

2. A method of determining viscosity of gelatin solutions with a maximum error of 0.5% has been described.
3. Gelatin solutions increase in viscosity with age at different rates depending upon concentration of gelatin, hydrogen-ion concentration, and kind of gelatin.
4. For any given gelatin solution a maximum viscosity is attained at an age of solution of about 24 hours. A decrease in viscosity after the maximum is reached indicates bacterial decomposition.
5. Gelatin solutions show a maximum viscosity at a p_H 3.0 to 3.5 at 25°.
6. The viscosity of gelatin solutions is not a simple function of concentration of gelatin.
7. Both hydrogen and hydroxyl ions catalyze the hydrolysis of gelatin solutions, the latter more rapidly than the former.
8. Excessive temperatures catalyze the hydrolysis of gelatin. Boiling gelatin solutions hydrolyzes them very rapidly.

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THE COMPRESSIBILITY OF BENZENE, LIQUID AND SOLID.

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Very few substances have had their compressibilities determined in both the liquid and the solid state. The comparison of the two different values is of considerable interest in relation to a study of the mechanism of the change of state in any given substance. Accordingly the present paper recounts such a comparison in the case of benzene, for which adequate data were lacking as regards the solid. The results were incidental to other researches, but seem to deserve separate publication.

Of liquid benzene, a careful determination, made in a glass piezometer, has already been described.¹ The object of repeating the determination was primarily to show whether or not the earlier apparatus, which had been used with a variety of substances, was adequate, by comparing a typical result with that yielded by a larger more complete piezometer free from the hysteresis to which glass is subject.

The piezometer used in the present research was the steel instrument already described in full in another previous paper.² In the case of liquid benzene, a weighed amount of about 30 cc. of this substance was placed in an inverted steel test-tube immersed under mercury (which filled the piezometer). The steel test-tube diminished the unnecessarily large volume

¹ T. W. Richards and J. W. Shipley, *THIS JOURNAL*, **38**, 989 (1916).

² T. W. Richards and E. P. Bartlett, *ibid.*, **37**, 470 (1915).

of the apparatus and kept the benzene from being entrapped in the washer and screw-thread. During the operation of filling, the utmost care was exercised against the introduction of air. From Amagat's measurement of the compressibility of air³ 1 cc. at 0° and 1 atmosphere changes in volume by 0.007 cc. between 100 and 500 atmospheres. Since the present method is sensitive to perhaps within 0.0001 cc., the presence of even 0.01 cc. of air should be avoided. Accordingly, after having been thoroughly cleaned and dried, the piezometer was filled with mercury through a funnel tube with a capillary outlet reaching to its bottom. The mercury thus rose quietly in the steel tube, without entrapping air. The iron washer was slipped edgewise under the mercury, and put in position with two glass rods. The piezometer was then ready to receive the tube containing the hydrocarbon. The benzene having been inserted, the cap-piece of the piezometer with the attached capsule, was carefully put in position and held firmly until the nut was screwed into place, when, with a special vise, the nut was tightened as much as possible, using a long lever to complete the closure.

It was by no means so easy to arrange the solid benzene for compression. In the first place, the steel piezometer was prepared as before in every respect for the reception of the tube containing the benzene, since its introduction was a process demanding great celerity, as will be seen.

The hydrocarbon was enclosed in a glass tube of 17.82 cc. capacity, drawn down to a capillary opening. This tube had been filled by placing it in a large test-tube containing the liquid, and by alternately exhausting and admitting pressure. Unfortunately benzene dissolves a considerable amount of air,⁴ which separates when the liquid is frozen. Accordingly, when the tube was completely full of benzene, the whole apparatus was immersed in ice water, still keeping it at low pressure. As the liquid froze, the dissolved air was set free. Because, however, the crystals entangled a few bubbles, the benzene was melted and frozen again several times successively, until no further air appeared on freezing. The apparatus was finally warmed to about 23° and the tube removed, wiped, and weighed as quickly as possible on a balance already holding the known approximate weights. Slight warming brought the benzene exactly to the orifice, when the tube was quickly inverted and immediately inserted in the waiting piezometer. The only surface exposed was that in the capillary about a millimeter in diameter; so that evaporation, or solution of air, must have been negligible in the very brief time concerned. The remainder of the closing of the piezometer was conducted just as usual, and so were the details of the application of pressure.

