

CCXXXVI.—*Adiabatic and Isothermal Compressibilities of Liquids between One and Two Atmospheres' Pressure.*

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THE present paper constitutes an extension of a previous one (T., 1913, **103**, 1675) on the compressibility of liquids, in which a new and precise method for the determination of compressibilities at low pressures was described.

Since the publication of the previous results, it was discovered that a small correction to the observed values had been overlooked. This was due to neglecting the small change in pressure on the liquid caused by the change of level of the liquid in the vertical capillary tube (see the previous paper). Although this pressure is very small compared with the total external pressure change, it introduces a correction greater than the general experimental error, and must therefore be taken into account. Fortunately, this correction can be accurately calculated from the observed data, and, on the average, causes the results to be raised by about 0.5 per cent. All the previously obtained results have accordingly been corrected, and the corrected values are contained in the tables in this paper. The necessity of this correction is to be regarded as a disadvantage of the piezometer. It has also been noticed that for rather viscous liquids, such as aniline, the capillary tube requires a long time to drain, and for easily vaporised liquids, such as ether, slight errors are introduced by the evaporation of a little liquid in the capillary tube during an experiment. To avoid these disadvantages and sources of error, the piezometer was modified, as is fully described below. In order to test the accuracy of the previous results (corrected as explained above), a few of the determinations were repeated, in each case with the new piezometer. As will be seen from the following tables, the differences between the old and new results are, in general, very small, which gives considerable confidence in the validity and precision of the method.

In order to determine the isothermal compressibility from the adiabatic value, use is made of the following thermodynamic equation:

$$\beta = \alpha + \frac{1 \left(\frac{dv}{dt} \right)^2}{J_v C_p}$$

where β and α are the isothermal and adiabatic compressibilities

respectively, v the specific volume, J the mechanical equivalent of heat, C_p the specific heat at constant pressure, and T is the absolute temperature.

In the previous work, in order to obtain values of dv/dt and of C_p , the results of other investigators were relied on. In the case of C_p , errors, even moderately large, have a comparatively small effect on the accuracy of β , but in the case of dv/dt the effect of errors is considerable. It was found that in many cases the values of dv/dt which had been calculated from the specific-volume data of various investigators contained considerable errors, and it was therefore necessary to make a series of accurate specific-volume determinations for each liquid, from which accurate values of dv/dt could be calculated. The practical part of the work is therefore divided into two parts, namely, the determination of adiabatic compressibilities at different temperatures and the determination of specific volumes.

Apparatus: The New Form of Piezometer.

The construction of the piezometer can best be understood by referring to the diagram. The liquid to be investigated is contained in the inner vessel, A , of ordinary soda-glass, filled completely up to and between the two taps, T and T_1 , and the mercury thread in the horizontal capillary tube, B . The two tubes C and D are attached by stout rubber tubing to a small air-pump and manometer. On increasing the pressure, the mercury thread is depressed in the graduated tube, B . When the temperature is constant, the pressure is released, and the change in position of the mercury thread in B is noted. The filling of the piezometer is effected by first exhausting it of air, by attaching the side-tube E to a strong pump, and then allowing the liquid to enter through the tap T . When almost filled, the capillary tube B is dried, the mercury thread allowed to enter, and then the last few c.c. of air expelled from the apparatus by warming. It is emptied by inverting the instrument and attaching the tube E to a suitable exhausted receptacle.

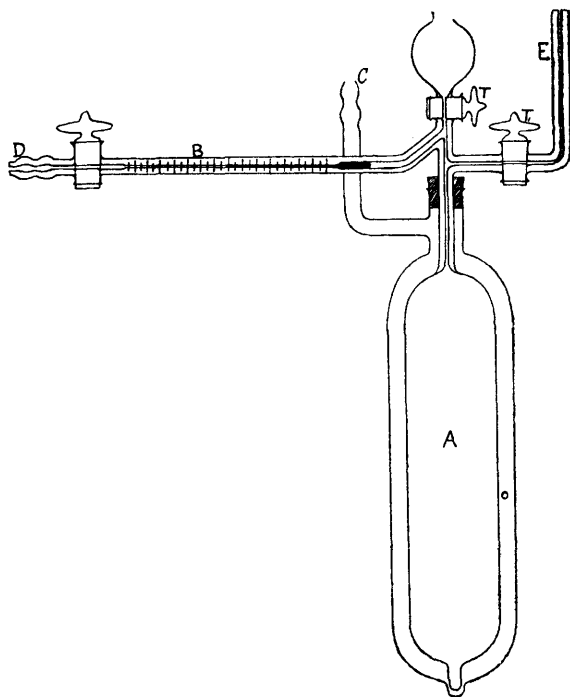
For further details of the rest of apparatus, and the manner of working, the previous paper must be consulted. No correction beyond that of the compressibility of the glass is necessary. For the compressibility of the glass, the result of Amagat (2.18×10^{-6}) has been taken as correct.

The volume of the piezometer used was about 450 c.c., and the diameter of the graduated capillary tube depended on the compressibility of the liquid in the apparatus, but was such as to give

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a change of reading of about 6 to 10 cm. for a pressure change of about one atmosphere.

