286. *The Liquid Dinitrogen Tetroxide Solvent System. Part III. The Electrical Conductivity of Liquid Dinitrogen Tetroxide.*

By C. C. Addison, J. Allen, H. C. Bolton, and J. Lewis.

The specific conductivity of liquid dinitrogen tetroxide has been found to be $1{\cdot}3 \times 10^{-12}$ ohm^{-1} cm.$^{-1}$ at 17°. A conductivity cell and electrical circuit suitable for measurements of high resistances are described and the experimental features which may give rise to erroneously high conductivity values are discussed. The sign, and an approximate value for the temperature coefficient of conductivity have been determined and the possible mechanisms of electrical conduction in liquid dinitrogen tetroxide are considered.

A knowledge of the electrical conductivity of liquid dinitrogen tetroxide was required for the interpretation of electrical measurements on solutions of various compounds in this liquid. Faraday (*Phil. Trans.*, 1840, **130**, 61) observed that the liquid distillate obtained by heating lead nitrate was a poor conductor of electricity; Frankland and Farmer (*J.*, 1901, **79**, 1356), finding the specific conductivity to be less than 2×10^{-8} ohm^{-1} cm.$^{-1}$, considered that the liquid was unable to behave as an ionising medium. Heberlein (see Mellor, " A Comprehensive Treatise, etc.," Vol. 8, p. 536) obtained values of $1{\cdot}16 \times 10^{-8}$ to $14{\cdot}2 \times 10^{-8}$ ohm^{-1} cm.$^{-1}$ over a temperature range of $-10°$ to $+20°$.

A number of reactions in liquid dinitrogen tetroxide, involving nitrosyl compounds and nitrates, may be interpreted as " acid–base " reactions (Part I, *J.*, 1949, S 211, and following papers) on the basis of the dissociation $N_2O_4 \rightleftharpoons NO^+ + NO_3^-$ in the liquid state. In considering such reactions, it is not essential that this ionisation should occur to any appreciable extent in the pure liquid, but rather that the N_2O_4 molecule should serve as a potential source of these ions. In this respect the system is analogous to that of liquid ammonia, in which the ionisation $2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$ is fundamental, although the specific conductivity of 10^{-11} ohm^{-1} cm.$^{-1}$ (Carvallo, *Ann. Physik*, 1914, **208**, 224) indicates that the degree of ionisation in pure liquid ammonia is very slight. Nevertheless, in a study of the nature of reactions involving liquid dinitrogen tetroxide it is of importance to determine whether such dissociation occurs to any appreciable extent in the pure liquid. To this end, various physical properties of the pure liquid have been studied. The present paper is restricted to conductivity studies; preliminary experiments indicated that the specific conductivity of the pure liquid was considerably smaller than previously recorded values, and since the electrical conductivity gives some indication of the presence of ionic species, its value has been determined accurately.

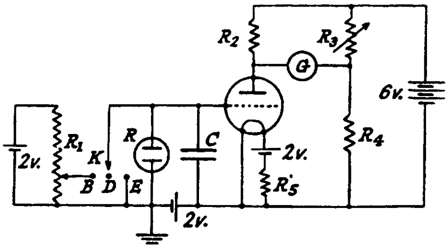
EXPERIMENTAL.

Preparation of Liquid Dinitrogen Tetroxide.—The liquid was prepared from lead nitrate (see Part II, *J.*, 1949, S 218). Dry powdered lead nitrate was heated in a steel tube; the evolved gases were passed down a water-cooled condenser fitted with a trap at the bottom. About one quarter of the dinitrogen tetroxide condensed here, together with any traces of metallic, and some of the aqueous, impurities. The remaining gas was then passed through a 40 × 2 cm. Pyrex glass tube packed with fresh phosphoric oxide, and was liquefied in a condenser [similar to that shown in Fig. 1 (*a*), Part II (*loc. cit.*), but without a thermometer] cooled to $-15°$ in an ice-salt mixture. Before use, the condenser was washed in turn with water, alcohol, and ether, warmed to 100°, and the ether vapour removed by blowing through dry nitrogen. Finally, the condenser was heated in a flame, cooled in a vacuum desiccator, attached to the tetroxide generator by a ground-glass joint, and guarded by a phosphoric oxide tube as described in Part II (*loc. cit.*). An empty bath was then placed round the condenser, and with this at room temperature, dinitrogen tetroxide gas was allowed to flow through until the apparatus was flushed free from air. Freezing mixture was then added slowly to the bath, and the temperature of the condenser decreased at such a rate that a steady out-flow of gas was maintained from the condenser. If the condenser was cooled rapidly, the fall in pressure due to the condensation of the tetroxide led to a rapid ingress of air and the consequent risk of entry of water vapour. Throughout the whole preparation the outflow of tetroxide from the condenser was maintained. Under these conditions the end of the phosphoric oxide guard tube became moist with nitric acid. To avoid the possibility of nitric acid flowing back into the condenser, the guard tube was bent downwards.

