·2° [see Fig. 2(*b*)], and the less easily determined eutectic composition, differ quite markedly from their values. The two lowest temperatures measured by Baume and Robert [3] were —107° (according to their interpretation these values lay on either side of the eutectic). Freezing points in the region between the eutectic composition and $x = 1{\cdot}5$ are very difficult to determine accurately. Fig. 2(*c*) represents one of the more favourable examples. In other cases we found only a very slight change in slope in the region of the expected freezing point. Nevertheless, two quite independent sets of observations in this region were in good agreement (S. W. B. and A. J. V.). It seems probable that Baume and Robert,[3] during their cooling-curve determinations in the region of the eutectic, missed the freezing point and obtained in each case a eutectic temperature measured as —107°. Extrapolation on this basis would give them an anomalously low eutectic temperature coupled with a eutectic composition too rich in nitric oxide.

FIG. 1. *The freezing point–composition curve in the system nitrogen dioxide–dinitrogen trioxide.*



○ This work (A. J. V.); ▽ this work (S. W. B.); △ Whittaker *et al.*;[2] × Baume and Robert;[3] □ Wittorf.[4]

FIG. 2. *Cooling curves obtained in the system nitrogen dioxide–dinitrogen trioxide.*



The compositions correspond to (*a*) $x = 1{\cdot}774$, (*b*) $x = 1{\cdot}560$, (*c*) $x = 1{\cdot}545$, (*d*) $x = 1{\cdot}500$.

At the composition $x = 1{\cdot}5$ we found that under certain conditions the freezing-point curve was that to be expected for a pure compound [see Fig. 2(*d*)]. If the dinitrogen trioxide was held at —95° for two hours and the cooling curve then measured, a sharp freezing point was obtained. However, on cooling the system rapidly from —78° to —95° and then carrying out a normal cooling curve measurement, we were unable to obtain a clear-cut freezing point, even with shocking by liquid air *via* the touch-off tube. It is possible that this behaviour is due to a slow rate of attainment of equilibrium at low temperatures. The rapidly cooled sample solidified very quickly once nucleation had started. This usually occurred in the region of the eutectic temperature but without the appearance of any large pressure changes. We suspect that the anomalous behaviour is due to capricious supercooling.

Leifer [7] has, on the basis of isotope exchange experiments, suggested that solid dinitrogen trioxide can only exist in equilibrium with its components. As solid dinitrogen trioxide will be in equilibrium with gaseous dinitrogen trioxide, which will also be in

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[6] Addison and Thompson, *J.*, 1949, 5218.

[7] Leifer, *J. Chem. Phys.*, 1940, **8**, 301.

equilibrium with its decomposition products, the exchange between gas and solid is to be expected. The speed of reaction may indicate a high rate of diffusion in the solid, but does not prove that there is any inherent instability. When solid crystallises from a liquid of the composition $NO_{1\cdot5}$, the vapour pressure remains approximately constant. If solid solutions of a composition richer in nitrogen dioxide were to crystallise out, the pressure would rise abruptly. Alternatively, a compound enriched in nitric oxide is unlikely to crystallise from such solutions at temperatures in the region of —100°. We consider that pure dinitrogen trioxide crystallises out from solutions having the composition $x = 1\cdot5$.

It is noteworthy that N.B.S. Circular 500 [8a] quotes —111° for the freezing point of dinitrogen trioxide, *i.e.*, more than 10° below our value of —100·7°. However, Wittorf[4] obtained the value >—104·5°, while Baume and Robert[3] found >—100°. Our final results are presented in the Table.

Freezing points in the system nitrogen dioxide–nitric oxide.

x	2·000	1·991	1·985	1·982	1·974	1·936	1·876	1·846
F. p. ...	$-11{\cdot}2_9^\circ$	$-11{\cdot}9_3^\circ$	$-12{\cdot}2_0^\circ$	$-12{\cdot}3_8^\circ$	$-13{\cdot}0_0^\circ$	$-15{\cdot}7_2^\circ$	$-20{\cdot}3_6^\circ$	$-23{\cdot}4_4^\circ$
x	1·816	1·785	1·747	1·656	1·644	1·606	1·591	1·575
F. p. ...	$-27{\cdot}0_6^\circ$	$-30{\cdot}7_7^\circ$	$-36{\cdot}5_4^\circ$	$-57{\cdot}0_0^\circ$	$-59{\cdot}2_6^\circ$	−81·0°	−89·0°	−98·7°
x	1·561	1·560	1·549	1·545	1·516	1·508	1·504	1·500
F. p. ...	−105·8°	−106·2°	−104·3°	−103·8°	−101·0°	−100·7°	−100·2°	$-100{\cdot}7_4^\circ$

EXPERIMENTAL

All work was carried out in a vacuum system.