The average error of the adiabatic compressibility determinations does not appear to be greater than 0.1 per cent. Probably the greatest constant error lies in the correction for the compressibility of the glass, but this must be comparatively small, for it was shown in the previous communication that results obtained with a copper piezometer, which requires a much smaller correction than glass,



are in good agreement with the results obtained with a glass piezometer.

Determination of Values of dv/dt .

In order to be able to calculate accurate values for the function dv/dt , very accurate specific-volume data—carried out to the fifth decimal place at least—are necessary. The dilatometer is not capable of giving such a degree of accuracy, and hence the longer method of the pycnometer had to be used. The ordinary Sprengel

form of pycnometer is liable to considerable error for volatile liquids, owing to evaporation in the two capillary tubes, and for viscous liquids there is always an appreciable quantity of liquid which clings to the sides of the unfilled part of the capillary tube. A new form of pycnometer was therefore devised which has only one capillary tube instead of two. On the capillary tube is etched a fine mark, and the open end is widened out and provided with a ground-glass stopper. The instrument had an approximate volume of 70 c.c. The empty part of the instrument above the mark on the capillary tube can be thoroughly freed of adhering liquid. The filling and emptying of the pycnometer is effected by attaching to it a small dropping funnel provided with a side-tube and tap, through which the instrument is exhausted. The liquid is then run in, and fills the pycnometer completely. The liquid does not come into contact with any rubber connexions during the filling, and is always kept in contact with dry air only. The filling under exhaustion also serves to free the liquid from dissolved air.

As the capillary stem of the instrument may be made to any degree of fineness, the adjustment of the volume may be made to a very superlative degree of accuracy. The weighing of the pycnometer was made to 0.1 milligram, and all weights were reduced to a vacuum. The thermostat used consisted of a large 40-litre water-bath provided with a motor-driven stirrer and a thermoregulator; the temperature remained constant to less than 0.01° . It may be said, therefore, that practically all error lay in the temperature reading. For this purpose, a series of finely graduated thermometers was used, capable of being read with accuracy to less than 0.01° , which had been standardised by comparison with the normal hydrogen thermometer. In addition, they were compared with another set of thermometers, and the fixed points (melting and boiling points) were tested, and the melting point of sodium sulphate ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, 32.38° : Richards and Wells, *Zeitsch. physikal. Chem.*, 1890, **26**, 690) was carefully determined. At no point was the correction greater than 0.02° . The error of temperature readings was probably not, on the average, greater than 0.01° .

Now for liquids the value of dv/dt of which is less than 0.001, an error in the temperature reading of 0.01° causes an error in the specific volume for a liquid of average density which affects the sixth decimal place only. Hence it is reasonable and logical to calculate the specific volumes to six decimal places. At the higher temperatures the degree of accuracy would be rather less than this, on account of a somewhat greater temperature error.

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The volume of the pycnometer was accurately determined at different temperatures by weighing it filled with boiled, distilled water. These calibrations were also repeated, using distilled mercury in place of the water.* The calibrations were repeated at various times to see whether the volume of the pycnometer was altering with time, but no change was observed.

The Pure Liquids.

All the liquids used were highly purified. They were generally fractionally distilled or frozen, and, where possible, they were dried over phosphoric oxide. The fractionation was continued until a liquid of constant boiling point was obtained, and the density was unchanged by further distillation. In the following table are given the constants (boiling points and densities at 0°) of the pure liquids used, where these had come within the scope of accurate measurement. (Only boiling points below 100° were accurately measured.) The corrections of the boiling points to normal pressure were made by calculating the values of dt/dp from the Clapeyron-Clausius latent heat relation, which is a much more satisfactory method than the use of tables of experimental values of dt/dp , a function extremely difficult to measure with accuracy.

Liquid.	Density at 0°.	Boiling point at 760 mm.
Carbon disulphide.....	1.29304	46.25°
Ethyl acetate.....	0.92468	77.15
Ethylene chloride	1.28248	83.45
Chloroform	1.52649	61.21
Toluene	0.88412	—
Aniline.....	1.03893	—
Nitrobenzene	1.20323 at 20°	—
<i>m</i> -Xylene.....	0.88151	—
Ethyl bromide	1.49821	38.40
Ethyl iodide	1.98038	72.52
Benzene	0.88946 at 10°	80.28
Ether	0.73639	34.60
Methyl alcohol	0.81040	64.72
Ethyl alcohol	0.80645	78.32
Chlorobenzene	1.12780	—

Adiabatic Compressibilities and Specific Volumes.

In the following tables are given for each liquid the experimental results of the adiabatic compressibilities. For the liquids which had been previously investigated, the values corrected, as explained in the introduction, are given, together with a few

* The specific volumes of water given by Thiesen, Scheel, and Diesselhorst (Landolt-Börnstein, "Tabellen") were used, and for mercury the results of Chappuis (*ibid.*).

supplementary values obtained by means of the new form of piezo-meter.

For each liquid, also, the experimental specific-volume data are given, together with the constants in the equation $V_t = V_0 + at + bt^2$. It was exceedingly laborious to find an equation containing four terms on the right-hand side to fit the experimental results for the whole temperature range, and it was better to find two equations of three terms each covering a range of not more than 40° .

In the following table, t° expresses the temperature in degrees centigrade, α is the adiabatic compressibility, and v the specific volume.