In order to ensure complete drying of the dinitrogen tetroxide in its passage through the phosphoric oxide column (immediately before the condenser) the gas was generated slowly, and liquefied in the condenser at the rate of about 5 ml. per hour. The liquid was redistilled (when required) directly from the condenser through phosphoric oxide columns of effective length 100 cm. and recondensed in a similar receiver with the same precautions as outlined above. To reduce the resistance to gas flow, the columns contained alternate bands of phosphoric oxide (3 cm.) and glass wool (1 cm.).

The product could be solidified at $-11{\cdot}2°$ to a colourless solid. [*Note.* The freezing point of liquid dinitrogen tetroxide was wrongly recorded in Part II as $-9{\cdot}3°$. This should have read $-11{\cdot}2°$, and the value recorded on the pure tetroxide axis in the $NOCl$–N_2O_4 phase diagram should be adjusted accordingly. All other points in this diagram are correct as recorded.]

FIG. 1.



R_2 = 4,700 *ohms*.
R_3 = 70,000 ,,
R_4 = 270,000 *ohms*.
R_5 = 10 ,,

Measurements of Electrical Resistance.—Preliminary experiments had shown liquid dinitrogen tetroxide to have a low electrical conductivity. It was therefore necessary to employ a method capable of measuring very high resistances. The method used involved measurement of the rate of decay of potential difference across a standard condenser, when the plates were connected through the high resistance. In this case, the high resistance consisted of a conductivity cell (described below) containing the liquid dinitrogen tetroxide. The voltage on the condenser must be measured by some instrument having a resistance considerably greater than the conductivity cell; for this purpose a G.E.C. electrometer valve, type E.T.I., was used. In this valve a high input resistance is achieved by having the grid connection isolated from other electrodes by a long glass neck. At the bias voltage (2 volts negative), the valve characteristics were such that the grid current was less than 10^{-16} amp. The electrical circuit employed is shown in Fig. 1; R represents the conductivity cell, and R_1 was a simple potentiometer device used to charge the mica condenser C, of capacity 0·01 μF. The Tinsley galvanometer G had a sensitivity of 16 cm. per microamp. at a mirror-scale distance of 1 m. The insulating parts of the simple three-way switch K were made from polystyrene. Other resistances were as stated. All accumulators used were of large capacity.

The circuit was shielded electrically by mounting the valve, switch, condenser, and resistances (other than R and R_1) in an earthed metal box. In order to prevent the formation of a film of moisture on the glass surface of the valve, and the consequent decrease in valve resistance, a tray of phosphoric oxide was placed inside the metal box some hours before a determination was carried out. The leads to the conductivity cell R were of stout (16 S.W.G.) uncovered copper wire, which passed unsupported through, and without touching, the shielding box.

The calculation of the value of R is based on the usual equation for rate of decay of voltage V across a condenser capacity C. At a given time t, $V_t = V_0e^{-t/CR}$. The voltage concerned is the extra grid voltage applied from the potentiometer. In the initial calibration, it was necessary to confirm that the galvanometer deflection θ was proportional to V. In order to do this, switch K was set to point E, and R_3 adjusted to bring the galvanometer spot to the point of zero deflection on the scale. The switch was moved from E to B, thus applying an extra voltage (of the order of 0·5 volt or less) to the grid, and the resulting deflection measured. This was repeated for various settings of R_1, and it was confirmed that the deflection was proportional to this extra voltage. The above equation can therefore be written as $\theta_t = \theta_0e^{-t/CR}$, whence $R = t/2{\cdot}303C.\ \log_{10}(\theta_0/\theta_t)$.

