The Magnetic Susceptibilities of the Vapors of Benzene and Carbon Tetrachloride

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An apparatus has been constructed for measuring at elevated temperatures and at independently controlled pressures the magnetic susceptibility of vapors of substances which are normally in the liquid or solid state. Besides greatly increasing the range of substances for which such measurements can be made, the measurement at elevated temperatures is believed to permit considerably greater accuracy than has been attained previously in the susceptibility measurements on vapors. Determinations of the susceptibilities of the vapors of benzene and carbon tetrachloride have been carried out at 110°C. The extreme limits of uncertainty in the results are estimated to be 3 percent. The values found for the mass susceptibilities of the vapors are in very close agreement with values which have been obtained for the liquids.

INTRODUCTION

INVESTIGATIONS of the magnetic susceptibility of vapors and gases have been concerned mainly with substances which are gases at ordinary temperatures. The first and most extensive measurements of magnetic susceptibilities of substances which are liquids at ordinary temperature were made by Vaidyanathan.[1,2] Using a Curie balance-type of apparatus, Vaidyanathan investigated the vapors of twelve organic compounds whose boiling points range from 30° to 100°C. Nine of these substances were reinvestigated by the Faraday test-body method. The values obtained by the two methods differed by an average of about 9 percent. For most of the substances investigated the measured values of the susceptibilities of the vapors differed from the best values for the liquids by no more than the estimated experimental error. For benzene and carbon disulfide, however, the differences were about 35 percent and were considered to be too large to be accounted for by experimental error.

Sivaramakrishnan[3] measured the susceptibility of benzene vapor by the Faraday method and obtained a value intermediate between the two values of Vaidyanathan. Rao and Varadachari[4] pointed out that both Vaidyanathan and

Sivaramakrishman had assumed the validity of Boyle's law for the vapors. Using corrected vapor densities they found much better agreement between vapor and liquid benzene, but stated that for carbon disulphide the susceptibility of the vapor was still 30 percent greater than for the liquid.

Yanus and Shur[5,6] investigated the vapors of benzene and carbon disulfide by a method that does not involve the use of a test body. They concluded that the susceptibilities of the vapors of both substances are practically the same as those of the liquids. A like result was obtained for bromine vapor.[7]

Except for Yanus and Shur's investigation of bromine vapor, which was carried out at 60°C, all the measurements of the magnetic susceptibilities of vapors of substances which are normally liquids have been carried out at room temperature. Because of the low vapor densities at room temperature and of the difficulty of accurately determining the density, and because of the difficulty of avoiding errors caused by surface adsorption on the test body, it is doubtful that the accuracy and reliability of these measurements are comparable with those of the most accurate measurements on gases.

The apparatus used in this investigation was designed to make measurements of the susceptibility of substances expected to be paramagnetic in the vapor state, and of substances which are

[1] V. I. Vaidyanathan, Phys. Rev. **30**, 512 (1927).
[2] V. I. Vaidyanathan, Ind. J. Phys. **2**, 1935 (1928).
[3] G. Sivaramakrishnan, J. Annamalai Univ. **3**, 48 (1934).
[4] S. R. Rao and P. S. Varadachari, Nature **134**, 812 (1934).
[5] R. I. Yanus and J. Shur, Nature **134**, 101 (1934).
[6] J. Shur, Physik. Zeits. Sowjetunion **11**, 194 (1937).
[7] J. Shur and R. I. Yanus, Physik. Zeits. Sowjetunion **7**, 501 (1935).

known to be highly associated in the liquid state. Most of these substances have a relatively high boiling point. Both to increase the range of substances which could be tested and to obtain the highest accuracy, it was considered essential to have an apparatus with which measurements could be carried out over a considerable range of temperatures and at independently controlled pressures.

Because of the war it was necessary to discontinue the experiments after making measurements on benzene and carbon tetrachloride. These substances were chosen for the initial measurements because they were considered most suitable for the thorough testing of the apparatus. Because the results are believed to be more accurate than any previously reported for vapors, it was felt that they should be published.

APPARATUS AND EXPERIMENTAL PROCEDURE

The magnetic measurements were made by the Faraday test-body method. This consists of the comparison of the torques produced by a non-homogeneous magnetic field on a test body when suspended in the gas or vapor to be measured, and when suspended in a gas of known susceptibility. In the present investigation the method of obtaining the homogeneous field and the design of the test body were patterned largely on those of Rao and Sivaramakrishman.[8] Figure 1 shows the apparatus used.

