

# Studies of Solution. I.

## The Change of Molecular Solution Volumes in Solutions.

By

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### 1. Introduction.

It is not recognizable that a solution would generally be formed by a simple physical mixture of solute and solvent. Solute and solvent, according to their relative properties, may form solutions in all possible proportions or in certain limited proportions. In the latter case, if there is an excess of solute, we obtain a purely physical mixture of a saturated solution and the solute. The fact of the existence of a saturated solution tells us that the constitution of a solution is something different from a simple physical mixture. Is, therefore, a solution a chemical compound? No, evidently not; because, the composition of solution may be varied continuously within certain limits.

A solution which is neither a physical mixture nor a chemical compound, must, therefore, be formed by a kind of affinity between solute and solvent that is different both from chemical affinity and physical attractive force.

The term "physico-chemical affinity"<sup>1</sup> may be employed to designate this attractive force. The origin of these attractive forces may

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<sup>1</sup> L. Gruwitsch (Zs. physik. Chem., **87**, 333, (1914) and J. Russ. Phys. Chem. Soc., **47**, 805. (1915)) has studied the phenomena of partition and absorption in solution and explained the differences between three kinds of attractive forces, chemical, physical and physico-chemical.

perhaps be the same, and their differentiation may depend only upon the manner of their expressions; but, as physical attractive force and chemical affinity have been treated practically as quite different forces, so physico-chemical affinity may be treated as a special kind of attractive force. Physical attractive force is not of specific nature and it is expressed by a certain function of distance, but chemical affinity is very specific for substances and it is usually expressed by a comparatively simple function of the concentrations of components. At present, the definition and expression of physico-chemical affinity is not known, yet I think it an interesting method of study of solution to treat it as a problem of such an affinity.

In a study of solution from such a stand point, the usual chemical methods can not be employed and we are compelled to be content with the study of variation of certain physical properties of solution in accordance with the change of its composition.

As the physical properties of solution, viscosity, surface tension, specific gravity, optical properties, electric conductivity, heat capacity, vapour pressure, osmotic pressure, etc, have been studied by many chemists and physicists; most of these physical constants can not be determined separately by parts where solute and solvent play their rôles respectively. Thus there is no appropriate method for the study of solution but a discussion of the difference between the physical properties of real solution and those of the ideal solution which obeys the *admixture law*. Certain of these properties, however, such as electric conductivity and osmotic pressure, are favorable for our purpose as they depend upon only one component of a solution in lower concentrations, though in concentrated solutions, it is impossible to neglect the influence of the other component. Only one property, that is vapour pressure, may be separately determined as the partial pressures of solute and solvent; but the vapour phase is a kind of phase different from that of solution, therefore the conclusion<sup>1</sup> about the state of solution deduced from the studies of vapour pressures is indirect.

If there be a property which can separately be determined with respect to solute and solvent in the state of solution itself, there is confidence that the study of this property would make some important contribution to the knowledge of the nature of solution. As one such property, I have chosed the *molecular solution volumes* of solute

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<sup>1</sup> F. Dolezalek: Zs. physik. Chem., **64**, 727 (1908).

and solvent in solution. This is not perhaps the best for the present purpose ; but I have no clue to any other which might better suit.

## 2. The Method of Determination of Molecular Solution Volumes of Solute and Solvent in Solution.

The change of volume in the formation of solution has been noticed from early times in the study of solution ; and the fact that solution changes its volume according to temperature, pressure and concentration shows that the volume of a given substance in solution is variable.

In order to discuss something about the volume of solute or solvent in solution, it is necessary to make the assumption that the total volume of a solution was made up as the sum of the two volumes which are occupied by the solute and solvent respectively. Taking into consideration the Richards' conception<sup>1</sup> of the compressible atoms or assuming that the free volume in solution is very small against its total volume, the above assumption is not non-plausible. The author designates such volumes as the "molecular solution volumes",<sup>2</sup> to distinguish them from the "molecular volume", as defined as (molecular weight)/(density).

