

Diamagnetism of Alkyl Acetates†

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Susceptibility measurements on the first five primary alkyl acetates and on methanol, made with the manometric balance of Wills and Boeker over the range 5°–70°, are described. The results show a very slight variation of susceptibility with temperature and an indication of increasing temperature dependence for higher members of the acetate series. The molecular susceptibility of CH₂ is

found to be additive in agreement with Pascal's law. The magnetic properties of NiCl₂ solutions are discussed with special regard to the work of Fahlenbrach, and experiments on NiCl₂ solutions as used for calibrating the manometric balance are described. No variation in the calibration depending on the method of preparing the solutions was found.

DIAMAGNETISM OF ALKYL ACETATES

IN the study of the influence of temperature on the susceptibility of organic compounds it is of interest to determine the effect of a regular change in constitution of the molecule such as occurs, for instance, in the chain compounds. The results of Cabrera and Fahlenbrach¹ on the primary alcohols have shown the value of investigating a series as a whole as compared with measurements on a single substance chosen as typical of a group.

In the present investigation susceptibility determinations over a range of temperatures were made on the first five of the primary alkyl acetates, *viz.* methyl, ethyl, *n*-propyl, *n*-butyl, and *n*-amyl, and on methanol. In continuing the work on susceptibilities inaugurated by Wills and Boeker² the alkyl acetates were chosen with a view to supplementing the magnetic data obtained (at room temperature) for the same series by Boorse³ in his measurements of magnetic birefringence. These acetates may be regarded as formed by the successive addition of a CH₂ group to an acetic acid molecule and experiments upon them may be expected to furnish a test of the diamagnetic additivity of the CH₂ group.

Preliminary to the measurements on the organic liquids just mentioned a study was made of the magnetic properties of nickel chloride solutions used in calibrating the magnetic balance

employed in the present investigation in order to make sure that there could be no error in the calibration resulting from a possible variation on the magnetic moment of nickel such as has been recently reported by Fahlenbrach,⁴ whose experiments indicated that the susceptibility of nickel chloride in solution might depend upon the concentration and method of preparing the solutions.

APPARATUS AND METHOD

The apparatus used was the manometric balance of Wills and Boeker.² This is a device for balancing the force exerted by a magnetic field upon a standard liquid by a corresponding force exerted by a second magnetic field upon a liquid whose susceptibility is to be measured. Several modifications, to be mentioned presently, were made, however, resulting in greater facility of operation and economy in the amount of material used. A schematic diagram is shown in Fig. 1 from which certain details have been omitted for the sake of simplicity. P_0 and P indicate the rear faces of two twin pairs of pole pieces which are cemented to the two core faces of an electromagnet. The balance itself is made of Pyrex glass throughout and consists of two branches, one of which is filled with the standard liquid and the other with the liquid whose susceptibility is to be measured. The two liquids are separated by mercury (indicated by the shaded areas of the diagram). Filling can be accomplished by means of the thistle tubes at the top, or, after a preliminary filling, by drawing

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¹ B. Cabrera and H. Fahlenbrach, *Zeits. f. Physik* **85**, 568 (1933).

² A. P. Wills and G. F. Boeker, *Phys. Rev.* **42**, 687 (1932).

³ H. A. Boorse, *Phys. Rev.* **46**, 187 (1934).

⁴ H. Fahlenbrach, *Ann. d. Physik* **13**, 265 (1932); **14**, 521 (1933).

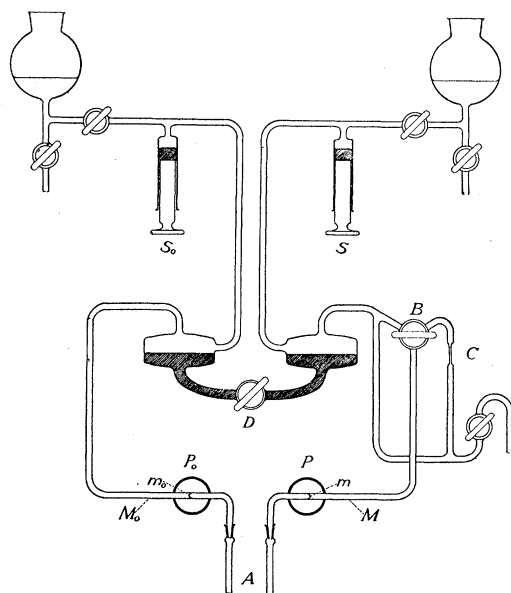


FIG. 1. The manometric balance.

liquid up through the auxiliary tubes A^5 which connect with the apparatus by means of ground glass joints. When the apparatus has been filled the liquid in each branch is drawn back by means of two glass syringes S_0, S so that the two menisci are in the horizontal portions of the meniscus tubes M_0, M between the two pairs of pole pieces corresponding to P_0 and P , as indicated by m_0 and m . These syringes, which replace the heating coils used by Wills and Boeker to adjust the menisci, are operated by fine-thread screws;* their plungers are lubricated with glycerine and are separated from the liquid in the tubes by mercury. The positions of the menisci are determined by cross-hair settings in two telescopes* equipped with micrometer eyepieces. With the stopcock D open and the three-way stopcock B^6 turned to connect the meniscus

⁵ In the original apparatus the only provision for filling was the thistle tubes at the top and this required the use of a large amount of liquid for flushing. The present arrangement makes it necessary to flush only a relatively small portion of tubing.

* Not shown.

