

# Density and Compressibility of Four Higher Alcohols for Pressures to 2800 Kg. per Sq. Cm.

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Data are reported on the density and compressibility of glycerol, 1,3-butanediol, 2-methyl-2,4-pentanediol, and 1,5-pentanediol, over the range  $-50^{\circ}$  to  $80^{\circ}$  C. from atmospheric pressure to 2800 kg. per sq. cm. The data are estimated to be accurate to better than 1 part in 2000. At atmospheric pressure the reciprocal density was linear with temperature. As a function of temperature and pressure, the density can be represented within experimental accuracy by a Tait equation of the form  $\rho^{-1}(T,P) = \rho^{-1}(T,O) - a_0 \log_e \{ [P + B(T)] / [1.0332 + B(T)] \}$ . The ratio of specific heats is determined for glycerol and 1,3-butanediol using the density and ultrasonic velocity data.

IN LIQUID STATE STUDIES, the volume dependence of various dynamic parameters is of considerable interest. Volume theories which attempt to relate viscosity, self-diffusion, electrical conductivity, and/or relaxation times to the volume of a liquid have been partially successful in a variety of liquids and polymers. Recent examples of this approach are found in the work of Williams, Landel, and Ferry (17), Cohen and Turnbull (3), Macedo and Litovitz (7), Matheson (10), and Hogenboom, Webb, and Dixon (5). To test these theories adequately in a given liquid, a wide range of data on the parameter under study must be available and accurate volume data must exist.

Liquids which supercool are particularly convenient for such studies because of the wide range over which data may be obtained. Viscosity, dielectric, and mechanical relaxation data in many liquids which supercool are available above and in the supercooled regions as a function of both temperature and pressure. Two to ten decades of data are common. However, accurate volume data in the supercooled region are generally not available, particularly as a function of pressure.

Recently a densitometer was developed for measuring the change in volume of a liquid over a wide range of temperatures and pressures (9). This device has been used to measure the pressure dependence of the specific volume of three hydrogen-bonded liquids which supercool easily (glycerol, 1,3-butanediol, and 2-methyl-2,4-pentanediol) and one hydrogen-bonded liquid which does not supercool (1,5-pentanediol). This paper reports these volume data and the thermodynamic parameters derived from them.

## EXPERIMENTAL

The densitometer measures relative changes in the volume of fluids over wide ranges of temperature and pressure. It employs a nickel alloy bellows, whose displacement is determined by means of a differential transformer arrangement located external to the pressure and temperature environment. Hydrostatic pressure is applied to the sample-filled bellows, using ethyl alcohol as a pressure-transmitting fluid. A diagram of the apparatus is shown in Figure 1.

The pressure vessel housing the bellows is mounted in a commercial air temperature bath. Temperature is measured by a copper-constantan thermocouple mounted inside the pressure vessel at a point near one end of the bellows. The internal temperature of the vessel is maintained constant to within  $0.05^{\circ}$  C. Pressure is measured

in the line connecting the pressure vessel to the pressure pump by a Heise Bourdon pressure gage. The measured temperature is estimated to be accurate to within  $\pm 0.1^{\circ}$  C., and the measured pressure to within approximately  $\pm 0.5\%$ .

Details of the device were reported by Madigosky (9). The calibration described in this reference is relative, being based on measurements made in water. This calibration has been modified for the measurements reported here. A calibrated buret was attached to the bellows system and the actual volume change measured as a function of the displacement of the end of the bellows. Water was used as the fluid in this measurement, the temperature maintained at  $23^{\circ}$  C., and the pressure atmospheric. By this means an absolute calibration of the bellows was obtained. The proportionality constant between the displacement of the end of the bellows and change in volume of the bellows was found to be slightly dependent on the displacement. An additional modification was made in the original device by replacing the quartz rod connecting the movable end of the bellows to the transformer core with a stainless steel rod. The shortening of this rod by hydrostatic pressure was measured as a function of pressure and temperature. A correction to the measured bellows displacement was then included in the data reduction process. We estimate that the measured volume changes using the above technique are accurate to 1 part in 2000.

