The Rankine Magnetic Balance and the Magnetic Susceptibility of H_2O, HDO and D_2O

HAIG P. ISKENDERIAN

Columbia University, New York, N. Y.

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Details are given of the construction of a Rankine magnetic balance which realizes the full theoretical sensitivity of this type of instrument. The volume magnetic susceptibilities of stated mixtures of light and heavy water relative to that of ordinary water are reported, and from these data the relative mass susceptibilities of HDO and D_2O are deduced. The mass susceptibility of H_2O is assumed to be -0.7200×10^{-6}, in terms of which that of HDO is -0.6807×10^{-6} and of D_2O is -0.6466×10^{-6}.

IN 1933 Professor A. O. Rankine described in principle a novel form of magnetic balance whose nature and high theoretical sensitivity suggested its eminent fitness as an instrument to measure the relative magnetic susceptibilities of feebly magnetic substances.[1] Rankine later constructed a balance embodying these principles, but this instrument failed to function with the requisite sensitivity, chiefly because of ferromagnetic impurity in some of the structural materials.[2]

The present paper contains a description of a Rankine balance which realizes the full theoretical sensitivity of this type of instrument. The balance has been used to measure the diamagnetic susceptibilities of mixtures of light and heavy water with an accuracy of about 0.06 percent, and the results of these measurements form a second part of this report.

THE RANKINE MAGNETIC BALANCE

If a bar magnet stands parallel to the plane surface of a magnetizable medium the induced polarity on the surface exerts a force on the magnet, which is an attraction if the substance is paramagnetic and a repulsion if it is diamagnetic, and which depends in magnitude on the magnetic susceptibility of the material. If, now, the magnet is mounted, with its axis vertical, at one end of a horizontal beam supported by a vertical torsion fiber, this force will produce a torque about the fiber axis and the beam will rotate. The relative magnetic susceptibilities of different materials. can be deduced theoretically from the magnitudes

of such rotations, or, preferably, from the relative magnitudes of small nonuniform magnetic fields which, acting on the magnet, return it to a fiducial position close to the surface.

The theoretical sensitivity of such an instrument is very high, but is completely vitiated in practice by the fact that neither the earth's magnetic field nor the horizontal component of the magnet's moment can be nearly enough annulled to reduce the consequent residual directive torque on the beam to a value comparable with that exerted by a fine suspension fiber. In the Rankine balance the theoretical sensitivity is in large measure regained by the simple expedient of suspending the magnet from the beam on a torsion fiber of the same nature as that which supports the beam itself. It is apparent that with such an arrangement the control exerted by extraneous magnetic fields which are uniform over the magnet can operate at worst to halve the sensitivity. In fact, it can readily be shown[3] that the effective torsional coefficient, τ, of the instrument is given by the expression

$$\tau = \tau' + [(1/\tau'') + (1/\mu'H)]^{-1},$$

in which τ is the ratio of the torque on the beam due to the force between specimen and magnet, to the resulting angular displacement, τ' and τ'' are the torsional coefficients of the two fibers, respectively, μ' is the horizontal magnetic moment, and H is the extraneous uniform horizontal magnetic field. The present values of these constants are $\tau' = 3 \times 10^{-4}$ dyne cm/radian, $\tau'' = 3 \times 10^{-5}$ dyne cm/radian, $\mu' = 0.3$ e.m.u. and

[1] Rankine, Proc. Phys. Soc. **46**, 1 (1934).
[2] Rankine, Proc. Phys. Soc. **46**, 391 (1934).
[3] Rankine, reference 1, p. 11.

$H=0.16$ oersted, so that the term in $\mu'H$ is negligible in comparison with the others.

The foregoing considerations apply only when the extraneous field is uniform over the magnet. A nonuniform field exerts on the magnet a force, and on the beam a directive couple, of the same nature as, and possibly much larger than, that which it is desired to observe. In the presence of such forces the balance may be difficult, if not impossible, to use, and its sensitivity may be materially impaired. However, nonuniform fields can readily be eliminated by removing ferromagnetic bodies from the neighborhood of the instrument, and in particular *by constructing the balance of materials which contain no ferromagnetic impurity.* The latter specification is by far the most important item in the design of a successful instrument.