Carbon Disulphide.

t° .	$\alpha \times 10^6$.	t° .	v .
	Old results corrected.		
0.0	52.95	0.0	0.773370
12.77	57.94	11.66	0.783857
12.58	57.74	16.97	0.788768
20.30	60.61	23.74	0.795154
29.21	63.91	30.72	0.801888
33.39	65.49	39.07	0.810144
40.05	69.13		
	New results.		
19.83	60.43		
27.18	63.35		
34.02	66.36		

$$v_t = 0.773370 + 0.0008818 t + 0.0.1510 t^2.$$

Chloroform.

t° .	$\alpha \times 10^6$.	t° .	v .
	Old results corrected.		
0.0	59.30	0.0	0.655097
14.14	65.91	10.31	0.663408
20.96	68.99	15.94	0.668131
29.42	74.00	25.07	0.675942
36.77	78.20	32.06	0.682088
44.80	83.11	40.35	0.689644
54.31	90.65	47.40	0.696278
	New results.		
0.0	58.54	54.60	0.703199
9.31	62.65		
24.31	70.75		
35.20	77.35		
49.89	87.25		

$$v_t = 0.655097 + 0.0.79260 t + 0.0.1576 t^2. \quad (0-30^\circ).$$

$$v_t = 0.680294 + 0.0.88323(t-30) + 0.0.1945(t-30)^2. \quad (30^\circ-60^\circ).$$

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Toluene.

t° .	$\alpha \times 10^6$.	t° .	v .
Old results corrected.			
Glass piezometer.			
12.42	64.19	0.0	1.131065
16.01	65.85	14.98	1.148860
27.10	71.16	21.17	1.162369
38.74	77.32	25.78	1.168689
50.26	83.81	30.74	1.168689
60.16	90.84	40.00	1.180721
68.56	97.32	50.13	1.19148
84.11	109.8	73.05	1.22494
Copper piezometer.			
0.0	58.74	79.73	1.23529
12.41	64.10	79.24	1.23443
47.10	82.10	99.17	1.26660
57.72	89.00		
67.60	96.88		
90.00	115.3		
New results.			
21.50	68.00		
36.43	76.05		
29.42	72.11		
47.27	82.46		

$$v_t = 1.131065 + 0.0011630 t + 0.0_5 1959 \cdot 2. \quad (0-40^{\circ}).$$

$$v_t = 1.19131 + 0.0013918 (t - 50^{\circ}) + 0.0_5 2834 (t - 50^{\circ})^2.$$

Benzene.

t° .	$\alpha \times 10^6$.	t° .	v .
Old results corrected.			
Glass piezometer.			
9.55	61.40	11.92	1.12687
20.38	66.76	14.40	1.13023
30.52	72.35	17.90	1.13506
36.38	75.64	24.42	1.14402
42.76	79.80	47.95	1.17822
49.54	84.92	58.33	1.19402
49.67	84.62	62.30	1.20025
65.40	97.58	72.06	1.21589
Copper piezometer.			
16.15	63.99		
21.91	67.86		
31.33	72.81		
41.30	79.42		
50.29	85.59		
62.97	95.20		
New results.			
15.96	64.16		
32.03	73.24		
54.58	88.56		
64.00	96.45		

$$v_t = 1.124278 + 0.0013508(t - 10) + 0.0_5 1860(t - 10)^2.$$

$$v_t = 1.18129 + 0.0015038(t - 50) + 0.0_5 3086(t - 50)^2. \quad [50-80^{\circ}].$$

Ether.

t° .	$\alpha \times 10^6$.	t° .	v .
Old results corrected.			
Glass piezometer.			
0.0	114.3	0.0	1.35793
11.19	129.4	13.29	1.38615
18.54	139.6	23.90	1.41004
25.30	149.5	28.00	1.41963
30.69	158.3		
Copper piezometer.			
14.63	134.5		
21.11	142.8		
27.52	151.3		
New results.			
10.91	128.24		
18.54	138.62		
24.93	149.05		
29.50	157.73		

$$v_t = 1.35793 + 0.0020514t + 0.0_5542t^2.$$

Ethyl Alcohol.

t° .	$\alpha \times 10^6$.	t° .	v .
Old results corrected.			
0.0	83.92	0.0	1.239998
15.52	94.45	14.21	1.258698
28.41	102.04	23.98	1.272043
35.28	105.99	39.15	1.293690
43.54	112.36	46.32	1.30459
51.90	118.9	54.01	1.31638
62.05	128.5	62.71	1.33047
72.31	139.6	72.07	1.34631
New results.			
0.0	83.81		
12.64	91.37		
17.82	94.22		
27.50	100.7		
39.62	109.37		
52.65	120.05		
60.02	126.69		
72.50	139.95		

$$v_t = 1.239998 + 0.0012909t + 0.0_51767t^2.$$

$$v_t = 1.29494 + 0.0014749(t - 40) + 0.0_53958(t - 40), \quad [40-70^{\circ}].$$

Carbon Tetrachloride.

