

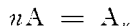
DETERMINATION OF MOLECULAR WEIGHTS BY DISTRIBUTION EXPERIMENTS¹.

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According to Nernst² and Aulich³ and others⁴ it is possible to find the relation existing between the molecular weights of a substance in two immiscible solvents by distributing it between them. The simplest derivation of this law is the following :

Assume the formula of a substance to be A_n in one solvent, and A in the other immiscible one, where n is equal to 1, or greater. The chemical reaction in the two-layer, heterogeneous system, then, will be



and the application of the law of mass action will lead to the relation

$\frac{C_{A_n}}{C_A^n} = \text{constant}$, where C_{A_n} and C_A are the concentrations in moles, per

unit of volume, of the substances A_n and A in the two layers.

This constant is of course independent of the single values of C_{A_n} and C_A , and dependent only upon the temperature.

If $n = 1$, the substance being a gas which is distributed between a liquid and a space above it, we have Henry's law, *i. e.*, $\frac{C_{\text{gas}}}{C_{\text{in solution}}} = \text{constant}$. When $n = 2$, as is the case when the solvents are water and benzene, and the substance benzoic acid, it is found that $\frac{C_{\text{water}}}{C_{\text{benzene}}} = \text{constant}$, at any one temperature and independent of the total amount of benzoic acid present in the system.

In place of concentration, *i. e.*, moles per liter, we can employ grams per unit volume. Thus, since $C_1 = \frac{w_1}{M_1}$, $C_2 = \frac{w_2}{M_2}$, and $M_1 = nM_2$ we find that — constant = C_1/C_2^n — can also be written in the form $((M_1/M_2^n) \text{ constant}) = w_1/w_2^n$, where w_1 and w_2 are the grams in the two layers per unit of volume. In other words, so long as at all dilutions M_1/M_2^n is a constant, we can use w_1/w_2^n in place of C_1/C_2^n . And, conversely, if w_1/w_2^n is a constant for all dilutions, M_1 must be equal to M_2^n .

¹ Abstract from the Dissertation (Columbia 1907) of H. K. Benson.

² Z. physik. chem., 8, 110, (1891).

³ Ibid, 8, 105, (1891).

⁴ See Hantzsch and Sebald, *ibid*, 30, 268, (1896); Hantzsch and Vagt, *ibid*, 38, 705, (1901); Roloff, *Ibid*, 13, 341, (1894); Jakowkin, *Ibid*, 20, 19, (1896); Hendrixson, Z. anorg. Chem., 13, 73, (1897); Riecke, Z. physik. Chem., 7, 108, (1891); H. Fischer, Dissertation, Breslau, (1905); Herz and Lewy, Z. electrochem., 11, 818, (1905) and others.

The substances studied in this investigation were those which absorb heat on dissolving, and show variation in the molecular weight with the concentration, according to the freezing point method; together with those which were necessary to interpret these. The results of the distribution experiments, expressed in grams per cc., are as follows:

I. ACETIC ACID BETWEEN WATER AND ETHER.			
	W_w	W_e	$\frac{W_w}{W_e}$
	0.0044	0.0025	1.76
	0.0200	0.0101	1.98
	0.0694	0.0370	1.88
	0.0768	0.0364	2.11
	0.1152	0.0616	1.87
		Average	1.92
II. ACETIC ACID BETWEEN MOLTEN $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ AND ETHER.			
	W_s	W_e	$\frac{W_s}{W_e}$
	0.0124	0.0175	0.709
	0.0216	0.0285	0.757
	0.0249	0.0358	0.696
	0.0518	0.0767	0.675
	0.0933	0.1229	0.759
	0.1298	0.1940	0.669
		Average	0.711
III. ACETIC ACID BETWEEN MOLTEN $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ AND ETHER.			
	W_s	W_e	$\frac{W_s}{W_e}$
	0.0092	0.0072	1.28
	0.0216	0.0194	1.11
	0.0261	0.0249	1.05
	0.0533	0.0508	1.05
	0.0869	0.0869	1.00
		Average	1.09
IV. ETHYL ALCOHOL BETWEEN WATER AND ETHER.			
	W_w	W_e	$\frac{W_w}{W_e}$
	0.0116	0.0164	0.707
	0.0289	0.0496	0.583
	0.0543	0.0833	0.652
	0.0660	0.1157	0.570
	0.0689	0.1127	0.611
	0.102	0.1896	0.538
		Average	0.610