⁶ The stopcock B controls a by-pass arrangement which was introduced to permit drawing in fresh liquid whenever desired without disturbing the particles in C . The frequent occurrence of sticking at the menisci when water or aqueous solutions are under test and the untrustworthiness of such readings when even a small trace of sticking is present make necessary frequent cleaning of the tubes

tube M with the capillary tube C , the left meniscus is kept at a predetermined fixed position, while that of the right is varied until balance is obtained. Balance is indicated by the lack of motion of suspended particles in C as observed by a microscope* when the field is thrown on and off. If both branches are filled with the same liquid at the same temperature the balance position gives the zero setting, i.e., the setting for which the fields acting on the two menisci are equal. If now the temperature of the liquid within M_0 is changed (temperature is regulated by means of water jackets* surrounding M_0 and M) or if the liquid within M_0 is replaced by a different liquid, the right meniscus m must be moved into a region of different field strength in order to restore balance. The difference between this new setting and the zero, as determined by the micrometer eyepiece of the telescope, corresponds to a change in susceptibility on the right which can be computed when the apparatus has been calibrated.

If the two meniscus tubes M_0 and M contain liquids whose volume susceptibilities are κ and κ_0 , respectively, and whose free surfaces are in contact with a medium of susceptibility κ_a (air or helium), then the condition for balance under the influence of the magnetic fields when the field strengths at the menisci are H_0 and H , respectively, is:

$$\frac{1}{2}(\kappa - \kappa_a)H_0^2 = \frac{1}{2}(\kappa_0 - \kappa_a)H^2,$$

which may be written

$$\kappa/\kappa_0 = H^2/H_0^2 + (\kappa_a/\kappa_0)(1 - H^2/H_0^2), \quad (1)$$

or, to a sufficient degree of approximation,

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

In measuring temperature variations of susceptibility the liquid is usually the same in both tubes and is maintained in contact with helium by means of a helium bulb* which can be connected with the meniscus tube outlets. One meniscus tube is kept at 20°C while the temper-

with chromic acid cleaning solution and the by-pass proved an important time saver in both cleaning and filling.

* Not shown.

ature of the other is varied. Noting that when helium is used κ_a/κ_0 is negligible, we have from (1) for the case where M is at 20° :

$$\frac{\kappa}{\kappa_{20}} = \frac{H^2}{H_0^2} \quad \text{or} \quad \frac{\chi}{\chi_{20}} = \frac{\rho_{20}}{\rho} \frac{H^2}{H_0^2}, \quad (3)$$

where ρ represents the density and χ the mass susceptibility κ/ρ .

The method of calibrating the field, i.e., the determination of the ratio H^2/H_0^2 for different settings of the variable meniscus, as described in previous papers, has been modified in the present work as follows. The calibrating solutions of nickel chloride were prepared from a mother solution of nickel chloride that had been made neutral against air—not, as in the previous work, against helium—at 20.7°C . A calibrating solution, prepared by adding to m grams of this neutral solution μ grams of water, has a mass susceptibility χ_n determined by the following relation (Wiedemann's law):

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

where χ_s is the mass susceptibility of the neutral solution and χ_0 the susceptibility of water. If we let ρ_s represent the density of the neutral solution and put $m/\mu = \delta$, we have:

$$\frac{\chi_n}{\chi_0} = \frac{1}{1 + \delta} \left(1 + \delta \frac{\rho_0 \kappa_a}{\rho_s \kappa_0} \right), \quad (4)$$

since the volume susceptibility of a solution neutral against air must equal the volume susceptibility of air. In terms of volume susceptibilities (4) becomes:

$$\frac{\kappa_n}{\kappa_0} = \frac{\rho_n}{\rho_0} \frac{1}{1 + \delta} \left(1 + \delta \frac{\rho_0 \kappa_a}{\rho_s \kappa_0} \right). \quad (5)$$

In calibrating the apparatus the right branch is filled with water and the left with a nickel chloride calibrating solution. Then the two menisci, which are left in contact with air, are adjusted as described above until balance is obtained. To determine the ratio H^2/H_0^2 for the two meniscus positions at balance, corresponding to a scale reading s , say, for the right-hand meniscus, the expression for κ_n/κ_0 from (5) is substituted for κ/κ_0 in (2), from which we obtain upon reduction the relation:

$$\frac{H^2}{H_0^2} = \frac{\rho_n}{\rho_0} \frac{1}{1 + \delta} = \frac{1}{1 + \delta \rho_0/\rho_s}, \quad (6)$$

neglecting terms smaller than 10^{-5} since variations in H^2/H_0^2 smaller than this cannot be detected. In this way, by using a series of calibrating solutions, the ratio H^2/H_0^2 as a function of s can be determined and a calibration curve constructed. (Cf. Fig. 2.) The field was calibrated over a range sufficient to accommodate a 7.3 percent change in volume susceptibility corresponding to an actual displacement of m from its zero position of about 2.5 mm or about $1/6$ the diameter of the pole face P . Eq. (6) presupposes, of course, that the calibration is carried out at the temperature of neutrality. The expression on the right is obtained by assuming that the volume of a calibrating solution is simply the sum of the volumes of the neutral solution and water that were mixed in its preparation. Since a neutral solution contains approximately 2 percent nickel chloride, any error in assuming additivity of volumes is negligible.

The advantage of this method becomes apparent when it is noted that Eq. (6) is exactly the equation that applies if the field is calibrated with the liquids in contact with helium instead of air and the calibrating solutions are prepared from a mother solution neutral against helium.⁷ That is, this method enables one to calibrate with open meniscus tubes without correcting for the susceptibility of air.

The susceptibilities of the organic liquids are determined relative to water by balancing the liquid whose susceptibility is to be measured against a comparison solution of nickel chloride⁸ prepared in the same way as the calibrating solutions, except that this comparison solution must be made from a solution neutral against helium. The susceptibility κ_n of such a comparison solution is given by the equation:

$$\kappa_n = \frac{\rho_n}{\rho_0} \frac{\kappa_0}{1 + \delta} \quad (7)$$

and, if κ_L be the susceptibility of the liquid, we

⁷ Cf. Wills and Boeker, reference 2.

⁸ The diamagnetism of organic liquids is generally too small to permit balancing directly against water in the manometric balance.

