

III.—*The Liquid Volume of a Dissolved Substance.*

By JOHN SCOTT LUMSDEN.

THE following investigation was undertaken in order to obtain some information regarding the volume assumed by a solid, liquid, or gas when dissolved in a liquid on which it exerts no chemical action.

It is well known that the values determined for atomic volumes and atomic refractions from experiments made on pure liquids hold with fair accuracy when applied to solids and liquids in solution; and the inference is, that a liquid retains its own volume when dissolved and that a solid assumes in solution the volume which the

same weight would have if it existed as a liquid at the same temperature.

If that inference is correct, or if it can be proved to vary from exactness in a rational manner, a law of the liquid volume of a dissolved substance is revealed and the experimental results here recorded show that there is such a law, which holds, not only for the volume assumed by a solid or liquid, but also for the volume taken by a dissolved gas.

At the beginning of the investigation it was found necessary to exclude from consideration solutions in which water was the solvent, since solution in water is of the nature of combination and is always accompanied by a marked shrinking in volume; a further contraction also occurs if the dissolved substance becomes ionised.

The first experiments were designed to prove that a dissolved substance behaves as a liquid and does not undergo any sudden change in volume as the temperature is raised above its normal melting point or boiling point. A number of substances of widely different composition were chosen; these were dissolved in various solvents and the volume of the molecular weight in grams of each substance was measured at several temperatures. A quantity of substance was weighed in a short-necked, stoppered flask, the solvent was added and the flask was reweighed. A pycnometer was filled with the solution obtained in this way by inserting the point of the instrument into the flask and withdrawing the liquid, and a similar pycnometer was filled with the solvent. The pycnometers were then placed together in a thermostat and after remaining a sufficient time at the desired temperature they were removed, dried, and weighed. The capacity of each pycnometer was carefully determined at several temperatures and by interpolation the capacity at any desired temperature was obtained. All the weighings were corrected to the weight in a vacuum and the densities are referred to water at 4°, thus making the number which expresses the molecular volume represent also the volume in cubic centimetres of the molecular weight in grams of the substance at the temperature given.

The molecular volume in solution was calculated by the usual formula: $V_m = \frac{M + s}{D} - \frac{s}{d}$, where M is the molecular weight of the substance, D the density of the solution, d the density of the solvent, and s the weight of the solvent used to dissolve the molecular weight in grams of the substance.

Molecular Volume of Naphthalene in Toluene.

2.7933 grams of naphthalene were dissolved in 19.7216 grams of toluene :

Temp.	Sp. gr. toluene.	Sp. gr. solution.	Vol. of 128 g. naphthalene.	
			In solution.	As liquid.
15°	0.8706	0.8885	123.28	—
25	0.8612	0.8791	124.25	—
40	0.8476	0.8653	126.05	(79.9°)
60	0.8296	0.8473	128.42	130.92 *
80	0.8113	0.8287	131.05	(98.4°)
100	0.7931	0.8104	133.64	133.04 †

* Schiff, *Annalen*, 1884, **223**, 261.

† Nasini, *Gazzetta*, 1885, **15**, 84.

Molecular Volume of Phenylacetic Acid in Toluene.

3.1889 grams of acid were dissolved in 19.6646 grams of toluene :

Temp.	Sp. gr. toluene.	Sp. gr. solution.	Vol. of 136.08 g. acid.	
			In solution.	As liquid.
15°	0.8706	0.8998	119.91	*
25	0.8612	0.8906	120.60	(76.6°)
40	0.8476	0.8770	122.04	125.50
60	0.8296	0.8590	123.84	(86.2°)
80	0.8113	0.8405	125.88	126.41
100	0.7931	0.8223	127.90	(89.5°)
				126.73

* Schiff, *Annalen*, 1884, **223**, 260.

Molecular Volume of Thymol in Benzene.