The non-homogeneous field is produced by the arrangement shown in Fig. 1(b). The pole pieces tapered from a height of 10 cm and a width of 6 cm, to a height of 8 cm and a width of 4 cm. The air gap was 5 cm in width. Vertical cylindrical iron bars having a diameter of 2 cm were placed symmetrically at the sides to increase the inhomogeneity of the field. This arrangement produced a field which was symmetrical about two vertical planes, one parallel and the other perpendicular to the direction of the field at the center of the gap. When the magnet was energized the field strength at the center of the gap was approximately 3000 oersteds.

The test body consisted of four thin glass tubes

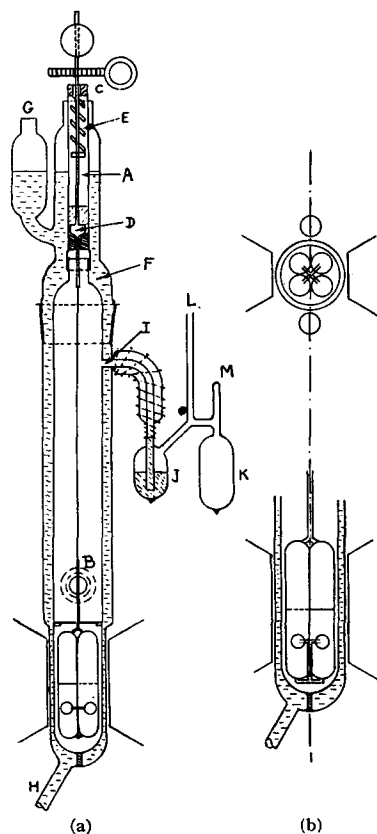[8] S. R. Rao and G. Sivaramakrishman, Proc. Phys. Soc. London **46**, 318 (1934).

FIG. 1.

12 mm in diameter, sealed together at the top as shown in Fig. 1(b). Two of the tubes were 8 cm long and were located on opposite sides of the central axis. They were closed and evacuated. Each of the other pair of tubes was of half-length and was open at the bottom. This design, which differs essentially from that of Rao and Sivaramakrishman only in that the latter used full-length open tubes, was intended to minimize errors resulting from surface adsorption. For, when oriented in the field as shown in the figure, the surface area exposed to the vapor at a given field strength and at corresponding distances from the symmetric planes was approximately the same for the open as for the closed tubes, the former having a double surface. The weight of the test body was approximately 8 grams.

In order to obtain an approximate magnetic balance when the test body was suspended in a vacuum, a small glass ball was placed below each of the open tubes. They were held in

position by small glass rods attached to a central stem.

The test body was suspended from rod (A) of Fig. 1(a) by means of a 50 cm phosphor bronze wire having a diameter of about 0.03 mm. A null method was used for comparing torques on the test body. This consisted of balancing the torque on the test body by a rotation of the rod (A) by means of a worm screw. Angular positions were observed by means of mirrors, one at the top of rod (A) and the other on the stem of the test body. The latter mirror was observed through two windows (B) separated by an evacuated space.

The rod (A) was held in position by a bearing (C) and a ground joint (D). A continuous pressure was maintained on the ground seat by means of a spring acting on a collar attached to the rod. The ground joint was made gas tight by a small amount of Wood's metal above the joint.

A constant temperature was maintained by the circulation of a liquid from a thermostatically controlled temperature bath through the chamber (F) which surrounds the tube containing the vapor. There was no mechanical connection between the apparatus and the outer circulating system. The liquid entered at (G) from an overflow of the bath and flowed out at (H) into a pump which returned the liquid to the bath. Except for the part between the pole pieces, the apparatus was well insulated.

The highest temperature at which the apparatus could be operated was limited by the available circulating fluids. All the experiments here reported were made at 110°C using ethylene glycol as the circulating fluid. However, in preliminary experiments, measurements were made at temperatures up to 270°C using vegetable oil. At high temperatures some instability was experienced because of vapor convection currents. To minimize these currents a thin diaphragm was inserted across the tube immediately above the test body.

