Determination of Magnetic Susceptibilities of Paramagnetic Gases by an Improved Viscometer Method

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An improved viscometer method has been applied to the determination of the magnetic susceptibility of a paramagnetic gas and found to be of use in the analysis of a paramagnetic gas mixed in a diamagnetic gas. The magnetic susceptibilities of oxygen and nitrogen monoxide have been determined to within ±0.5% using a saturated aqueous solution of sodium chloride as the working liquid.

The present authors reported an improved viscometer method[1] for the determination of the magnetic susceptibilities of diamagnetic liquids by measuring the time of flow of liquid under nitrogen through the capillary of a modified Ubbelohde type viscometer under an external magnetic field.

In the present study, some applications of the viscometer method will be described concerning the magnetic susceptibilities of paramagnetic gases and the analysis of paramagnetic species in a gaseous mixture, *e.g.*, oxygen in air.

Theoretical

A capillary viscometer cell of modified Ubbelohde type as shown in Fig. 1 was placed in a magnetic field so that the lower end of the capillary was in the center of the pole gap of an electromagnet, while the capillary extended vertically, through the inhomogeneous region, outside the field. The liquid in the capillary of the cell was forced to flow down by the dual action of the gravitational and magnetic forces acting on it and its enviromental gas which was in contact with the liquid and circulating in the dead space below the capillary.

Assuming a liquid of certain volume requires time t_H to flow through the capillary of the viscometer under action of an external magnetic field of strength, H, then it follows that

$$\frac{1}{t_H} = C\left[\rho_L g\tilde{h} + \frac{1}{2}(\kappa_L - \kappa_G)H^2\right], \tag{1}$$

where C is a constant determined by the geometry of the cell and the viscosity of the flowing liquid, g is the acceleration due to gravity, $\tilde{h}$ is the mean effective head of liquid, ρ_L is the density of the liquid, κ_L represents the volume magnetic susceptibility of the liquid phase (L) in equilibrium with the gas phase (G) whose susceptibility is κ_G, where the gas is supposed to dissolve in the liquid without chemical reaction (solbility β). In the absence of a field, $1/t_0 = C\rho_L g\tilde{h}$ which gives from Eq. 1:

$$\tau_G \equiv \left(\frac{t_0 - t_H}{t_H}\right)_G = \frac{H^2}{2g\tilde{h}\rho_L}(\kappa_L - \kappa_G), \tag{2}$$

where

$$\kappa_L = \kappa^\circ_L + \beta\kappa'_G, \tag{3}$$

κ°_L is the volume magnetic susceptibility of the pure liquid and κ'_G that for the dissolved gas. Generally speaking, the gas considered may be mixture, the most simple case being the two component system consisting of, from the magnetic point of view, a diamagnetic (D) and a paramagnetic (P) species with respective volume fractions x_D and x_P. It is apparent that

$$x_D + x_P + x_V = 1, \tag{4}$$

where x_V is the volume fraction of the working liquid vapor with which the gases are in contact. Denoting by κ°_D and κ°_P the volume magnetic susceptibilities of the dia- and paramagnetic species respectively both in the gaseous pure states at a given temperature T and pressure P, the apparent susceptibility, κ_G, of a gas mixture may thus be written as follows:

$$\kappa_G = \kappa^\circ_D x_D + \kappa^\circ_P x_P + \kappa^\circ_V x_V, \tag{5}$$

where κ°_V denotes the susceptibility of the saturated vapor of the working liquid in the pure state at a given condition of T. Assuming the gas is in equilibrium in contact with the working liquid in the viscometer at constant temperature and pressure and denoting by β°_D and β°_P the solubilities of the two gaseous species D and P, in the pure states respectively, (under the same conditions of T and P) the solubility of a gaseous mixture composed of D and P in a certain liquid may be written as follows:

$$\beta = \beta^\circ_D x_D + \beta^\circ_P x_P. \tag{6}$$

Then, the volume fractions x'_D and x'_P of the two species (D and P) dissolved in the liquid may be expressed as follows:

$$x'_D \equiv \frac{\beta^\circ_D}{\beta}x_D, \qquad x'_P \equiv \frac{\beta^\circ_P}{\beta}x_P, \tag{7}$$

