XLVI.—*The Molecular Weights of Nitrogen Trioxide and Nitric Peroxide.*

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IT was shown by Dr. Sydney Young and myself in a paper read before the Physical Society (*Proc. Phys. Soc. Lond.*, 1887, **9**, 45), that the Messrs. Natanson's experiments on the relations between the pressure, temperature, and volume of nitric peroxide, interpreted by the light of the equation $p = bt - a$ (see previous communications to the Physical Society), lead to the probable conclusion that at low temperatures the formula of the peroxide is N_2O_4 , and that no more complex molecular groupings are formed than those corresponding to $2NO_2$. But owing to experimental difficulties, it appears to be impossible to prove this statement with absolute certainty from experiments on the density of the substance in the gaseous state.

A means of determining the molecular weight of liquid and solid substances has, however, recently been placed at the disposal of chemists by the brilliant researches of M. Raoult. In a series of memoirs published in the *Annales de Chimie et de Physique* [5], **20**, 217; **28**, 133; [6], **2**, 66, 93, 99, 115; **4**, 401; **8**, 289, 317) he has proved that the depression of the freezing point of a liquid caused by the presence of dissolved liquid or solid is proportional to the absolute amount of substance dissolved, and inversely proportional to its molecular weight. This law holds for the great majority of substances with which he has experimented, and the exceptions are so few in number, and so striking, as to call for further research to explain their anomalous behaviour. With glacial acetic acid as solvent, however, among nearly 150 substances with which he experimented, there are barely half-a-dozen whose behaviour proved abnormal.

This method makes it possible to determine the molecular weight of liquid nitric peroxide; and it also throws light on the question whether nitric peroxide undergoes further dissociation at low temperatures by dilution, which may be regarded as equivalent to reduction of pressure, if the liquid and gaseous states be compared with one another.

Experiments (an account of which follows) tend to show that not merely is the formula of nitric peroxide N_2O_4 at temperatures in the neighbourhood of 16° , but also that no appreciable alteration in molecular weight is produced by considerably increasing the relative number of molecules of the peroxide in a given volume.

The accompanying diagram shows a convenient form of the apparatus required for such experiments. A wide test-tube is closed by an india-rubber cork A, perforated with two holes. Through one of these a piece of wide glass tubing B passes, in which a stirrer CC moves freely up and down. The thermometer D serves to show the temperature of the liquid, while by surrounding the tube by a beaker E with hot or cold water as required, the temperature may be raised a few degrees above, or depressed a few degrees below the freezing point of the solvent.

A quantity of acetic acid, fractionated from water, amounting to 41.02 grams, was weighed out. It melted at 16.680° . A small bulb containing 0.378 gram of nitric peroxide was added and broken in the acetic acid by crushing it with the stirrer. The melting point of the acid was lowered by this addition to 16.300° . The depression is therefore 0.380° . Had one part of peroxide been added to 100 parts of acetic acid, the depression would have been, according to this measurement, 0.4214° . And $0.4214 \times 94.6 = 39$ (Raoult's constant for acetic acid); hence the molecular weight of the peroxide appears from this experiment to be 94.6. Without disturbing the apparatus, a second bulb of peroxide weighing 0.5085 gram was crushed in the acid, and the melting point was now 15.825° ; the total depression amounting to 0.855° . Calculating as before, the depression for 1 gram per 100 is 0.3956, and the molecular weight 98.58. Subsequent additions were made as follows:—

1.5405 gram lowered the melting point 1.590° ;	mol. wt. = 92.11.
2.2080 " " "	2.280 " = 92.07.
3.1510 " " "	3.215 " = 93.18.
3.679 " " "	3.865 " = 90.29.

A second determination gave the following result:—

Acetic acid taken, 40.05 grams, melting at 16.675° ; the addition of 0.893 gram of the peroxide lowered the melting point to 15.768° ; depression = 0.907° . Depression produced by 1 gram per 100 would therefore amount to 0.4068° ; and the molecular weight is therefore 95.87.

It must therefore be concluded that the molecular weight of nitric peroxide in the liquid state at about 16° is 92, and its formula consequently is N_2O_4 . It is also manifest that the relative number of molecules of the peroxide in a given volume of acetic acid may be decreased from 8.97 to 0.92 without materially altering the molecular weight; no dissociation, therefore, would appear to take place on dilution.

Similar experiments were tried with nitrogen trioxide prepared by dissolving N_2O_4 in acetic acid and passing NO through the cooled mixture; but they gave no reliable results owing to the dissociation of the trioxide, which is rapid at 16° .