

THE GROUND-STATE OF THE Se_2 MOLECULE.

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THE diatomic molecules of the lighter elements of the sixth family of the Periodic Table show the peculiarity that contrary to the behaviour of other groups the ground-level is a triplet state. Ordinarily, one should expect that on combination of two atoms, each of which is in a ^3P state, a molecule with $^1\Sigma$ as its ground-level should result and that the possible triplet states are excited ones. It has, however, been established by experiment¹—and upto a certain extent also theoretically—that in the O_2 , S_2 and SO molecules the ground-level is $^3\Sigma$ and that the $^1\Sigma$ level is some way above it.

There is some doubt, whether or not this condition still prevails with the other elements of that group. It is possible that as one proceeds to heavier atoms the $^1\Sigma$ state may come below $^3\Sigma$. Spectroscopical investigations have so far not been able to bring about a decision and it is still unknown, whether the ground-states of Se_2 , Te_2 , SeO , etc., are $^3\Sigma$ or $^1\Sigma$ states.¹

So it appeared worthwhile to ascertain the magnetic properties of Se_2 vapour and to bring about a decision in this way. A Weiss-Foëx transmission balance would have been the proper apparatus for that purpose, especially if accurate values for the susceptibility of Se_2 vapour were to be found out. That type of balance was, however, not at our disposal. On the other hand, the actual value of the susceptibility of the vapour is not of particular importance; what is really wanted, is a qualitative experiment to show whether the vapour is paramagnetic or diamagnetic. Furthermore, there is no point in exaggerating the accuracy of the magnetic measurements, because the vapour pressure of Se_2 at various temperatures is not sufficiently well known to justify the employment of a more sensitive apparatus. Therefore, the simplest possible arrangement was decided upon.

A furnace made of a double filament of coiled nichrome wire was placed between the poles of an electro-magnet of about 7000 gauss. In the earlier experiments the pole-pieces of the magnet were cooled with water, but later

on it was found that it really did not matter, because it was possible to insulate the furnace so well with a mixture of asbestos and clay, that even without cooling the field remained unchanged in the degree of accuracy attained.

The sample was hanging inside the furnace and was suspended from an analytical balance with the help of a silica fibre. The selenium was carefully purified, special care was taken to prevent the surface of the grains from being contaminated by a layer of oxides. It was then sealed in a silica tube in the vacuum, the evacuation being driven to a point when the cathode ray discharge practically ceased. Care was also taken to remove any air adsorbed on the walls of the tube, before the sample was introduced.

The method of reading was a null method, the force exerted by the magnet being counterbalanced by the addition of weights. This force, according to the different tubes used, varied between 0.0016 and 0.0038 g.

The temperatures were measured with the help of a pyrometer (thermocouple and millivoltmeter); the gauging was checked with the help of various standard temperatures (b.p. of sulphur, m.p. of sodium chloride, etc.).

The measurements on the empty and evacuated tubes showed not the slightest change in the force exerted by the magnet between room temperature and 1100° C.; the changes in the field, which were due to a slight warming of the pole-pieces and to heating the air between them, were apparently below the sensitivity of the apparatus.

The tubes containing selenium exhibited on heating a considerable reduction of the force exerted by the magnet and thus showed that the selenium vapour formed in them was *paramagnetic*.

A few examples of the measurements taken are as follows:—

TUBE III.

Weight (empty) = 2.3842 g.
Capacity = 1.0429 cm³.
Se inside = 0.0186 g.

Temperature	Magnetic Force
23° C.	— 0.0036 g.
481° C.	— 0.0036 g.
648° C.	— 0.0036 g.
783° C.	— 0.0033 g.
923° C.	— 0.0032 g.
1110° C.	— 0.0030 g.

TUBE IV.

Weight (empty) = 1.4141 g.
Capacity = 0.3910 cm³.
Se inside = 0.0189 g.

Temperature	Magnetic Force
23° C.	— 0.0024 g.
440° C.	— 0.0024 g.
523° C.	— 0.0023 g.
648° C.	— 0.0022 g.
783° C.	— 0.0020 g.
970° C.	— 0.0018 g.
1110° C.	— 0.0016 g.

From these results there is not the least doubt that on heating a considerable quantity of a paramagnetic vapour is created in the tubes. On the other hand, it was not possible to calculate a value for the susceptibility of Se₂ vapour with any semblance of accuracy, because the amount of Se₂ formed in the tubes was quite unknown. The formula of Preuner and Brockmüller² for the equilibrium between Se₆ and Se₂ gave by far too low values for the quantity of Se₂ present. On the other hand, there is no reason to suppose that the paramagnetic susceptibility of free Se₂ molecules should in any way be different from that of O₂, particularly in consideration of the fact, that there is an excellent agreement between the theoretical value for a ³Σ' state and the one measured on oxygen.³

Experiments with sulphur made along with those on selenium confirmed qualitatively the results previously obtained by Néel.⁴ As to the actual amount of the susceptibility of S₂ calculated by him, the present authors are of opinion that the same holds good as in the case of Se₂ and that in spite of the accuracy of his magnetic measurements the amount of S₂ present in the sulphur vapour is not sufficiently well known to justify any statement as to the numerical value of the susceptibility. The discrepancy found by Néel between his value and the theoretical one is probably due to that cause rather than to a real deviation.

Experiments to ascertain, whether Te₂ vapour is dia- or paramagnetic, are in progress. Here higher temperatures are necessary than for sulphur and selenium, and the furnace employed in those cases was insufficient for tellurium.

The apparatus described proved to be a quick and efficient means of ascertaining the magnetic nature of vapours, particularly in cases, when it is either not necessary or—owing to lack of knowledge as to the vapour pressure—not possible to obtain accurate values of the susceptibility.

REFERENCES.

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- ⁴ L. Néel, *C.R.*, 1932, **194**, 2035.