and

$$x'_D + x'_P = 1. \tag{8}$$

For the magnetic contribution, κ'_G, from the gas dissolved in the liquid (L) assuming that the intermolecular interaction between the liquid and dissolved gas is not strong, in analogy to Eq. 5, it may be written as

$$\kappa'_G = \kappa^\circ_D x'_D + \kappa^\circ_P x'_P. \tag{9}$$

Converting the magnetic susceptibility of the i-th species, κ_i, per unit volume into that, χ_i, per unit mass by definition $\kappa_i \equiv \rho_i\chi_i$, and putting $\rho_L \doteqdot \rho^\circ_L$ (ρ°_L is the density of the pure liquid), Eq. 2 may be rewritten with the abbreviation $H^2/2g\tilde{h} \equiv K$:

$$\tau_G = K\left[\chi^\circ_L - \frac{\rho^\circ_D x_D}{\rho^\circ_L}(1-\beta^\circ_D)\chi^\circ_D - \frac{\rho^\circ_P x_P}{\rho^\circ_L}(1-\beta^\circ_P)\chi^\circ_P - \frac{\rho^\circ_V x_V}{\rho^\circ_L}\chi^\circ_V\right], \tag{10}$$

where ρ°_L, ρ°_P, and ρ°_V are the densities of the dia- and paramagnetic gases, D and P, and the vapor of the liquid in the pure states, respectively, at a given T and P. For the paramagnetic gas system ($x_P = 1 - x_V$, $x_D = 0$);

$$\tau_P = K\left[\chi^\circ_L - \frac{\rho^\circ_P(1-x_V)}{\rho^\circ_L}(1-\beta^\circ_P)\chi^\circ_P - \frac{\rho^\circ_V x_V}{\rho^\circ_L}\chi^\circ_V\right], \tag{11}$$

and for the diamagnetic gas system ($x_P = 0$, $x_D = 1 - x_V$);

$$\tau_D = K\left[\chi^\circ_L - \frac{\rho^\circ_D(1-x_V)}{\rho^\circ_L}(1-\beta^\circ_D)\chi^\circ_D - \frac{\rho^\circ_V x_V}{\rho^\circ_L}\chi^\circ_V\right], \tag{12}$$

assuming t_H is measured under the same field strength, *i.e.*, with a common K. Then invariably, irrespective of the working liquid used;

$$\frac{\tau_G - \tau_D}{\tau_P - \tau_D} = \frac{x_P}{x_P + x_D} = \phi_P, \tag{13}$$

where Eq. 4 is considered and ϕ_P is the volume fraction of the paramagnetic component in the gaseous sample. From Eq. 13, it is now possible to make a magnetic a nalysis of a gaseous mixture which is known to involveonly one paramagnetic species. (See below).

In addition to this, the susceptibility of the paramagnetic species in the gaseous state may be obtained in four ways:

(i) from Eq. 10,

$$\chi^\circ_P = -\frac{\rho^\circ_L(\tau_G - K\chi^\circ_L)}{K\rho^\circ_P\phi_P(1-x_V)(1-\beta^\circ_P)}, \tag{14}$$

(ii) from Eq. 11,

$$\chi^\circ_P = -\frac{\rho^\circ_L(\tau_P - K\chi^\circ_L)}{K\rho^\circ_P(1-x_V)(1-\beta^\circ_P)}, \tag{15}$$

(iii) from Eqs. 10 and 12,

$$\chi^\circ_P = -\frac{\rho^\circ_L(\tau_G - \tau_D)}{K\rho^\circ_P\phi_P(1-x_V)(1-\beta^\circ_P)}, \tag{16}$$

(iv) from Eqs. 11 and 12,

$$\chi^\circ_P = -\frac{\rho^\circ_L(\tau_P - \tau_D)}{K\rho^\circ_P(1-x_V)(1-\beta^\circ_P)}, \tag{17}$$

where the second terms of Eqs. 10 and 12 and the last terms of Eqs. 10, 11, and 12 have been considered negligible. Allowing for a deviation of 0.5—1% (approximately -0.5×10^{-6} e.m.u.), one may use Eq. 16 or 17.