t° .	$\alpha \times 10^6$.	t° .	v .
Old results corrected.			
Glass piezometer.			
0.0	63.38	0.0	0.612869
12.43	69.33	17.41	0.625728
20.77	73.24	37.90	0.641815
29.09	78.38	46.89	0.649243
38.29	83.88	53.76	0.655021
47.10	90.70	62.63	0.662735
57.72	99.28	72.43	0.671525
67.63	106.74		
Copper piezometer.			
16.16	70.72		
27.10	76.98		
38.69	84.23		
60.10	101.55		
New results.			
0.0	63.04		
16.27	71.25		
24.08	75.54		
38.97	84.82		
45.85	89.30		
53.25	95.68		

$$v_t = 0.612869 + 0.0_3 71724t + 0.0_5 1227t^2.$$

$$v_t = 0.643530 + 0.0_3 81438(t - 40) + 0.0_5 1507(t - 40)^2. \quad [40-70^{\circ}].$$

Chlorobenzene.

t° .	$\alpha \times 10^6$.	t° .	v .
Old results corrected.			
0.0	49.19	0.0	0.886685
13.40	54.04	24.32	0.907701
24.24	57.54	38.89	0.920830
35.53	61.83	47.94	0.929336
43.97	65.37	60.63	0.941635
52.79	69.59	73.54	0.954282
62.02	74.36		
71.67	78.87		
80.47	83.3		
New results.			
0.0	49.38		
23.78	57.39		
41.26	64.09		

$$v_t = 0.886685 + 0.0_3 84104t + 0.0_5 9506t^2.$$

$$v_t = 0.921848 + 0.0_3 91697(t - 40) + 0.0_5 1265(t - 40)^2. \quad [40-80^{\circ}].$$

Methyl Alcohol.

t° .	$\alpha \times 10^6$.	t° .	v .
0.0	88.94	0.0	1.233821
13.55	98.06	11.33	1.250072
15.17	99.18	24.42	1.269553
21.37	102.93	41.65	1.29639
29.65	109.04	55.20	1.31899
30.80	109.70	58.31	1.32430
24.33	105.64		
39.09	115.93		
43.69	120.12		

$$v_t = 1.233821 + 0.0014089t + 0.0_5 2240t^2.$$

$$v_t = 1.278104 + 0.0015261(t - 30) + 0.0_5 3740(t - 30)^2. \quad [30-60^{\circ}].$$

Ethyl Bromide.

t° .	$\alpha \times 10^6$.	t° .	v .
0.0	72.99	0.0	0.667463
10.56	79.45	5.17	0.672046
19.17	85.74	8.75	0.675293
25.23	90.80	17.58	0.683562
31.98	96.53	25.42	0.691098
		31.54	0.697345

$$v_t = 0.667463 + 0.0_387466 t + 0.0_32307 t^2.$$

Aniline.

t° .	$\alpha \times 10^6$.	t° .	v .
0.0	32.94	0.0	0.962534
10.66	34.54	5.25	0.966759
20.42	36.35	21.89	0.980373
30.38	38.25	30.63	0.987713
39.57	40.25	50.12	1.004489
49.69	42.76	41.65	0.997117
60.04	45.08	62.35	1.015319
73.56	48.88	79.04	1.03074
85.70	52.43	98.95	1.05003
85.50	52.10		

$$v_t = 0.962534 + 0.0_379697 t + 0.0_68005 t^2.$$

$$v_t = 1.004384 + 0.0_386953 (t - 50) + 0.0_51288 (t - 50)^2. \quad [50-100^{\circ}].$$

Ethylene Chloride.

t° .	$\alpha \times 10^6$.	t° .	v .
0.0	48.17	0.0	0.779738
10.81	51.95	5.55	0.784571
19.31	55.31	15.41	0.793457
20.51	55.53	21.03	0.798638
30.52	60.08	31.98	0.808962
25.45	57.72	40.13	0.816912
27.25	58.56	50.74	0.827579
39.15	64.16	59.77	0.837043
50.23	69.95	74.98	0.853591
59.79	75.67		
73.50	85.02		

$$v_t = 0.779738 + 0.0_386779 t + 0.0_51459 t^2.$$

$$v_t = 0.816785 + 0.0_39842 (t - 40) + 0.0_51943 (t - 40)^2. \quad [40-80^{\circ}].$$

Acetic Acid.

t° .	$\alpha \times 10^6$.	t° .	v .
18.98	75.10	19.36	0.951801
29.55	81.36	24.97	0.957685
39.51	87.19	29.54	0.962388
39.37	86.73	34.26	0.96737
49.23	93.57	39.57	0.973016
60.80	102.03	49.69	0.98393
77.44	114.00	60.04	0.99551
		73.46	1.01078
		79.11	1.01755
		99.07	1.04250

$$v_t = 0.952461 + 0.0010266 (t - 20) + 0.0_51212 (t - 20)^2.$$

$$v_t = 0.99546 + 0.001110 (t - 60) + 0.0_52405 (t - 60)^2. \quad [60-100^{\circ}].$$

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Nitrobenzene.

t° .	$\alpha \times 10^6$.	t° .	v .
14.67	37.33	12.95	0.826309
21.10	38.91	21.25	0.831984
30.77	41.10	30.73	0.838538
40.00	43.26	39.10	0.844402
50.13	45.43	49.99	0.852209
60.15	48.41	58.53	0.858420
73.07	52.26		
82.00	54.92		

$$v_t = 0.826343 + 0.0_3 67665(t - 13) + 0.0_6 162(t - 13)^2. \quad [13 - 60^{\circ}].$$