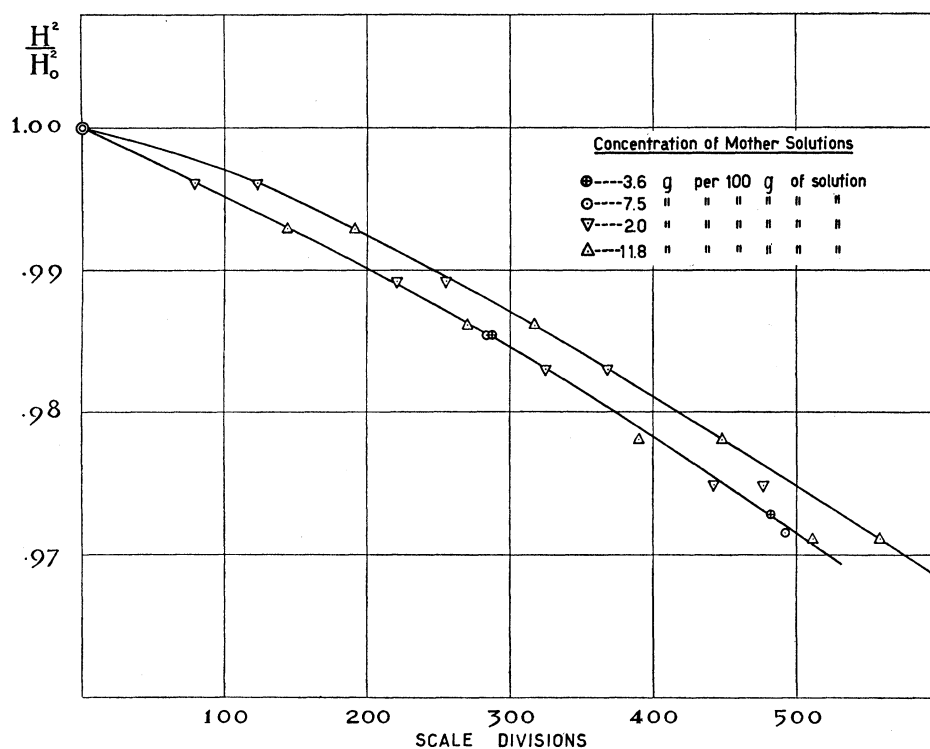


FIG. 2.

have by substituting κ_L/κ_n for κ/κ_0 in (1), using the value of κ_n from (7):

$$\frac{\chi_L}{\chi_0} = \frac{\rho_0}{\rho_L} \frac{\kappa_L}{\kappa_0} = \frac{\rho_n}{\rho_L} \frac{1}{1+\delta} \left[\frac{H^2}{H_0^2} + \frac{\kappa_a}{\kappa_0} \left(1 - \frac{H^2}{H_0^2} \right) \right].$$

The absolute susceptibilities are then computed by taking for the susceptibility of water $\chi_0 = 0.72 \times 10^{-6}$

NICKEL CHLORIDE AS A MAGNETIC STANDARD

The methods for calibrating and for determining the absolute susceptibilities assume that the susceptibility of aqueous solutions prepared by diluting neutral nickel chloride solutions may be computed by Wiedemann's law. This is equivalent to assuming that the magnetic moment of nickel in the calibrating solutions is independent of concentration, since departures from the rule of additivity embodied in Wiedemann's law are generally regarded as indicative of a change in magnetic state. In support of this assumption may be cited the work of

Bruins,⁹ Brant,¹⁰ Foëx,¹¹ Cabrera and Dupérier,¹² all of whom found the susceptibility of nickel in solution independent of concentration and put the magnetic moment of Ni^{++} at 16 Weiss magnetons. All but Brant, who worked at room temperature only, investigated the dependence on temperature and found that nickel in solution obeyed Curie's law. However, more recently Foëx and Kessler¹³ and Fahlenbrach¹⁴ have reported experiments indicating that the magnetic moment of nickel was not constant. The former found a variety of nickel that obeyed Weiss' law and had a moment of 17 W.m. This moment was nevertheless independent of concentration and after the solution had been heated over 100°C the nickel was found to have the usual moment 16. Fahlenbrach's results, on

⁹ Bruins, Akad. Amsterdam **18**, 246 (1915) (cited by Foëx, see note 15).

¹⁰ L. Brant, Phys. Rev. **17**, 697 (1921).

¹¹ G. Foëx, Ann. d. Physik (9) **16**, 224 (1921).

¹² B. Cabrera and A. Dupérier, J. de physique **6**, 121 (1925); nickel nitrate was used.

¹³ G. Foëx and B. Kessler, Comptes rendus **192**, 1638 (1931).

¹⁴ H. Fahlenbrach, reference 4.

the other hand, seemed to show that the magnetic moment of the nickel ion as calculated from the susceptibility of aqueous nickel chloride solutions depended in some cases both on the concentration and on the method of preparing the solutions. Fahlenbrach made up mother solutions of nickel chloride having concentrations of 7.310, 4.217, 9.32, 4.16, 8.29 g per 100 cc of solution, all showing approximately the same moment for nickel, and found for dilutions of the first two more concentrated solutions a magnetic moment independent of concentration and identical with the moment of the mother solutions (15.5). But dilutions of the weaker mother solutions showed increasing moment with increasing dilution. Finally, in the case of an immediate dilution (i.e., a dilution made immediately after preparation) of the 8.29 solution he found a larger moment than for an equal dilution of the same mother solution made several days later. In all cases the nickel obeyed Weiss' law.¹⁵