Experimental

Materials. Nitrogen and oxygen were obtained from commercial sources with purities exceeding 99.9%. The mixed gases were prepared from these. The gases and air were dried by passage through silica gel and phosphorus pentoxide; commercial 99.0% nitrogen monoxide was used without further drying. Benzene, carbon tetrachloride, 2,2,4-trimethylpentane, and cyclohexane were Dotite Primasol solvents, while toluene, ethyl acetate, hexane, heptane, and acetone were Dotite Spectrosol solvents (Dojindo Co.) and used without purification. Sodium chloride (G. R. grade) was recrystallized twice from water. The water was purified by sub-boiling distillation from a quartz still after deionization.

Capillary Cells. A detailed figure of the cell has been given in a previous paper.[1] The two types of cell used in the present work were found to have slightly different cell-constants, K, *i.e.*, 38.9_3 and 38.7_2 Oe^2 dyn^{-1} cm^{-1}, respectively, at 1 kOe and $13.7_6 \times 10^3$ and $14.7_2 \times 10^3$ Oe^2 dyn^{-1} cm^{-1}, respectively, at the respective maximum magnetic field strengths. The cell constants were determined from Eq. 12 for water under nitrogen, ignoring the second and last terms in Eq. 12 and using -0.720×10^{-6} e.m.u. for the magnetic susceptibility of pure water.[2] Figure 1 and Tables 1 and 2 are derived from using the first type cell and Fig. 2 and Table 3 from the second type.

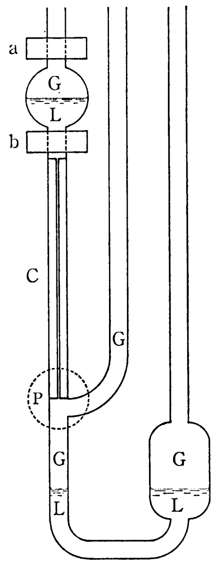

Fig. 1. Schematic representation for the G-L contact in a viscometer cell. P, the position of the pole pieces of electromagnet; a and b, detectors of viscometer; C, capillary; G, sample gas; L, working liquid.

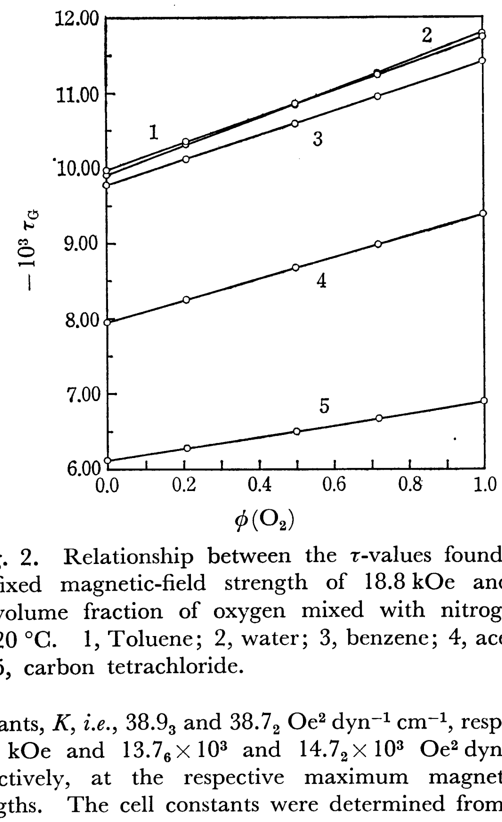

Fig. 2. Relationship between the τ-values found at a fixed magnetic-field strength of 18.8 kOe and the volume fraction of oxygen mixed with nitrogen at 20 °C. 1, Toluene; 2, water; 3, benzene; 4, acetone; 5, carbon tetrachloride.

