

**628.** *The Vapour Pressure of Anhydrous Copper Nitrate, and its Molecular Weight in the Vapour State.*

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Reaction of copper metal with a mixture of dinitrogen tetroxide and ethyl acetate yields the compound  $\text{Cu}(\text{NO}_3)_2 \cdot \text{N}_2\text{O}_4$ , which loses dinitrogen tetroxide to give anhydrous copper nitrate at  $85^\circ$ . When heated to higher temperatures *in vacuo*, the anhydrous salt sublimes, and condenses as deep blue-green crystals. Vapour pressures have been recorded up to  $226^\circ$ , at which temperature the vapour becomes unstable. The heat of sublimation is 15.6 kcal./mole. Molecular-weight measurements on the vapour show it to be monomeric. Attempts to determine the molecular weight by a transport method were unsuccessful, but indicated that the decomposition temperature of the vapour is lowered in the presence of other gases. Possible structures for the copper nitrate molecule are discussed.

BRIEF reference has recently been made to the volatility of anhydrous copper nitrate.<sup>1</sup> Vapour pressures over a temperature range and molecular weights in the vapour state have now been determined. References to the preparation of anhydrous cupric nitrate are conflicting. Thus, it is stated to be unknown,<sup>2</sup> but also that it separates as a white or pale green crystalline meal from solutions rich in nitric acid.<sup>3</sup> Ditti<sup>4</sup> claims to have prepared the compound by dissolving copper nitrate hydrate (which had been heated until red fumes were evolved) in hot anhydrous nitric acid and allowing it to cool, but repetition failed to yield an entirely anhydrous product. Guntz and Martin<sup>5a</sup> studied the reaction of copper metal with silver nitrate dissolved in an anhydrous solvent (acetone, phenyl cyanide or liquid ammonia). They considered that a cupric salt was produced in these solvents, though Morgan<sup>6</sup> has shown that displacement of silver from a silver nitrate solution in acetonitrile gives the cuprous salt. Complete replacement occurred but evaporation of the resulting solution gave a copper nitrate-solvent addition compound of variable composition. Efforts to remove this solvent resulted in thermal decomposition of the nitrate. Guntz and Martin also refluxed a mixture of hydrated copper nitrate (from which most of the water had been removed by heating) with dinitrogen pentoxide in anhydrous nitric acid. The analysis of the pale blue solid which separated corresponded with anhydrous copper nitrate.<sup>5b</sup> Reaction of copper oxide with acetyl nitrate was used by Chrétien and Boh<sup>7</sup> to prepare the anhydrous nitrate, again as a pale blue powder.

<sup>1</sup> Addison and Hathaway, *Proc. Chem. Soc.*, 1957, 19.

<sup>2</sup> Sidgwick, "The Chemical Elements and their Compounds," Oxford Univ. Press, 1950, p. 155.

<sup>3</sup> Remy, "Treatise on Inorganic Chemistry," Elsevier Publishing Co., New York, 1956, Vol. II, p. 388.

<sup>4</sup> Ditti, *Ann. Chim. Phys.*, 1879, **18**, 320; *Compt. rend.*, 1879, **89**, 576.

<sup>5</sup> Guntz and Martin, (a) *Bull. Soc. chim. France*, 1910, **7**, 313; (b) 1909, **5**, 1004.

<sup>6</sup> Morgan, *J.*, 1923, **123**, 2901.

<sup>7</sup> Chrétien and Boh, *Compt. rend.*, 1945, **220**, 822; Boh, *Ann. Chim. France*, 1945, **20**, 421.

Ferraro and Gibson<sup>8</sup> heated dinitrogen tetroxide with freshly prepared cupric oxide in a sealed tube at 87° and 14.7 atm. pressure for 7.5 hours. This gave a jade-green microcrystalline solid, to which the formula  $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{NO}_2$  was assigned, which decomposed at 90°—140°/10<sup>-5</sup> mm. to anhydrous copper nitrate, but the volatility of the latter was not observed.