In Fahlenbrach's paper the results are presented graphically to show the reciprocal of the Ni^{++} susceptibility as a function of the absolute temperature, the points that determine the curves having been computed from the observational data. The absence of numerical data on the susceptibilities of the nickel chloride solutions themselves makes difficult any estimate of the bearing of his findings on our use of nickel chloride as a standard. Obviously, however, if the same sort of variation in the susceptibility of nickel occurs in our calibrating solutions our method of measuring susceptibilities is quite unreliable. Hence, although our ability to reproduce results after many months, using different sets of calibrating solutions differently prepared, provides considerable indirect evidence for the reliability of our method, it was deemed important to determine whether variations in the

method of preparing the calibrating solutions had any influence on the calibration. For this purpose four mother solutions were prepared, two having concentrations such that their dilutions should, in the light of Fahlenbrach's results, show no dependence of susceptibility on concentration, and two whose dilutions should show such dependence. From these were prepared four neutral solutions (the weakest mother solution was made up to be as near neutral at room temperature as possible) and these neutral solutions were then used to prepare calibrating solutions having concentrations ranging from 0.008 to 0.06 g NiCl_2 per 100 g of solution. With these the apparatus was then calibrated in the regular manner. Fig. 2 shows two calibration curves made on different occasions for somewhat different parts of the field, but with the same solutions. All calibration points corresponding to the same mother solutions are marked with the same index. These mother solutions had concentrations of 3.6, 7.5, 11.8, 2.0 and the corresponding indices are shown in the legend. Although these points show more scattering than the later calibrations that were used for the acetate measurements, there is no evidence that the calibration is dependent upon the original concentrations of the mother solutions. For the range of concentrations here used the general indication is that the susceptibilities of the calibrating solutions, as computed by Wiedemann's law, depend only on the neutral solutions so that any set of calibrating solutions gives the same result independent of the concentrations of the mother solutions. These results are not, of course, a contradiction of Fahlenbrach's findings since they serve only to establish the uniqueness of the calibration curves.

PREPARATION OF CHEMICALS

Samples of the five acetates were obtained from the Eastman Kodak Company. In addition, a sample of ethyl acetate (reagent grade) was secured from Merck. All were carefully distilled and only the best fraction of each was used for the determination of the absolute susceptibilities. The boiling points are shown in Table II. The measurements of temperature variation of susceptibility include runs made with other fractions of the distillate as well. The methanol was triple

¹⁵ Foëx, J. de phys. et rad. (7) 3, 337 (1932); (7) 4, 517 (1933), has regarded these results as evidence of a new magnetic state of nickel and suggests their explanation on the basis of a principle of uniformization according to which in any given sample the paramagnetic ion can exist in only one state, which state might be assumed to prevail during any change of state in the sample (solution, dilution) provided the change were slow enough. While the agreement of Fahlenbrach's curves with Weiss' law supports this principle, Fahlenbrach's emphasis on uniformity of procedure in preparing solutions makes doubtful the applicability of Foëx's suggestion as an explanation for the dependence on concentration.

distilled from the synthetic product of the Chemical Solvents Company, the last distillation being over magnesium.

SUSCEPTIBILITY-TEMPERATURE MEASUREMENTS

The results of the measurements of relative temperature variation are summarized in Table I; in Figs. 3 and 4 the experimental curves showing volume susceptibility as a function of temperature for propyl and amyl acetates are reproduced. The experimental curves for all six liquids show much the same characteristics and these two may be taken as typical. The values κ/κ_{20} for the volume susceptibilities relative to 20° given in the table have been found by interpolation with the aid of the experimental curve for each substance and from these values the relative mass susceptibilities χ/χ_{20} have been computed. In addition, the table gives for each liquid the average and greatest deviations, Δ_{ave} and Δ_m , of the experimental points from the κ/κ_{20} curve. Experimental points have been indicated only for κ/κ_{20} in Figs. 3 and 4 since the χ/χ_{20} curves are simply the plot of the values given in the tables.

The experiments on methanol were made as a preliminary investigation of the difficulties that might be encountered with hygroscopic liquids. Methanol was chosen for this purpose because

of its low cost compared with the acetates and to provide a comparison with the work of other experimenters. It was found necessary not only to dry the helium before admitting it to the apparatus but to put a layer of calcium chloride on the floor of the helium bulb before reproducible measurements could be made on methanol.

A similar difficulty was found in the case of methyl and ethyl acetates, but the use of calcium chloride failed to overcome it. Ultimately, by taking a zero reading at 20° after each determination at a higher (or lower) temperature and correcting for slight zero shifts it was possible to obtain reproducible results for methyl acetate up to about 45° and for ethyl acetate to about 50°. When these temperatures were exceeded zero shifts too large to be corrected occurred and the attempt to go higher had to be abandoned. Just what the changes were that took place at these temperatures is not fully understood.

With the remaining three acetates there was practically no difficulty of this sort and it was possible to carry them up over 70°, beyond which temperature the behavior of the apparatus becomes too unstable and constant temperature too difficult to maintain for precise measurement.

Methanol and the first three acetates show very nearly the same slight decrease in dia-

TABLE I.