To verify the absolute calibration described above, the pressure dependence of the density of distilled water was measured at  $0^{\circ}$  and  $40^{\circ}$  C. and compared with the data of Bridgman (2). The root mean square deviation between the data of Bridgman and the data of this paper is 1 part per 1000 (Table I). The shapes of the curves of  $\rho(T,P)$  vs. pressure for the two sets of data are slightly different, as indicated by the systematic change in the differences given in the last column of the table.

The samples of 1,3-butanediol, 2-methyl-2,4-pentanediol, and 1,5-pentanediol used in these tests were Fisher Scientific Co. "highest purity" liquids (Fisher Catalog Nos. 5566, 1828, and 5941). No further purification was attempted. The glycerol sample was reagent grade (Fisher Catalog No. G33) and contained approximately 0.3% water by weight.

The bellows was loaded under vacuum with the liquids to be measured, sealed, and then placed in the thermostated pressure container. Isothermal data were taken on the displacement of the movable end of the bellows as a function of pressure. Data were taken for both increasing and decreasing pressure, between 20 and 30 points at each temperature. The difference between the position of the mov-

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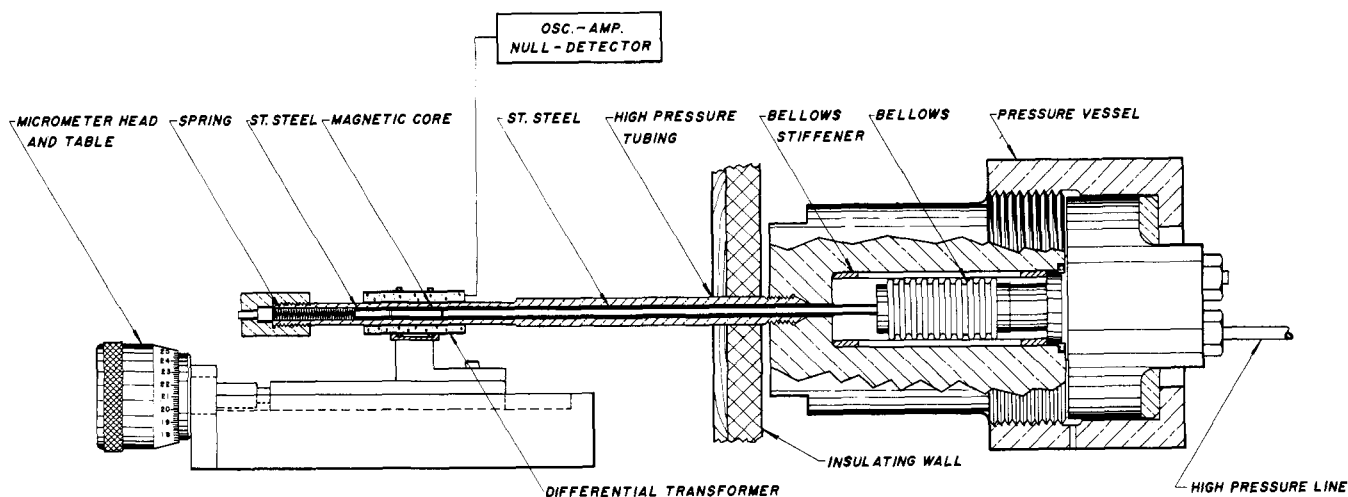


Figure 1. Assembly drawing of apparatus for measuring relative volume

Table I. Measured Density of Water as a Function of Pressure Compared with Data of Bridgman