Such molecular solution volumes of solute and solvent in solution have been seldom studied separately. Recently G. P. Baxter<sup>3</sup> studied the change of volume of solutions of alkali halides and tried to explain the complex phenomena by the theory of compressible atoms ; but he did not turn his attention to the change of molecular solution

<sup>1</sup> See J. Amer. Chem. Soc., **36**, 2417 (1914).

<sup>2</sup> J. Traube has first introduced the term molecular solution volume (See Smiles : The Relation between Chemical Constitution and some Physical Properties, p. 124.) If  $A_s$  is the molecular weight of a solute in grams,  $l$  the quantity of solvent which is present for every mol of solute,  $d$  the density of the solvent,  $d_s$  the density of the solution, the molecular solution volume of Traube is related to that of the solute of the author,  $\varphi_s$ , as follows :

$$\varphi_s = \frac{A_s + l}{d_s} - \frac{l}{d}.$$

In the present case, as the change of the volume of solvent is also taken into consideration, the second term of the above expression must be a function of the molecular solution volume of solvent such as  $\varphi_s = \frac{A_s + l}{d_s} - \frac{l}{A_w} \varphi_w$  where  $\varphi_w$  and  $A_w$  are the molecular solution volume and the molecular weight of solvent respectively.

<sup>3</sup> J. Amer. Chem. Soc., **33**, 922 (1911).

volumes of solute and solvent. Twelve years ago Carl Forch<sup>1</sup> attempted to determine the molecular solution volumes of solute and solvent in solution separately, but since his studies were limited to comparison of the molecular solution volumes of solutes in several kinds of solutions in a definite concentration, his work has drawn little attention and no one has continued the study of solution after such a manner. Forch's method however appears the only one whereby to determine the property of solution in separate parts with respect to solute and solvent.

Explanation of this method: If  $m_s$  mols of solute be present in one litre of solution of sp. gr.  $s$ , the mols of solvent  $m_w$ , in the solution is

$$m_w = \frac{1000s - m_s A_s}{A_w},$$

where  $A_s$  and  $A_w$  are the molecular weights of solute and solvent respectively.

If  $\varphi_s$  and  $\varphi_w$  be the molecular solution volumes of solute and solvent respectively, we have the following relation:

$$m_s \varphi_s + m_w \varphi_w = 1000.$$

The molecular solution volumes are of course functions of concentration, say

$$\varphi_s = f_1(m_s, m_w) \quad \text{and} \quad \varphi_w = f_2(m_s, m_w),$$

but within the range where the change of concentration is not so large, we get the following two equations:

$$\left. \begin{aligned} m_{s_1} \varphi_s + m_{w_1} \varphi_w &= 1000 \\ m_{s_2} \varphi_s + m_{w_2} \varphi_w &= 1000 \end{aligned} \right\} \quad (1)$$

From these equations we can calculate two unknown quantities  $\varphi_s$  and  $\varphi_w$ . That is, if we take two solutions which have known concentrations, we can calculate the molecular solution volumes of solute and solvent in the solution which has the mean concentration of the two solutions here chosen. To know the concentrations of the solute and solvent of a solution, we must determine the sp. gr. of the solution which has the known weight percentage of solute.

From equation (1)

<sup>1</sup> Ann. Physik, [iv] **12**, 591 (1903). In the Forch's paper the term "molecular volume" of solute and solvent in solution is used, but not "molecular solution volume."

$$\left. \begin{aligned} \varphi_s &= \frac{1000(m_{w_1} - m_{w_2})}{m_{s_2}m_{w_1} - m_{s_1}m_{w_2}} \\ \varphi_w &= \frac{1000(m_{s_2} - m_{s_1})}{m_{s_2}m_{w_1} - m_{s_1}m_{w_2}} \end{aligned} \right\} \quad (2)$$