2.0108 grams of thymol were dissolved in 14.1864 grams of benzene :

Temp.	Sp. gr. benzene.	Sp. gr. solution.	Vol. of 150 g. thymol.	
			In solution.	As liquid.
15°	0.8846	0.8943	154.74	*
25	0.8742	0.8842	156.01	(49.3°)
35	0.8639	0.8740	157.50	157.91
45	0.8536	0.8638	158.99	(58.3°)
55	0.8432	0.8535	160.58	159.08
65	0.8328	0.8432	162.26	(64°)
				159.78

* Schiff, *Annalen*, 1884, **223**, 259.

Molecular Volume of Dichlorobenzene in Carbon Tetrachloride.

2.0677 grams were dissolved in 30.3615 grams of carbon tetrachloride :

Temp.	Sp. gr. CCl ₄ .	Sp. gr. solution.	Vol. of 146.9 g. dichlorobenzene.	
			In solution.	As liquid.
15°	1.6039	1.5794	113.93	—
25	1.5845	1.5608	114.77	—
35	1.5652	1.5425	115.48	(53°)
45	1.5462	1.5244	116.33	117.53
55	1.5275	1.5065	117.18	(63°)
65	1.5075	1.4876	117.95	118.36

* Schiff, *Annalen*, 1884, **223**, 263.

Molecular Volume of o-Nitrophenol in Chloroform.

1.1628 grams of nitrophenol were dissolved in 12.9120 grams of chloroform :

Temp.	Sp. gr. CHCl ₃ .	Sp. gr. solution.	Vol. of 139 g. nitrophenol.	
			In solution.	As liquid.
15°	1.4898	1.4774	102.80	*
25	1.4721	1.4605	103.56	(35°)
35	1.4531	1.4423	104.31	106.48
45	1.4344	1.4247	105.06	(45.2°)
55	1.4163	1.4071	105.91	107.38
				(55°)
				108.29

* Schiff, *Annalen*, 1884, **223**, 263.

Molecular Volume of Chloroform in Toluene :

Temp.	Sp. gr. toluene.	Sp. gr. solution.	Vol. of 119.4 g. chloroform.	
			In solution.	As liquid.
40°	0.8472	0.9647	82.98	(20°) 80.21 *
60	0.8290	0.9427	85.39	(40) 83.33
80	0.8105	0.9203	88.02	(60) 84.62

* Thorpe, *Trans.*, 1880, **37**, 196.

Molecular Volume of Bromine in Carbon Tetrachloride.

3.4716 grams of bromine were dissolved in 28.3596 grams of CCl₄ :

Temp.	Sp. gr. CCl ₄ .	Sp. gr. solution.	Vol. of 79.96 g. bromine.	
			In solution.	As liquid.
40°	1.5555	1.6379	27.70	26.22 *
50	1.5362	1.6178	27.98	26.52
60	1.5173	1.5981	28.27	26.83
70	1.4969	1.5769	28.57	—
75	1.4892	1.5687	28.74	—

* Thorpe, *Trans.*, 1880, **37**, 174.

Molecular Volume of Naphthalene in Quinoline :

Temp.	Sp. gr. quinoline.	Sp. gr. solution.	Vol. of 128 g. naphthalene.	
			In solution.	As liquid.
15°	1·0978	1·0887	123·73	
40	1·0785	1·0691	126·40	(79°)
80	1·0478	1·0378	130·85	130·34 (130·7°)
120	1·0150	1·0057	134·61	136·78
160	0·9826	0·9735	139·20	(173·8°) 141·99
200	0·9489	0·9394	144·93	(193·6°) 143·37
220	0·9319	0·9234	146·56	(217°) 147·57

* Lossen and Zander, *Annalen*, 1884, **225**, 111.