Ethyl Iodide.

t° .	$\alpha \times 10^6$.	t° .	v .
0.0	59.71	0.0	0.504927
12.17	65.01	10.33	0.510881
23.86	70.85	19.15	0.516144
40.85	80.28	39.32	0.528808
52.10	88.08	24.20	0.519172
62.60	95.83	46.45	0.533512
		53.80	0.538464
		62.72	0.54462

$$v_t = 0.504927 + 0.0_3 56522t + 0.0_5 1072t^2.$$

$$v_t = 0.522849 + 0.0_3 6295(t - 30) + 0.0_6 1114(t - 30)^2. \quad [30 - 60].$$

m-Xylene.

t° .	$\alpha \times 10^6$.	t° .	v .
0.0	57.27	0.0	1.134417
15.10	63.44	18.83	1.155500
21.38	66.49	22.62	1.159877
30.92	71.15 (?)	29.62	1.16808
32.73	71.67	39.37	1.179694
40.59	75.82	50.54	1.193367
49.72	80.75	59.28	1.20438
61.60	88.00	75.92	1.22627
75.83	97.21	78.86	1.23012
		98.86	1.25867

$$v_t = 1.134417 + 0.0010925t + 0.0_5 1461t^2.$$

$$v_t = 1.192698 + 0.0012402(t - 50) + 0.0_5 2002(t - 50)^2. \quad [50 - 100^{\circ}].$$

Ethyl Acetate.

t° .	$\alpha \times 10^6$.	t° .	v .
0.0	70.30	0.0	1.081456
19.28	83.02	18.22	1.10751
21.89	84.81	27.18	1.121117
30.62	91.50	34.05	1.131909
34.13	94.93	41.04	1.143210
40.47	100.34	52.23	1.161970
50.14	109.39	59.93	1.17552
62.35	122.9	73.21	1.19994
62.90	123.6		

$$v_t = 1.081456 + 0.0013700t + 0.0_5 3282t^2.$$

$$v_t = 1.14154 + 0.0_2 16247(t - 40) + 0.0_5 4028(t - 40)^2. \quad [40 - 80^{\circ}].$$

Water.

t°	$\alpha \times 10^6$ Old results corrected.	t°	$\alpha \times 10^6$ New results.
2.40	50.10	9.71	48.35
6.45	49.05	11.51	48.03
14.12	47.18	10.98	48.13
19.37	46.00	14.23	47.31
24.42	45.21	19.38	46.21
35.75	44.08	20.38	46.09
46.95	43.19	24.98	45.34
63.51	42.80	24.29	45.37
75.33	42.67	29.46	44.56
86.75	42.81	34.62	43.76
90.22	42.88	38.90	43.69
		47.95	43.04
		60.65	42.55
		73.50	42.57
		84.40	43.00

Isothermal Compressibilities and Values of dv/dt .

Values of dv/dt were determined by differentiating the equations given in the foregoing tables. For the wider temperature ranges where two equations were necessary, it was found that there was usually a slight break in the continuity of the dv/dt values at the intermediate point. This break was removed by plotting the results, and then drawing a smoothed curve, from which values of dv/dt were read. In addition, the accuracy of the results was checked by calculating them in another way. The mean value of dv/dt between each pair of succeeding points was determined by subtracting the specific volumes and dividing by the temperature difference. The result was taken to refer to the mean temperature. Then, by plotting a curve of all the values thus obtained, results were obtained at regular temperature intervals, which, in general, agreed excellently with the values obtained from the equations.

From the values of dv/dt and the adiabatic compressibilities, values of the isothermal compressibility β have been calculated by aid of the thermodynamic equation given in the introduction. A knowledge of the specific heat at constant pressure (C_p) is also necessary. As already explained, comparatively large errors in the latter quantity affect the calculated values of β but slightly, and so no special determinations of specific heats have been made, but results obtained by other investigators have been relied on. For benzene and carbon tetrachloride, the specific heat determinations of Mills and McRae (*J. Physical Chem.*, 1910, **14**, 797; 1911, **15**, 54) have been used in the calculations. Schiff's results (*Annalen*, 1886, **234**, 300; *Zeitsch. physikal. Chem.*, 1887, **1**, 376) were employed in the cases of toluene, *m*-xylene, ethyl acetate,

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and chlorobenzene; Regnault's results ("Relations des Expériences" and *Mem. de l'Acad.*, 1862, **26**, 262) for carbon disulphide, ether, ethylene chloride, ethyl iodide, chloroform, and ethyl alcohol. In the case of aniline, Griffith's results (*Phil. Mag.*, 1895, [v], **39**, 47, 143) were used. In a few other cases, the values of the specific heats employed in the calculations are the mean values of several observers. These are given in the tables.