METHANOL				ETHYL ACETATE				<i>n</i> -BUTYL ACETATE			
<i>T</i>	ρ/ρ_{20}	κ/κ_{20}	χ/χ_{20}	<i>T</i>	ρ/ρ_{20}	κ/κ_{20}	χ/χ_{20}	<i>T</i>	ρ/ρ_{20}	κ/κ_{20}	χ/χ_{20}
10	1.0124	1.0119	1.0005	5	1.0201	1.0210	1.0009	6	1.0162	1.0164	1.0002
20	1.0000	1.0000	1.0000	10	1.0135	1.0140	1.0005	10	1.0116	1.0117	1.0001
30	0.9876	0.9880	0.9996	20	1.0000	1.0000	1.0000	20	1.0000	1.0000	1.0000
40	0.9752	0.9760	0.9992	30	0.9864	0.9860	0.9996	30	0.9883	0.9882	0.9999
50	0.9628	0.9638	0.9990	40	0.9727	0.9719	0.9992	40	0.9765	0.9769	1.0004
				50	0.9591	0.9580	0.9989	50	0.9647	0.9656	1.0009
$\Delta_m(\kappa/\kappa_{20}) = 0.0010$		$\Delta_{ave}(\kappa/\kappa_{20}) = 0.0004$		$\Delta_m(\kappa/\kappa_{20}) = 0.0010$		$\Delta_{ave}(\kappa/\kappa_{20}) = 0.0004$		60	0.9527	0.9535	1.0008
								70	0.9407	0.9408	1.0001
								$\Delta_m(\kappa/\kappa_{20}) = 0.0005$		$\Delta_{ave}(\kappa/\kappa_{20}) = 0.0002$	
METHYL ACETATE				<i>n</i> -PROPYL ACETATE				<i>n</i> -AMYL ACETATE			
<i>T</i>	ρ/ρ_{20}	κ/κ_{20}	χ/χ_{20}	<i>T</i>	ρ/ρ_{20}	κ/κ_{20}	χ/χ_{20}	<i>T</i>	ρ/ρ_{20}	κ/κ_{20}	χ/χ_{20}
5	1.0206	1.0216	1.0010	10	1.0125	1.0130	1.0005	10	1.0109	1.0117	1.0008
10	1.0138	1.0144	1.0006	20	1.0000	1.0000	1.0000	20	1.0000	1.0000	1.0000
20	1.0000	1.0000	1.0000	30	0.9874	0.9871	0.9997	30	0.9890	0.9885	0.9995
30	0.9861	0.9856	0.9995	40	0.9747	0.9740	0.9993	40	0.9779	0.9786	1.0007
40	0.9861	0.9856	0.9991	50	0.9619*	0.9610	0.9991	50	0.9668	0.9682	1.0015
				60	0.9493*	0.9481	0.9988	60	0.9555	0.9570	1.0016
$\Delta_m(\kappa/\kappa_{20}) = 0.0010$		$\Delta_{ave}(\kappa/\kappa_{20}) = 0.0004$		70	0.9361*	0.9350	0.9989	70	0.9441	0.9445	1.0004
				$\Delta_m(\kappa/\kappa_{20}) = 0.0004$		$\Delta_{ave}(\kappa/\kappa_{20}) = 0.0002$		$\Delta_m(\kappa/\kappa_{20}) = 0.0010$		$\Delta_{ave}(\kappa/\kappa_{20}) = 0.0003$	

* Extrapolated.

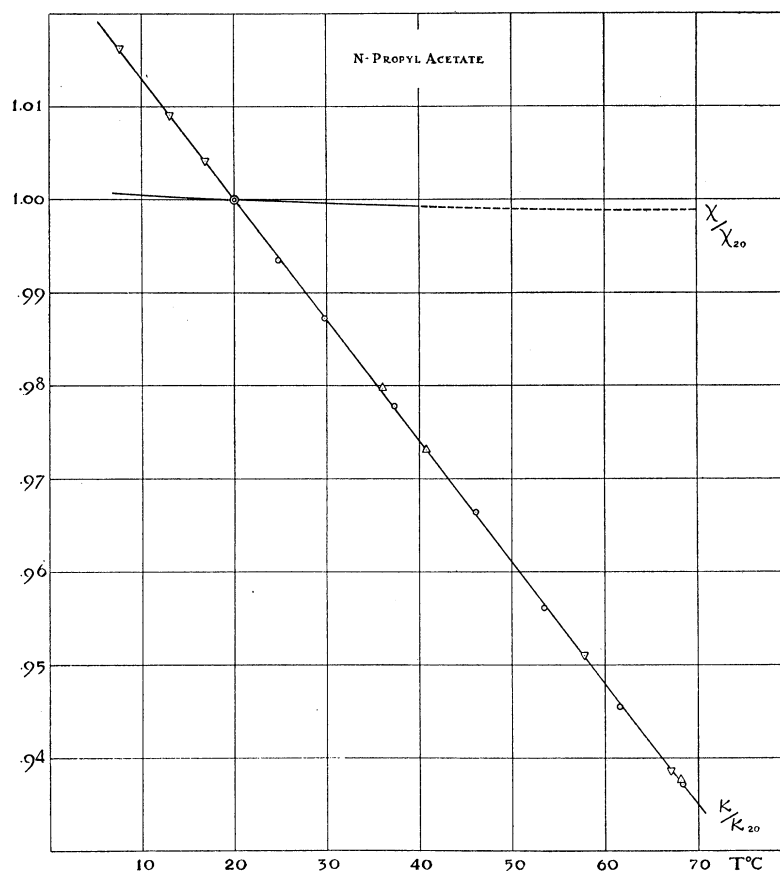


FIG. 3.

magnetism with $(1/\chi_{20})(\Delta\chi/\Delta T)$ very close to 0.00005 in each case. The dotted line in the case of propyl acetate indicates that the densities have been extrapolated (see below). Butyl and amyl acetate, on the other hand, show an increase in diamagnetism above 20° —slight for butyl and appreciable for amyl. The indication is that within the temperature range of these experiments there is a very slight temperature dependence of the mass susceptibility that increases for the higher members of the series, which is in accord with the findings of Cabrera and Fahlenbrach for the alcohols. However, in no case does the variation of χ exceed 0.2 percent.