These molecular volumes are represented by curves on the accompanying diagram and the continuity of the curves makes it apparent that with rise of temperature the increase of volume is regular and that no breaks occur at the normal melting points or boiling points of the dissolved substances. Liquids, such as bromine and chloroform, when in solution were raised to temperatures above their boiling points, but their volumes did not undergo any sudden change; similarly, solids such as naphthalene and thymol when in solution were raised to temperatures above their melting points, but their curves of volume are continuous; and in the example given of a solution of naphthalene in quinoline, the change of temperature includes the regions at which the naphthalene normally exists as solid, liquid, and gas, yet there are no breaks in the curve of volume. In solution there is, therefore, only one phase, namely, the liquid phase, and a substance in solution at any temperature behaves as a simple liquid.

The next point on which information was sought was the relation between the volume of a pure liquid and its volume when dissolved.

The substances employed in the foregoing experiments had in every case been examined by previous workers and their volumes determined in the liquid state at several temperatures. From these measurements, the molecular volumes were calculated, and the values obtained are given in the last columns of the preceding tables and are indicated on the volume diagram by dotted lines. It is seen that naphthalene and phenylacetic acid dissolved in toluene have volumes in solution almost identical with their volumes as pure liquids; bromine in carbon tetrachloride, thymol in benzene, and chloroform in toluene show greater volumes in solution, whilst nitrophenol in chloroform and dichlorobenzene in carbon tetrachloride have smaller volumes when dissolved.

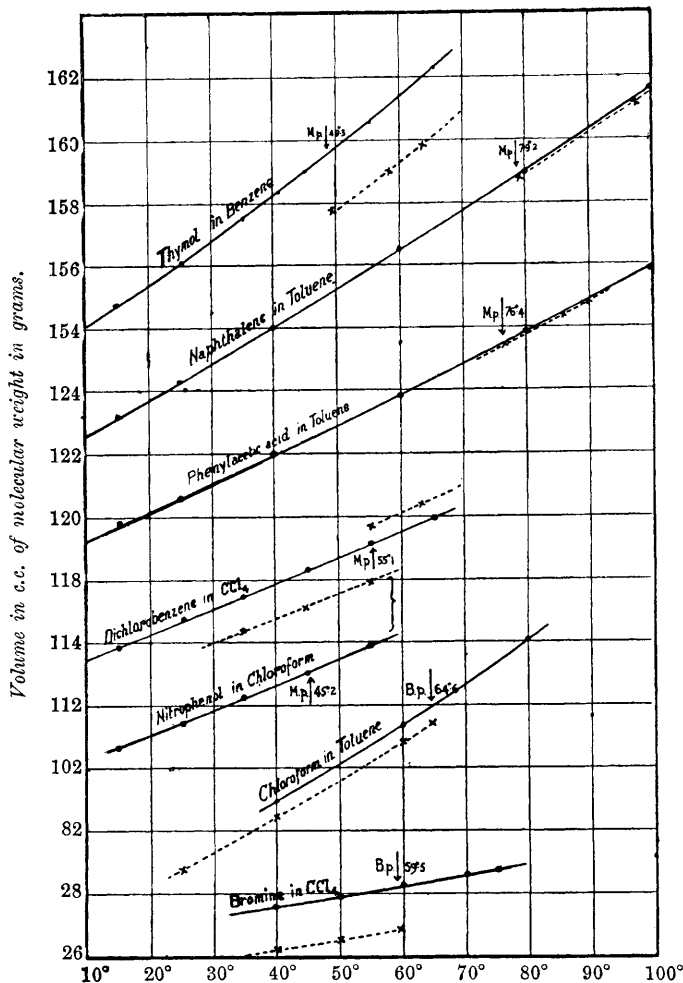
Two liquids may therefore be mixed without any change of volume

taking place, but usually mixing is attended either by a small contraction or a small expansion.

Some very accurate experiments on the mixing of carefully purified

FIG. 1.

Molecular volumes of various substances in solution.