Benzene.

t° .	$\alpha \times 10^6$.	dv/dt .	$\beta \times 10^6$.
0	56.00	0.001316	81.95
10	61.00	1351	88.45
20	66.32	1387	95.65
30	72.00	1424	103.15
40	78.26	1464	111.41
50	85.12	1509	120.51
60	92.99	1561	130.03
70	101.91	1623	143.16
80	111.5	1694	156.5

Carbon Tetrachloride.

t° .	$\alpha \times 10^6$.	dv/dt .	$\beta \times 10^6$.
0	63.25	0.0007200	91.03
10	68.14	7417	98.31
20	73.28	7642	105.96
30	78.85	7884	114.34
40	85.32	8147	123.94
50	92.90	8432	134.97
60	101.20	8743	147.15
70	109.60	9071	159.81

Carbon Disulphide.

t° .	$\alpha \times 10^6$.	dv/dt .	$\beta \times 10^6$.
0	53.21	0.0008818	81.44
10	56.79	9120	87.52
20	60.50	9422	93.84
30	64.52	9724	100.55
40	69.08	10026	107.92
50	74.6	1033	116.3

Ether.

t° .	$\alpha \times 10^6$.	dv/dt .	$\beta \times 10^6$.
0	114.30	0.002051	152.97
10	127.05	2159	170.31
20	140.85	2268	188.97
30	158.7	2376	211.8
35	169.0	2430	244.7

Ethylene Chloride.

t° .	$\alpha \times 10^6$.	dv/dt .	$\beta \times 10^6$
0	48.23	0.0008678	70.05
10	51.60	8970	75.15
20	55.42	9260	80.73
30	59.80	9560	86.97
40	64.59	9875	93.75
50	69.78	0.001022	101.20
60	75.80	1060	109.73
70	82.53	1100	119.17
80	89.95	1143	129.60

Aniline.

t° .	$\alpha \times 10^6$.	dv/dt .	$\beta \times 10^6$.
0	32.89	0.0007980	41.31
10	34.47	8120	43.57
20	36.25	8270	45.86
30	38.20	8428	48.34
40	40.32	8595	51.04
50	42.63	8775	53.95
60	45.18	8967	57.15
70	47.83	9180	60.51
80	50.57	9420	64.07
90	53.45	9690	67.87

Chlorobenzene.

t° .	$\alpha \times 10^6$.	dv/dt .	$\beta \times 10^6$.
0	49.40	0.0008410	67.02
10	52.66	8600	71.12
20	56.03	8783	75.23
30	59.69	8985	79.82
40	63.73	9200	85.02
50	68.10	9438	90.42
60	72.88	9683	96.28
70	78.00	9938	102.64
80	83.50	0.001019	109.29

Toluene.

t° .	$\alpha \times 10^6$.	dv/dt .	$\beta \times 10^6$.
0	58.75	0.001163	79.34
10	63.03	1200	84.94
20	67.50	1239	90.80
30	72.45	1281	97.28
40	78.10	1328	104.70
50	84.12	1379	112.76
60	90.80	1433	121.57
70	98.16	1490	131.23

Ethyl Iodide.

t° .	$\alpha \times 10^6$.	dv/dt .	$\beta \times 10^6$.
0	59.72	0.0005652	85.59
10	64.10	5868	92.40
20	68.73	6081	99.53
30	73.87	6296	107.29
40	79.73	6516	115.86
50	86.45	6735	125.40
60	93.80	6958	135.72
70	101.75	7186	146.80

Ethyl Acetate.

t° .	$\alpha \times 10^6$.	dv/dt .	$\beta \times 10^6$.
0	70.30	0.001370	96.29
10	76.43	1434	104.98
20	83.41	1500	114.72
30	91.22	1567	125.3
40	99.86	1635	137.0
50	109.25	1708	149.8
60	120.1	1784	164.2
70	133.4	1864	181.4

Chloroform.

t° .	$\alpha \times 10^6$.	dv/dt .	$\beta \times 10^6$.
0	58.54	0.0007940	85.90
10	62.98	8230	92.94
20	68.31	8538	101.15
30	74.10	8863	110.04
40	80.48	9218	119.96
50	87.33	9598	130.74
60	94.70	0.0010005	142.46

m-Xylene.

t° .	$\alpha \times 10^6$.	dv/dt .	$\beta \times 10^6$.
0	57.27	0.0010925	75.39
10	61.40	1121	80.47
20	65.69	1149	85.69
30	70.35	1179	91.38
40	75.48	1210	97.57
50	80.93	1243	103.90
60	87.04	1279	111.56
70	93.40	1316	119.24
80	100.00	1356	127.30

Ethyl Alcohol.

t° .	$\alpha \times 10^6$.	dv/dt .	$\beta \times 10^6$.
0	83.85	0.001288	99.95
10	89.52	1326	106.28
20	95.55	1365	113.07
30	102.20	1413	120.61
40	109.62	1470	129.12
50	117.82	1542	138.78
60	126.65	1624	149.34
70	137.04	1719	161.8
75	142.95	1825	168.9

Water.

t° .	$\alpha \times 10^6$.	dv/dt .	$\beta \times 10^6$.
0	50.75	-0.0,68	50.78
10	48.38	+0.0,88	48.43
20	46.15	+0.0,207	46.45
30	44.52	304	45.20
40	43.60	380	44.69
50	43.02	455	44.62
60	42.70	526	44.89
70	42.60	592	45.44
80	42.76	655	46.31
90	43.05	720	47.43
100	43.35	782	48.63

Ethyl Bromide.

t° .	$\alpha \times 10^6$.	dv/dt .	C_p .*	$\beta \times 10^6$.
0	72.99	0.0008747	0.210	109.05
10	79.05	9208	0.213	119.34
20	86.45	9669	0.216	131.18
30	94.84	0.0010129	0.219	144.20
40	103.70	1059	0.223	157.3

* Calculated from results of Regnault (*loc. cit.*) and Battelli (*Atti R. Accad. Lincei*, 1907, [v], 16, i. 243).