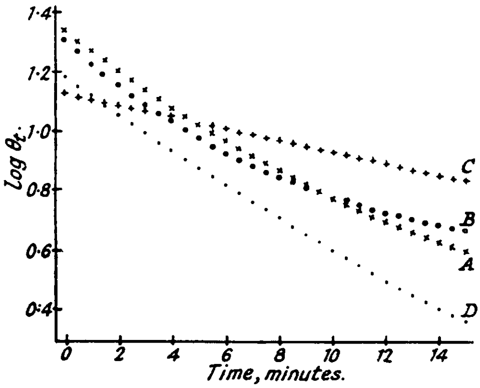
In a determination of R, the switch K was put to E, and the galvanometer set to zero deflection. The switch was then moved to B to charge the condenser C. The potentiometer was then isolated from C by switching from B to D, and the condenser voltage allowed to decay by discharge through R.

A graph of log θ against t was plotted as in Fig. 2, and the slope of the straight line used to calculate R. The capacity of the condenser was measured on a Marconi impedance bridge, and was found to be 0·0100 μF. ± 1%.

Conductivity Cell.—The cell used is shown in Fig. 3. In several standard types the leads are held rigid, and insulated from one another, by various forms of wax. Preliminary experiments showed that the bulk (or surface) conductivity of such waxes was frequently greater than that of the dinitrogen tetroxide itself. Under these conditions an accurate determination of the conductivity of the tetroxide was impossible. In the cell used, the leads to the electrodes were of 24 S.W.G., uncovered platinum wire, and were sealed directly through the glass walls of the cell; thereafter, the leads were separated by several cm. of air space. The electrodes, prepared from sheet platinum, had dimensions 3 × 1·3 cm., and were placed approximately 1 cm. apart. The cell constant, determined by using aqueous potassium chloride solution, was 3·81. The electrodes were contained in a glass tube about 6 cm. long and 3 cm. in diameter. This was sealed to a narrower tube 18 cm. long, carrying a B14 ground-glass joint C as shown.

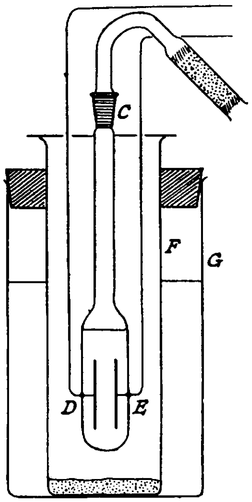
Before being filled with liquid tetroxide, the inside of the cell was scrupulously dried. This was done by washing with water, alcohol, and ether in turn; the cell was warmed to about 60°, and ether vapour removed in a stream of dry nitrogen. A narrow tube containing phosphoric oxide, sufficiently long to pass between the electrodes, and perforated at intervals, was then inserted into the cell. This drying tube was attached to a B14 ground-glass cone; the cell, thus sealed, was then allowed to stand for some days to remove traces of water from the inside walls. At the same time as the drying tube was removed from the cell, the guard tube protecting the condenser was removed, and the cone connected directly to C. Enough liquid was then poured over to cover the electrodes (about 35 ml.), and the cell protected by a guard tube as shown.

FIG. 2.



Curve.	*Condition of cell surface.*
A	*Cell exposed to atmosphere.*
B	*Cell in* P_2O_5 *drying chamber for* 1 *hour.*
C	*Clean, dry surface* (10 *hours' drying*).
	Adsorbed film of nitric acid.

FIG. 3.



Surface Conduction.—The major error in determination of the resistance between the electrodes arises from surface conduction through films of moisture or acid absorbed on the outer surface of the glass cell between the sealing points D and E. If no attempt was made to dry the air immediately surrounding the cell, this surface conduction resulted in a log θ–t curve of type A (Fig. 2). Change in the slope of this curve indicates that the measured resistance, and thus the conductivity of the film, varies with time, and under no such conditions was a linear relation between log θ and t obtainable. The cell was therefore housed in a tall glass jacket F (Fig. 3) having a layer of phosphoric oxide at the bottom, and closed at the top by a cardboard lid. The leads from the cell passed, without contact, through two holes in this lid. The function of the long glass neck on the cell was to remove that part of the cell between D and E as far as possible from any water vapour which may diffuse through the holes in the lid. As the film of moisture was removed, the resistance increased. Curve B (Fig. 2) was obtained one hour after the cell was placed in jacket F. The rate of change of slope of curve B is greater than for curve A, indicating that the film is being removed; the overall slope, determined from the first and last experimental points, is less in B than in A, indicating an increase in resistance. After 10 hours' drying in F, the curve changed to the straight line C, and from this slope the true resistance was calculated.