Magnet. The electromagnet is the same type as used in the previous work.[1] The pole pieces of the magnet were set at a separation of approximately 8 mm for the first type cell and approximately 7 mm for the second type. The highest magnetic field strengths available at a maximum current of 4 A were 18.8 and 19.5 kOe, calibrated with

TABLE 1. τ-VALUES MEASURED IN VARIOUS GASES AND OXYGEN CONTENT IN DRIED AIR AT 20 °C

Liquid	$10^3\tau(N_2)$[a)]	$10^3\tau(\text{Air})$[a)]	$10^3\tau(O_2)$[a)]	$\phi(O_2)$[c)]
Water	-9.90_7	-10.30_5	-11.79_8	0.21_0
Carbon tetrachloride	-6.11_0	-6.27_1	-6.89_2	0.20_6
Acetone	-7.95_3	-8.25_3	-9.38_6	0.20_9
Ethyl acetate	-8.57_9	-8.88_8	-10.06_5	0.20_7
Hexane	-11.95_6	-12.26_5	-13.47_0	0.20_4
Heptane	-11.95_2	-12.32_1	-13.75_2	0.20_5
2,2,4-Trimethylpentane	-12.16_7	-12.52_8	-13.86_7	0.21_2
Cyclohexane	-11.05_7	-11.40_1	-12.71_9	0.20_7
Benzene	-9.78_6	-10.13_4	-11.43_3	0.21_1
Toluene	-9.98_5	-10.35_0	-11.74_5	0.20_7
	Gas-chromatographic analysis			0.210±0.005
	Literature value[b)]			0.2099

a) Mean values obtained from more than 20 measurements at 18.8 kOe. b) International critical Tables, Vol. 1. c) Calculated using Eq. 12.

TABLE 2. MAGNETIC SUSCEPTIBILITY OF OXYGEN MEASURED WITH VARIOUS FLOWING LIQUIDS, IN 10^{-6} e.m.u. AT 20 °C

Liquid	ρ_L g cm^{-3}	p[a)] mmHg	ρ_G[b)] g cm^{-3}	β[c)] cm^3 cm^{-3}	χ from	
					air[d)]	oxygen
Water	0.998	17.5	0.001345	0.0333	$105._8$	$105._6$
Carbon tetrachloride	1.598	91	0.001216	0.2996	$104._6$	$106._6$
Acetone	0.792	184.8	0.001052	0.2736	$107._7$	$107._9$
Benzene	0.880	74.8	0.001244	0.2186	$109._1$	$108._4$
Toluene	0.867	22.2	0.001336	0.179	$99._9$	$101._1$
		Literature values[c,e)]			104.1—108.2	

a) The vapor pressure of liquids at 20 °C: International Critical Tables, Vol. 3. b) Converted from the partial pressure of oxygen under a total pressure of 785 mmHg at 20 °C in the measuring cell, where the standard density, 0.001435 g cm^{-3} at 0 °C, 1 atm is assumed for pure oxygen (International Critical Tables, Vol. 3). c) Gmelin's Handbuch der Anorganischen Chemie, 8 Auflage. d) Assuming $\phi(O_2)=0.2099$. e) International Critical Tables, Vol. 6.

a Yokogawa gauss meter, type 3251. The magnetizing current was automatically kept at a constant value (±0.01%) throughout the measurements.

Measurements. Prior to the measurements the liquid in the cell was saturated with the gas under study by passing the gas through the liquid for about 10 min and the dead space of the cell fully replaced by the gas by means of an operation tube connected to the cell. The τ-value was measured for nitrogen before and after every measurement of τ to check for changes in the liquid under study. Exchange of the two gases was achieved by means of 3-way stop valve that allowed either of the two gases to flow continuously through the operation tube so that the gases and the liquid in the cell was never exposed to the air. The temperature and pressure were kept constant at 20±0.01 °C, and 785±1 mmHg and 798±1 mmHg for the first and second type cells respectively. Details of the automatic measurements have been fully described in a previous paper.[1)] The density of the liquid was measured using a Shibayama Scientific Co. densimeter, type SS-D-200; more than 20 measurements were conducted to yield a mean flow time from which the magnetic susceptibility could be calculated.