The present work provides an alternative interpretation of some experiments by Neumann and Sonntag,<sup>9</sup> who treated copper oxide with gaseous dinitrogen tetroxide for some days at 25°, obtaining a brown-black microcrystalline product (termed anhydrous copper nitrate) which decomposed above 80° to a product regarded as a basic nitrate. It is now known that the compound  $\text{Cu}(\text{NO}_3)_2 \cdot \text{N}_2\text{O}_4$  has a dissociation vapour pressure of dinitrogen tetroxide of 1 atm. at 83.5°, and that copper nitrate does not decompose to a basic nitrate at this temperature. Neumann and Sonntag did not give full analyses of their products, and it seems probable that their experiments were concerned with the preparation and decomposition of the addition compound  $\text{Cu}(\text{NO}_3)_2 \cdot \text{N}_2\text{O}_4$ .

The method now given is believed to be the simplest for the preparation of anhydrous copper nitrate. By sublimation of the amorphous powder so obtained, the nitrate can be obtained as large blue-green crystals.

#### EXPERIMENTAL

*Preparation and Sublimation of Anhydrous Copper Nitrate.*—A freshly abraded strip (10 g.) of pure copper was added to a mixture of 20 ml. of dinitrogen tetroxide with 20 ml. of dried ethyl acetate in a 17 × 3 cm. glass tube closed by a B24 ground joint and phosphoric oxide guard tube. Nitric oxide was evolved vigorously and the colour of the solution changed from red to dark green. Reaction was complete after 4 hr. at room temperature. Unchanged copper was then removed, the solution (which increased appreciably in viscosity during reaction) was filtered in a closed system, and excess of liquid dinitrogen tetroxide added until precipitation of  $\text{Cu}(\text{NO}_3)_2 \cdot \text{N}_2\text{O}_4$  was complete. This was filtered off, washed with liquid dinitrogen tetroxide, and transferred to a 17 × 3 cm. tube where the excess of tetroxide was removed under a vacuum at 0°.

The thermal decomposition  $\text{Cu}(\text{NO}_3)_2 \cdot \text{N}_2\text{O}_4 \longrightarrow \text{Cu}(\text{NO}_3)_2 + \text{N}_2\text{O}_4$  was effected by immersing the tube in an oil bath, and maintaining the vacuum while raising the temperature slowly to 120°; anhydrous copper nitrate remains as a pale blue amorphous powder. A 0.5 cm. layer of cleaned and dried glass wool was then packed on the surface of the copper nitrate in the bottom of the tube, which was re-evacuated and arranged so that the oil level in the bath was about 3 cm. above the surface of the glass wool. The bath temperature was raised to 200°, whereupon copper nitrate rapidly sublimed, the sublimate collecting on the walls of the tube, leaving only about 0.3 cm. of clear glass above the oil level. The sublimation of 10 g. of copper nitrate was complete in about 4 hr. A small amount of dark olive-green powder (less than 5% of the starting material) remained. The sublimate was a deep blue-green crystalline mass, but if the sublimation was arrested early long needles could be isolated [Found: Cu, 33.83; N, 14.85.  $\text{Cu}(\text{NO}_3)_2$  requires Cu, 33.85; N, 14.93%]. Slower sublimation is possible at much lower temperatures; thus at 130°, 100 mg. quantities have been collected in 2—3 hr., and smaller quantities at as low as 100°. Anhydrous copper nitrate is very deliquescent, and all manipulations are carried out in a dry-box.

*Melting Point.*—When a sealed capillary was plunged into a bath at 255° the sample shrunk with signs of wetting, and at 256° the solid melted to a green liquid. In a similar experiment at 260°, the sample melted to an emerald-green liquid which almost immediately decomposed with evolution of bubbles of gas. The m. p. is therefore 255—256°. The nitrates of the alkali metals and of silver have lower m. p.s than the chlorides and the above value is consistent with this pattern (cf.  $\text{CuCl}_2$ , m. p. 498°).

*Vapour Pressures.*—Preliminary investigations indicated that a satisfactory technique must allow for the following points: (a) There appears to be no fluid suitable for use in a manometer. If mercury was used, a yellow solid was formed on the walls of the vessel containing

<sup>8</sup> Ferraro and Gibson, *J. Amer. Chem. Soc.*, 1953, **75**, 5747.