³ Amagat, *Compt. rend.*, 111, 871 (1890), and 116, 946 (1893).

⁴ T. W. Richards, E. K. Carver, and W. C. Schumb, *THIS JOURNAL*, 41, 2019 (1919). Reference will be found in this paper to earlier work of Just, Garelli and Falcicola, etc.

The piezometer was suspended in the thermostat for several minutes, and the meniscus set at a height estimated to break contact at a pressure slightly below 100 megabars. The space above the meniscus was filled with water, the platinum point screwed on, cotton placed in the openings at the top, and the piezometer carefully lowered into the pressure cylinder, which was then packed in ice. The further operations were precisely like those which have been so often described before.

Apparently, the density of solid benzene (which is needed for calculating the results) has never been determined. Various values at 0° are given in tables, but if these were directly determined, the measurements must have been made on the under-cooled liquid. On account of the great tendency of the liquid to dissolve air, the measurement of the specific gravity of solid benzene is not very easy. A rough determination made in the 17.82-cc. tube showed that its density is slightly over 1.000. This is confirmed by the very careful determination of the change in volume upon melting of benzene (thoroughly free from air) of Julius Meyer,⁵ who found that one gram of benzene increases 0.1333 cc. in volume on melting. If the density of liquid benzene at its melting point is 0.8941, the density of the solid would then be 1.0151. This value (which probably differs only very slightly from the density at 0°) was used in the following calculation.

Both the benzene and toluene had been very carefully purified. The benzene had been prepared by Dr. J. W. Shipley,⁶ and the toluene by Dr. F. Barry.⁷

The compressibility determinations follow. The first three columns give three successive pressure measurements, p_0 , p_1 , p_2 ; the next two, the weights of mercury added (w and w_2) to obtain p_1 and p_2 ; the last two columns record the values for the weights calculated for two successive pressure ranges of exactly 200.00 megabars, and the calculation was made

DATA.

COMPRESSIBILITY OF LIQUID BENZENE AT 20° (E. P. B.)
Density of Benzene ($20^\circ/4^\circ$) = 0.8788; Weight taken 25.016 g.
(Pressures in megabars).

Pressures.			Actual weights mercury.		Calculated weights mercury	
p_0 .	p_1 .	p_2 .	w_1 .	w_2 .	100-300. (w_1) cor.	300-500. (w_2) cor.
109.5	300.9	...	5.7395	6.0269
100.4	300.6	500.5	6.0265	5.1592	6.0243	5.1656
100.5	301.0	500.9	6.0298	5.1565	6.0197	5.1652
Average weights of added mercury with benzene in apparatus =					6.0236	5.1654
Average weights with mercury alone filling completely the						
apparatus =					0.3363	0.3313

⁵ Julius Meyer, *Z. physik. Chem.*, **72**, 225 (1910).

⁶ Richards and Shipley, *THIS JOURNAL*, **36**, 1830 (1914); also **41**, 2022 (1919).

⁷ Richards and Barry, *ibid.*, **37**, 996 (1915).

COMPRESSIBILITY OF SOLID BENZENE AT 0° (J. H. H.).

Density of Benzene (0°/4°) = 1.0151, Weight taken 15.685 g.

p_0 .	Pressures.		Actual weights mercury.		Calculated weights mercury.	
	p_1 .	p_2 .	w_1 .	w_2 .	100-300.	300-500.
89.90	292.86	519.06	1.6795	1.7630	1.6511	1.5617
110.37	302.37	488.02	1.5804	1.4364	1.6496	1.5448
108.11	296.63	490.76	1.5619	1.5015	1.6615	1.5399
Average weights of added mercury with benzene in						
					apparatus = 1.6541	1.5488
Average weights of added mercury with glass tube filled						
					with mercury = 0.4836	0.4772

by determining exactly the dv/dp values at about 100, 300, and 500 megabars in each case, in special trials, but could have been taken from a carefully plotted curve.