$T, ^\circ\text{C.}$	$P, \text{ Kg./Sq. Cm.}$	$\rho(T,P), \text{ G./Cc.}$		Difference, Parts per Thousand
		Measured	Bridgman <sup>a</sup>	
40	1.0332	0.99224 (1)		
	500	1.0115	1.0121	-0.6
	1000	1.0295	1.0304	-0.9
	1500	1.0459	1.0472	-1.3
	2000	1.0618	1.0630	-1.2
	2500	1.0775	1.0774	+0.1
	3000	1.0907	1.0910	-0.3
0	1.0332	0.99987 (1)		
	500	1.0224	1.0236	-1.2
	1000	1.0427	1.0442	-1.5
	1500	1.0612	1.0628	-1.6
	2000	1.0784	1.0798	-1.4
	2500	1.0947	1.0950	-0.3
	3000	1.1096	1.1093	+0.3

<sup>a</sup> Calculated from data of Bridgman (2).

able end of the bellows at atmospheric pressure and its position as a function of pressure was fitted by a fifth-order polynomial in pressure for each temperature. These polynomials were then used as the source of raw data.

The density at atmospheric pressure of the liquids under test was measured as a function of temperature, using a standard pycnometer technique, to an accuracy of better than 1 part in 2000.

## RESULTS

In each of the four liquids studied, the measured density changes at atmospheric pressure were found to vary linearly with temperature to within the accuracy of the measurement over the complete temperature range of approximately 90°C. The density at atmospheric pressure,  $\rho(T,O)$ , was thus assumed to have the form  $\rho(T,O) = b_0 - b_1T$ . Formulas for each liquid are given in Table II; the temperature ranges over which measurements were taken are shown in the last column of this table. The densities calculated from these formulas are estimated to be accurate to within 1 part in 2000.

Picirelli and Litovitz (13) and Meister *et al.* (11) have published  $\rho(T,O)$  data for glycerol, 1,3-butanediol, and 2-methyl-2,4-pentanediol over somewhat smaller temperature ranges than those reported here. Although they use a form for  $\rho(T,O)$  different from that used here and

Table II. Density Formulas at Atmospheric Pressure

Liquid	$\rho(T,O), \text{ G./Cc.}$	Temp. Range, °C.
Glycerol	$1.2723 - 6.55 \times 10^{-4}T$	-50 to 80
1,3-Butanediol	$1.0166 - 6.66 \times 10^{-4}T$	-50 to 40
2-Methyl-2,4-Pentanediol	$0.9364 - 7.49 \times 10^{-4}T$	-50 to 40
1,5-Pentanediol	$1.0010 - 6.08 \times 10^{-4}T$	-30 to 40

claim only 0.5% accuracy, values of  $\rho(T,O)$  calculated from their data agree to within 0.1% with the data reported here.

Accurate specific volume changes in glycerol as a function of temperature in the range 0° to 300°C. are listed by Laurie (6). These data show a larger volume expansion than the present data; however, over the temperature range -50° to 80°C., the densities determined from the two sets of data agree within the accuracy of the present measurements.

The pressure dependence of the density,  $\rho(T,P)$ , can be expressed in terms of the bellows displacement by

$$\rho(T,P) = \frac{W}{V(T,O) - K\Delta L(T,P)} \quad (1)$$

where  $W$  is the weight of the sample,  $V(T,O)$  is the volume of the sample at atmospheric pressure,  $K$  is the calibration constant of the bellows, and  $\Delta L(T,P)$  is the change in the length of the bellows corrected for the small error introduced by the pressure dependence of the rod connecting the movable end of the bellows and the ferrite core of the differential transformer. The volume of the sample at atmospheric pressure is determined from  $W/\rho(T,O)$ . Values of  $\rho(T,P)$  were computed from Equation 1 for convenient increments of pressure (14 increments) at each temperature, using  $W$  and  $\rho(T,O)$  and the polynomial representation of  $\Delta L(T,P)$ .