In order to obtain true linear decay as shown by C, it was necessary to wash with water, and dry the outside of the cell immediately before placing it in jacket F (*i.e.*, after filling with tetroxide). If this precaution was not observed, and if the cell was allowed to come into contact with dinitrogen tetroxide vapour before being placed in the jacket, the slope of the log θ–t curve was observed to diminish on drying the cell, but the curvature could never be completely eliminated. Curve D (Fig. 2) is typical of the final results obtained under these conditions. This effect is attributed to the formation between

D and *E* on the cell surface, of a film of nitric acid produced by hydrolysis of the tetroxide. Unless this film was washed away by water, it could not be removed after placing the cell in *F*. The greater overall slope of curve *D* than of curves *A*, *B*, and *C* is consistent with the higher conductivity which a film of nitric acid might be expected to show, compared with a corresponding water film.

The resistance of the empty cell and associated circuit was also determined. This was found to be $1{\cdot}3 \times 10^{13}$ ohms. This high value confirmed that the drying procedure for both cell and electrometer valve was sufficient to reduce surface conduction to negligible proportions; it was possible to neglect the resistance of the cell and circuit in calculating the resistance of the liquid dinitrogen tetroxide.

Variation in Temperature.—For the measurement of resistance below room temperature, jacket *F* was surrounded by a further vessel *G*. With the cell in position, and the surrounding atmosphere in *F* dry, crushed ice was added to vessel *G*, which was then stoppered. By this means the temperature in the cell was decreased slowly. For a given quantity of added ice, preliminary experiments showed that the cell reached a steady temperature after about one hour. A resistance measurement, requiring about 15 minutes, could then be carried out with little change in temperature. For these measurements, the guard tube was replaced by a thermometer having a ground-glass cone fitting into socket *C* (Fig. 3), and of such a length that the bulb was immersed in the cell liquid. In order to measure resistances below 0°, it would be necessary to modify the apparatus to ensure more rigorous exclusion of moisture from the neighbourhood of the cell. However, the arrangement shown in Fig. 3 was found to be quite efficient over the temperature range for which results are recorded below.

RESULTS AND DISCUSSION.

The results, given in Table I (where the specific conductivity κ is in ohm^{-1} cm.$^{-1}$), indicate that there is a slight variation in conductivity from one preparation to another; in view of the extremely low order of conductivity, such variations are unavoidable. It is clear that the drying system employed in the preparation of the tetroxide was efficient, since further redistillation through phosphoric oxide (Preparations 1, 4, and 5) did not decrease the conductivity. In fact, the reverse occurred, repeated redistillation of the tetroxide increasing rather than decreasing the conductivity. This is considered to arise from the passage of the tetroxide through an additional number of glass vessels before reaching the conductivity cell. The second of the two results recorded in each case for preparations 7 and 8 are duplicate measurements carried out about 7 hours after the first measurements, and indicate that the conductivity was constant within experimental error. These two experiments are considered to be the most accurate. Since any unconscious relaxation of the experimental precautions can only increase the conductivity, we consider Experiment 7 to approach most nearly to ideal conditions, and throughout later work we quote the electrical conductivity of liquid dinitrogen tetroxide as $1{\cdot}3 \times 10^{-12}$ ohm^{-1} cm.$^{-1}$ at 17°. This conductivity is the value obtainable from dinitrogen tetroxide prepared and purified as described above; it is possible that purification of the liquid to a higher degree than was required in this work may result in an even lower value for the conductivity than that quoted above.

TABLE I.

Prep. no.	Temp.	$10^{12}\kappa$.	Prep. no.	Temp.	$10^{12}\kappa$.
1 *	19·5°	2·61	6	20·4°	2·24
2	18·3	2·71	7	17·3	1·34
3	18·5	7·05		17·0	1·24
4 *	18·0	8·08	8	20·0	1·92
5 *	20·0	5·90		20·0	2·00

* N_2O_4 redistilled.

The direction, and order of magnitude, of the temperature coefficient of conductivity has also been determined. For this purpose Preparation 6 (Table I) was used, and the conductivity values over a range of temperature are recorded below. Over this narrow temperature range the conductivity increased almost linearly with temperature, with a coefficient of $8{\cdot}5 \times 10^{-14}$ ohm^{-1} cm^{-1}./degree.

Temperature	7·3°	13·6°	19·5°	20·4°
$10^{-12}\kappa$ (ohm^{-1} cm.$^{-1}$)	1·17	1·71	2·19	2·24

In Table II the conductivity value and the sign of the temperature coefficient are compared with the corresponding properties of liquids which have been established as solvent systems.