Results and Discussion

The experimental results obtained at different mixing ratios of oxygen and nitrogen are shown in Fig. 2. In all cases a straight line relation may be seen, which can be expressed by the following empirical formula;

$$\tau_G = [\tau(O_2)-\tau(N_2)]\phi(O_2) + \tau(N_2), \qquad (18)$$

where $\tau(O_2)$ and $\tau(N_2)$ represent the τ-values measured with a working liquid under flowing of pure oxygen and pure nitrogen, respectively, and $\phi(O_2)$ represents the volume fraction of oxygen in the gas. This equation is identical with that of Eq. 13. The volume fraction of oxygen in air was calculated with the aid of Eq. 13 from the τ-values measured on various working liquid, and the results are shown in Table 1. The observed values of $\phi(O_2)$ for air are found to be reproducible within ±1% and are in good agreement with the literature as well as those given by gas-chromatographic analysis.

The magnetic susceptibility of pure oxygen was estimated with the aid of Eq. 15, from the experimental τ-values as listed in Table 1, where the volume fraction ϕ_P is assumed equal to 0.999, the purity of the oxygen in the gas cylinder used here, the results of which are shown in Table 2 together with the necessary physical data. In most cases, the τ-values obtained were always reproducible to within ±0.05% and the estimated values of χ for oxygen were found to be reproducible to within ±0.5%, in good agreement with the literature except for the case of toluene. Thus, it has been demonstrated that the magnetic susceptibility

TABLE 3. MAGNETIC SUSCEPTIBILITIES OF OXYGEN AND NITROGEN MONOXIDE, IN 10^{-6} e.m.u. AT 20 °C
SATURATED AQUEOUS SODIUM CHLORIDE USED AS THE WORKING LIQUID

H kOe	$10^3\tau(N_2)$	$10^3\tau(NO)$	$10^3\tau(O_2)$	$\kappa^{a,b)}$		$\chi^{b,c)}$	
				NO	O_2	NO	O_2
12.2	-3.84_1	-4.14_4	-4.54_4	0.064_9	0.149_2	$49._5$	$106._7$
15.0	-5.78_3	-6.22_7	-6.84_0	0.063_2	0.149_0	$48._2$	$106._5$
17.2	-7.63_5	-8.22_7	-9.04_4	0.063_8	0.150_5	$48._7$	$107._6$
18.6	-8.98_1	-9.67_5	-10.63_5	0.063_6	0.150_2	$48._5$	$107._3$
19.5	-9.83_1	-10.58_9	-11.64_0	0.063_4	0.150_0	$48._4$	$107._3$
			Literature values[d,e]			48.7 ±0.25	104.1 —108.2

a) The volume susceptibilities at 798 mmHg. b) Calculated by taking the purities, 0.990 (NO) and 0.999 (O_2), for the ϕ_P values, and assuming 13.6 mmHg for the vapor pressure of water saturated with sodium chloride under the total pressure 798 mmHg. (International Critical Tables, Vol. 3.) c) Calculated using densities, 0.001310 g/cm³ (NO) and 0.001399 g/cm³ (O_2), at 798 mmHg. d) Gmelin's Handbuch der Anorganischen Chemie, 8 Auflage. e) International Critical Tables, Vol. 6.

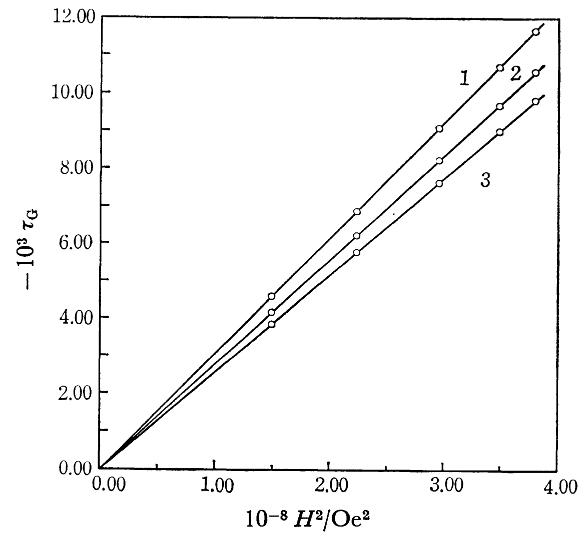

Fig. 3. Relationship between the τ-values found in different gases and the external magnetic-field strength at 20 °C when water saturated with sodium chloride was used as a working liquid. 1, Oxygen; 2, nitrogen monoxide; 3, nitrogen.

of a paramagnetic species mixed singly in diamagnetic gases may be determined by the viscometer method when the working liquid is selected and the gas non-reactive and the vapor pressure and solubility data of the gas in the liquid available. At least, all liquids used here appeared not to be denaturalized throughout the measurements, since no changes in the $\tau(N_2)$-value could be found before and after the measurement of the $\tau(O_2)$-value, were concluded.