The vapor was introduced through the side tube (I) which dipped into the liquid reservoir (J). A non-uniformly wound heating coil surrounding the tube produced a temperature gradient along the tube, the highest temperature occurring at the top. Vapor was introduced into the system by slowly admitting gas into an outer glass system connected to the reservoir, thus forcing the liquid up the tube until the desired vapor pressure was attained. The vapor pressure characteristic of the temperature of the top of the liquid column was equal to the outer gas pressure less the hydrostatic pressure of the liquid column. Thus the vapor pressure could be easily controlled and its value could be accurately determined. This method of controlling vapor pressures is essentially that of Zahn.[9]

CO_2 was used as the comparison gas. Its susceptibility is relatively large and is probably as accurately known as that of any other diamagnetic gas. Before admitting the gas into the apparatus it was passed through a tube containing heated copper shavings to remove any traces of oxygen and through a tube containing anhydrone to remove water vapor.

Experiment showed that the torque produced on the test body when in a magnetic field was proportional to the pressure. So, to obtain a calibration measurements were made at only two pressures. A lower pressure of 2 cm of mercury was used, as it was found that at pressures below $\frac{1}{2}$ cm of mercury there was appreciable drift in the neutral position, possibly caused by thermal effects.

A reading was made as follows: With no current in the magnet coil, the rod (A) was rotated until the test body had the desired position as indicated by the mirror attached to its stem. The magnetic field was then brought up to a fixed value and the rotation of rod (A) necessary to restore the position of the test body was noted. The magnet-coil circuit was then opened and another determination of the zero point was made.

This procedure was followed, first with CO_2 at a pressure of about 2 cm, then for the same gas at a pressure of about 70 cm, and then repeated again at the low pressure of about 2 cm. The difference in the rotations necessary to balance the effect of the field at the two pressures was thus determined. Successive trials gave consistent results. The sensitivity was such that a rotation of rod (A) of one degree corresponds to a change of volume susceptibility of approximately 2×10^{-10}.

[9] C. T. Zahn, Rev. Sci. Inst. 1, 299 (1930).

Before introducing the test liquid the apparatus was evacuated and filled with CO_2 through the tube (L). The tube (M) was then broken off and the CO_2 was permitted to flow slowly from (L) out through (M) during the entire time the latter was open to the atmosphere. The test liquid was introduced into the reservoir (K) through (M) and about a third of the liquid was boiled off. It was then solidified by surrounding the reservoir with a low temperature bath. Tube (M) was again resealed.

With the test substance in a solid state the apparatus was evacuated. The low temperature bath was then transferred from reservoir (K) to reservoir (J) and about one-half the liquid was distilled into (J).

Measurements were then made at low and high vapor pressures using the same procedure as was outlined for CO_2 above. To obtain a low vapor pressure of no more than a few cm of mercury the reservoir was surrounded by a cold-water bath.

The benzene and carbon tetrachloride used were the best obtainable product of Eimer and Amend and were redistilled before using.

RESULTS

The measurements with the apparatus gave a direct comparison of volume susceptibilities of the vapors and of CO_2. The results can be translated into a comparison of the mass susceptibilities only if the densities are known. At the highest pressures used the densities of benzene and carbon tetrachloride vapors are expected to be several percent greater than the perfect gas values. For a better approximation the densities were calculated on the basis of Berthelot's law. The results are given in Tables I and II. Five separate determinations were made for each vapor.

TABLE I. Mass susceptibility of benzene vapor at 110°C.

Cm Hg		$-x \times 10^6$	
Lower pressure	Higher pressure	Boyle's law	Berthelot's law
8.5	33.3	0.700	0.690
8.5	67.5	0.706	0.688
5.0	65.0	0.724	0.697
5.0	65.1	0.722	0.695
4.0	65.8	0.730	0.713
mean		0.716	0.697

TABLE II. Mass susceptibility of carbon tetrachloride vapor at 110°C.

Cm Hg		$-x \times 10^6$	
Lower pressure	Higher pressure	Boyle's law	Berthelot's law
3.0	59.7	0.441	0.431
4.0	57.4	0.447	0.438
1.6	26.07	0.436	0.432
2.5	66.0	0.437	0.427
7.0	57.0	0.440	0.430
mean		0.440	0.432

DISCUSSION

The following unique features of the apparatus and method used in this investigation are believed to be important for the attainment of the highest accuracy and reliability in measurements on vapors:

(a) By carrying out measurements at 110° it was possible to use much larger vapor densities and at the same time to limit the vapor pressures to a smaller fraction of the saturation pressure than in previous experiments. The result has been to increase the effective sensitivity, to limit the amount of adsorbed vapor on the test body and to minimize its relative importance, and to permit a more accurate estimate of the vapor density.

