of an oil, b. p. 74–76° (8 mm.) (130–132° (34 mm.)), apparently identical with that obtained from addition of bromine to the *trans* diacetate and from treatment of the tetrabromide with silver acetate. Distillation in a nitrogen atmosphere gave a colorless lachrymatory product, which discolored rapidly.

Anal. Calcd. for $C_{10}H_{16}O_4Br_2$: Br, 44.41. Found: Br, 44.10.

***trans*-2,3-Dimethyl-2-butene-1,4-diol.**—Ten grams (0.0500 mole) of *trans*-1,4-diacetoxy-2,3-dimethyl-2-butene and 31.5 g. (0.100 mole) of pulverized barium hydroxide octahydrate were stirred together in 50 ml. of ethanol under reflux for five hours. After precipitation of inorganic salts with carbon dioxide, the concentrated filtrates gave 2.7 g. (46%) of the diol, a white crystalline solid, m. p 57–58° after recrystallization from ethanol. The bis-phenylurethan, prepared by warming the diol with phenyl isocyanate and recrystallizing from chloroform, melted at 157.0–157.5°.

Anal. Calcd. for $C_{20}H_{22}O_4N_2$: C, 67.77; H, 6.26; N, 7.91. Found: C, 67.60; H, 6.20; N, 7.82.

***cis*-2,3-Dimethyl-2-butene-1,4-diol.**—By a procedure analogous to the foregoing, substituting potassium hydroxide in the saponification, the corresponding *cis*-1,4-diacetoxy-2,3-dimethyl-2-butene gave a liquid diol, b. p. 110–115° (5 mm.). The bis-phenylurethan melted at 147.0–148.0° after recrystallization from chloroform. A mixture of the two phenylurethans melted at 132–140°.

Anal. Calcd. for $C_{20}H_{22}O_4N_2$: C, 67.77; H, 6.26; N, 7.91. Found: C, 67.35; H, 6.16; N, 7.85.

2,3-Dibromo-2,3-dimethylbutane.—As this dibromo compound could be formed by addition of hydrogen bromide to 2,3-dimethylbutadiene, and its recorded melting points vary from 140 to 192°, a reference sample was prepared for comparison with the 1,4-dibromides obtained in the present work. The product from pinacol and aqueous hydrobromic acid[20] after careful drying and sublimation in a vacuum, melted at 177–177.5° in a *sealed tube.*

Anal. Calcd. for $C_6H_{12}Br_2$: Br, 65.50. Found: Br, 65.23.

The compound has a camphoric odor and sublimes quite readily.

Dipole Moment Measurements.—Thiophene-free benzene for use as solvent in the dipole moment measurements was dried for three days over calcium oxide, distilled over sodium, and stored over sodium wire. Physical constants were: b. p. 79.0–79.4° (745 mm.), $n^{25}\text{D}$ 1.4973, $d^{25}\text{D}$ 0.8725. Samples were weighed by difference from dropping bottles directly into the solvent and the dielectric constant was measured immediately, at several concentrations, each solution being diluted to prepare the succeeding one.

The apparatus used employs the heterodyne-beat method,[21] with an oscillator of 1.57 megacycles frequency. The measuring cell, of about 135 ml. volume, resembled that described by Smyth.[22] All measurements were made with the cell in a thermostat at 25.00 ± 0.06°.

Summary

The addition of bromine to 2,3-dimethylbutadiene has been reëxamined. Three geometrically isomeric pairs of compounds of the general formula, $A—CH_2—C(CH_3)=C(CH_3)—CH_2—A$, have been prepared in which A is —Br, $—OCOCH_3$, and —OH and the configurations have been correlated by measurement of the dipole moments.

The dipole moments of the solid tetrabromide, 1,2,3,4-tetrabromo-2,3-dimethylbutane, m. p. 138.5–139°, and of the crystalline 1,4-dibromide (*trans*) obtained from butadiene have been measured also.

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[20] Thiele, *Ber.*, **27**, 454 (1894).

[21] Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Co., Inc., New York, N. Y., 1931; Le Fèvre, "Dipole Moments," Chemical Publishing Co., New York, N. Y., 1938.