THE ABSOLUTE SUSCEPTIBILITIES

The absolute susceptibilities, volume, mass, and molecular (computed on the basis of $\chi = 0.720 \times 10^{-6}$ for water) are given in Table II

and are shown graphically in Fig. 5. In each case the volume susceptibilities represent the mean of from four to eight independent observations. The curve labeled χ_M indicates the agreement with Pascal's law of the additivity of atomic susceptibilities. The general formula for the alkyl acetates may be written $\text{HCH}_3\text{CO}_2(\text{CH}_2)_n$, with $n=1$ for methyl, $n=2$ for ethyl, etc. If the atomic susceptibilities are strictly additive a plot of the molecular susceptibility of each acetate against n should be a straight line of the form:

$$(\chi_M)_n = (\chi_M)_{\text{Ac. acid}} + n(\chi_M)_{\text{CH}_2},$$

that is, a straight line having a slope equal to the molecular susceptibility of CH_2 and an intercept on the ordinate equal to the molecular susceptibility of acetic acid. The values for CH_2 and acetic acid in Table II have been computed from the acetate susceptibilities by the method

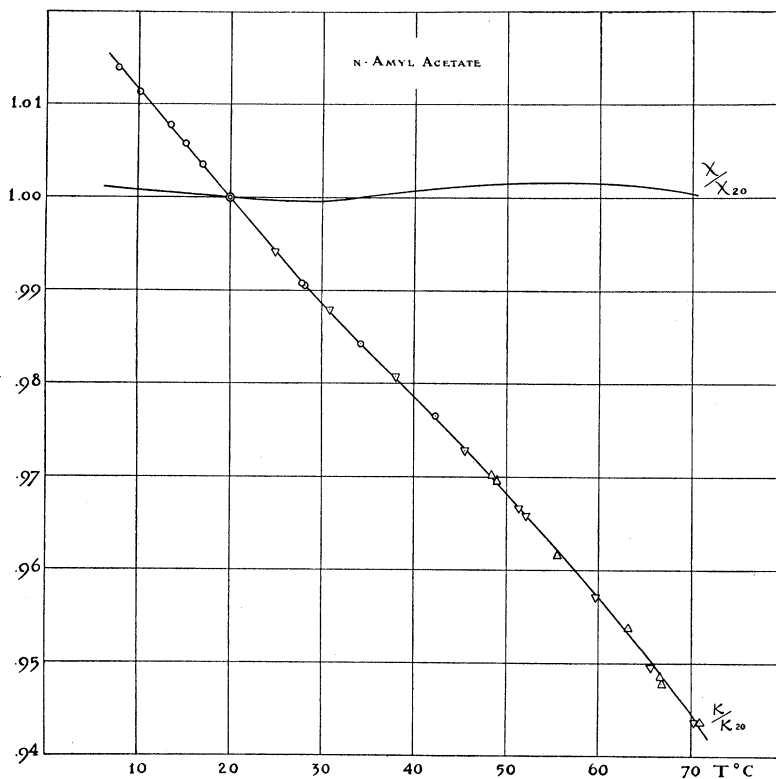


FIG. 4.

TABLE II.

	B.P.†	Mol. Wt.	Density (20.7°)	$-x_{20,7} \cdot 10^6$	$-x \cdot 10^6$	$-x_M \cdot 10^6$	$-\Delta x_M \cdot 10^6$	$-x \cdot 10^6$ (other authors)
Methanol CH ₃ OH	64.6	32.03	0.7907	0.5289	0.669 ₀	21.42		0.683 (P) 0.650 (I) 0.674 (CF)
Methyl acetate C ₃ H ₆ O ₂	56.6-56.9	74.05	0.9328	0.5320	0.570 ₃	42.23	-0.04	0.590 (P) 0.586 (B)
Ethyl acetate C ₄ H ₈ O ₂	76.7-76.9	88.06	0.8997	0.5515	0.613 ₀	53.98	0.00	0.627 (P) 0.608 (I) 0.621 (B)
n-Propyl acetate C ₅ H ₁₀ O ₂	101.4-102.0	102.08	0.8855	0.5704	0.644 ₂	65.75	0.06	0.646 (B)
n-Butyl acetate C ₆ H ₁₂ O ₂	126.4-126.6	116.09	0.8804	0.5840	0.663 ₃	77.00	-0.40	
n-Amyl acetate C ₇ H ₁₄ O ₂	148.0-148.4	130.11	0.8735	0.5979	0.684 ₅	89.06	0.05	
Acetic acid C ₂ H ₄ O ₂		60.03	1.0485	0.5338	0.509 ₁	30.56*		0.526 (P) 0.535 (CF) 0.520 (S) 0.534 (K) 0.528 (B)
CH ₂						11.67*		$-x_M \cdot 10^6$ 11.86 (P) 11.36 (B) 11.48 (CF) 14.5 (Bi)

* Computed.

† The boiling points have not been corrected for barometric pressure.

(P) P. Pascal, Ann. de chim. et phys. (8) **19**, 5 (1910).(I) T. Ishiwara, Sci. Rep. Tôhoku Univ. **3**, 303 (1914).(CF) B. Cabrera and H. Fahlenbrach, Zeits. f. Physik **85**, 568(1933);
89, 682 (1934).(B) S. Bhatnagar *et al.*, Phil. Mag. **18**, 449 (1934).(S) Alpheus W. Smith and Alva W. Smith, J. Am. Chem. Soc. **40**,
1218 (1918).(K) K. Kido, Sci. Rep. Tôhoku Univ. **21**, 149 (1932).(Bi) F. Bitter, Phys. Rev. **33**, 149 (1932).