<sup>9</sup> Neumann and Sonntag, *Z. Electrochem.*, 1935, **41**, 611.

copper nitrate, produced by a gas-phase reaction with mercury vapour. Of the low-vapour-pressure oils, Silicone fluid M.S. 550 and Apiezon high vacuum grease L (which is liquid at the temperatures used) both showed signs of chemical attack. An all-glass system incorporating a spiral gauge was therefore used. (b) On being heated, solid copper nitrate evolves small quantities of decomposition products ( $\text{NO}_2 + \text{O}_2$ ) as well as copper nitrate molecules. The vapour pressure of the latter is of the order of a few mm. Hg; this is independent of the volume of the containing vessel, whereas the pressure set up by decomposition products from a given quantity of solid is decreased as the containing vessel becomes larger. The vessel must therefore be big enough for the pressure due to copper nitrate vapour to be readily identified. (c) The state of the surface of solid nitrate has a critical influence. The rate of development of pressure at a given temperature decreases with time, even though the proportion of the solid decomposing is almost negligible. It appears that decomposition occurs first at the surface of the solid, producing a layer of decomposition product (copper oxide or a basic nitrate) which acts as a barrier to vaporisation of copper nitrate molecules. Vapour-pressure measurements were therefore carried out only on freshly sublimed solid. (d) The whole of the vessel containing the vapour must be at the temperature of measurement, otherwise copper nitrate will immediately condense on any cool spot. (e) Copper nitrate will vaporise into a vacuum to give

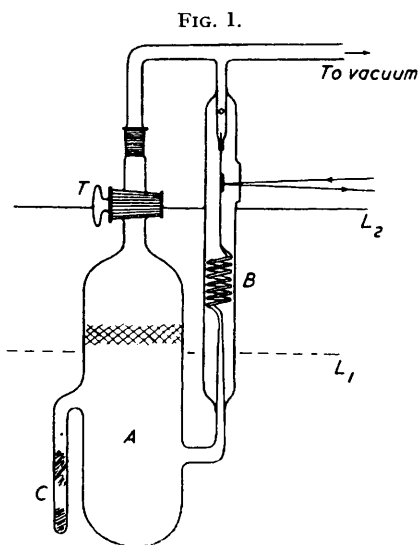
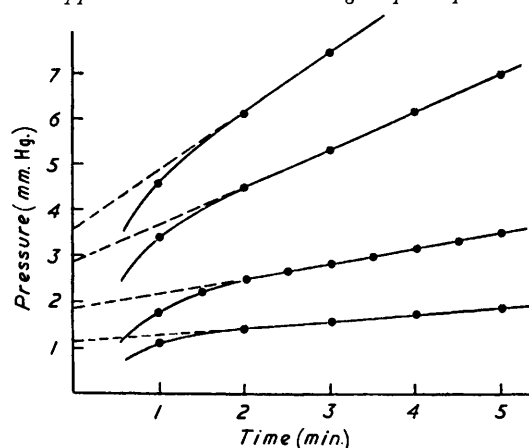


FIG. 1.

FIG. 2. Rate of development of pressure when anhydrous copper nitrate is heated in a large vapour space.



Temperatures, from top to bottom, 222.6°, 215.2°, 202.0°, 189.5°.

its full equilibrium vapour pressure, but not in presence of other gases (see molecular-weight measurements by the transport method below).

The apparatus used is shown in Fig. 1. To a vessel *A* (520 ml.) was attached a glass-spiral gauge *B* (sensitivity 90° deflection per atm.). The spiral gauges were kindly prepared by Mr. S. Kettle of the Inorganic Laboratories, Cambridge; such gauges are undamaged by sudden temperature changes from room temperature to 250°. Before the vapour-pressure measurements, the gauge *B* was calibrated to read pressure in *A* against vacuum in *B* (*i.e.*, outside the spiral), and the change in the zero (vacuum-vacuum) reading of the spiral with temperature was determined by immersing the empty apparatus in the bath at various temperatures.

Sublimed copper nitrate was placed in the bottom of tube *C*, followed by a plug of glass wool, and *C* then sealed into *A* as shown. The apparatus was degassed by flaming under vacuum, and placed in an oil-bath at 200° so that the oil was at level  $L_1$ . The vacuum being maintained, copper nitrate sublimed from *C* and condensed as a band of crystals round the inner walls of *A* a little above  $L_1$ . This provided a large surface area of fresh copper nitrate for subsequent ready vaporisation. The apparatus was then withdrawn from the oil-bath, the side arm *C* drawn off, and the apparatus and optical system mounted rigidly. The oil-bath (controlled to within  $\pm 0.1^\circ$ ) was then raised round the apparatus to the oil level  $L_2$ . It was essential that tap *T* should be partly immersed, to prevent condensation of copper nitrate on

the barrel. When  $T$  was partly immersed, the optical window in  $B$  was just above the oil surface.