[22] Smyth, THIS JOURNAL, **50**, 1547 (1928).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SOUTHWESTERN COLLEGE, WINFIELD, KANSAS]

Dielectric Constants of the Methanol–Water System from 5 to 55°[1]

BY PENROSE S. ALBRIGHT[2] AND LOUIS J. GOSTING[3]

It is desirable to have available accurate dielectric constant data for several liquids or solutions so they may be used as standards in different dielectric constant ranges as well as for many other purposes. Benzene and water are excellent standards for the low and high dielectric constant ranges, respectively. For the middle range, the lower aliphatic alcohols are one of the satisfactory groups of liquids for this purpose since they are quite easily purified, the lower members of the series are miscible with water in all proportions, and they have suitable dielectric constants.

Unfortunately, the data for the first member of this series, methanol, and its aqueous solution have been inconsistent. Jones and Davies[4] have summarized the data up to 1939 and have added their values for the dielectric constants of the methanol–water system at 20 and 25°. Their values, as do ours, differ considerably from the dielectric constant results for the methanol–water solutions, over a wide range of temperatures, as measured by Åkerlöf.[5]

It has been the purpose of this research to determine the dielectric constants of the methanol–water system in the temperature range 5 to 55°, using the equipment described below.

Experimental

Materials.—Conductivity water was prepared by three distillations. Tap water was first given an ordinary distillation. This distillate was distilled from a mixture of dilute sulfuric acid and potassium permanganate. The

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[4] Jones and Davies, *Phil. Mag.*, **28**, 307 (1939).

[5] Åkerlöf, THIS JOURNAL, **54**, 4125 (1932).

final distillation was from a dilute sodium hydroxide solution. This water at 25.00° was used as a reference standard for the entire experiment.

Methanol from the Carbide and Carbon Chemicals Corporation was purified by four distillations as described previously in this Journal.[6] It had a density at 25.00° of 0.78654 *in vacuo* which compares with 0.78660 given by the "International Critical Tables."

Mixtures were made in glass-stoppered flasks. After measuring the dielectric constant of each mixture, its density was taken in a modified form of the Ostwald pycnometer and checked against the values given in the "International Critical Tables."

Apparatus.—The apparatus consisted of the radio frequency bridge circuit described by Albright[7] with the following changes.

1. The equipment was made entirely a. c. operated. A Sargent 110-volt a. c. "all-wave" regenerative receiver was used as a detector to determine bridge balance, and a Clough–Brengle, wide-range, a. c. operated, radio frequency oscillator provided the input signal.
2. The voltage supplied to the receiver and oscillator was stabilized by a Sola constant voltage transformer.
3. The dielectric cell was provided with improved thermal insulation, and a new constant temperature bath was built so that the cell which contained the liquid being measured could be maintained at any temperature between 5 and 55° within 0.01°. The thermometer used was checked against a thermometer calibrated by the National Bureau of Standards.
4. The precision condenser was carefully calibrated.
5. The resistances R_3 and R_4 now consist of vertical glass tubes in which are sealed platinum grids. A solution of 0.030 *M* potassium chloride was used in R_3. The resistance of R_4 was easily varied by admitting 0.10 *M* potassium chloride solution in the bottom of the tube, and distilled water in the top. By varying the height of the mixture, the concentration, and hence the resistance, of the solution between the grids was varied. Due to the small areas of these grids, their relatively large separation of about two centimeters, and the small change of dielectric constant of potassium chloride solutions with the concentration, the capacitance changes of these resistors is negligible over the range of resistance changes involved.
6. The inductance of electrical leads in the cell arm of the bridge was further reduced. It is necessary that this inductance be kept very low when making measurements with solutions of appreciable conductance, such as water, since the shift of resistance from the cell to R_4, when turning the cell from minimum to maximum capacitance, will vary the amount of current flowing through the residual inductance in the lead wires. This source of error was found by decreasing the resistance of R_3 and R_4 to successively lower values, while measuring the apparent dielectric constant of water in the cell. The dielectric constant (after extrapolation to zero frequency as described below under "data") appeared to increase slightly as the resistances of R_3 and R_4 were decreased. When the cell was filled with a very dilute solution of hydrochloric acid the effect was much more pronounced, due to the increased conductivity. The following table illustrates the magnitude of these changes of apparent capacitance of the dielectric cell as a function of R_3. The data were obtained with about 15 cm. of extra wire in the leads to both R_3 and R_4, thus providing a small amount of extra inductance in the circuit. Measurements were made on nitrobenzene, conductivity water, and 0.0001 *M* hydrochloric acid to show the dependence of this error upon the conductivity of the liquid in the cell. Values shown in the table are expressed in units of capacitance of the precision condenser, and are proportional to the apparent dielectric constant of the liquid. Measurements were made at 30.00°. On making a more direct electrical connection, thus removing most of the 15 cm. of extra wire in the leads to R_3 and R_4, the dependence of the apparent dielectric constant on R_3 decreased greatly, as shown below. These measurements were made on conductivity water at 25.00°