V. ETHYL ALCOHOL BETWEEN MOLTEN $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ AND ETHER.

W_f	W_e	$\frac{H_f}{W_e}$
0.0039	0.00387	1.01
0.025	0.0247	1.01
0.025	0.0210	1.19
0.0388	0.0332	1.14
0.0463	0.0369	1.26
0.098	0.0764	1.27

Average 1.15

VI. ETHYL ALCOHOL BETWEEN MOLTEN $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ AND BENZENE.

W_a	W_b	$\frac{W_f}{W_b}$
0.288	0.0382	7.54
0.4566	0.0606	7.53

VII. ETHYL ALCOHOL BETWEEN WATER AND BENZENE.

W_a	W_b	$\frac{W_a}{W_b}$
0.040	0.0385	1.04
0.0693	0.0683	1.02
0.160	0.1316	1.22
0.262	0.1936	1.36

Equal volumes of the two solvents were used throughout, in each case the system being agitated at 25° until equilibrium was established. The acetic acid was titrated with a standard base, using phenolphthalein as indicator. The content of alcohol in the two layers was found by the Method of Thorpe and Holmes¹. 25 cc. of the layer were removed and placed in a separating funnel, diluted to 100 cc. with water, saturated with sodium chloride and mixed with 40 cc. of petroleum ether. After shaking for five minutes the layers were allowed to separate and the lower one withdrawn for distillation. The layer of petroleum ether was washed several times with saturated salt solution and the washings added to the main portion. The latter was next distilled through a Hopkins head and condenser into a 50 cc. flask, protected against evaporation by an adapter. The flask, after distillation had continued until one-fourth of the original solution had distilled over, was filled to the mark with distilled water. To determine the alcohol in grams in this distillate, the specific gravity was determined by aid of a Sprengel-Ostwald pycnometer and from that, by means of the conversion table of Morley²; the percentage of alcohol by weight determined. This weight was the amount of alcohol present in the original 25 cc.

Discussion of Results

Before using ether as the second solvent it was necessary to find the molecular weights of alcohol and acetic acid, when dissolved in it. As

¹ J. Chem. Soc., 83, 314, (1903).

² This Journal, 26, 1185. (1904).

these cannot be found by aid of the freezing point, and since solute, as well as solvent, distils when heated the boiling point method is not applicable, there is no direct method. The method used was as follows: The molecular weights of ethyl alcohol and acetic acid in water have been determined up to high concentrations¹; and increase but slightly with increased concentration. Solutions of acetic acid and ethyl alcohol in water were shaken with equal volumes of ether, and gave (see tables I and IV) practically constant results, within the experimental error. Tables II, III, and V also show constancy in the ratio for acetic acid between ether and $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$, and alcohol between ether and $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$. This proves, then, that acetic acid and alcohol have practically the same molecular weights in ether as they have in water (which is nearly independent of concentration, as shown by the freezing point method); and that this molecular weight is really the same as that in molten $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, notwithstanding that the freezing point leads, according to Morgan and Benson, to absurd figures at high concentrations. Further, according to the coefficient of distribution the molecular weight of alcohol in benzene, (table VII) even ignoring the experimental error, does not vary as greatly with the concentration as it does according to the freezing points of Beckmann², who finds the value $M = 318$ for a solution containing 32.45 grams of alcohol to 100 of benzene.

Throughout, of course, all consideration of ionization has been omitted, for in all cases considered it is negligible, as compared with the experimental error; and simplicity rather than great exactness was thought important.

Summary.

I. The molecular weights of ethyl alcohol and acetic acid in ether are the same as in water, *i. e.*, $\frac{C_w}{C_e}$, for both acetic acid and alcohol is constant and independent of dilution.

II. The molecular weights of alcohol and acetic acid in molten $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and in $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ derived from the coefficient of distribution, are the same as in water, although freezing point measurements, according to Morgan and Benson, using the ordinary formula, lead to absurd values in concentrated solutions.

III. The molecular weight of alcohol in benzene, derived from the coefficient of distribution, apparently does not vary with the concentration to such a great extent as it does when derived from the freezing point method.

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¹ Jones and Murray, *Am. Ch. J.*, **30**, 205, (1903).

² *Z. physik. Chem.*, **2**, 728, (1888).