After  $T$  was closed the pressure in  $A$  was recorded at  $\frac{1}{2}$  min. intervals. The type of pressure-time curve obtained is shown in Fig. 2. Each curve falls into two sections, an initial rapid rise in pressure representing vaporisation of copper nitrate, followed by a slower linear increase due to decomposition of the solid. Extrapolation of this line (which was straight for at least 10 minutes' heating) to zero time gives the true vapour pressure of copper nitrate. It is therefore important that the time scale should be correctly chosen. A finite time is required for the heat from the oil-bath to pass through the walls of  $A$  and to bring the copper nitrate to the temperature of the bath. When a measurement was started, the bath was therefore raised round the apparatus with  $T$  open and the whole apparatus under a vacuum.  $T$  was kept open until the copper nitrate reached the bath temperature, which was indicated by the appearance of copper nitrate crystals in its barrel.  $T$  was then closed and this time taken as zero.

This technique being used, values obtained are given in Table 1.

TABLE 1. Vapour pressure of anhydrous copper nitrate.

Temp. ( $^{\circ}$ )	157.0	172.8	186.4	189.5	202.0	215.2	222.6
Vapour pressure (mm. Hg)	0.32	0.59	0.99	1.15	1.87	2.84	3.59

The pressure values quoted are believed to be accurate to  $\pm 0.02$  mm. Hg.

*Vapour-phase Decomposition.*—Below  $225^{\circ}$ , the walls of  $A$  (Fig. 1) remained clear throughout an experiment. At higher temperatures the vapour pressures became much higher than

FIG. 3. Vapour pressure of anhydrous copper nitrate (mm. Hg).

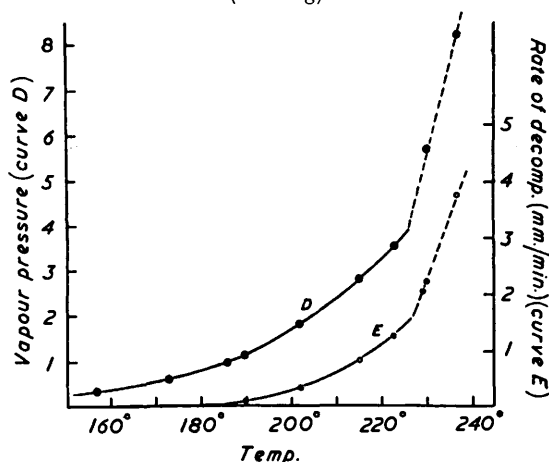
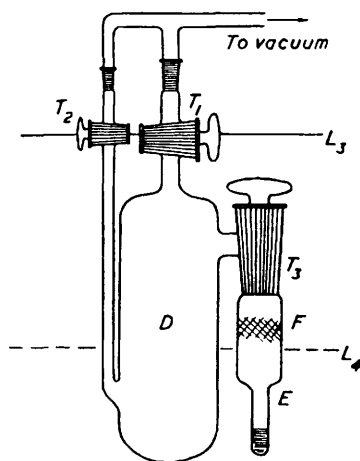


FIG. 4.



expected from extrapolation of the values in Table 1, and the walls were rapidly covered with a fine, dark deposit, indicating decomposition of the vapour. The vapour pressure-temperature curve ( $D$ , Fig. 3) shows a sharp break; the graph of  $\log p$  against  $1/T$  is straight over the temperature range at which the vapour is stable, and the break in this graph at the decomposition temperature shows that the vapour begins to decompose very sharply at  $226^{\circ}$ . The gradients of the straight portions of the pressure-time curves (Fig. 2), obtained by use of similar quantities of solid copper nitrate, are also plotted against temperature in Fig. 3 (curve  $E$ ) and again show a break at  $226^{\circ}$ . The stability of copper nitrate vapour is therefore greater than that of the solid; in the absence of high pressure of other gases (see below) there is no evidence for decomposition of the vapour below  $226^{\circ}$ , whereas the decomposition of the solid is measurable even below  $190^{\circ}$  (Fig. 2). The higher pressures and gradients above  $226^{\circ}$  (Fig. 3) result from the fact that the oxygen-nitrogen dioxide mixture responsible is now produced by decomposition of copper nitrate in both the solid and the vapour state.