(b) The design of the test body to give equal exposed surface in each of the four quadrants further minimized the effect of adsorbed vapors.

(c) The large air gap and relatively large separation between the test body and pole pieces made for high stability as evidenced by a negligible change in the calibration constant over a period of several months and by its insensitivity to small adjustments in the horizontal position of the suspension support.

(d) Experiment showed that the rather lengthy procedure which was used in this investigation for making magnetic measurements was essential to obtain consistent results. The usual procedure of observing the change in torque produced by a constant field when vapors or gases are introduced or when the density is varied was used in preliminary tests, but did not give as consistent results, probably because of the small shifts in zero position which were frequently observed when the density was increased or decreased. Similar shifts were observed by Vaidyanathan.[2]

Aside from accidental errors of measurement,

possible sources of error were considered to be adsorption of vapor on the test body, uncertainty in the density of the vapors, and uncertainty in the susceptibility of the comparison CO_2. In view of the measures taken to minimize the effects of adsorbed vapors the error caused by this factor is believed to be negligible. This is supported by the fact that the results appear to be independent of the vapor pressures used.

To check the accuracy of Berthelot's law for determining the vapor density, data for benzene are available from the very careful measurements of Ramsay and Steele.[10] On p. 513 of the article by Ramsay and Steele are summarized the results of measurements of PV/mT for two samples of benzene, each at temperatures of 99.7° and 129°C, and at four pressures between 320 and 680 mm Hg. Here P, V, and T are the observed pressure, volume, and temperature, respectively, and m is the mass of the sample. Calculation of PV/mT by Berthelot's equation at each of the indicated temperatures and pressures gives values which differ from the experimental values in no case by more than 0.2 percent and in most cases by no more than 0.1 percent. Corresponding data are not available for carbon tetrachloride, but for the saturated vapor the density obtained using Berthelot's law at 110°C is about 1.5 percent less than the experimental value given by Young,[11] while for benzene the calculated value is approximately 1 percent too small. Since the vapor pressures used in the present experiment were less than 40 percent of the saturation pressure it is considered that the uncertainty in the densities is not more than 0.2–0.3 percent.

The molar susceptibility of CO_2 was taken to be -20.8×10^{-6}. This value was given by Stoner,[12]

TABLE III.

Observer	$-\chi \times 10^6$ for CCl_4 Reported values	$-\chi \times 10^6$ for C_6H_6 Reported values	Corrected[4] for density
Vaidyanathan[1]	0.514±0.030	1.06 ±0.064	0.827
Vaidyanathan[2]	0.500±0.038	0.948±0.075	0.760
Yanus and Shur[5]		0.756±0.038	
Sivaramakrishman[3]		0.796	0.732
Reber and Boeker	0.432±0.013	0.697±0.021	

who estimated the extreme limits of error to be about 2 percent. Subsequently Rao and Sivaramakrishman[8] obtained a value of $-20.88 \pm .08 \times 10^{-6}$ and Sivaramakrishman[3] reported a value of -20.79×10^{-6}.

Considering all sources of error the extreme limits of uncertainty in the susceptibilities as given by the averages of the last columns of Tables I and II are considered to be about 3 percent.

Table III gives the susceptibilities of the vapors of benzene and carbon tetrachloride and the approximate limits of error which have been reported by various observers. For convenience of comparison all reported values have been converted into gram-mass susceptibilities. The last column gives the values of the susceptibilities of benzene obtained by Rao and Vardichari from the results of Vaidyanathan and Sivaramakrishman by correcting for deviations from Boyle's law. Corrections were not given for carbon tetrachloride. It is observed that all previous values of the susceptibility of benzene vapor are larger than the value obtained by the writers, though Sivaramakrishman's corrected value is only 5 percent larger and that of Yanus and Shur is only 8 percent larger than the value obtained in this investigation.

The susceptibilities of benzene and carbon tetrachoride liquids probably have been studied more extensively than those of any other organic compounds. Seely[13] gives for benzene an average value of -0.7038×10^{-6} obtained from the results of ten observers and for carbon tetrachloride an average value of -0.4308×10^{-6} obtained from the results of seven observers. On comparing these values with those of four of the most recent observers[13-16] who studied both liquids it is found that the maximum difference is 0.5 percent for carbon tetrachloride and 0.9 percent for benzene.

