MAY 1, 1933 PHYSICAL REVIEW VOLUME 43

The Diamagnetism of Carbon Tetrachloride, Benzene and Toluene at Different Temperatures

GILBERT F. BOEKER, *Department of Physics, Columbia University*

(Received March 8, 1933)

An account is given of experiments on the variation, with temperature, of the diamagnetism of benzene, toluene and carbon tetrachloride. The results indicate that the mass susceptibilities of these liquids decrease only slightly, if at all, with increasing temperatures; the change was less than one percent in each case.

IN a previous paper,[1] a description was given of a new and very sensitive device for measuring very small changes in magnetic susceptibility of liquids. Some preliminary results on the variation with temperature of the diamagnetism of water were also given. The results obtained showed certain anomalies, which might possibly be explained on the assumption that the diamagnetism of water depends somewhat on its recent thermal history. If, with the same apparatus, such anomalies are not shown in normal liquids, they cannot be due to peculiarities of the apparatus itself and their interpretation must be looked for elsewhere.

It was therefore decided to make a series of experiments on certain liquids which, in view of their other known properties, might be expected to be normal in their magnetic behavior. The liquids selected were carbon tetrachloride, benzene and toluene.

THEORY AND PROCEDURE

The apparatus used in the present investigation was the same as that used in the investigation mentioned above; for details relating to it the reader is referred to the previous paper.[1]

The principle of the measuring device employed, called a manometric balance, is that of balancing the actions of two magnetic fields on two liquid columns (joined by a mercury column and contained in Pyrex tubes). The strengths of the magnetic fields at the free surfaces, or menisci, being designated by H and H_0, the condition for balance is:

$$\tfrac{1}{2}\kappa H_0^2=\tfrac{1}{2}\kappa_0 H^2, \tag{1}$$

where κ indicates the volume susceptibility of the liquid whose meniscus is in the field H_0, and κ_0 that of the liquid whose meniscus is in the field H. It is customary to express the results of susceptibility measurements in terms of specific susceptibilities, and in our case these are designated by χ, χ_0 so that: $\chi=\kappa/\rho$, and $\chi_0=\kappa_0/\rho_0$, where ρ, ρ_0 denote the densities of the liquids. We can then write in place of Eq. (1):

$$\chi/\chi_0=(\rho_0/\rho)(H/H_0)^2. \tag{2}$$

In general χ_0 represents the specific susceptibility of a standard liquid such as water maintained at a standard temperature T_0, and χ the specific susceptibility of the liquid under test at some temperature T. The densities ρ, ρ_0 can usually be derived from the tables, and if not, can be specifically determined.

Balance is actually effected as follows: The meniscus of one of the liquids (that under experimentation) being kept in a constant field H_0, the other is moved until it reaches a position where the corresponding field strength H is such as to produce a balance, and the positions of the menisci with respect to their corresponding fields are then determined with the aid of two micrometer-telescopes.

The ratio of the magnetic field strengths H, H_0 is determined by a process of calibration whereby a solution of nickel chloride, whose volume susceptibility κ_n can be determined as explained

---

[1] A. P. Wills and G. F. Boeker, Phys. Rev. **42**, 687 (1932).

below, is placed in one branch of the apparatus with its meniscus in the constant field H_0. This solution is balanced against pure water in the other branch of the apparatus, the meniscus of which, at balance, is in a field H, both liquids being maintained at the standard temperature. Usually the surfaces of the liquids were in contact with helium gas, the susceptibility of which is negligible; but in the process of calibration it is more convenient to have the menisci in contact with air; the susceptibility of the air must then be taken into account.

If κ_a denote the volume susceptibility of the air, when balance obtains we shall then have in place of (1):

$$\tfrac{1}{2}(\kappa_n-\kappa_a)H_0^2=\tfrac{1}{2}(\kappa_0-\kappa_a)H^2$$

and hence:

$$\left(\frac{H}{H_0}\right)^2=\frac{\kappa_n/\kappa_0-\kappa_a/\kappa_0}{1-\kappa_a/\kappa_0},$$

where κ_a/κ_0 is a small quantity. With sufficient approximation the last equation can be written:

$$\left(\frac{H}{H_0}\right)^2=\frac{\kappa_n}{\kappa_0}+\frac{\kappa_a}{\kappa_0}\left(\frac{\kappa_n}{\kappa_0}-1\right)+\left(\frac{\kappa_a}{\kappa_0}\right)^2\left(\frac{\kappa_n}{\kappa_0}-1\right). \quad (3)$$

