IMPROVED APPARATUS FOR THE DETERMINATION OF MOLECULAR WEIGHTS

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Isotonic solutions of two substances in the same solvent have equal vapour pressures, at the same temperature. The state of equilibrium is represented by the equation

$$\frac{m_1}{m_2} = \frac{w_1}{w_2} \cdot \frac{v_2}{v_1}$$

(w_1, w_2 , are the respective weights of the substances of molecular weights m_1, m_2 , dissolved in the solvent of volumes v_1, v_2). If two such solutions, maintained at the same temperature, have their vapours in communication by means of a suitable gauge, the indicator will remain stationary.

Unlike the previous methods described by the author, the success of which depends entirely on the regularity with which the solutions can be made to boil, this method is entirely free from this difficulty.

Apparatus

Two graduated boiling tubes and another similar ungraduated tube are each fitted with a three-holed rubber stopper; through each stopper of the graduated tubes passes a dropping funnel with a glass tap, the lower end of the funnel being drawn out to a point and reaching the bottom of the tube (or else, a piece of glass tubing, drawn out to a point, may be fitted by means of a piece of rubber tubing to the end of the funnel just below the cork). The two boiling tubes are connected by a gauge, fitted with a tap; a suitable liquid, one that is not affected by the vapour of the solvent, is used as index. The graduated tubes are both connected with the third tube by means of inverted U-pieces, also fitted with

¹ Jour. Chem. Soc., 87, 1474 (1905). Proc. Chem. Soc., 21, 304 (1905). Chem. News, 93, 96 (1906).

taps. The third tube is furnished with a tube with tap. The three tubes should be arranged in the form of a triangle, so that the apparatus is self-supporting.

Method

(By using equal weights of the substances whose molecular weights are to be compared, the working and calculations are considerably simplified; the above equation, by putting $w_1 = w_2$, becomes $m_1/m_2 = v_2/v_1$). The weighed quantities of the two substances (about 0.1–0.5 gram) are introduced into the graduated boiling tubes, the stoppers fixed in position, and the necessary connections with the third

Fig. 1

tube made. The taps in the funnels and gauge are kept closed; a little of the solvent is added to the funnels to ensure that no air may find its way into the apparatus. The third tube is then connected, by means of the glass tap, with an exhaust pump, and as high a vacuum as possible is obtained. The taps in the $\cap$ -tubes are then closed. The solvent is now added from the funnels, care being taken that

it is not all drawn in, as risk of introducing air must be avoided; sufficient solvent must be introduced to cover the lower ends of the funnels. The substances must be left to dissolve, the process being quickened by slightly agitating the apparatus (which will also assist in producing uniformity of concentration). The tap in the gauge is cautiously opened (if care be not taken, the liquid serving as index may be forced into one of the solutions), and the movement of the indicator observed. This moves toward the tube in which the vapour pressure is smaller; consequently, if the solvent is added drop by drop into that tube, a stage—the equilibrium stage—is reached when the index is stationary, and the volumes of the solutions are read off. More liquid is next added to one of the solutions, and equilibrium again re-established by careful addition of solvent to the other, when another reading of the volumes is taken. This process is repeated as often as is desirable. Whenever liquid is added to the solutions, the apparatus should be agitated or left to itself for some time in order to insure uniformity of concentrations.

Precautions

The ends of the funnels should be drawn out to fine stems, otherwise thick-walled tubing will introduce error in the reading of the volumes, corrections in such cases being rather laborious to apply. It is extremely difficult to ensure that the taps are perfectly air-tight, and that no air finds its way into the tubes.

Advantages

(1) The apparatus is of fairly simple construction, and is not difficult to manipulate. (2) Good quantitative results could be obtained were it possible to completely overcome the mechanical difficulty of rendering the taps perfectly air-tight. (3) There is a wide choice of solvents (the more volatile the solvent, the better the results). (4) The method may be found useful in the study of the phenomena of "dissociation" and "association."

Suggestions

It is possible that, instead of using glass taps which are very difficult to render quite air-tight, it would be advantageous to employ pressure tubing with clips.