In the case of toluene as the working liquid, a considerably low magnetic susceptibility was obtained for oxygen, the deviation being up to 6%. Such a large deviation can not be accounted for by intermolecular interactions such as the charge transfer between the dissolved oxygen and the liquid. A possible explanation may be that the solubility value of oxygen in toluene used here is somewhat erroneous since the value is too small compared with other liquids. On the other hand, the solubility data for the less-familiar gases, *e.g.*, nitrogen monoxide, are rarely found in the literature. Consequently it is advisable to use a liquid in which the solubility of gases is negligibly small, the limit of $\beta<0.001$ being sufficient. Concentrated aqueous solutions of inorganic salts having strong salting out effects may be of use. Water saturated with sodium chloride may be a liquid that can be used conveniently; *i.e.*, one volume of saturated aqueous solution dissolves only 0.00107 volumes of oxygen at 20 °C and 1 atm.[3]

The experimental results obtained by the viscometer method using saturated aqueous solutions of sodium chloride and various gases are shown in Fig. 3. In every case a straight line relation can be seen between τ and H^2, passing through the origin in agreement with Eq. 2. The saturated solution used here was found by analysis to dissolve sodium chloride at 26.17_6 wt% with a density 1.1990 g cm^{-3}, only slightly lower than that reported in the literature,[4] 26.43 wt% and 1.1999 g cm^{-3}, respectively. The magnetic susceptibility, χ_L, of this solution, measured by the present method was found to be $-0.667_8\times10^{-6}$ e.m.u., very closely in agreement with $-0.667_6\times10^{-6}$ e.m.u. estimated by Wiedemann's additivity law using the magnetic susceptibilities of -0.720 and -0.520×10^{-6} e.m.u.,[2] respectively for water and solid sodium chloride. Furthermore, the use of a saturated sodium chloride solution as the working liquid in the viscometer method at the same field strength using the same cell and measuring τ_G and τ_D separately, allowing for a maximum error of approximately ±0.5% at most, the following conventional equation, may be used instead of the more rigorous Eq. 16,

$$\kappa_P^\circ = \rho_P^\circ\chi_P^\circ = \frac{0.800_7}{(1-x_V)\phi_P}\left(\frac{\tau_G}{\tau_D}-1\right)\times 10^{-6}\ \text{e.m.u.}, \qquad (19)$$

where two approximations, $\beta_P^\circ=0$ and $\tau_D=K\chi_L^\circ$ are assumed. From the experimental values of τ measured at different magnetic field strengths, the magnetic susceptibilities of oxygen and nitrogen monoxide have been computed using Eq. 19 and are listed in Table 3. In the range of magnetic fields investigated the results obtained were found to be in good agreement with each other in either species of gases and those reported in the literature. However, according to the experience of the authors, the stronger the field in which the measurements are conducted, the more reliable are the results obtained. Consequently, for the magnetic susceptibilities of oxygen and nitrogen monoxide the values 107.3 and 48.4×10^{-6} e.m.u., respectively are prefered, found at 19.5 kOe, the highest level of the magnetic field strength available in the present study.

The advantages of the present method are: (1) no structural delicacy of the apparatus for its simple mechanism; (2) the measuring system since it is fully automatic, the successive analysis of a gas with respect to paramagnetic species may be possible; (3) it is easy to obtain results with considerable accuracy without taking a lot of precision; (4) the use of saturated aqueous solution of sodium chloride is very convenient for determining the susceptibility of paramagnetic gas species to a sufficient accuracy avoiding considerations of the solubility effect of gases. In addition pure sodium chloride is readily available and ample physicochemical data of its aqueous solutions exists.

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