Nitrogen Dioxide.—This was prepared as described previously,[9] and distilled into ampoules having an easily broken tip. The ampoules were weighed, introduced into the system, and broken, and the contents distilled into the cryoscope. The weight of nitrogen dioxide introduced into the system was found by weighing the residual glass from the ampoule.

FIG. 3. *Nitric oxide ampoule.*

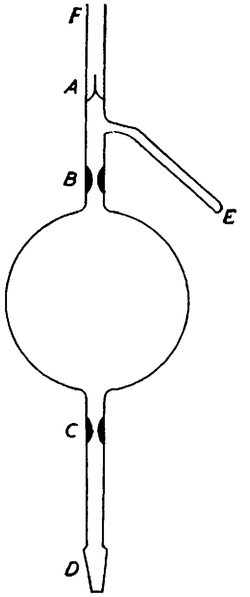
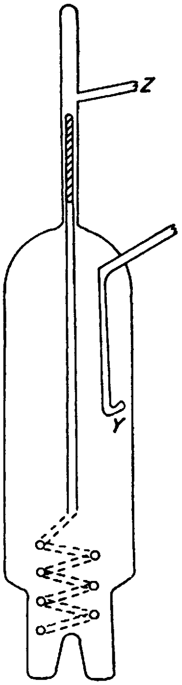


FIG. 4. *Cryoscope system.*



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[8] (*a*) Rossini, Wagman, Evans, Levine, and Jaffe, Nat. Bur. Stand., Circular 500, 1952; (*b*) Guye and Drougenine, *J. Chim. phys.*, 1910, **8**, 473.

[9] Beattie and Bell, *J.*, 1957, 1681.

Nitric Oxide.—The preparation has already been described,[9] although on the present occasion (A. J. V.) we were unable to obtain colourless nitric oxide. We suspect that the pale blue colour is due to traces of other oxides of nitrogen. The nitric oxide was introduced into the system in a variety of ways: (*a*) from weighed bulbs connected to the apparatus and equipped with breakers, (*b*) *via* two diaphragm taps plus a cold finger, (*c*) by using the apparatus shown in Fig. 3. In this case nitric oxide was passed into a calibrated bulb, and the pressure measured at 25°. The nitric oxide was then completely distilled into the cold finger *E*, and the constriction *C* was sealed. The whole of the apparatus shown in Fig. 3 was weighed before and after this operation. All joints were greased with " Halocarbon " grease. To introduce nitric oxide into the all-glass cryscope system the bulb was joined on at *F*, the cold finger *E* surrounded by liquid nitrogen, and constriction *B* sealed. Septum *A* was then broken, and the nitric oxide allowed to distil into the cryoscope. In this way the total volume of the system was kept sensibly constant.

Diaphragm Taps.—These were standard taps (supplied by Springham's) having fluorocarbon diaphragms. The only modification made to these taps was to bolt the diaphragms in position by clamping them between retainers completely spanning the tap.

Cryoscopes.—The cryoscopes used were of the type shown in Fig. 4. The push-up was made of especially thinned glass and contained the five-junction copper–constantan thermocouple embedded in paraffin wax. In cases where analyses were carried out, *Y* was a sample tube, while *Z* also led to a spiral-gauge manometer and pressure-measuring system. The cryoscope was enclosed in a copper jacket packed with alumina and sealed at the top with paraffin wax to avoid trouble from condensation. The thermocouples were standardised by using ice, solid carbon dioxide, and liquid oxygen as calibrants. A Cambridge vernier potentiometer, together with a sensitive galvanometer, were used to enable temperatures to be read to an accuracy of 0·01°.

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