To determine the value of κ_n in terms of κ_0, a solution of nickel chloride in water was prepared which was neutral against helium gas at the standard temperature 22.7°C. With this neutral solution, several diamagnetic solutions were made, each of which was prepared by adding a mass m of neutral solution to a mass μ of pure water. By Wiedemann's law:

$$(m+\mu)\chi_n=\mu\chi_0,$$

whence

$$\chi_n/\chi_0=1/(1+\delta), \quad \text{where} \quad \delta=m/\mu.$$

If ρ_n, ρ_0, respectively, denote the density of such a diamagnetic solution and that of pure water, and if χ_n, κ_n denote the mass and volume susceptibilities of the diamagnetic solution, and χ_0, κ_0 those of pure water, then, since $\rho_n\chi_n=\kappa_n$ and $\rho_0\chi_0=\kappa_0$, we can write:

$$\kappa_n/\kappa_0=(\rho_n/\rho_0)(1/(1+\delta)). \quad (4)$$

THE MAGNETIC SUSCEPTIBILITIES OF CARBON TETRACHLORIDE, BENZENE AND TOLUENE RELATIVE TO WATER

In order to determine the ratio of the magnetic susceptibility of each organic liquid used to that of water, the liquid was balanced against an aqueous nickel chloride solution, the susceptibility of which was known in terms of that of water. The menisci being in contact with air, when balance obtains we have in place of (1):

$$\tfrac{1}{2}(\kappa_L-\kappa_a)H^2=\tfrac{1}{2}(\kappa_n-\kappa_a)H_0^2 \quad (5)$$

where κ_L is the volume susceptibility of the organic liquid; in what follows the subscript L refers to this liquid. The other symbols have the significance previously assigned to them. From Eqs. (4) and (5) we obtain:

$$\frac{\chi_L}{\chi_0}=\frac{\rho_n}{\rho_L(1+\delta)}\left[\left(\frac{H_0}{H}\right)^2+\frac{\kappa_a}{\kappa_n}\left(1-\left[\frac{H_0}{H}\right]^2\right)\right]. \quad (6)$$

The mass susceptibility of water at 22.7°C is taken as -0.720×10^{-6},[2] and, with this value for water, the value for the mass susceptibilities of carbon tetrachloride, benzene and toluene, given in the last column of Table I, were obtained.

The benzene and carbon tetrachloride were of the best available grade obtainable from

TABLE I. *Mass susceptibilities.* I.C.T., International Critical Tables (Pascal, Ishiwara); T and S, Trew and Spencer, Proc. Roy. Soc. **A131**, 209 (1931); S.P.R., S. P. Ranganadham, Ind. J. Phys. **6**, Part 5, 421 (1931); R and S, S. R. Rao and G. Sivaramakrishnan, Ind. J. Phys. **6**, Part 6, 509 (1932); G.F.B., Gilbert F. Boeker.

	I. C. T.	T and S	S. P. R.	R and S	G. F. B.
Carbon tetrachloride	-0.429×10^{-6}	-0.542×10^{-6}	-0.4313×10^{-6}	-0.432×10^{-6}	-0.433×10^{-6}
Benzene	$-.712\times10^{-6}$	$-.732\times10^{-6}$	$-.7042\times10^{-6}$	$-.702\times10^{-6}$	$-.698\times10^{-6}$
Toluene	$-.729\times10^{-6}$	——	——	——	$-.712\times10^{-6}$

---

[2] -0.720×10^{-6} is the commonly accepted value for 20°C.

Merck; the toluene was a C.P. product of Eimer and Amend and was redistilled. Each liquid was vigorously boiled before using in order to eliminate dissolved gases.

VARIATIONS OF SUSCEPTIBILITIES WITH TEMPERATURES

(a) Carbon tetrachloride

In Fig. 1 a curve is shown giving the ratio of the mass susceptibility at temperature T to that at 20°C for the temperature range 10 to 50°C and also a curve is given for the volume susceptibility of a sample of carbon tetrachloride obtained from the Merck Chemical Company; the points represented by the Δ's indicate results of an experiment on a sample of carbon tetrachloride obtained from the Baker Chemical Company.

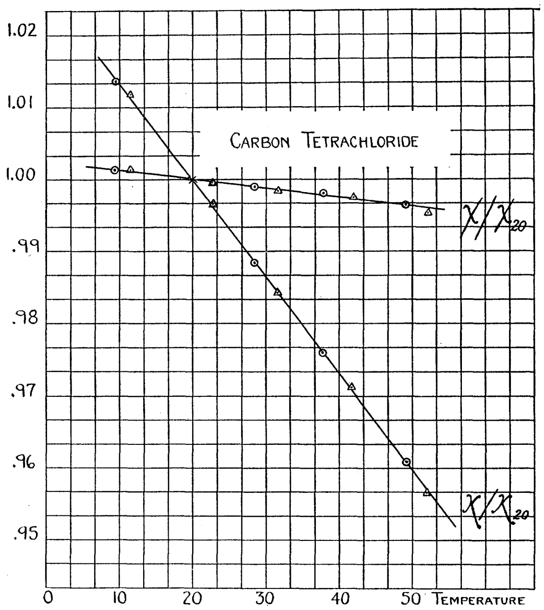

FIG. 1. The ratios of the susceptibilities of carbon tetrachloride *vs.* temperature.