The computed values of  $\rho(T,P)$  can be conveniently represented by a Tait equation of the form

$$-\left. \frac{dv(T,P)}{dp} \right|_T = \frac{C}{P + B(T)} \quad (2)$$

where  $v$  is the specific volume and  $C$  is a constant for all  $T$  and  $P$ .  $B(T)$  is a temperature-dependent parameter.

For the liquids studied,  $B(T)$  can be represented by the linear function

$$B(T) = a_1 - a_2 T \quad (3)$$

Manipulation of Equation 2 yields

$$\rho^{-1}(T,P) = \rho^{-1}(T,O) - a_0 \log \frac{P + B(T)}{P_0 + B(T)} \quad (4)$$

where  $a_0 = C/M$ ,  $M$  is the molecular weight, and  $P_0$  is the atmospheric pressure. Using the data computed from Equation 1 in Equations 3 and 4, the constants  $a_0$ ,  $a_1$ , and  $a_2$  have been determined by a least squares fit technique. These constants and the appropriate temperature and pressure ranges are given in Table III for the four liquids measured. The root mean square error between the values of  $\rho(T,P)$  calculated from Equations 3 and 4 and the experimental values determined by means of Equation 1 are also given in Table III for each of the liquids. Curves of density vs. pressure for liquids studied are given in Figures 2 to 5.

Actual measured data are not given because of the excellence of fit of the data to Equation 4. Values of density calculated from Equation 4 and the constants of Tables II and III are more accurate than the measured points, because of the smoothing of random errors by the fitting

process. Values of density calculated from these formulas are considered accurate to better than 1 part in 2000.

An expression for the isothermal compressibility,  $\beta_T = -(1/v)(dv/dP)$ , may be obtained in terms of the Tait equation parameters by differentiating the reciprocal density expression, Equation 4. The resulting expression is

$$\beta_T = a_0/[P + B(T)] \quad (5)$$

The pressure dependence of  $\beta_T$  at 20° C. determined from Equation 5 and the constants of Tables II and III is given in Table IV for the four liquids studied. These compressibilities are estimated as accurate to within 5%.

Table V compares values of  $\beta_T$  for glycerol at atmospheric pressure with values determined from density data by other workers. The agreement between the present data and the literature values is excellent.

The isothermal compressibility may also be determined from ultrasonic low frequency compressional modulus and specific heat data by using

$$\beta_T = \beta_S + \frac{T\alpha^2}{\rho c_P} \quad (6)$$

$$\beta_S = 1/K_0 \quad (7)$$

Table III. Tait Equation Constants for Temperature and Pressure Dependence of Density of Liquids Listed

Reciprocal density given by  $\rho^{-1}(T,P) = \rho^{-1}(T,O) - a_0 \log_e \{ [P + B(T)]/[1.0332 + B(T)] \}$  where  $B(T) = a_1 - a_2(T + 273.2)$ . Pressure in kg./sq. cm. absolute and  $T$  in degrees Centigrade. Pressure range atmospheric to 2800 kg./sq. cm. except where noted.

Liquid	$a_0$	$a_1$	$a_2$	RMS of Fit ( $\times 10^4$ )	Temp., Range, °C.
Glycerol	0.1115	12,550	20.55	1.8	-50 to 80
1,3-Butanediol	0.1134	6298	12.19	2.7	-40 to 30
2-Methyl-2,4-pentanediol	0.1148	4670	10.19	8.3	-50 to 30
1,5-Pentanediol <sup>a</sup>	0.1366	7782	14.83	5.8	-20 to 35

<sup>a</sup> Pressure ranges atmospheric to 1800 kg./sq. cm. at -20° C. and atmospheric to 2400 kg./sq. cm. at -10° C.