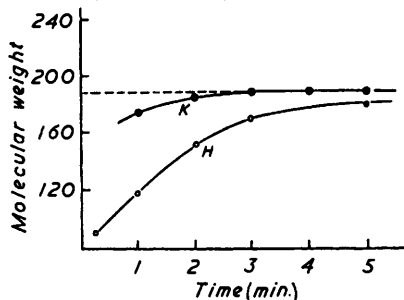
By extrapolation of the  $\log p-1/T$  graph, the vapour pressure of copper nitrate at its m. p. ( $256^{\circ}$ ) would be 8.7 mm. Hg if the vapour did not decompose.

*Molecular Weight in the Vapour Phase.*—This determination involved measurement of the

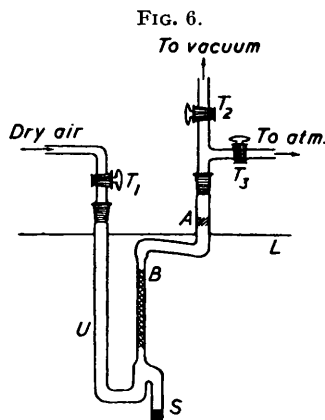
quantity of copper nitrate present in a given volume of vapour at a known temperature. The apparatus (Fig. 4) was designed so that when equilibrium pressure was established, the solid could be isolated from the vapour. Taps  $T_1$  and  $T_2$  were at the same level so that each could lie in the surface ( $L_3$ ) of the oil. A side tube  $F$  was attached to vessel  $D$  (capacity 740 ml.) through a hollow-barrelled 10 mm. bore tap  $T_3$  arranged so that its barrel would lie below  $L_3$ . The apparatus was flamed under vacuum, and a narrow tube containing copper nitrate covered by a glass wool plug sealed to tube  $F$  at  $E$  as shown. With all taps open to vacuum, the oil-bath at  $200^\circ$  was raised to level  $L_4$ , and copper nitrate sublimed into  $F$ . The oil level was then raised to  $L_3$ , with  $T_1$  and  $T_2$  open and  $T_3$  closed. The temperature of the bath was adjusted to  $217^\circ$ , and the apparatus allowed 10 min. to achieve this temperature.  $T_1$  was then closed and  $T_3$  opened to allow copper nitrate vapour to pass into  $D$ .  $T_2$  was kept open until copper nitrate was seen to condense in this tap (which usually occurred 6–7 sec. after opening  $T_3$ );  $T_2$  was then closed. This step ensured the removal from  $D$  of as much as possible of the gaseous decomposition products which had accumulated in  $F$ , and also confirmed the passage of copper nitrate vapour from  $F$  into  $D$ .

$T_3$  was then closed and  $T_1$  opened, thus drawing the vapour from  $D$  though the barrel of  $T_1$ , where it condensed. To increase the amount of copper nitrate available for analysis, the

FIG. 5. *Molecular weight of anhydrous copper nitrate vapour at  $217^\circ$ .*



The broken line represents the molecular weight of the monomer (187.6).



above process could be repeated several times, thus accumulating an amount of copper nitrate in  $T_1$  equivalent to a multiple of the volume of  $D$ . Since  $T_3$  must be closed before  $T_1$  is opened, it was necessary to ensure that  $T_3$  remained open long enough for the equilibrium vapour pressure of copper nitrate to be established in  $D$ . A series of experiments were therefore carried out which were identical except that  $T_3$  was kept open for different periods. The results are given in Table 2 (row 4), where the Time is that allowed and the Weight is that of copper nitrate condensed per evacuation of the vessel (calculated from the weight of copper-ethylenediamine-mercury iodide complex).