The data from which the curves for Merck's carbon tetrachloride were constricted are given in Table II. The temperatures T in the first column indicate temperatures at which the liquid was balanced against the same liquid kept at the standard temperature (22.7°C). The ratios[3] of the field strengths $(H/H_0)^2$ at the menisci when balance obtains, are given in the second column. From Eq. (1) these numbers represent the ratios of the volume susceptibilities of the liquid at temperatures T to that at the standard temperature (22.7°C). The ratios of the volume susceptibilities to that at 20°C, given in the third column, were obtained from numbers in the second column by a simple transformation; to determine the corresponding ratios of the mass susceptibilities, given in the last column, the ratios of the volume susceptibilities in the third column were multiplied by the ratios of the densities given in the fourth column. The density ratios were obtained from data given in the *International Critical Tables.*

TABLE II. *Data on carbon tetrachloride.*

T	$(H/H_0)^2=\kappa/\kappa_{22.7}$	κ/κ_{20}	ρ_{20}/ρ_t	χ/χ_{20}
9.5	1.0173	1.0139	0.9874	1.0011
22.7	1.0000	0.9966	1.0033	0.9999
28.5	0.9919	0.9885	1.0105	0.9989
37.95	0.9793	0.9760	1.0223	0.9978
49.4	0.9642	0.9609	1.0372	0.9966

No variation of the magnetic susceptibility of carbon tetrachloride depending on its previous thermal treatment could be detected; the susceptibility of the liquid was measured at 22.7°C, then the temperature was lowered to about 4°C and held there for approximately one-half hour; the temperature was again raised to 22.7°C and after a period of twenty minutes, the magnetic susceptibility was found to be the same within experimental error. Corresponding results were found for similar experiments at higher temperatures.

(b) Benzene

In Fig. 2 curves are given for χ/χ_{20} and for κ/κ_{20} as functions of the temperature for benzene obtained from Merck Chemical Company, obtained in a manner quite analogous to that outlined for carbon tetrachloride. The results shown by these curves were confirmed by repeated experiments on the same liquid. The results of a temperature run upon a sample of benzene obtained from the Baker Chemical

---

[3] The method of obtaining this ratio is described, in detail, in the previous paper, reference 1.

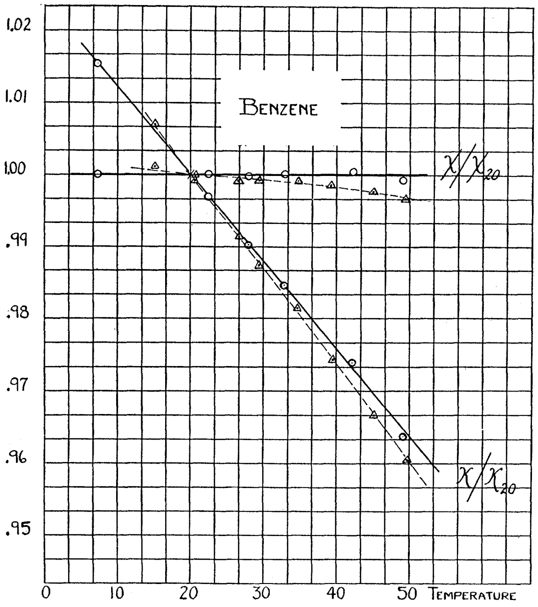

FIG. 2. The ratios of the susceptibilities of benzene *vs.* temperature.

Company are indicated by the Δ's. The lack of agreement is striking, and is probably due to a difference in the composition of the liquids themselves.

The data for the curves shown above for Merck's benzene are given in Table III. The significance of the numbers in the various columns and the method of finding them are identical with those outlined above in the case of carbon tetrachloride. As in the case of carbon tetrachloride, no variation of the magnetic susceptibility with previous thermal treatment could be detected.