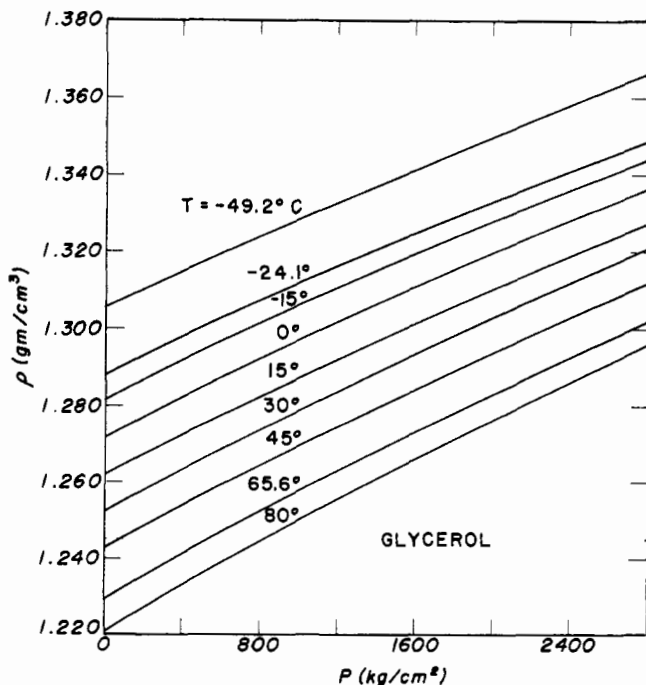


Figure 2. Density of glycerol as a function of pressure

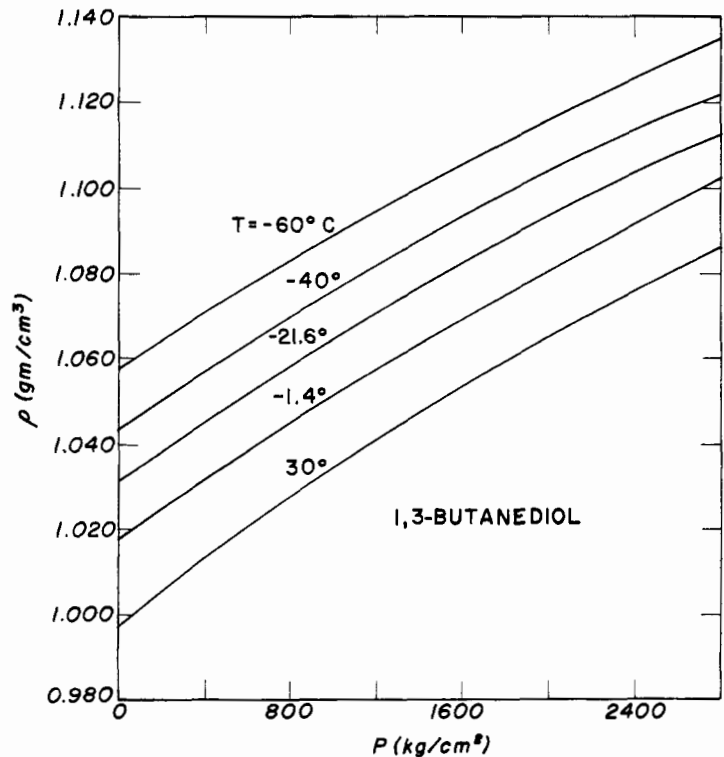


Figure 3. Density of 1,3-butenediol as a function of pressure

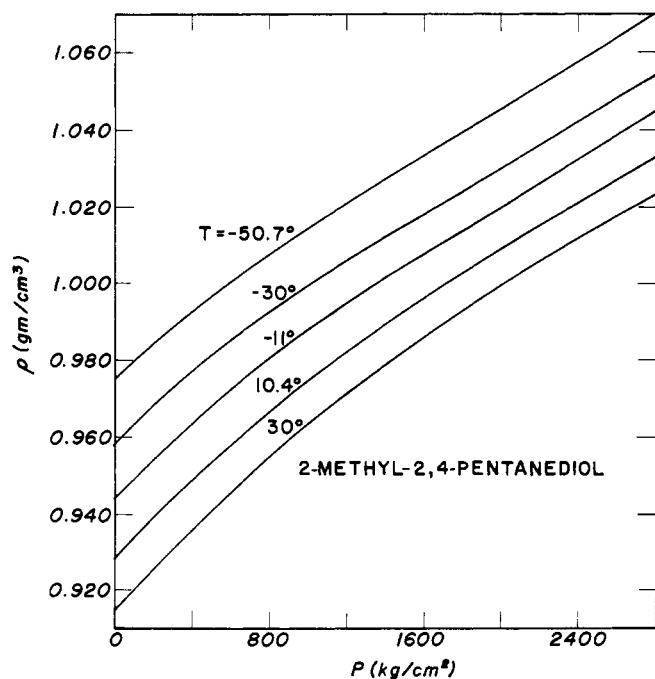


Figure 4. Density of 2-methyl-2,4-pentanediol as a function of pressure

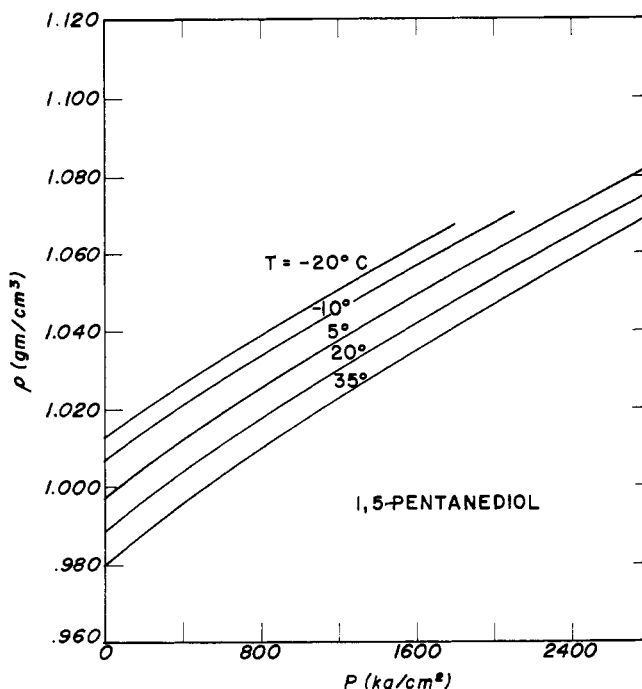


Figure 5. Density of 1,5-pentanediol as a function of pressure

Table IV. Pressure Dependence of Compressibility and Expansion Coefficient Calculated from Equation 4 at 20° C.

$\beta_T$  in units of  $10^{-6}$  sq. cm./kg. and  $\alpha_T$  in units of  $10^{-4}/^\circ\text{K}$ .

P, Kg./Sq. Cm.	Glycerol		1,3-Butanediol		2-Methyl-2,4-pentanediol		1,5-Pentanediol	
	$\beta_T$	$\alpha_T$	$\beta_T$	$\alpha_T$	$\beta_T$	$\alpha_T$	$\beta_T$	$\alpha_T$
1	21.5	5.20	41.8	6.64	62.9	8.13	39.3	6.15
1000	19.0	5.91	31.7	8.30	41.5	11.1	31.6	7.73
2000	17.1	6.48	25.7	9.38	31.3	12.7	26.5	8.84
3000	15.6	6.96	21.7	10.2	25.3	13.7	22.9	9.69

where  $K_0$  is the low frequency compressional modulus,  $\alpha$  is the thermal expansion coefficient, and  $c_p$  is the specific heat. In glycerol,  $K_0$  has been measured by Slie and Madigosky (15), who found that

$$K_0(T,P) = K_0(T) + 1.08 \times 10^{-3}P \quad (8)$$

where  $K_0(T,P)$  is in units of  $10^{10}$  dynes per sq. cm. The atmospheric modulus is given in the same units, by

$$K_0(T) = 4.91 - 0.0122T \quad (9)$$

where  $T$  is in degrees Centigrade. The modulus of Equation 8 is estimated to be accurate to within  $\pm 4\%$  for  $15^\circ < T < 65^\circ\text{C}$ . and  $1 < P < 3000$  kg. per sq. cm. Equation 9 has the same accuracy for  $-5^\circ < T < 65^\circ\text{C}$ .