With liquid ammonia, as with liquid dinitrogen tetroxide, developments in the technique of drying the liquid and apparatus have led to progressive decreases in the values for conductivity quoted in the literature. The positive sign of the temperature coefficient is taken from the work of Frenzel (*Z. Electrochem.*, 1890, **6**, 477) and Goodwin and Thompson (*Physical Rev.*, 1899, **8**, 38) although the conductivity values recorded by these authors are of the order of 10^{-7} and 10^{-4} ohm⁻¹ cm.⁻¹, respectively.

The extremely low order of electrical conduction found for liquid dinitrogen tetroxide is in accord with observations made on many other pure liquids. In water and liquid ammonia (which have dielectric constants which are high compared with that of dinitrogen tetroxide) any ions produced by dissociation may be considered to be free to migrate, but although these ions have a high mobility the electrical conductivity is slight. This has been interpreted (Sidgwick, *Ann. Reports*, 1934, **31**, 42) as arising from the association of the molecules in the liquid state, with the formation of zwitterions which cannot contribute to the conductivity. In liquid dinitrogen tetroxide the N–N bond is so weak that association between neighbouring molecules may well occur. This, together with the limited ionic freedom which results from the low dielectric constant, gives rise to conditions in the liquid which are even less favourable for the conduction of electricity than in the case of water and liquid ammonia.

TABLE II.

	κ (ohm^{-1} cm.$^{-1}$).	Temp. coeff.		κ (ohm^{-1} cm.$^{-1}$).	Temp. coeff.
Liquid N_2O_4	$1{\cdot}3 \times 10^{-12}$ at 17°	Positive	Water	(*b*) 4×10^{-8} at 18°	Positive
Liquid NH_3	(*a*) 10^{-11} at $-33{\cdot}4°$	Positive	BF_3	(*c*) $8{\cdot}0 \times 10^{-3}$ at 25°	Negative

(*a*) Carvallo (*loc. cit.*).
(*b*) Kohlrausch and Heydweiller (*Z. physikal. Chem.*, 1894, **14**, 317).
(*c*) Banks, Emeléus, and Woolf (*J.*, 1949, 2861).

The small degree of conduction which does occur in liquid dinitrogen tetroxide may arise from either ionic or electronic conduction. If conduction is ionic, the low conductivity value indicates that the number of free ions is extremely small, and this is consistent with the low value observed for the dielectric constant (Part IV, following paper). The most probable ionic species are NO^+, NO_3^-, NO_2^+, and NO_2^-; the general chemistry of each ionic species suggests that they are thermally stable over the temperature range involved, and therefore a positive temperature coefficient would be expected. The negative coefficient for bromine trifluoride is attributed by Banks, Emeléus, and Woolf (*loc. cit.*) to the thermal instability of the ions responsible for conduction.

The term electronic conductivity is used here in its widest sense, to imply the transference of electricity by electrons rather than by charged ions. This form of electrical conductivity is normally associated (*e.g.*, in metals) with a negative temperature coefficient and a high conductivity value, but the peculiar nature of the NO_2 group makes this form of conduction theoretically possible. This group is known to exist in the three forms NO_2^+, NO_2, and NO_2^-; the paramagnetism of the uncharged group shows the presence of an unpaired electron, and the stability of the NO_2^+ and NO_2^- ions indicates the ability of the NO_2 group to donate or accept electrons. It is therefore possible to consider the passage of an electric current through the liquid as occurring by the transfer of electrons along a type of Grotthuss chain of NO_2 groups. In the present experiments, the potential difference across the electrodes did not exceed 2 volts. If an electronic mechanism operates, a different value for the conductivity may be obtained if a high potential difference is applied across the electrodes; this aspect is being investigated. The N_2O_4 molecule is diamagnetic, and is less likely to partake in such a mechanism. The low order of conductivity may then be related to the small concentration of NO_2 groups in the liquid tetroxide. Soné (*Sci. Rep., Tohoku Imp. Univ.*, 1922, **11**, 139), from a study of magnetic susceptibility, has deduced that liquid dinitrogen tetroxide undergoes homolytic dissociation to the extent of 0·15% at 0° and 0·72% at 20°. If the conductivity is electronic, and is a property of the NO_2 groups, then the positive temperature coefficient which would arise from the increase in dissociation with temperature may outweigh the negative coefficient usually associated with electronic conduction in systems where no such dissociation can occur.

We are indebted to the Department of Scientific and Industrial Research for a Maintenance Grant to one of us (J. L.).

THE UNIVERSITY, NOTTINGHAM. [*Received, December* 16*th*, 1950.]