Acetic Acid.

t° .	$\alpha \times 10^6$.	dv/dt .	C_p .*	$\beta \times 10^6$.
15	72.80	0.001019	0.480	88.71
20	75.73	1029	0.485	91.98
30	81.55	1048	0.494	98.48
40	87.50	1068	0.504	105.10
50	94.10	1093	0.514	112.55
60	101.18	1122	0.523	120.66
70	108.65	1157	0.533	129.37
80	116.30	1200	0.542	138.57

* From results of Schiff, Timoféev, Lüdeking and others. (See Landolt-Börnstein, "Tabellen.")

Methyl Alcohol.

t° .	$\alpha \times 10^6$.	dv/dt .	C_p .*	$\beta \times 10^6$.
0	88.95	0.001409	0.570	107.59
10	95.30	1451	0.588	114.94
20	101.95	1495	0.606	122.7
30	109.18	1543	0.625	131.0
40	117.02	1599	0.643	140.3
50	125.48	1666	—	—

* From results of Regnault (*loc. cit.*), Kopp (*Ann. Phys. Chem.*, 1848, [ii], 75, 98), Timoféev, (*Compt. rend.*, 1891, 112, 1261) and Walker and Henderson (*Trans. Roy. Soc. Canada*, 1902, [ii], 8, 105).

Nitrobenzene.

t° .	$\alpha \times 10^6$.	dv/dt .	C_p .*	$\beta \times 10^6$.
0	36.40	0.0006730	0.338	44.70
10	38.61	6852	0.345	47.30
20	40.90	6975	0.352	49.98
30	43.22	7097	0.358	52.79
40	45.70	7219	0.365	55.58
50	48.37	7342	—	—
60	50.28	—	—	—

* From results of Regnault (*loc. cit.*) and Schlamp (*Ann. Phys. Chem.*, 1896, [iii], 58, 759).

Discussion of Results.

As has been stated, the general order of error in the results for the adiabatic compressibility is about 0.1 per cent. This is, however, independent of any possible error in the accepted value (Amagat's value) for the compressibility of glass. In any case,

even supposing that this value contains, say, a 10 per cent. error, then the consequent error in the value of the adiabatic compressibility is only 0.3 per cent. in an average case. It is evident, therefore, that very little error can arise from this source. The accuracy of the calculated values of β depends chiefly on the accuracy of the values of α . Errors in the determinations of dv/dt and C_p have little effect on the value of β . For example, a 5 per cent. error in the value of C_p introduces only an error of 1 to 1.5 per cent. in the value of β .

It must be remarked that whilst the observed values of the adiabatic compressibility refer to a mean pressure of about 1.5 atmospheres, those of dv/dt and of C_p refer to the normal atmospheric pressure. The effect of pressure on the value of α is so small, however, that the results may be considered as all referring to the atmospheric pressure, without any appreciable error being made. In none of the experiments was observed a change of α with a change of pressure of about half an atmosphere. It may be claimed, then, that the values of the compressibility obtained by this method for low pressures are far more accurate than results obtained by the direct method, which yields very discordant results on account of the evolution of a very small but important quantity of heat during compression. The effect of this evolution of heat on the results obtained by the direct method will be easily appreciated from what is explained in the note at the end of this paper.

In every case except water the value of both the adiabatic and isothermal compressibility increases with rise of temperature, the increase being the greater for the isothermal compressibility. For water, both compressibilities show minimum values.

The theoretical application of the results obtained in this work are reserved for a future paper.

Note on some Previous Determinations of the Compressibilities of Liquids at Low Pressures.

On comparing the compressibility measurements at low pressures with some results of early investigators, it was found that results which were considered by their authors to be isothermal are really adiabatic.

On studying the work of Quincke (*Ann. Phys. Chem.*, 1883, [iii], **19**, 401), it was found that, judging from his method of determination, his results could not possibly be isothermal, but were undoubtedly adiabatic. The same was found to be the case for the determinations of Grassi (*Ann. Chim. Phys.*, 1851, [iii], **31**, 437), of Amaury and Deschamps (*Compt. rend.*, 1869, **68**, 1564),

and of Collodon and Sturm (*Ann. Chim. Phys.*, 1827, [ii], 36, 113), and of a few other investigators. It is important to point out the true nature of the results of these investigators, because they have always been recorded in tables of physical constants and properties of liquids as isothermal compressibilities (see, for example, Landolt-Börnstein, "Tabellen," 1912).

Their results differed very considerably from the isothermal compressibility determinations of later investigators, a matter which appears to have caused some surprise, although the reason of the discrepancy was apparently never discovered.

When a liquid is compressed by a small pressure—say, by one atmosphere—there occurs a small rise in temperature amounting to a few thousandths of a degree, yet sufficient, if neglected, to cause a difference of 10 to 40 per cent. in the observed isothermal compressibility, and, as can be easily imagined, the elimination of such a small change of temperature is exceedingly difficult.