TABLE 2. *Condensation of copper nitrate from vapour.*

Time (min.)	0.25	1.0	2.0	3.0	4.0	5.0	5.0	5.0
Temp.	$217^\circ$	$217^\circ$	$217^\circ$	$217^\circ$	$217^\circ$	$217^\circ$	$180^\circ$	$198^\circ$
Weight (g.)								
Apparatus 1 (560 ml.)	0.00489	0.00651	0.00840	0.00932	—	0.00966	—	—
Apparatus 2 (Fig. 4) (740 ml.)	—	0.0125	0.0133	0.0135	0.0134	0.0135	0.0127	0.0131

From each experiment the apparent molecular weight of copper nitrate in the vapour was calculated and the results are shown in Fig. 5 as the curve  $K$ . The molecular weight rapidly rises to, and levels off at, the value corresponding to the monomer  $\text{Cu}(\text{NO}_3)_2$ , which thus represents the state of this compound as vapour. The results in row 3 (Table 2) and curve  $H$  (Fig. 5) were obtained with an apparatus in which a straight-bore tap was used at  $T_3$  (Fig. 4). This interposed a longer tube between  $F$  and  $D$ , and equilibrium vapour pressure was established more slowly.

This molecular weight is probably independent of temperature. Measurements at  $180^\circ$

and 198° (Table 2) gave molecular weights of 175 and 180 respectively. At these temperatures the lower equilibrium pressures may be more slowly attained with the type of apparatus used and this is probably responsible for the slightly lower molecular weights observed.

*Molecular Weight by the Transport Method.*—The total pressures recorded in the vapour-pressure measurements (Fig. 2) did not normally exceed 10 mm. Hg. Attempts to determine the molecular weight of copper nitrate by the transport method were made primarily to examine the behaviour of copper nitrate vapour in the presence of other gases. Air, thoroughly dried and at atmospheric pressure, was used in the apparatus shown in Fig. 6. Anhydrous copper nitrate was placed in side arm *S* of the U-tube *U*, and the tube evacuated through *T*<sub>2</sub> with *T*<sub>1</sub> and *T*<sub>3</sub> closed. An oil-bath at 210—220° was raised round *U* to level *B*, whereupon copper nitrate condensed in the outgoing arm of *U* (5 mm. bore). By gradual lowering of the oil level, this arm was almost filled with crystals for a distance of 5 cm., after which the oil-bath was removed, and dry air admitted to the cool apparatus. The bath was then brought to the desired temperature, and raised round the U-tube to the final level *L* shown in Fig. 6. The apparatus was allowed 3 min. to attain bath temperature; a very slow stream of dry air was then passed through the apparatus *via T*<sub>1</sub> and *T*<sub>3</sub>. Copper nitrate was transported from the U-tube, and condensed as crystals at point *A*. Occasionally, needles formed which tended to fall away when the apparatus was moved; the tube below *A* was therefore bent as shown to form a trap for such crystals. After an experiment, the tube was cut at this trap, and the quantity of copper nitrate transported was determined by analysis. Results are given in Table 3.

From the data in Table 3, and on the assumption that copper nitrate gives the same equilibrium vapour pressure in contact with air as it does in a vacuum, it is possible to calculate molecular weights *M* (col. 6). These are much lower than the value for the monomer formed

TABLE 3. *Transport of copper nitrate by air at atmospheric pressure.*

Expt. No.	Rate *	Duration of expt. (min.)	Cu(NO <sub>3</sub> ) <sub>2</sub> transported per l. of air	Temp.	<i>M</i> (apparent)
1	0.546	60	0.00982	204°	90
2	1.053	60	0.00810	204	74
3	1.310	60	0.00845	203	77
4	1.469	60	0.00756	204	69
5	2.090	60	0.01020	204	93
6	0.700	60	0.0184	217	112
7	1.500	60	0.0229	217	139
8	2.275	60	0.0210	217	128
9	4.460	30	0.0156	217	95
10	1.87	60	0.0255	220	141
11	1.87	60	0.0272	224	131

\* l. of dry air per hr. corrected to 760 mm. at 20°.

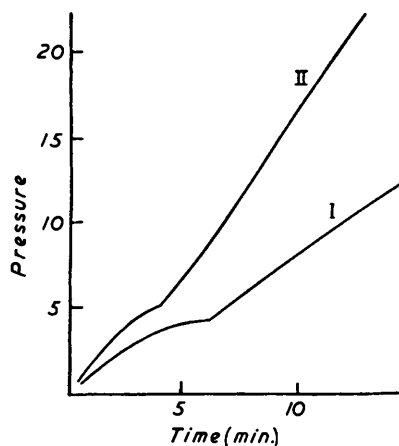
in the absence of foreign gases, and the results indicate either that gas–solid equilibrium was not achieved, or that the stability of cupric nitrate vapour is influenced by the presence of other gases. The former is unlikely, since the weight of copper nitrate transported per litre of air does not increase as flow-rate decreases (cf. expts. 1—5 with 6—9); in fact, in some cases the reverse is true (cf. expt. 5 with 4, and 7 with 6). Experiment 9 was carried out for a shorter period to ascertain whether the smaller quantity transported was due to ageing of the copper nitrate surface during vaporisation, but again a low value was obtained.