It may be found necessary to maintain the solutions at a uniform temperature by placing the apparatus in a trough of water or in some suitable thermostat.

The following is a simplified form of the apparatus. Each graduated tube is fitted with a two-bored rubber stopper.

Fig. 2

through which pass the funnel and gauge; the funnels are fitted with one-bored rubber stoppers, connected by a T-piece in communication with an exhaust pump. The weighed quantities of the substances are introduced, the necessary connections made, the apparatus exhausted, the taps in the funnels closed, the T-piece with the stoppers removed, the solvent added, and the estimations made (see figure).

Results

In all cases, ether was used as solvent, and concentrated sulphuric acid as index. The volumes (v_1v_2) were measured in cubic centimeters.

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I. Compared *p*-dibrombenzene (m_1, v_1) with *p*-chlor-nitrobenzene (m_2, v_2). Equal weights of each (0.3 gram)

$$m_1/m_2 = 236/157 = 1.5$$

	v_1	v_2	v_2/v_1
(1)	5.0	7.5	1.50
(2)	8.0	11.75	1.47
(3)	10.0	14.75	1.48
(4)	11.0	16.25	1.48
Mean			1.48

II (Test.) Determination of M. W. of unknown substance (m_1, v_1) by comparison with *p*-chlor-nitro-benzene (m_2, v_2). Equal weights (0.4 gram each)

	v_1	v_2	v_2/v_1
(1)	5.0	7.5	1.50
(2)	7.5	11.0	1.33
(3)	8.0	11.5	1.44
(4)	10.25	14.0	1.36
Mean			1.41

$$\therefore m_1 = m_2 \cdot v_2/v_1 = 157 \times 1.41 = 221.$$

M. W. of α -brom- β -naphthol = 223.

Same compared with 1-chlor-2-4-dinitro-benzene (m_2, v_2)

	v_1	v_2	v_2/v_1
(1)	5.0	5.5	1.10
(2)	7.0	8.4	1.20
(3)	9.0	10.1	1.12
(4)	10.0	11.1	1.11
(5)	12.0	13.3	1.11
Mean			1.13

$$\therefore m_1 = 202 \times 1.13 = 228.$$

III Compared picric acid (m_1, v_1) with 1-chlor-2-4-dinitro-benzene (m_2, v_2). Equal weights (each 0.35 gram)

$$m_1/m_2 = 229/202 = 1.13.$$

	v_1	v_2	v_2/v_1
(1)	5.0	5.5	1.10
(2)	10.0	11.5	1.15
(3)	15.0	16.5	1.10
Mean			1.12

IV (Test.) Determination of M. W. of unknown substance (m_1, v_1) by comparison with *p*-dibrom-benzene (m_2, v_2). Equal weights (0.4 gram)

	v_1	v_2	v_1/v_2
(1)	6.5	5.0	1.30
(2)	13.2	10.0	1.32
(3)	14.5	11.0	1.32
Mean			1.31

$$\therefore m_1 = m_2 \div (v_1/v_2) = 236 \div 1.31 = 180.$$

M. W. of 2-4-dinitro-toluene = 183.

Same by comparison with α -naphthylamine (m_2, v_2)

	v_1	v_2	v_2/v_1
(1)	5.0	6.3	1.26
(2)	7.0	8.9	1.27
(3)	9.0	11.1	1.23
(4)	12.0	14.9	1.24
Mean			1.25

$$\therefore m_1 = 143 \times 1.25 = 179.$$

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V (Test.) Determination M. W. of unknown substance (m_1 , v_1)
by comparison with 1-chlor-2-4-dinitro-benzene (m_2 , v_2).
Equal weights (0.3 gram)

	v_1	v_2	v_1/v_2
(1)	6.5	4.0	1.62
(2)	7.25	4.5	1.61
(3)	8.25	5.5	1.50
(4)	9.0	6.0	1.50
(5)	10.75	7.0	1.55
(6)	12.25	8.0	1.53

