ON THE MAGNETIC SUSCEPTIBILITIES OF VAPORS OF ORGANIC LIQUIDS

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Abstract

The apparatus employed in this investigation consists essentially of a thin closed diamagnetic bulb suspended from one end of the beam of a modified Curie balance. The vapor under investigation surrounds this bulb. The complete balance is in an air-tight chamber of suitable shape. The bulb moves horizontally and at right angles to a non-homogeneous field, causing a twist in the suspension fibre of the balance beam. The diamagnetism of the bulb is compensated as nearly as possible by enclosing the requisite quantity of air, so that at room temperature there is very little magnetic force acting on it, if surrounded by a vacuum. Now if a diamagnetic vapor is introduced, the bulb apparently becomes paramagnetic and is drawn towards the stronger part of the field, and *vice versa* if a paramagnetic vapor be introduced. Values relative to air were obtained in all cases. All the vapors examined were diamagnetic. The molecular susceptibilities determined for the vapor state were in many cases nearly equal to those calculated from the liquid state, but in some cases they appear to be higher. This is specially true in the case of CS_2 and C_6H_6, the molecules of which are known to possess a high degree of magnetic anisotropy[1] in the liquid state. The results for these two substances await confirmation by independent investigations by other methods.

Introduction

NO LITERATURE seems to exist in connection with the magnetic susceptibilities of vapors. In the liquid state the problem has been extensively studied by Pascal, Henrichsen, Koenigsberger, Ishiwara and others. Many interesting conclusions emerged from Pascal's investigations of organic liquids and atomic susceptibility constants were deduced. In the investigation of molecular and atomic structure the diamagnetic susceptibilities of substances in the gaseous form are of greater interest than of those in the liquid state. Furthermore, a comparison of the gaseous and liquid states is of great importance as it might throw light on the still unsolved problem of the nature of the liquid state.

Experimental

The essential parts of the experimental arrangements are shown diagrammatically in Fig. 1. The magnetic balance consists essentially of a hollow glass bulb B, which is sealed and suspended by a silk loop from one end of a light aluminum bar AD, the latter being suspended by a torsion fibre. This bulb is blown out of feebly diamagnetic glass the diamagnetism being compensated as nearly as possible by enclosing within the bulb the requisite quantity of air and sealing its stem. It hangs in a suitable non-homogeneous field. The bulb C attached to the other end of the balance beam counterpoises the weight of B, and in addition its volume is so adjusted that the hydro-

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[1] Raman and Krishnan, Proc. Roy. Soc. **A113**, 511 (1927).

static buoyancy due to introducing gases is completely neutralized. The balance chamber has a suitable shape and is perfectly air-tight. The balance is capable of moving within it over a short range without touching the walls. The concave mirror *M* serves in taking deflections of the beam by the usual lamp and scale arrangement. A side-tube attached to the balance chamber near the bulb *B*, carries a delicate thermometer.

When the magnet is excited the bulb *B* is slightly attracted or repelled in vacuum because of the imperfection in compensation and because of the fact that temperature fluctuations change the susceptibility of the contained air. By a proper rotation of the torsion head the beam is adjusted to lie along the axis of the chamber. If we introduce a diamagnetic vapor into the balance chamber, the bulb becomes apparently paramagnetic and is drawn towards the stronger parts of the field. On the other hand, if air or some other paramagnetic gas is introduced, the bulb appears to be diamagnetic to this medium and is repelled. Preliminary adjustments were made so that *B* moves in a perfectly horizontal plane and at right angles to the non-homogeneous field causing a twist of the suspension fibre of the balance beam. From the deflections, values relative to air are obtained in all cases.

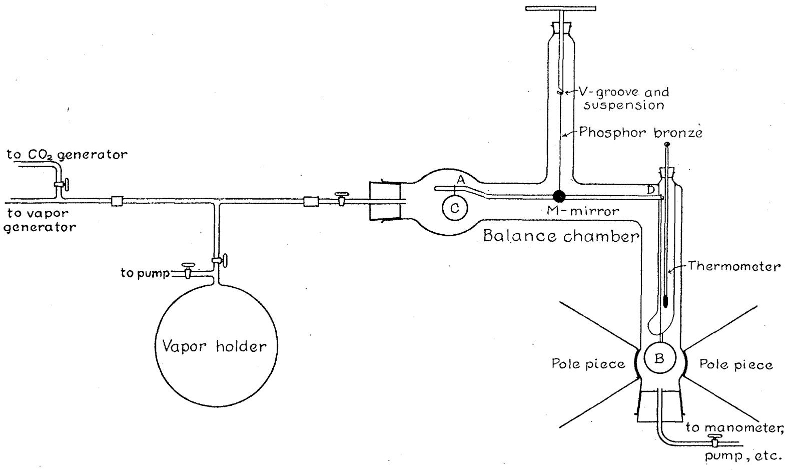

Fig. 1. Diagram of apparatus.

The sensitiveness was generally such as to produce a deflection of 2 to 4 mm of the spot of light on a scale placed at a distance of 100 cm, corresponding to the change of susceptibility caused by altering the pressure of air by 1 mm. Since in all cases, air was used to calibrate the scale and since the deflections with a diamagnetic gas are oppositely directed to those for air, the rotatable head was so adjusted after an experiment as to make it possible to have the calibration deflections cover the same range as those for the gas. When the sensitiveness was kept low, this adjustment was not found necessary. The field strength was generally about 2000 Gauss.