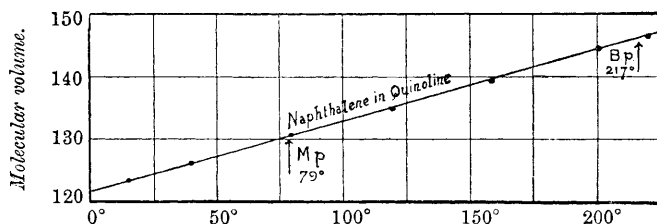
liquids are recorded by Young and Fortey (Trans., 1902, 81, 742 and 772; 1903, 83, 45), and by Thorpe and Rodger (Trans., 1897, 71, 367), and in order to indicate the extent of the change of volume

accompanying mixing, I give the measurements made by these investigators:

Mixtures of	Volumes.	Instead of Ob- 100 c.c. servers.	
Toluene and ethylbenzene	Equimolecular	99.966	Y. & F.
Hexane and octane	"	99.966	"
Carbon tetrachloride and benzene	"	99.849	"
" " methyl alcohol	"	99.820	"
Ethyl acetate and ethyl propionate	"	100.015	"
Benzene and toluene	"	100.161	"
Chlorobenzene and bromobenzene	"	100.000	"
Benzene and ethyl alcohol	31 per cent. alcohol	100.000	"
Ether and chloroform	84 per cent. chloroform	99.185	T. & R.
Carbon disulphide and methyl iodide	78.4 per cent. methyl iodide	100.217	"

FIG. 2.

Molecular volume of naphthalene in quinoline.



In no case do these measurements by Young and Fortey indicate a change of volume on mixing as great as one-fifth of 1 per cent., and according to Thorpe and Rodger, a mixture of the two dissimilar liquids, ether and chloroform, is accompanied by a change which does not exceed 1 per cent.

Referring again to the volume diagram it will be observed that the curve indicating the volume of the pure liquid at different temperatures runs parallel with the curve showing the volume of the substance in solution. One learns from this that whatever change takes place on mixing two liquids at one temperature, the same amount of change will take place on mixing them at another temperature. It also leads to a second important generalisation: if the volume of a pure substance over the range of temperature when it is liquid can be represented by a curve which coincides with or runs parallel to the volume curve of the substance in solution, then, as the trend of the solution curve is regular, it may safely be concluded that if the pure substance remained liquid, its volume, at any temperature below or above the temperature of the normal liquid state, would be represented by a point on an extension of the liquid volume curve continued parallel to the curve of the volume in solution.

It follows directly from this that, if the two curves coincide, the conditions of the law of liquid volume are fulfilled, and the law may be stated thus: *When a substance in the liquid state dissolves without change of volume, the same substance when in the state of solid or gas will, when dissolved in the same solvent, change to the volume which the same weight of it would have if it were a pure liquid at the temperature of solution.* Should, however, the two curves run parallel, the deviation from the law may be expressed as follows: *When a substance in the liquid state, on being dissolved, changes in volume by a certain amount, the same substance, when in the state of solid or gas, will, when dissolved, assume a volume which differs from the volume which it would have if liquid at the same temperature, by the same amount.*

These two definitions may be combined in a general statement: the volume occupied by a substance in solution is the same as that of the pure substance at the same temperature if it were liquid; or if it is not identical, it deviates by the same amount at all temperatures.

When two pure liquids were mixed it was seen that the change in volume was very small, and the deviation from conformity with the law of liquid volume can in no instance be considerable, yet it seemed of interest to inquire further concerning the cause of the change of volume when two liquids are brought together.

The cause must be looked for in the distribution of the particles of the solute throughout the solvent producing an adjustment of spacing, since it might be expected that molecules differing in size, shape, and weight, when mixed, will arrange themselves so that the new volume is not exactly the sum of the volumes added. The change, moreover, cannot entirely be ascribed to the dissolved substance; the solvent must also be affected, and if that is the case it is evident that the true volume which a substance occupies when in solution cannot be measured, since the amount of change of each constituent is unknown.