Mean 1.55

$$\therefore m_1 = m_2 \div (v_1/v_2 = 202 \div 1.55 = 130.$$

M. W. of *p*-chlor-aniline = 127.

Same by comparison with *p*-nitraniline (m_2 , v_2)

	v_1	v_2	v_1/v_2
(1)	5.5	5.0	1.10
(2)	7.6	7.0	1.08
(3)	9.8	9.0	1.09
(4)	11.0	10.0	1.10
(5)	13.2	12.0	1.10

Mean 1.07

$$\therefore m_1 = m_2 \div (v_1/v_2) = 138 \div 1.09 = 127.$$

VI Comparison of iodoform (m_1 , v_1) with hydrazobenzene (m_2 , v_2).
Equal weights of each (0.4 gram)

$$m_1/m_2 = 394/184 = 2.14$$

	v_1	v_2	v_2/v_1
(1)	8.0	17.5	2.19
(2)	9.75	20.0	2.05
(3)	11.5	23.75	2.07
(4)	12.0	24.75	2.06

Mean 2.09

VII Compared hydrazobenzene (m_1, v_1) with 1-brom-2-4-dinitro-benzene (m_2, v_2). Equal weights (each 0.4 gram)

$$m_2/m_1 = 247/184 = 1.34$$

	v_1	v_2	v_1/v_2
(1)	6.75	5.0	1.35
(2)	8.25	6.0	1.37
(3)	12.25	9.0	1.36
(4)	13.25	10.0	1.32
(5)	16.25	12.0	1.35
(6)	17.50	13.0	1.35
(7)	20.00	15.0	1.33

Mean 1.35

VIII Compared 1-brom-2-4-dinitro-benzene (m_1, v_1) with diphenyl-amine (m_2, v_2). Equal weights (0.35 gram each)

$$m_1/m_2 = 247/169 = 1.46$$

	v_1	v_2	v_2/v_1
(1)	5.0	7.5	1.50
(2)	8.0	12.25	1.53
(3)	10.0	15.0	1.50
(4)	12.0	17.75	1.48

Mean 1.50

IX Compared β -naphthylamine (m_1, v_1) with picric acid (m_2, v_2). Equal weights (each 0.4 gram).

$$m_2/m_1 = 229/143 = 1.60$$

	v_1	v_2	v_1/v_2
(1)	8.0	5.0	1.60
(2)	10.0	6.25	1.60
(3)	12.0	7.5	1.60
(4)	12.25	7.75	1.61
(5)	16.0	10.0	1.60
(6)	18.75	12.0	1.56

Mean 1.59

X (Test.) Determination of M. W. of unknown substance (m_1 , v_1) by comparison with β -naphthylamine (m_2 , v_2). 0.4 gram of each

	v_1	v_2	v_1/v_2
(1)	6.0	5.0	1.21
(2)	7.25	6.0	1.21
(3)	8.5	7.0	1.21
(4)	10.75	9.0	1.19
(5)	11.75	10.0	1.17
(6)	14.5	12.0	1.21

Mean 1.19

$$m_1 = m_2 \cdot v_2 / v_1 = 143 / 1.19 = 120.$$

M. W. of *p*-chlor-aniline = 127.

XI Compared *p*-toluidine (m_1 , v_1) with α -naphthylamine (m_2 , v_2).
Equal weights of each (0.4 gram)

$$m_2/m_1 = 143/107 = 1.33$$

	v_1	v_2	v_1/v_2
(1)	7.7	5.0	1.34
(2)	10.7	8.0	1.33
(3)	13.5	10.0	1.35
(4)	17.4	13.0	1.34

Mean 1.34

XII Comparison of *m*-dinitro-benzene (m_1 , v_1) with *p*-nitro-toluene (m_2 , v_2). Equal weights (each 0.4 gram)

$$m_1/m_2 = 168/137 = 1.22$$

	v_1	v_2	v_2/v_1
(1)	6.1	5.0	1.22
(2)	9.7	8.0	1.21
(3)	12.1	10.0	1.21
(4)	14.6	12.0	1.21
(5)	17.1	14.0	1.22
(6)	18.2	15.0	1.21

Mean 1.21

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