The vapor was generated from a bulb containing the pure liquid. To displace any trace of air in the vapor holder, carbon dioxide from a Kipp's apparatus was passed through it for an hour; this was then pumped out and filled many times with the vapor.

The chief source of error is introduced by the rise of temperature due to the heating of the coils of the magnet and a correction is applied for this. There was some difficulty due to the absorption of the vapor by rubber cork surfaces and this was minimized by coating the inside with water glass. There were also oscillations of the balance caused by letting the vapor into evacuated balance chamber. These were reduced by careful manipulation of the taps. To avoid condensation of the vapor on the balance bulbs, the pressures at which measurements were made were less than the saturation pressures at atmospheric temperature.

RESULTS

The results of one calibration are given in Table I.

TABLE I

Calibration with air.

Temperature	Pressure	Deflection	Temperature correction	Corrected readings
23.5°C	0 mm	300	0	300
23.7	9	271.5	2.4	274
23.9	16	251	4.8	256
24.2	24.5	229	8.4	237
24.5	33	210	12	222
24.7	40.5	194.5	14.4	209

On plotting the observations of the last columns, the gradient of the deflection-pressure curve is obtained and hence the number of divisions corresponding to the change in the volume susceptibility due to a change of 1 mm in pressure of air. This is equal to 2.44 divisions per mm at a mean temperature of 24°C.

The results for hexane vapor are presented in Table II.

TABLE II

Observations on hexane vapor.

Temperature	Pressure	Deflection	Temperature correction	Change of deflection	Relative pressure change	Change of deflection per mm
23.3°C	0 mm	256		39.1	114 mm	0.343
23.6	114	291.5	3.6			
23.9	14	253.5	−3.6	34.4	100	.344

Generally three experiments were conducted with each vapor, in some cases under different sensitiveness. Taking the volume susceptibility of air as 0.0308×10^{-6} at 0°C and 760 mm according to Také Soné,[2] the volume susceptibility of the vapor at the temperature of observation is obtained after the necessary corrections for the change of volume susceptibility of air according to Curie's law. The volume susceptibility of the vapor for the

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[2] Také Soné, Phil. Mag. **39**, 305 (1920).

molar volume is calculated assuming it to obey Boyle's law. This is called the mol. susceptibility in Table III.

TABLE III

Mol. susceptibility of various substances in the vapor and liquid state.

Substance	mol. sus. $\times 10^6$ vapour	mol. sus. $\times 10^6$ liquid*
Methyl acetate	51	45, Pe. 45, A. 53, K.
Ethyl formate	50	45, Pe.
Carbon-tetrachloride	79	70, Hn.
Chloroform	73	70, Ml. 62, Hn.
Ether	70	60, A. 63, Hn.
N. Pentane	82	68, A.
N. Hexane	89	80, A.
N. Heptane	97	92, A.
Methyl formate	38	33, A.
Acetone	34	40, A.
Carbon disulphide	75	45, Hn.
Benzene	83	57, Pe. 56, B and Z.

* In L. B. Tables Hn, Henrichsen; Pe, Pascal; Ml, Meslin; K, Koenigsberger. A, Additive law. B and Z. Berkman & Zocher. Zeits. f. Phys. Chemie. **124**, 318 (1926). The molar susceptibilities are calculated to the nearest numbers from the data given by the authors.

On calculating the value of the susceptibility of the CH_2 group from the difference in the values for $C_3H_6O_2$ and $C_2H_4O_2$ it is found to be 11.2×10^{-6}, nearly the same as was deduced by Pascal from liquid measurements. Because of various experimental difficulties met with in the measurements in the vapor state, the results are accurate only up to about 6 percent.

DISCUSSION OF EXPERIMENTAL RESULTS

The susceptibility per gram molecule determined from the vapor state is in many cases nearly equal to that determined from the liquid state. In the case of CS_2 and C_6H_6 the gram molecular susceptibility in the vapor state appears to be much higher than can be accounted for by experimental errors. The two isomers methyl acetate and ethyl formate have the same susceptibility. In many organic compounds Oxley[3] found a change of susceptibility in passing from the crystalline solid to the liquid state. Honda[4] and Owen[5] found that many elements undergo a change of susceptibility at their melting points. Whether the approach of the neighboring molecules in the liquid state is sufficient to cause any such change as was observed in the cases mentioned above is now uncertain. As such an enormous difference as was observed in CS_2 is difficult to reconcile with our present state of knowledge, arrangements for further investigation by a different method are being made, and it is premature at present to attempt an explanation.

In conclusion I wish to express my gratitude to Professor C. V. Raman, F.R.S., at whose suggestion this problem has been taken up. The investigation was carried out in the Laboratory of the Indian Association for the Cultivation of Science.

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[3] A. E. Oxley, Phil. Trans. **A214,** 109 (1914).

[4] Honda, Ann. d. Physik **32,** 1027 (1910).

[5] Owen, Ann. d. Physik **37,** 657 (1912).