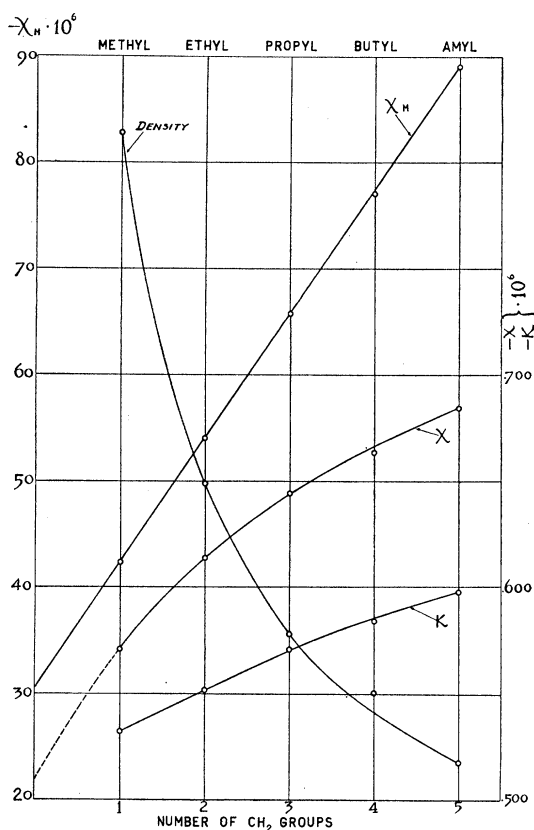


FIG. 5.

of least squares and the χ_M curve drawn accordingly. In this computation, however, butyl acetate was not included because of its apparently irregular position in the series as revealed in each of the curves in Fig. 5. This irregularity is most striking in the case of the densities.¹⁶ (No ordinates have been indicated for the density curve; it merely indicates relative values at 20.7°.) As a matter of fact, the values for CH_2 (-11.68×10^{-6}) and for acetic acid (-30.60×10^{-6}) obtained if butyl acetate is included differ little from those in the table, but the curve fits by no means as well, the average deviation of the points being more than doubled. For the curve as drawn this deviation does not exceed 0.1 percent. The actual deviations are given in the column $\Delta\chi_M$.

In view of the temperature variation of χ the

question of the agreement with Pascal's law at higher temperatures arises. A computation made for 50°, omitting methyl acetate, which was not measured at this temperature, gives -11.72×10^{-6} and -30.45×10^{-6} for CH_2 and acetic acid with about the same scattering as before, which would indicate a decrease in the diamagnetism of acetic acid with temperature of about the same order as the first three acetates and an increase with temperature of the diamagnetism of CH_2 .

DENSITIES

The densities used in computing the mass susceptibilities of methanol, methyl, ethyl and propyl acetates were taken from the *International Critical Tables*. For methanol and ethyl acetate these are in good agreement with values reported in 1930 by the Bureau International d'Étalons Physique-Chimique.¹⁷ For propyl acetate the equation in the *I.C.T.* is limited to the range 0°–40°C and the probable error is put at 0.001. Young's values¹⁸ for propyl acetate extend well beyond the 70° range needed, but his values would give an increase in χ about twice that shown in Fig. 4. The curve as drawn is much more consistent with the behavior of the other acetates.

The densities of butyl and amyl acetates were measured by Miss Mildred Kammer of the Columbia University Department of Chemistry under the direction of Professor V. K. LaMer, using portions of the same material that had been used for the susceptibility measurements. For butyl acetate four determinations were made by pycnometer at 0°, 20°, 50°, 70°C and for amyl acetate five determinations at 0°, 20°, 35°, 50°, 70°C. The equations computed from these results together with the average deviation of the experimental points are:

Density of *n*-butyl acetate from $t = 0^\circ$ to $t = 70^\circ\text{C}$:

$$\rho_t = 0.90151 - 1.01079 \times 10^{-3}t - 0.380 \times 10^{-6}t^2 \pm 4 \times 10^{-5}$$

Density of *n*-amyl acetate from $t = 0^\circ$ to $t = 70^\circ\text{C}$:

$$\rho_t = 0.89316 - 0.9481 \times 10^{-3}t - 0.388 \times 10^{-6}t^2 \pm 6 \times 10^{-5}$$

¹⁶ In this connection it is perhaps worth noting that Cabrera and Fahlenbrach found the greatest departure from regularity in the case of butyl alcohol.

¹⁷ J. chim. phys. 27, 411 (1930).

¹⁸ S. Young, Proc. Roy. Dub. Soc. 12, 434 (1910).

The densities of butyl acetate agree very well with values computed from Gartenmeister's volume equation.¹⁹ For amyl acetate they differ by about 2 percent although the relative change in density is very nearly the same. The agreement with the results of Lieben and Rossi²⁰ on butyl and amyl acetate and of Lievens²¹ on amyl acetate is by no means so good.

The densities of the neutral solutions in terms of water at 20° were:

For solution neutral *vs.* air at 20.7° $\rho_s 20/\rho_0 20 = 1.0203$;
For solution neutral *vs.* helium at 20.7° $\rho_s 20^\circ/\rho_0 20^\circ = 1.01978$ (Miss Kammer).²²

DISCUSSION OF ERRORS

The important sources of error to be considered in appraising the absolute values given for the volume susceptibilities in Table II are the susceptibility of air, slight variations in the neutral solution in the course of time (this is negligible for the calibrating solutions because of their small nickel chloride content), the difference in surface tension between the organic liquids and the nickel chloride solutions,²³ and finally errors of observation. An estimate of these gives the probable error in the volume susceptibilities as $\pm 0.0009 \times 10^{-6}$, of which observational errors account for about $\pm 0.0003 \times 10^{-6}$.

As for the mass susceptibilities, in view of the uncertainty of the density values and in the absence of chemical tests for purity a fourth figure cannot be regarded as significant.

The figures for the average deviation in the tables of temperature variation may be considered a measure of the precision of these measurements.

¹⁹ Gartenmeister, *Lieb. Ann.* **233**, 259 (1886).

²⁰ Lieben and Rossi, *Lieb. Ann.* **158**, 169 (1871).

²¹ Lievens, *Chem. Soc. Belg.* **33**, 126 (1924).

²² If the susceptibility of NiCl₂ is computed in terms of water from this value of the density (assuming the volume of the solution to be greater than the volume of the water by a factor of 1.00059) the value $\chi = 36.4 \times 10^{-6}$ is obtained, some 10 percent higher than the value of Liebkecht and Wills (33.4) and the more recent values of Fahlenbrach (33.6) and Brant (33.8), though very much less than the 44.7 (undoubtedly too high) of Ishiwara in the I.C.T. Whether or not this difference is significant cannot be stated positively since no chemical analysis of the solution was made.