TABLE III. *Data for benzene.*

T	$(H/H_C)^2=\kappa/\kappa_{22.7}$	κ/κ_{20}	ρ_{20}/ρ_T	χ/χ_{20}
7.75	1.0184	1.0153	0.9850	1.0000
22.7	1.0000	0.9970	1.0033	1.0003
27.9	0.9931	0.9901	1.0098	0.9998
32.8	0.9875	0.9845	1.0159	1.0002
42.15	0.9765	0.9736	1.0279	1.0007
49.3	0.9666	0.9637	1.0371	0.9995

(c) Toluene

In Fig. 3 curves are given for χ/χ_{20} and for κ/κ_{20} as functions of the temperature, for toluene obtained from the Baker Chemical Company. The results of a temperature run on a sample of toluene obtained from Eimer and Amend are indicated by Δ's; this sample was carefully redistilled before using.

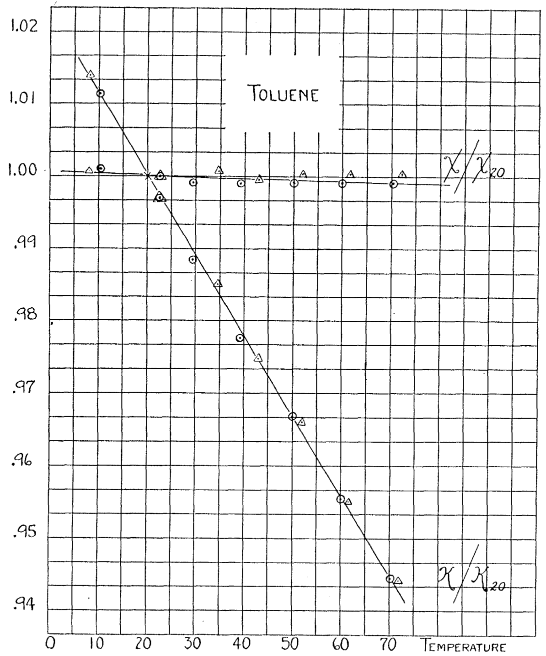

FIG. 3. The ratios of the susceptibilities of toluene *vs.* temperature.

The data for the run on Baker's toluene are given in Table IV; as in the case of carbon tetrachloride and benzene, no variation of the magnetic susceptibility with previous thermal treatment could be found.

TABLE IV. *Data on toluene.*

T	$(H/H_0)^2=\kappa/\kappa_{22.7}$	κ/κ_{20}	ρ_{20}/ρ_T	χ/χ_{20}
10.25	1.0142	1.0111	0.9897	1.0007
22.7	1.0000	0.9969	1.0029	0.9998
29.95	0.9917	0.9886	1.0108	0.9993
39.9	0.9806	0.9776	1.0220	0.9991
50.0	0.9699	0.9669	1.0336	0.9994
60.0	0.9586	1.9556	1.0456	0.9992
70.1	0.9473	0.9444	1.0581	0.9993

DISCUSSION

The variation of the magnetic susceptibilities of diamagnetic liquids has been studied by various observers. S. R. Rao and G. Sivaramakrishnan[4] conclude on the basis of the as yet unpublished work of N. Iyer that the mass susceptibility of the "ordinary" (normal ?) organic liquids do not vary with temperature. On the other hand they conclude, on the basis of the experiments of R. N. Mathur,[5] that if the liquids are highly associated this variation may become quite large. Mathur himself concludes, on the basis of his experiments, that the variation of the mass susceptibilities with temperature of the aromatic liquids is greater than for the aliphatic liquids. The results, however, of the present investigation on the aromatic liquids benzene and toluene indicate that the variation of their mass susceptibilities with temperature is very small, being less than one-half of a percent.

In the experiments described above, under favorable conditions[6] a variation in the ratio of volume susceptibilities of ±0.0002 can be detected; it is estimated that as far as the measurements themselves are concerned (neglecting impurities and assuming the validity of Wiedemann's law), the results may be in error by about ±0.0009.

Cognizance was of course taken of possible errors due to the presence of the vapor of the liquid in contact with the menisci; but various tests showed that the mass of this vapor was far from that of a saturated vapor at the temperature of the warmer meniscus and hence that no correction on account of the vapor was necessary.

The results obtained with the normal liquids, benzene, toluene and carbon tetrachloride constitute a thorough test of the behavior of the apparatus, and make it improbable that the apparent anomalies described in the previous paper on water[1] can be attributed to the apparatus itself.

I wish to express my appreciation for the help given to me by Professor A. P. Wills, under whose direction this investigation was carried out. I also wish to thank Mr. D. B. Woodbridge for many valuable suggestions and continued assistance.

---

[4] Ind. J. Phys. **6**, Part 6, 527 (1932).

[5] Ind. J. Phys. **6**, Part 3, 207 (1931).

[6] At the higher temperatures, the determination of the balance point becomes extremely difficult because of the increased drifting of the particles suspended in the liquid under test.