Calculated by the equations given in a previous paper⁸ these data give the following values for the compressibility of benzene.

RESULTS.

COMPRESSIBILITY OF LIQUID AND SOLID BENZENE.

	Compressibility $\times 10^4$.		
	Range 100-300.	Range 300-500.	Range 100-500.
Liquid Benzene at 20.00°.....	77.68	66.46	72.07
Solid Benzene at 0°.....	31.69	29.30	30.49

Evidently the compressibility of the solid is far less than that of the liquid, as is also its decrease with increasing pressure. Of course the comparison should properly be made with each phase at the same temperature; but the compressibility of the liquid cannot be determined at 0°. Some clue as to the effect of changing temperature may be found from the parallel behavior of liquid toluene. In the same apparatus as that used for solid benzene, one of us (E. P. B.) found that with 15.459 g. of toluene d_4^{20} 0.8845) the averaged values of (w_1) cor. and (w_2) cor. were respectively 3.4397 g. and 3.0370 g. These figures lead to the following values of the compressibility of toluene, which are compared with those previously found^{1,9} at 20°.

RESULTS.

COMPRESSIBILITY OF TOLUENE AT 0° AND 20°.

	Compressibility $\times 10^4$.		
	Range 100-300.	Range 300-500.	100-500.
Toluene at 0°.....	65.98	57.61	61.78
Toluene at 20.00°.....	74.07	63.93	69.00

The change of 20° affects the compressibility by about 10 or 11%. Probably the compressibility of benzene would show a somewhat larger

⁸ Richards, Stull, Mathews and Speyers, THIS JOURNAL, 34, 980 (1912), on last half of the page.

⁹ This value agrees exactly with that found in an earlier research, (*ibid.*, 34, 988, (1912)).

temperature effect, so that its liquid compressibility at 0° would be not far from 0.000063, (over the range 100 to 500 megabars) whereas that of the solid is only 0.0000305 — less than half the former.

The comparison of these results with those of other experimenters is interesting. In the first place, the result 72.07 for benzene at 20° confirms satisfactorily the most recent previous result 72.09 obtained with a quite different form of glass apparatus.^{1,10} This indicates consistency, and inspires confidence in both techniques. Evidently the needful precautions against complication by the hysteresis of glass had been properly observed.

Apparently the only earlier determination of the compressibility of solid benzene was that of Harry Essex.¹¹ He gives as the relative volumes of the substance at 0° , 0.87045, 0.84561 and 0.83277 at 1, 500 and 1000 kg/cm². respectively. The existence of these unusual results, which give an average compressibility $59. \times 10^{-6}$ over the first range, and 29.4×10^{-6} over the second range, had been among the reasons for the present study. In the light of our data, it seems possible that the benzene used by Essex had not been freed from air, of which he makes no mention. The presence of only about 1.5% by volume of air would account for the wide variation shown by his own figures, as well as the discrepancy between his and ours. In that case his values for the higher pressures are doubtless much more nearly correct than those for the lower pressures.

We are indebted to the Carnegie Institution of Washington for some of the apparatus used in this research.

Summary.

This brief paper records for the first time an accurate determination of the compressibility of solid benzene at 0° , namely $(\Delta V/\Delta PV_0)_T = 0.0000305$ over the range 100 to 500 megabars.

Incidentally, the compressibility of liquid toluene at 0° over the same range was found to be 0.0000618.

A new determination of the compressibility of liquid benzene at 20° confirmed satisfactorily the previous determination, giving the value 0.00007207 for the same range.

The compressibility of solid benzene is shown to be less than half that of liquid benzene at the same temperature. Thus another case, supporting the majority of those investigated, is found in which the solid shows much smaller compressibility than the liquid.¹² Interpretation of the result will be postponed until more cases of this kind have been studied.

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¹⁰ Richards and Shipley, *THIS JOURNAL*, **38**, 998 (1916). An earlier, less carefully found value, 72.4 (*ibid.*, **34**, 340 (1912)), is somewhat higher.

¹¹ Essex, *Z. anorg. Chem.*, **88**, 200 (1914).

¹² T. W. Richards, *THIS JOURNAL*, **37**, 1648 (1915).