Fig. 1 is a schematic diagram of the magnetic balance here to be described. The base is a circular disk of OFHC copper 21.5 cm in diameter, and is provided with three leveling screws. The cell S into which the specimen fluid is admitted is blown of Pyrex glass and is approximately 5 mm thick by 20 mm wide by 50 mm high. An entrance tube is provided at the bottom and an exit tube at the top.

The magnet DE is a right circular cylinder of 36 percent cobalt steel, 3 mm in diameter and 25 mm long. Its pole strength is 36 e.m.u. and its weight 1.5 g. A Duralumin hook pointed with tungsten is firmly attached to the top of the magnet in such position that the point of the hook lies on the prolongation of the cylinder axis. This point rests on a jewel set in the inner side of a Duralumin ring. The ring, with the magnet pendant below it, is supported in a vertical plane by a quartz fiber affixed with shellac to a pin attached to it at the top.

The fiber CD which supports the magnet is 22 cm long and is affixed with shellac to one end of a horizontal Duralumin beam BC, at the other end of which is a counterweight W. The beam is about 0.6 mm thick by 6 cm long, and the center of support is located 2 cm from the end which carries the magnet. A small mirror, and a hook similar to that which supported the magnet are attached to the beam at this point. The beam is suspended in the same manner as the magnet by
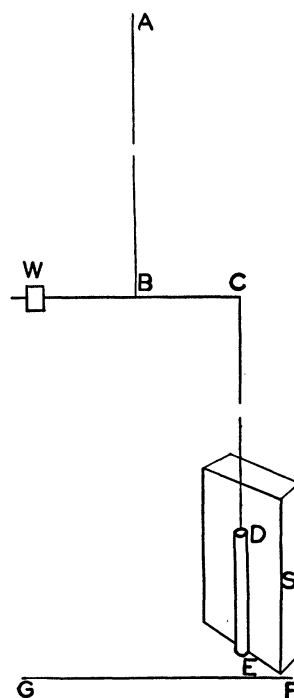

FIG. 1. Schematic diagram of the Rankine magnetic balance. AB and CD, quartz fibers; BC, Duralumin beam; W, counterpoise; DE, permanent magnet; S, specimen tube; GF, copper conductor.

a quartz fiber AB 28 cm long affixed at its upper end to a torsion head.

The torsion head is supported by three vertical Pyrex glass rods located at the vertices of an equilateral triangle 8.8 cm on edge. The rods are cemented at each end with glycol cement into OFHC copper bushings. This cement has been found to be both efficacious and free from ferromagnetic impurity. It is made by cooking a mixture of one gram molecular weight each of glycol and phthallic anhydride at 200°C for 2 hours, after which it is poured a little at a time into cold water.

A vertical screw on the torsion head permits the height of the entire suspended system to be so adjusted that the bottom of the magnet is about 0.5 mm from the copper base plate. The field of the eddy currents induced in the plate by the magnet when in motion effectively damps any oscillation of the system. When not in use the system can be lowered so that the beam rests on the top of a centrally located vertical glass rod.
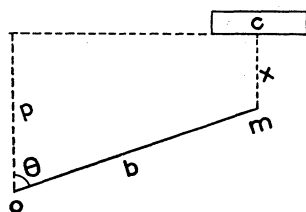
Two insulated conductors are mounted be-

FIG. 2.

neath the base plate so as to lie in the plane of the beam when in use. The field of a current in one of these serves to establish the fiducial position of the magnet and to return it thereto against the magnetic force exerted by the contents of the cell. This position is such that the surface of the magnet is about 3 mm from that of the cell, and is indicated by a light beam reflected from the mirror to a scale about 4 meters distant. The field of a current in the other conductor is used when needed as an additional control on the motion of the suspended system.

The apparatus is enclosed in a bell jar, which rests on the copper base plate, and is further protected against fluctuations in temperature by mounting it in a Celotex box covered with hair felt. The bell jar is evacuated when measurements are made.