The differences between the values of the mass susceptibilities of the vapors obtained in the present investigation and the average values for the liquids given by Seely are less than 1 percent.

Theoretically any appreciable difference be-

[10] W. Ramsay and B. D. Steele, Phil. Mag. 6, 492 (1903).
[11] S. Young, Proc. Roy. Dublin Soc. 12, 374 (1910).
[12] E. Stoner, *Magnetism and Matter* (Methuen and Company).

[13] S. Seely, Phys. Rev. 49, 812 (1936).
[14] S. P. Ranganadham, Ind. J. Phys. 6, 421 (1931).
[15] S. R. Rao and G. Sivaramakrishman, Ind. J. Phys. 6, 509 (1932).
[16] G. F. Boeker, Phys. Rev. 43, 756 (1933).

tween the mass susceptibilities of the vapor and liquid would appear to require inter-molecular forces in the liquid state sufficient to produce a substantial alteration of electronic orbits. Certainly, for liquids composed of symmetrical molecules such as benzene and carbon tetrachloride it would be difficult to account for inter-molecular forces of a type to effect importantly the susceptibility. It is noteworthy that neither Oxley[17] nor Cabrera and Fahlenbrach[18] found any detectible difference in the magnetic susceptibilities of benzene in the crystalline and liquid states, though small differences were found for other organic substances. Cabrera

[17] A. E. Oxley, Phil. Trans. **214A**, 109 (1914).
[18] B. Cabrera and H. Fahlenbrach, Zeits. f. Physik **85**, 568 (1933); **89**, 682 (1934).

and Fahlenbrach found that in general the change in susceptibility in passing from the crystalline to the liquid state was smaller the smaller the electric dipole moment of the molecules. Further evidence that inter-molecular forces do not have much effect on the susceptibility of non-polar liquids is given by measurements on non-polar liquid mixtures[13-15] which have shown that the additivity principle of susceptibility holds to within 0.5 percent. The results of the present investigation are consistent with the hypotheses that for benzene and carbon tetrachloride there is negligible difference between the mass susceptibilities in the vapor and liquid states.

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Statistical Mechanics of Binary Mixtures

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The possibility of specifying both the enumeration of the complexions of an assembly and the evaluation of its configurational energy in terms of the numbers of closest neighbor pairs of sites of various kinds, without introducing parameters explicitly to specify the occupation of individual sites, is considered. The formula obtained on such a basis by Alfrey and Mark is examined. Their work depends on an assumption which at first sight appears plausible. Furthermore, if this assumption could be justified, it would imply that the quasi-chemical equation, which has been introduced in the theory of regular assemblies as an *ad hoc* assumption, could be derived from the Boltzmann equilibrium law and the elementary formulas of algebraic combinations. If a pair of closest neighbor sites of which one is occupied by a molecule of species i and the other by a molecule of species j is called an $i-j$ pair, then it is shown that the assumption made by Alfrey and Mark is equivalent to neglecting the restrictions on the free allocation (amongst the $\frac{1}{2}zN$ pairs available in all) of pairs of different kinds which are inherent in the interconnections of an assembly of interacting particles. It is concluded, therefore, that the assumption in question is unjustified and leads to an incorrect result, and that consequently the quasi-chemical equation is correctly introduced as an *ad hoc* assumption.

1. INTRODUCTION

THE basic problem in the determination of the equilibrium properties of an assembly of interacting particles is the evaluation of the appropriate combinatory factor which is necessary in order to set up the partition function for the assembly. Much work has been devoted to this question. A detailed discussion of it can be dispensed with here as reviews[1,2] have appeared

[1] F. C. Nix and W. Shockley, Rev. Mod. Phys. **10**, 1 (1938).
[2] G. H. Wannier, Rev. Mod. Phys. **17**, 50 (1945).

elsewhere. We consider a simple binary mixture containing N_i molecules of a species i and N_j molecules of a species j on an array of N $(=N_i+N_j)$ sites formed by the points of a regular lattice. It is assumed further that the molecules of each species are of about the same size and roughly spherical in shape, and that the interaction energy of the assembly can be expressed as the sum of closest neighbor contributions. If X_{ii}, X_{ij}, and X_{jj}, respectively, are the numbers of $i-i$, $i-j$, and $j-j$ closest