All the transport experiments were carried out below the temperature (226°) at which copper nitrate vapour has been found to decompose, and in the presence of air at atmospheric pressure the vapour therefore decomposes at lower temperatures. This was supported by examination of that part of the U-tube (Fig. 6) between *B* and *A* which is traversed by the vapour. In all cases the internal wall was coated with a very thin dark green film similar in appearance to that formed on the walls of the vapour-pressure vessel (Fig. 1) above 226°. The identity of this copper compound has not yet been established; it is insoluble in water but readily soluble in dilute nitric acid. Copper nitrate vapour probably decomposes in the vapour-phase rather than by a heterogeneous process, the decomposition temperature being determined by the molecular weight, chemical nature, and the pressure of added gases.

The influence of total pressure has been illustrated by use of an apparatus similar to that shown in Fig. 1, except that the vessel *A* was replaced by a single narrow tube joining tap and

spiral gauge. The internal volume was thereby reduced from 520 ml. to 35 ml., and in this small volume the nitrogen dioxide and oxygen formed by decomposition of the solid nitrate give rise to much higher pressures than those indicated in Fig. 2. Typical pressure-time curves obtained on heating at 220° are shown in Fig. 7. Curve I was obtained on first heating. The apparatus was then evacuated and tap *T* closed, and curve II represents the subsequent development of pressure. Each curve shows a sharp break at about 5 cm. Hg total pressure. The initial part of the curve represents (NO<sub>2</sub> + O<sub>2</sub>) pressure from solid decomposition, together with the relatively small pressure of stable copper nitrate vapour. The decomposition temperature of the latter falls from the vacuum value of 226° to 220° under 5 cm. Hg pressure;

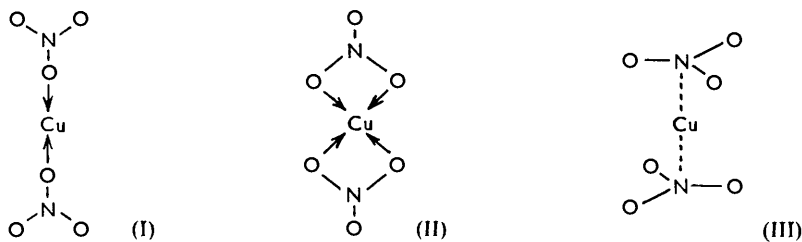
FIG. 7. Changes of pressure (cm. Hg) when anhydrous copper nitrate is heated at 220° in a small vapour space.



at higher pressures decomposition occurs *via* copper nitrate vapour also, and is therefore more rapid. These experiments present a unique problem in gas kinetics which we propose to explore more fully.

#### DISCUSSION

The most remarkable properties of anhydrous copper nitrate are its volatility, its monomeric state in the vapour, and its rich blue colour. These all indicate that a high degree of covalency exists in a molecule which would normally, on the basis of present knowledge, be regarded as fully ionic, and that in anhydrous compounds the nitrate group is capable of a type of bonding not hitherto realised. If we assume that each nitrate ion is bonded to the copper ion in the same manner, there are three possible structures for the molecule.



The unidentate nitrate group (I) is the form usually assumed for nitrate-complexes. However, the nitrate group is generally recognised as a weak ligand in co-ordination complexes, and is readily replaced by water. It seems inconsistent, then, that a metal-nitrate bond which is sufficiently strong to enable the molecule to exist as a monomer in the vapour phase should be of this form. There is no doubt however that covalency exists; from the infrared spectrum of nitrate-complexes it is possible to distinguish a covalent from an ionic nitrate group,<sup>10</sup> though it is not yet possible by this means to

<sup>10</sup> Gatehouse, Livingstone, and Nyholm, *J.*, 1957, 4222.

determine unequivocally the precise manner in which the  $\text{NO}_3$  group is bonded. The infrared spectrum of solid copper nitrate shows it to be pronouncedly covalent.<sup>11</sup>