The factors which determine the sensitivity of the balance can readily be deduced from Fig. 2, in which C denotes the cell, viewed from above, m a pole of the magnet, b the length of the beam between m and the (fixed) point of support at O, p the perpendicular from O to the plane of the cell, and x the distance from m to the cell. The force exerted upon m by the magnetic material in the cell is, approximately,[4] $\pi m^2 \kappa / 2x^2$, provided the volume susceptibility, κ, is small in comparison with unity. Accordingly, the equilibrium condition for the beam is

$$T_0 + T + \frac{\pi m^2 \kappa b \sin \theta}{2x^2} + \tau(\theta + \theta_0) = 0, \qquad (1)$$

in which T_0 denotes the torque on the beam due to extraneous fields and to the magnetization of the cell by the magnet, T that due to the current in the conductor, θ the angle between p and b, and θ_0 an unknown angular twist of the sus-

[4] Mason and Weaver, *The Electromagnetic Field*, p. 149.

pension fiber. It follows from this equation that if T_0 and T are held constant, then

$$\frac{\Delta\kappa}{\Delta\theta} = \frac{x^2}{\pi m^2 b \sin \theta}\left[\frac{2b \sin^2 \theta - x \cos \theta}{x^3}\pi m^2 b \kappa - 2\tau\right].$$

The optimum value of θ, i.e., the optimum orientation of the cell, is that which makes this expression a minimum for fixed values of b and x. However, accidental disturbances incident to the present arrangements do not warrant an effort to obtain greater sensitivity than that afforded by the orientation for which $\theta = 90°$. Under these circumstances the second term in the brackets is negligible in comparison with the first, and the theoretical uncertainty in κ is given by the formula $\Delta\kappa = (2b\kappa/x)\Delta\theta$, where $\Delta\theta$ is the uncertainty in θ. It follows that, with the present balance, an uncertainty of the order 10^{-10} may be expected in the measurement of susceptibilities of the order 10^{-6}. The observed precision measure of κ agrees with this estimate.

The experimental procedure for measuring the volume susceptibility, κ_x, of a specimen liquid relative to the susceptibility, κ_s, of a standard liquid is as follows:

The bell jar and cell are evacuated and the current, i_0, is noted which maintains the magnet in the fiducial position with respect to the cell. The equilibrium condition for the beam may then be written in the form

$$T_0 + c i_0 + \tau \theta_0 = 0, \qquad (2)$$

where c is a constant whose value depends on the moment of the magnet and its position relative to the current.

Next the cell is filled with the standard liquid, and the current, i_s, is noted which maintains the magnet in its former position. The equilibrium condition is

$$T_0 + f \kappa_s + c i_s + \tau \theta_0 = 0, \qquad (3)$$

TABLE I. *Comparison of data on benzene-nitrobenzene mixtures, obtained with the manometric and Rankine balances.*

	$\kappa \times 10^6$	
C	Manometric balance	Rankine balance
0.1086	0.6062	0.6070
.2296	.6074	.6077
.3356	.6083	.6078
.8821	.6115	.6125

where f is a constant whose value depends on the pole strength of the magnet and its position with respect to the cell. It follows from Eqs. (2) and (3) that

$$f\kappa_s = c(i_s - i_0). \qquad (4)$$

Lastly, the cell is filled with the specimen liquid, and the fiducial current, i_x, again noted. The equation corresponding to Eq. (4) is $f\kappa_x = c(i_x - i_0)$ and it follows that

$$\kappa_x/\kappa_s = (i_x - i_0)/(i_s - i_0). \qquad (5)$$

The currents, which are a few milliamperes, are measured with a L and N type K potentiometer. The standard liquid used throughout the present measurements was water, the volume susceptibility of which at the temperature of measurement, namely 21.3°C, was assumed to be -0.7186×10^{-6}.