At atmospheric pressure  $\beta_T$  has been determined for glycerol from Equation 6 using the modulus data above,  $C_p$  from Parks and Huffman (12), and  $\alpha$  data determined from Table III. The values thus obtained are presented in the last column of Table V. Approximately 90% of  $\beta_T$  in Equation 6 is determined by  $\beta_s$ ; thus the accuracy of  $\beta_T$  is governed primarily by the  $1/K_0$  term. Since  $K_0$  is accurate to 4%,  $\beta_T$  from Equation 6 is considered to be accurate to approximately 5%.

$\beta_T$  values in Table V, determined by the two methods above, differ by about 9%. This discrepancy may be attributed to the lack of necessary precision in determining the density, with the resultant lack of accuracy in the derivative with respect to pressure, from which the values of  $\beta_T$  in the first column of Table V are determined. Although the present density data are accurate to better

Table V. Isothermal Compressibility of Glycerol at Atmospheric Pressure

Values in second and third columns determined using only density data; those in fourth column determined from adiabatic modulus and  $C_p$  data.

T, °C.	$10^{-6}\beta_T$ , Sq. Cm./Kg.		
	From Eq. 5	Lit.	From Eq. 6
0	20.5		
15	21.2	21.4 (4)	22.2
20	21.5	21.0 (16)	23.2
		21.0 (1)	23.6
		24.3 <sup>a</sup> (14)	
30	22.1		24.3

<sup>a</sup> Value of 24.3 measured for pressure range of 0 to 1 atm. All other values taken from high pressure data.

than 1 part per 2000, considerably more precision is necessary to determine  $\beta_T$  from density data to within 1 or 2%. The choice of the form of  $B(T)$  in the density equation also slightly affects the resulting value of  $\beta_T$  at atmospheric pressure.

The ratio of specific heats,  $\gamma$ , may be determined from the above data by using

$$\gamma = \beta_T/\beta_s \quad (10)$$

The value of  $\beta_T$  in Equation 10 may be taken from either Equation 5 or 6. In glycerol at atmospheric pressure, using

Equations 5, 7, and 10,  $\gamma$  is found to be 1.02 and approximately independent of temperature. As a function of pressure this procedure gives for glycerol

$$\gamma(P) = 1.02 + 8 \times 10^{-5}P \quad (11)$$

over the temperature and pressure range studied. Equation 11 is estimated to be accurate to approximately 5%.

If  $\beta_T$  values from Equation 6 at atmospheric pressure are used, a somewhat higher value of  $\gamma$  is obtained. The authors have attempted to determine  $\gamma(P)$  for glycerol from Equation 6 by estimating the pressure dependence of  $C_p$  from Equation 4 using

$$\left. \frac{\partial C_p}{\partial P} \right|_T = -T \left[ \frac{\partial^2(\rho^{-1})}{\partial T^2} \right]_P \quad (12)$$

Although this procedure is inaccurate, it indicates that  $C_p$  is approximately independent of pressure over the temperature range of interest. Within this approximation Equations 6 and 10 yield

$$\gamma(P) = 1.12 + 8 \times 10^{-5}P \quad (13)$$

which is independent of temperature and has the same pressure dependence as that found in Equation 11.