TABLE I

DEPENDENCE OF APPARENT MINIMUM-MAXIMUM CELL CAPACITANCE DIFFERENCES ON R_3 AND THE CONDUCTIVITY OF THE SOLUTION IN THE CELL

(before reducing length of leads to R_3 and R_4)
Temperature = 30.00°

Concn. of KCl in R_3, *M*	Nitrobenzene	Conductivity water	0.0001 *M* HCl
0.05	11.55	26.20	
.10		26.24	27.0
.30	11.55	26.43	30.2
.50	11.55	26.57	33.1

TABLE II

DEPENDENCE OF APPARENT MINIMUM-MAXIMUM CELL CAPACITANCE DIFFERENCES ON R_3

(after reducing lengths of leads to R_3 and R_4)
Temperature = 25.00°

Concn. of KCl in R_3, *M*	Capacitance diff. conductivity water
0.02	26.802
.10	26.815
.30	26.845
.50	26.870

Thus the errors from this source were shown to be less than one part in 5000 for the conductivities encountered in the methanol–water system. The importance of correction for, or removing, inductance in the leads when measuring solutions of appreciable conductivity is emphasized in the theoretical treatments of the subject by Davies and Jones[8] and by Shaw.[9]

Data.—Changes in C_3 corresponding to capacitance differences between the two cell positions were extrapolated to zero frequency by plotting the precision condenser differences against the square of the frequency, as suggested by Miller.[10] This eliminated inductive effects in the precision condenser and other parts of the circuit which had approximately constant resistance and were not corrected by the adjustments to decrease lead inductance mentioned under "apparatus." The extrapolation procedure was checked experimentally with conductivity water in the cell, using frequencies between 100 and 3000 kc. Values obtained with frequencies from 600 to 3000 kc. were found to be within 1 part in 2500 of lying on a straight line. The apparent dielectric constant at 2000 kc. was often at least five parts per thousand different from the value extrapolated to zero frequency. The slope of this extrapolation curve was not constant, but varied with the temperature and methanol concentration of the solution in the cell. At least four different frequencies between 650 and 2000 kc. were used for extrapolating each dielectric constant determination to zero frequency.

The dielectric constant of water at 25.00° was assumed to be 78.48 as reported by Albright.[7] This is in good agreement with values of several other workers, as summarized by Jones and Davies.[4] Other dielectric constant values for the system were calculated from this value by ratios of the capacitance changes extrapolated to zero frequency. These results were corrected for changes in the cell dimensions with temperature.

Results

The values shown in Table III were obtained for the dielectric constants of the methanol–water system after smoothing the original data, and shifting to even percentages. We prefer to pre-

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(6) Wright, Stuber and Albright, THIS JOURNAL, **61**, 228 (1939).

(7) Albright, *ibid.*, **59**, 2098 (1937).

(8) Davies and Jones, *Phil. Mag.*, **28**, 289 (1939).

(9) Shaw, *J. Chem. Phys.*, **10**, 609 (1942).

(10) Miller, THIS JOURNAL, **60**, 42 (1938).

sent these data in tabular form, rather than by equations.