An initial test of the Rankine balance showed its performance to be thoroughly satisfactory. Susceptibility measurements made with this instrument were in excellent accord with others made on the same substances with a Wills-Boeker manometric balance.[5] The specimen materials were mixtures of nitrobenzene in benzene. Typical data are given in Table I, in which the first column indicates the concentration by weight of nitrobenzene in benzene, the second, the volume susceptibility of the mixture as measured by Seely with the manometric balance,[6] and the third, the corresponding value obtained with the Rankine balance. The temperature at which the measurements were made was 21.8°C.

Another inference can be drawn from the concordance of these results. In the manometric balance the specimen material is placed in a field of approximately 15,000 oersteds, while in the Rankine balance it is subjected to a field of only about 100 oersteds. It appears, therefore,

that the susceptibilities of the mixtures relative to water are independent of field strength over this range.

EXPERIMENTAL RESULTS

The results of the observations on mixtures of light and heavy water are given in Table II. The first column gives the molar concentration of "heavy water," i.e., the ratio of the number of D atoms to the number of D plus H atoms in the mixture. The corresponding densities, shown in the second column, are calculated for the temperature 21.3°C with the formula[7]

$$\rho_f = 0.9979 + 0.1079f. \qquad (6)$$

The third column contains the .observed ratios of the volume susceptibilities of the mixtures to that of H_2O. The volume susceptibilities shown in the fourth column are calculated from these ratios and the value $\kappa_w = -0.7186 \times 10^{-6}$. The last column gives the mass susceptibilities of the mixtures, and is calculated from the data of the second and fourth columns with the formula $\chi = \kappa/\rho$.

The mass susceptibility of the constituent, HDO, of the mixtures can be computed from the observed mass susceptibility of any one mixture, on the assumption that the constituent susceptibilities are additive. The value thus obtained can then be used to *calculate* the susceptibilities of the remaining mixtures, and so the validity of this assumption can be tested. The equilibrium equation involved is $H_2O + D_2O \rightleftharpoons 2HDO$. The equilibrium constant of this reaction has been measured by Topley and Eyring.[8] Thus

$$(N_{12})^2/N_{11}N_{22} = 3.26, \qquad (7)$$

where N_{11}, N_{12}, N_{22} are the molar concentrations of H_2O, HDO and D_2O, respectively. Additional relations between the N's are

$$\left. \begin{array}{c} N_{22} + \tfrac{1}{2}N_{12} = f, \\ N_{11} + N_{12} + N_{22} = 1. \end{array} \right\} \quad (8)$$

and

The additivity law may be written in the form

$$m\chi = m_{11}\chi_{11} + m_{12}\chi_{12} + m_{22}\chi_{22}, \qquad (9)$$

where $m = m_{11} + m_{12} + m_{22}$,

$$m_{rs}/m = W_{rs}N_{rs}/(W_{11}N_{11} + W_{12}N_{12} + W_{22}N_{22}), \quad (10)$$

TABLE II. *The magnetic susceptibility of mixtures of H_2O, HDO and D_2O.*

f	ρ_f	κ/κ_w	$-\kappa \times 10^6$	$-\chi \times 10^6$
0	0.9979	1.	0.7186	0.7200
0.2	1.0195	0.9985	.7175	.7039
.4	1.0410	.9976	.7168	.6887
.6	1.0626	.9962	.7159	.6737
.8	1.0842	.9956	.7154	.6599
1.0	1.1058	.9949	.7149	.6466

[5] Wills and Boeker, Phys. Rev. **42**, 687 (1932).
[6] Seely, Phys. Rev. **49**, 812 (1936).
[7] Lewis and Luten, J. Am. Chem. Soc. **55**, 5061 (1933); Taylor and Selwood, J. Am. Chem. Soc. **56**, 998 (1934).
[8] Topley and Eyring, J. Chem. Phys. **2**, 217 (1934).

and W_{rs} denotes the molecular weight of the constituent. The N's corresponding to a given f are calculated with Eqs. (7) and (8), the mass ratios with Eq. (10), and, finally, χ_{12} with Eq. (9). The values of W_{rs} adopted in the present calculation are $W_{11}=18.015$, $W_{12}=19.021$ and $W_{22}=20.027$.