From these considerations it was reasonable to predict that alteration of the amount of solvent and the employment of different solvents would give different values for the volume of a dissolved substance, and the following experiments were made to obtain information on these points. Solutions were prepared containing approximately 5, 10, and 20 molecules of naphthalene in 100 molecules of benzene, toluene, xylene, and carbon tetrachloride. Four pyknometers were employed; one to contain the pure solvent, the others the three solutions made with this solvent. The pyknometers were heated in a thermostat to 15°, removed at the same time to ensure that they were all at exactly the same temperature, dried, and weighed:

Solvent.	Mols. naph- thalene.	Naph- thalene in grams.	Solvent in grams.	Sp. gr. solvent.	Sp. gr. solution.	Vol. of 128 g. naph- thalene.
Benzene	5	2.4151	32.0184	0.8848	0.8938	123.90
	10	2.3258	14.9250	„	0.9025	123.63
	20	2.0620	7.0862	„	0.9150	123.48
Toluene.....	5	2.0382	29.7285	0.8712	0.8802	123.43
	10	2.1583	15.8576	„	0.8883	123.30
	20	2.2576	7.6144	„	0.9046	123.17
Xylene	5	1.9115	30.8078	0.8678	0.8761	123.88
	10	2.0811	16.7844	„	0.8836	123.69
	20	3.8963	17.7555	„	0.8940	123.55
Carbon tetra- chloride	5	2.1084	54.9772	1.6043	1.5741	121.23
	10	2.7271	32.8754	„	1.5425	121.46
	20	5.4420	36.2363	„	1.5006	121.98

These molecular volumes of naphthalene, calculated as before on the assumption that each solvent retains the volume it has in the pure state, show that there is in solutions in benzene, toluene, and xylene a distinct diminution in volume with increase of concentration, whilst in carbon tetrachloride the volume becomes greater as the amount of solvent decreases. Several experiments with carbon tetrachloride gave the same result: a diminution in the volume of the dissolved substance on dilution.

The cause of these changes will be discussed later on.

An experiment was then made in order to find the change in volume of the dissolved substance when different solvents were used. Solutions containing approximately 10 molecules of naphthalene to 100 molecules of benzene, toluene, xylene, and carbon tetrachloride were prepared, these were heated at 15°, removed from the bath at the same moment, and weighed:

	Naph- thalene. in grams.	Solvent in grams.	Sp. gr. solvent.	Sp. gr. solution.	Vol. of 128 g. naph- thalene.
Benzene.....	2.8556	19.7194	0.8847	0.9014	123.52
Toluene	2.6164	25.8188	0.8708	0.8837	123.55
Xylene	2.3361	19.3979	0.8679	0.8832	123.67
Carbon tetrachloride ...	2.2266	27.4185	1.6043	1.5421	122.57

The volume of naphthalene is seen to be nearly the same in benzene, toluene, and xylene, but there is a great diminution when carbon tetrachloride is the solvent. These experiments prove that the volume occupied by a substance in solution at any given temperature alters with the solvent employed and also with the concentration of the solution.

The foregoing results enable one to form a conception of what takes place when two liquids are mixed.

If a pure liquid is a collection of like molecules which are in

constant motion jostling each other and changing their direction and motion at every moment, and that to permit of this jostling there are spaces between the molecules, then the question arises: is the interspace per molecule at the same temperature the same for each liquid? Kopp did not recognise the existence of interspaces, and in the atomic volumes deduced by him are included atom and space, and the sum of the atomic values make up the whole volume of the liquid; but according to Horstmann and Traube there must be added to the sum of the values which they assign to the atoms a co-volume of 25.9 c.c. at 15° in order to obtain the molecular volume, and this co-volume has a higher value as the temperature rises.

Now it is very improbable that the molecular interspaces in different liquids should have the same dimensions. The molecules differ in size, shape, and weight, and any value for the co-volume must be an average number from which the real value may in any given case differ considerably. If, however, the co-volume be different in different liquids, then, when two liquids are brought together, an adjustment of the dimensions of the interspaces will sufficiently account for the change in volume.