It can be easily understood, therefore, that early investigators, ignorant of this small change of temperature, and using thermometers scarcely sensitive enough to detect it, would obtain, not the isothermal compressibilities which they were attempting to measure, but really adiabatic compressibilities, or, more correctly in the majority of cases, results which lay between the adiabatic and isothermal values.

Quincke's method of investigation was very similar in principle to that described above. He operated at very low pressures, the highest he used being, in fact, little more than 50 cm. of mercury. The latent heat liberated in the compression would be so small as to be undetectable, and it is quite impossible that any appreciable quantity of this heat should have disappeared during an experiment. Moreover, he mentions that he worked as quickly as possible, as then better results were obtained. Quincke himself does not appear to have considered the possibility of the liberation of heat during the compression. In the table below, Quincke's results are compared with the adiabatic and isothermal values recorded in this paper. It will be seen that there is quite a close agreement between Quincke's results and the adiabatic values which leaves no room for doubt that Quincke's values are really adiabatic.

Grassi (*loc. cit.*) used a similar form of piezometer to that of Quincke, but he worked at higher pressures, up to 8 or 9 atmospheres. At the higher pressures, the heat produced in the compression would be so appreciable that much of it would be lost during the time of an experiment, but at the lower pressures the

compression would be adiabatic, or approximately so. Now, as the isothermal compressibility is much greater than the adiabatic, Grassi found, as a consequence, that the compressibility of a liquid increases with the pressure, whereas it really decreases. For instance, it will be seen in the table that for ether, alcohol, and chloroform the compressibility, according to Grassi, is greater at the higher pressures.

It will be noticed that where a comparison with the present author's results at one to two atmospheres is possible, Grassi's results agree quite well with the adiabatic values. It may be concluded, therefore, that for the lower pressures Grassi's results are approximately adiabatic, but at the higher pressures they lie between the adiabatic and the isothermal values.

Amaury and Deschamps (*loc. cit.*) made compressibility measurements between 1 and 10 atmospheres' pressure. For a change of pressure of 10 atmospheres there would be quite an appreciable change of temperature, but as they took minute readings of the volume change and eliminated what they considered to be accidental changes of temperature by plotting the readings against the time, and extrapolating to the zero point on the time ordinate, their results would be approximately adiabatic. The pressures for their experiments being higher than correspond with the author's results, it is to be expected that their values will be somewhat lower than the new adiabatic values.

From a study of the early experiments of Collodon and Sturm (*Ann. Chim. Phys.*, 1827, [ii], **36**, 113, 225; *Ann. Phys. Chem.*, 1828, **12**, 39), it would appear that their results were largely affected by the negligence of the latent heat of compression, and that their values are, as it were, partly adiabatic and partly isothermal.

Author	Liquid,	Temperature.	Pressure (atmospheres).	Compressibility $\times 10^6$ observed.	Adiabatic compressibility $\times 10^6$ (Tyler).	Isothermal compressibility $\times 10^6$ (Tyler).
Quinke (<i>loc. cit.</i>)	Water	0.0°	1—1.5	50.30	50.75	50.78
	Carbon disulphide	0.0	1—1.5	53.93	53.21	81.44
		17.0	1—1.5	63.78	59.35	92.30
		6.0	1—1.6	59.70	59.00	85.95
	Benzene	16.78	1—1.7	66.10	64.60	93.1
		0.0	1—1.5	82.82	83.85	99.95
	Ethyl alcohol	17.51	1—1.7	97.45	94.08	111.2
		0.0	1—1.5	115.57	114.30	152.97
	Ether	14.32	1—1.5	134.23	132.6	178.1

Author.	Liquid.	Temperature.	Pressure (atmospheres).	Compressibility $\times 10^6$ observed.	Adiabatic compressibility $\times 10^6$ (Tyrer).	Isothermal compressibility $\times 10^6$ (Tyrer).
Grassi (<i>loc. cit.</i>)	Water	{ 0.0°	Pressure found to have no influence on the com- pressibility.	50.3	50.75	50.78
		{ 4.1		49.9	49.77	49.77
		{ 10.8		48.0	48.20	48.25
	Ether	{ 0.0		1—7.82	131.0	—
		{ 0.0		1—3.41	111.0	152.97
		{ 14.0		1—1.58	140.0	177.6
		{ 13.8		1—8.36	153.0	—
	Ethyl alcohol	{ 7.3		1—2.30	82.8	104.5
		{ 7.3		1—9.40	85.3	—
		{ 13.1		1—1.57	90.4	108.3
		{ 13.1		1—8.97	99.1	—
	Chloroform	{ 8.5		1—1.26	62.5	91.7
		{ 12.0		1—1.30	64.8	95.0
		{ 12.5		1—1.92	76.3	—
Amaury and Des- champs, (<i>loc. cit.</i>)	Ethyl alcohol	{ 0.0	1—10	83.5	83.85	99.95
		{ 15.0	1—10	91.1	92.50	109.5
	Ether	{ 0.0	1—10	109.0	114.30	152.97
		{ 14.0	1—10	128.0	132.30	177.6
	Carbon disulphide	14.0	1—10	63.5	58.28	90.1

The results of other investigators were carried out at sufficiently high pressures to ensure the complete elimination of the heat of compression.

The practical part of the work was carried out in the Physical Chemistry laboratories of the University of Geneva.

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