An analysis of  $\beta_T(P)$  and  $\gamma(P)$  similar to that for glycerol was not possible for the other liquids studied because of the lack of modulus and specific heat data. In butanediol, however,  $\gamma(P)$  can be determined using the modulus data of Madigosky (8). For this liquid

$$K_0(T, P) = 2.61 - 0.01T + 1.2 \times 10^{-3}P \quad (14)$$

in units of  $10^{10}$  dynes per sq. cm. Using Equation 10 and  $\beta_T$  calculated from Equation 4,  $\gamma$  is approximately independent of temperature, and its pressure dependence is given by

$$\gamma(P) = 1.03 + 0.145 \times 10^{-3}P - 0.015 \times 10^{-6}P^2 \quad (15)$$

The thermal expansion coefficient,  $\alpha_T = [1/\rho][\partial(1/\rho)/\partial T]$ , may also be determined from Equation 4 and is given by

$$\alpha_T = \rho(T, P) \left[ \frac{b_1}{(b_0 - b_1 T)^2} - \frac{a_0 a_2 (P - 1.0332)}{(P + B)(1.0332 + B)} \right] \quad (16)$$

Equation 16 has been evaluated as a function of pressure for the liquids studied; the results at 20°C. are given in Table IV.

## CONCLUSIONS

Glycerol, a triol, is the densest of the four liquids studied. It also has the smallest thermal expansion and compressibility coefficients of the group.

Two of the diols studied, 1,3-butanediol and 1,5-pentanediol, have approximately the same density, gross pressure dependence, thermal expansion, and compressibility coefficients. This is to be expected because of the similarity in their molecular configurations.

The third diol, 2-methyl-2,4-pentanediol, has volume properties considerably different from those of the other two diols. It is the least dense of the four liquids studied; its gross pressure dependence, thermal expansion, and compressibility coefficients are considerably larger than those of the other liquids. These effects are undoubtedly due to the existence of the side chain methyl group. Finally, the ratio of specific heats for glycerol and 1,3-butanediol were found to be approximately equal and independent of temperature, but strongly pressure-dependent.

## LITERATURE CITED

- (1) American Institute of Physics Handbook, 2nd ed., McGraw-Hill, New York, 1963.
- (2) Bridgman, P.W., *J. Chem. Phys.* **3**, 397 (1935).
- (3) Cohen, M.H., Turnbull, D., *Ibid.*, **31**, 1164 (1959).
- (4) deMetz, J., *Wied. Ann.* **41**, 664 (1890).
- (5) Hogenboom, D.L., Webb, W., Dixon, J.A., *J. Chem. Phys.* **46**, 2586 (1967).
- (6) Laurie, J.W., "Glycerol and the Glycols," p. 163, Chemical Catalog Co., New York, 1928.
- (7) Macedo, P.B., Litovitz, T.A., *J. Chem. Phys.* **42**, 245 (1965).
- (8) Madigosky, W., private communication, Naval Ordnance Laboratory, Silver Spring, Md., 1968.
- (9) Madigosky, W.M., *Rev. Sci. Instr.* **37**, 227 (1966).
- (10) Matheson, A.J., *J. Chem. Phys.* **44**, 695 (1966).
- (11) Meister, R., Marhoeffer, C.J., Sciamanda, R., Cotter, L., Litovitz, T.A., *J. Appl. Phys.* **31**, 854 (1960).
- (12) Parks, G.S., Huffman, H.M., *J. Phys. Chem.* **31**, 1842 (1929).
- (13) Piccirelli, R., Litovitz, T., *J. Acoust. Soc. Am.* **29**, 1009 (1957).
- (14) Quincke, G., *Wied. Ann.* **19**, 401 (1883).
- (15) Slie, W., Madigosky, W., *J. Chem. Phys.* **48**, 2810 (1968).
- (16) Tammann, G., Ruhlenbeck, A., *Ann. Physik* **13**, (5) 63 (1932).
- (17) Williams, M.L., Landel, R.F., Ferry, J.D., *J. Am. Chem. Soc.* **77**, 3701 (1955).

RECEIVED for review July 1, 1968. Accepted December 9, 1968.