With regard to this adjustment, little can be inferred from the size and shape of the molecules, but considering only their mass, the direction of the change of volume may in many cases be explained. It was seen that when naphthalene was dissolved in carbon tetrachloride the volume was smaller than when the solvent was benzene, and that, whilst in carbon tetrachloride the volume diminished on dilution, in benzene the volume was greater as the amount of solvent was increased.

When the molecules of naphthalene were introduced amongst the heavier molecules of carbon tetrachloride they would be subjected to greater pressure than if they existed as liquid naphthalene, since the mass attraction between the molecules of carbon tetrachloride is greater than between naphthalene molecules. This cause would lead to a diminution of volume. At the same time the carbon tetrachloride molecules would be separated from each other by the intrusion of the naphthalene molecules; their mutual attraction would be diminished and expansion would result. The latter action must be the smaller since the experiment showed a contraction on mixture.

When more solvent was employed, the separated naphthalene molecules would be subjected to still greater attraction by the heavy carbon tetrachloride molecules and thus produce the diminution which was noticed on dilution.

In the case of naphthalene in benzene, the dissolved molecules are the heavier, they would be under less pressure than if in liquid naphthalene, and this would permit expansion; at the same time the

34 THE LIQUID VOLUME OF A DISSOLVED SUBSTANCE.

naphthalene molecules would be separated from each other, their mutual attraction would be diminished, and further increase of volume would take place. On adding more solvent the naphthalene molecules would become still more widely separated, their attraction for each other would again be lessened, and the expansion which was noticed on dilution would be brought about.

Observed changes in volume may therefore in many cases be accounted for by the mass attraction between the molecules of solvent and solute, but the shape and size of the molecules which are brought together must also affect the adjustment. Speaking generally, when the molecules of two substances resemble each other in size, shape, and weight, there will be little change on mixing, but when there is marked difference in the structure and weight of the molecules a considerable change may be expected.

The following is an illustration: methyl iodide was dissolved in carbon tetrachloride and in benzene and the molecular volumes determined:

Solvent.	Wt. of methyl iodide.	Wt. of solvent.	Sp. gr. solvent.	Sp. gr. solution.	Vol. of 141·97 g. methyl iodide.
Benzene.....	10·0459	26·5893	0·8847	1·0607	63·37
Carbon tetrachloride ...	6·8050	39·5385	1·6043	1·6778	62·09
Methyl iodide	—	—	2·2924	—	61·93

The volume of the pure methyl iodide is seen to differ very little from its volume in carbon tetrachloride, but the increase in volume is very marked when solution is in the much lighter liquid benzene.

One point in the preceding investigation demands notice: it was assumed as true that the curve of the volume of the substance in solution coincided with or ran strictly parallel to the curve of volume of the pure substance. The experimental results indicate that this is the case, and the examination of some measurements made by Thorpe and Rodger (*Trans.*, 1897, 71, 367) on the densities of mixtures of carbon tetrachloride and benzene and carbon disulphide and methyl iodide leads also to the conclusion that when definite weights of two liquids are mixed the amount of change of volume which occurs at one temperature is the same as the change at another temperature. But it is improbable that any such regularity should hold; for when two liquids have different rates of expansion the amount of change of volume on mixing must vary somewhat with the temperature. As this variation has not been experimentally noticed, one must conclude that it is very small, more especially when the dissolved substance bears no great proportion to the total volume, and it cannot be of sufficient magnitude to invalidate the law of liquid volume which is based on the parallelism of the volume curves.

In the foregoing discussion, proof has been adduced that the true volume of a dissolved substance cannot be known, and that the volume varies with the solvent and with the concentration of the solution ; but it has also been shown that the change in volume when two liquids are mixed is very small, and that the volume assumed in solution by a solid, liquid, or gas is never far removed from the volume that the same weight would occupy if liquid at the same temperature. The law of the liquid volume of a dissolved substance is therefore seldom strictly accurate, but it deviates so little from the truth that it deserves a definite position as a guide when dealing with problems relating to solutions in liquids where dissociation cannot take place.

UNIVERSITY COLLEGE,
DUNDEE.