The calculated value of χ_{HDO} corresponding to $f=0.2$ is -0.6807×10^{-6}. When this value is substituted in Eq. (9) the calculated mass susceptibilities of the remaining three mixtures are $\chi_{0.4}=-0.6885$, $\chi_{0.6}=-0.6739$, and $\chi_{0.8}=-0.6600$, all $\times10^{-6}$. These agree with the observed data of Table II with a maximum discrepancy of 2 in the fourth figure.

The present value of the molar susceptibility, χW, of D_2O is $-12.95\pm0.01\times10^{-6}$ compared with the value -12.97×10^{-6} for H_2O. Other investigators have obtained the values 12.90,[9] 12.76,[10] and 12.96±0.02,[11] all $\times-10^{-6}$. It should

[9] Selwood and Frost, J. Am. Chem. Soc. 55, 4335 (1933)·
[10] Cabrera and Fahlenbrach, Naturwiss. 22, 417 (1934).
[11] J. H. Cruickshank, Nature 268, 135 (1935).

be noted that the difference of amount 0.02×10^{-6} here found between the molar susceptibilities of H_2O and D_2O rests upon the adoption of the value 1.1058 for the density of D_2O at 21.3°C. An earlier measurement of this quantity by Lewis and Luten[12] yielded the value 1.1035, and the molar susceptibility of D_2O calculated from the present data with this figure is -12.97×10^{-6}. The experimental verification of the additivity law subsists whichever value is chosen.

In conclusion the writer gratefully acknowledges his indebtedness to Dr. W. B. Ellwood, of the Bell Telephone Laboratories, for his assistance in securing the magnet; to Dr. H. C. Urey, who supplied the mixtures of H_2O and D_2O; to Dean G. B. Pegram, in whose home in New York City this research was conducted; and to Dr. A. P. Wills, who suggested the problem and followed the progress of the work with helpful counsel and encouragement.

[12] Lewis and Luten, reference 7.

The Piezodielectric Effect and Electrostriction in Anisotropic or Isotropic Media

HAROLD OSTERBERG AND JOHN W. COOKSON
Department of Physics, University of Wisconsin, Madison, Wisconsin

A phenomenological theory of the piezodielectric effect in homogeneous isotropic or anisotropic solids is presented. This theory rests upon the assumption that the changes in the dielectric constants ϵ_{ij} are linear in the six components of applied mechanical stress. It is shown that 36 piezodielectric moduli are required for a complete description of the piezodielectric effect. The number of independent moduli is two in isotropic solids, eight in alpha-quartz and tourmaline, and twelve in Rochelle salt. The matrices for the piezodielectric and piezooptical moduli are identical in all crystal classes which we have considered. The term electrostriction is applied to the case in which the components of strain are quadratic functions of the applied electrical field. The character of electrostriction in any solid is predicted by considering the piezodielectric effect together with the first and second laws of thermodynamics. The relation of electrostriction to the piezodielectric effect is very similar to the relation of the converse piezoelectric effect to the direct piezoelectric effect. The equations for the components of "electrostrictive strain" in isotropic solids and alpha-quartz are given in detail. General expressions for "electrostrictive stress" are derived. The equations of motion of a perfectly elastic, piezoelectric and electrostrictive solid which is subjected to mechanical and electrical fields are then stated. From considerations of crystalline symmetry and Neumann's hypothesis it can be seen that every solid may exhibit electrostriction whereas relatively few solids are piezoelectric.

1. THE THEORY OF THE PIEZODIELECTRIC EFFECT

THE term *piezodielectric effect* is here applied to those changes in the dielectric constants ϵ_{ij} of a homogeneous solid which result from the application of mechanical stress. The following considerations are limited to the case in which

the changes are linear in the applied stress. Direct experimental evidence for this linearity has been recently obtained by A. H. Scott.[1]

Let the x, y and z components of the electric

[1] A. H. Scott, Nat. Bur. Stand. J. Research 15, 13 (1935).