²³ Since the positions of the two menisci are determined by setting the telescope cross-hairs tangent to the images of the menisci a slight error is introduced if the two menisci have not the same shape.

CONCLUSION

In the light of the experiments on nickel chloride solutions the suggestion of Cabrera and Fahlenbrach²⁴ that the anomalous behavior of water reported by Wills and Boeker² in their first paper might be accounted for by variation of the nickel chloride in the calibrating solutions must be regarded as incorrect. It is probable that the water results are to be explained as Wills and Boeker suggest²⁵ by a leakage of air in the helium bulb. Experience with the manometric balance has shown that this behavior is characteristic of a gradual displacement of helium by air in the apparatus.

The measurements of temperature variation show that the first five of the alkyl acetates belong to the large group of organic compounds that show very little variation of susceptibility with temperature. Such electric dipole measurements as have been made on the acetates suggest the same sort of association as exists in the alcohols and it would be interesting to have measurements on the higher members of this acetate series to see if they show the same increasing dependence on temperature as the higher alcohols.

The agreement with Pascal's law is very good—except for butyl acetate. However, comparison of these measurements with the results of other experimenters repeats the picture of conflict generally found in susceptibility data where measurements on the same substance may differ by two or three percent while individually a precision ten times as great is claimed. Attention should be called to Bitter's value for CH₂ obtained from measurements on the gases of the methane series. The 20 percent difference between the values for gases and for liquids is not unexpected in view of the change of state. The measurements of Vaidyanathan²⁶ on vapor susceptibilities indicate a discontinuity in the susceptibility curve in the change from the liquid to the vapor state for all the substances he measured and the increase in diamagnetism is

²⁴ H. Cabrera and B. Fahlenbrach, *Zeits. f. Physik* **82**, 759 (1933).

²⁵ A. P. Wills and G. F. Boeker, *Phys. Rev.* **46**, 907 (1934).

²⁶ V. I. Vaidyanathan, *Ind. J. Phys.* **11**, 135 (1928).

marked for pentane, hexane, and heptane, but it is unfortunate that the precision of vapor measurements is such as to make any comparison inconclusive.

I wish at this time to express my thanks to Professor A. P. Wills under whose direction

these experiments were carried out, to Professor V. K. LaMer for permitting the use of his laboratory for the density measurements, and to Mr. Samuel Seely and Mr. Erwin Watermeyer for their continued assistance in taking measurements.

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The Energy Levels of Inert-Gas Configurations

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THE energy levels for the configuration $n'p^5np$ have been calculated by Shortley,¹ neglecting the electrostatic interaction between the two groups of levels coming from different parents of the ionic doublet. From the matrices of electrostatic and spin-orbit interaction² in jj coupling he obtained four secular equations involving six radial integrals. These are a linear, a quadratic, a cubic, and a quartic equation, corresponding to values of $J=3, 0, 2,$ and $1,$ respectively. The solution of the cubic and quartic equations obviously involves a great amount of complicated arithmetic, and consequently in all cases where the electrostatic interaction between the two groups is small, Shortley found that a valid simplification can be made. If this interaction is neglected, the matrices may be reduced, and the cubic and quartic equations split up into linear and quadratic equations.

For small values of $n,$ however, this approximation is no longer valid, and the complete secular equations must be solved. Some work has already been done in this field by Inglis and Ginsburg,³ and again by Shortley,⁴ on the energy levels of the configuration $2p^53p$ of neon I.

The present calculations are an extension of this work and comprise the $2p^54p$ and $5p$ configurations of neon, $3p^54p$ and $5p$ of argon, $4p^55p$ of krypton, and $5p^56p$ of xenon. The six

radial integral parameters were first calculated from the observed energies as taken from Bacher and Goudsmit,⁵ making use of the linear and quadratic equations and expressions for the sum of the roots of the cubic and quartic. For this work it was found that the two parameters representing the spin-orbit interaction could be combined as follows

$$K = \frac{1}{4}(\zeta' - \zeta)$$

and consequently five equations involving five unknowns could be obtained:

$$\begin{aligned} 3a &= -F_0 - F_2 - 2K, \\ 0a &= -F_0 - 2\frac{1}{2}F_2 + 3G_0 + K \\ &\quad - [(-2\frac{1}{2}F_2 + G_0 - 3K)^2 + 2(2G_0 - 5F_2)^2]^{\frac{1}{2}}, \\ 0d &= -F_0 - 2\frac{1}{2}F_2 + 3G_0 + K \\ &\quad + [(-2\frac{1}{2}F_2 + G_0 - 3K)^2 + 2(2G_0 - 5F_2)^2]^{\frac{1}{2}}, \\ S_3 &= -3F_0 + 3F_2 + 12G_2, \\ S_4 &= -4F_0 - F_2 + 4K, \end{aligned}$$

where S_3 and S_4 represent the sums of the roots of the cubic and quartic equations.

The five parameters thus obtained were substituted in the original cubic and quartic equations and ζ' was then plotted graphically against the energy. This graphical method provided a comparatively simple means of adjusting not only ζ' , but the other parameters as well, since the properties of the curve could easily be studied.

After the parameters had been determined by the graphical method, they were finally adjusted

¹ George H. Shortley, *Phys. Rev.* **44**, 666 (1933).

² M. H. Johnson, Jr., *Phys. Rev.* **38**, 1628 (1931).

³ D. R. Inglis and N. Ginsburg, *Phys. Rev.* **43**, 194 (1933).

⁴ George H. Shortley, *Phys. Rev.* **47**, 295 (1935).

⁵ Bacher and Goudsmit, *Atomic Energy States* (McGraw-Hill, 1932).