The nitrate group does not usually enter co-ordination complexes as a bidentate ligand (II), although the  $\text{CO}_3^{2-}$  group readily does so. Crystallographic data<sup>12</sup> indicate that in the complex  $[\text{UO}_2(\text{NO}_3)_3]^-$  the uranyl group is normal to a plane in which lies a ring of six oxygen atoms (from three bidentate nitrate ions) surrounding the uranium atom. It has also been suggested that the ruthenium complex  $\text{Ru}_2\text{N}_6\text{O}_{15}$  may contain bidentate groups.<sup>13</sup> Structure (II) is therefore possible, but is less attractive than structure (III) which most readily explains the thermal properties of the compound.

From the vapour pressure-temperature relation (Fig. 3) the relevant thermodynamic functions for the vaporisation process have been calculated at three temperatures (Table 4).

TABLE 4.

$T$ ( $^{\circ}\text{K}$ )	$\Delta H$ (cal./mole)	$\Delta G$ (cal./mole)	$\Delta S$ [cal./(mole degree)]
453	15,600	6200	20.8
473	15,600	5730	20.9
493	15,600	5330	20.8

The heat of vaporisation  $\Delta H$  is surprisingly low, and is of the same order as values for the carbonyls of metals of the chromium group, and some metal *cyclopentadienyl* compounds (*e.g.*, ferrocene). This suggests that intermolecular forces are small, which led us to postulate the sandwich structure (III). It is possible, of course, that the structures in the solid and the vapour phase are different; the infrared spectrum of the vapour contains at least one absorption band which has not been observed for solid copper nitrate or any other solid nitrate, and is at present unassigned.<sup>11</sup> Structure (III) is therefore proposed primarily for the vapour phase, where an isolated molecule free from lattice forces can more readily attain molecular symmetry. The broken lines do not carry any implication regarding the number of electrons used in bonding, or their location, but they emphasise the fact that the three oxygen atoms in the co-ordinated nitrate ion are equivalent. Covalency may result from overlap of a bonding  $\pi$ -orbital of the nitrate ion with metal *d*-orbitals. The former is centrosymmetrical, which is consistent with sandwich-type bonding.

The structure of solid copper nitrate is now under examination (by Dr. S. C. Wallwork in these laboratories) by *X*-ray crystallography, so that detailed discussion of possible structures is unnecessary at this time. We may comment, however, that structure (III) represents hexaco-ordination of the copper ion by oxygen atoms, but a molecular model indicates Cu-O distances which are too long for strong bonding. Regular octahedral environment of the cupric ion rarely, if ever, occurs.<sup>14</sup> However, a distorted form of structure (III) is obtained if the co-ordination is regarded as square-coplanar (II) and each nitrate ion is then tilted so that the third oxygen atom is above (and below) the plane, giving four short and two long Cu-O bonds. The blue colour of the anhydrous nitrate is consistent with structure (II), or with (III) or its distorted form. It is of interest that the anhydrous carbonate complex  $\text{K}_2[\text{Cu}(\text{CO}_3)_2]$  also has an unexpectedly deep blue colour.<sup>15</sup>

It is now known that these unusual features of nitrate-ion bonding are not restricted to the copper compound; anhydrous ferric and mercuric nitrates are also volatile.<sup>16</sup>

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<sup>11</sup> Addison and Gatehouse, *Chem. and Ind.*, 1958, 464.

<sup>12</sup> Hoard and Stroupe, Atomic Energy Project Report, 1943, A, 1229; Jander and Wendt, *Z. anorg. Chem.*, 1949, **258**, 1; Zachariasen, *Acta Cryst.*, 1954, **7**, 795; see also Coulson and Lester, *J.*, 1956, 3650.

<sup>13</sup> Fletcher, "Proceedings of the International Conference on Co-ordination Complexes," Rome 1957, *Ricerca sci.*, 1958, in the press.

<sup>14</sup> Orgel and Dunitz, *Nature*, 1957, **179**, 462.

<sup>15</sup> Reynolds, *J.*, 1898, **73**, 262; Applebey and Lane, *J.*, 1918, **113**, 609.

<sup>16</sup> Addison, Hathaway, and Logan, *Proc. Chem. Soc.*, 1958, 51.