Table III

Dielectric Constants of the Methanol–Water System

Weight % methanol	Temperature, °C.					
	5.00	15.00	25.00	35.00	45.00	55.00
0.00	86.10	82.19	78.48	74.94	71.50	68.13
10.00	81.68	77.88	74.18	70.68	67.32	64.08
20.00	77.38	73.59	69.99	66.52	63.24	60.06
30.00	72.80	69.05	65.55	62.20	58.97	55.92
40.00	67.91	64.31	60.94	57.72	54.62	51.69
50.00	62.96	59.54	56.28	53.21	50.29	47.53
60.00	57.92	54.71	51.67	48.76	46.02	43.42
70.00	52.96	49.97	47.11	44.42	41.83	39.38
80.00	48.01	45.24	42.60	40.08	37.70	35.46
90.00	42.90	40.33	37.91	35.65	33.53	31.53
95.00	39.98	37.61	35.38	33.28	31.29	29.43
100.00	36.88	34.70	32.66	30.74	28.92	27.21

These values at 25.00° differ from the values of Jones and Davies[4] by less than one part in 500.

Summary

The dielectric constants of the methanol–water system have been measured for the temperatures of 5 to 55° by using an a.c. bridge circuit. It is believed that values given are accurate to within one part in 1000, or better, assuming that the dielectric constant of water at 25.00° is 78.48.[7]

Madison, Wisconsin Received November 19, 1945

[Contribution from the Chemical Laboratory of the University of California]

The Heat Capacity, Vapor Pressure, Heats of Fusion and Vaporization of Cyclopropane. Entropy and Density of the Gas[1]

By R. A. Ruehrwein[2] and T. M. Powell[3]

This paper is a report on the low temperature calorimetric investigations of cyclopropane. By means of these data and the third law of thermodynamics a value of the entropy of the gas has been obtained and this value compared with that calculated from spectroscopic and molecular data. The two values agree within their limits of error.

The measurements were made in a calorimeter with the laboratory designation Gold Calorimeter II. The apparatus and method of measurement have been described previously.[4]

Preparation and Purity of Cyclopropane.—The cyclopropane was obtained from the Ohio Chemical Company. It was purified by distilling through a vacuum-jacketed fractionating column packed with single-turn glass helices. From calorimetric measurements of the premelting effect the impurity was estimated to be 0.03 mole per cent.

The Melting Point of Cyclopropane.—A summary of the observations on the melting point is given in Table I.

Table I

Melting Point of Cyclopropane

0° C. = 273.10° K.

Time	% Melted	T, °K., resistance thermometer	T, °K., thermocouple
4/27			
10:18 p. m.	Heated into melting point		
11:05 p. m.	10	145.413	145.42
12:00 m.	10	145.397	145.40
4/28			
12:35 a. m.	10	145.392	145.40
1:03 a. m.	10	145.390	145.40
1:35 a. m.	Supplied heat		
10:50 a. m.	30	145.491	145.50
11:20 a. m.	30	145.490	145.49
2:16 p. m.	Supplied heat		
5/1			
12:01 a. m.	56	145.515	145.54
12:39 a. m.	Supplied heat		
11:00 a. m.	80	145.515	145.54
		Accepted value	145.54

The Vapor Pressure of Cyclopropane.—The vapor pressure was measured with a Société Génévoise cathetometer with a precision of 0.002 cm. It was used as a comparison instrument for a standard meter suspended between the arms of a mercury manometer. The manometer was in a case in which the air was circulated to ensure a uniform temperature. The acceleration of gravity was taken as 979.973 cm. sec.$^{-2}$ for this location and the standard acceleration as 980.665 cm. sec.$^{-2}$. The meniscus corrections were taken from the work of Cawood and Patterson[5] and data given in the "I.C.T."[6] were used to correct the observations to international cm. of Hg.

The data have been represented by the equation, 183.1 to 241.1° K.

$$\log_{10}P \text{ (inter. cm. Hg)} = 9.03877 - \frac{1348.2}{T} - 0.00823\,T + 7.45 \times 10^{-6}T^2 \quad (1)$$

The vapor pressure observations are compared

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[1] Presented to the American Association for the Advancement of Science, Pasadena Meeting, June, 1941.

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[3] Present address: Standard Oil Co., Richmond, Calif.

[4] (a) Blue and Giauque, This Journal, **57**, 991 (1935); (b) Giauque and Wiebe, *ibid.*, **50**, 101 (1928); (c) Giauque and Johnston, *ibid.*, **51**, 2300 (1929); (d) Giauque and Egan, *J. Chem. Phys.*, **5**, 45 (1937).

[5] Cawood and Patterson, *Trans. Faraday Soc.*, **29**, 514 (1933).

[6] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., 1926, Vol. I.