Now, if the weight percentages of the solute in the two solutions chosen be denoted by  $a_1$  and  $a_2$ , and the specific gravities of these solutions by  $s_1$  and  $s_2$  respectively, then

$$\varphi_s = \frac{1000[(100 - a_1)s_1 - (100 - a_2)s_2]A_s}{[a_2(100 - a_1) - a_1(100 - a_2)]s_1s_2} pA_s. \quad (3)$$

In the same way :

$$\varphi_w = \frac{1000[a_1s_1 - a_2s_2]A_w}{[a_1(100 - a_2) - a_2(100 - a_1)]s_1s_2} = qA_w. \quad (4)$$

As may be seen, the above equations (3) and (4) are independent to each other, with respect to their molecular weights, therefore the above method of calculation is also applicable to the determination of the molecular solution volumes of solute and solvent when the molecular weight of one of them is unknown. Moreover, if their molecular weights are both unknown, the relative volume change may be calculated in quite the same way. Therefore this method of calculation is also applicable to the case where the solute or solvent have ionized or polymerized in the solution.

In the present work, the change of molecular solution volumes in aqueous solutions of cane sugar and of alkali halides by the changes of temperature and concentration has been determined.

### 3. The Molecular Solution Volumes of Solute and Solvent in Aqueous Solutions of Cane Sugar.

Plato<sup>1</sup> has determined very accurately the specific gravities of aqueous solutions of cane sugar. From his values, the data needed in the calculation of the molecular solution volumes were taken and the molecular solution volumes of cane sugar and water in the solutions have been calculated as shown in the following tables, where  $s$  denotes the specific gravity of solution and  $m_s$  and  $m_w$  the numbers of mols of cane sugar and water per litre and  $\varphi_s$  and  $\varphi_w$  the respective molecular solution volumes.

<sup>1</sup> Zs. Zuckerindustrie, **56**, 982. 1079, (1900); Landolt-Börnstein's Tabellen, p. 311.

TABLE I.

0.0°C.

%	$s$	$m_s$	$m_w$	$\varphi_s$	$\varphi_w$
0	0.999868	0	55.500}	204.7	18.019
5	1.02033	0.14909	53.801}	206.6	18.015
10	1.04135	0.30433	52.020}	208.4	18.004
20	1.08546	0.63447	48.200}	209.9	17.986
30	1.13274	0.99314	44.012}	211.3	17.968
40	1.18349	1.38347	39.415}	213.0	17.891
50	1.23775	1.80865	34.352}	214.7	17.804
60	1.29560	2.27181	28.765}	216.1	17.700
70	1.35719	2.77645	22.600}		
60	1.29560	2.27181	28.765}	215.8	17.719
65	1.32591	2.51871	25.759}	216.4	17.665
70	1.35719	2.77645	22.600}		

TABLE 2.

10.0°C.

%	$s$	$m_s$	$m_w$	$\varphi_s$	$\varphi_w$
0	0.999727	0	55.491}	208.9	18.021
5	1.01960	0.14899	53.765}	209.6	18.019
10	1.04016	0.30400	51.962}	210.5	18.018
20	1.08353	0.63333	48.114}	211.6	17.998
30	1.13014	0.99085	43.911}	212.9	17.970
40	1.18020	1.37964	39.305}	214.3	17.920
50	1.23382	1.80286	34.242}	215.8	17.844
60	1.29117	2.26404	28.667}	217.1	17.737
70	1.35230	2.76644	22.518}		
60	1.29117	2.26404	28.667}	216.7	17.767
65	1.32125	2.50986	25.668}	217.4	17.701
70	1.35230	2.76644	22.518}		

TABLE 3.

20.0°C.

%	$s$	$m_s$	$m_w$	$\varphi_s$	$\varphi_w$
0	0.998230	0	55.408		
5	1.01784	0.14873	53.671	210.7	18.048
10	1.03813	0.30339	51.860	211.3	18.047
20	1.08094	0.63180	47.999	212.0	18.042
30	1.12698	0.98806	43.789	213.1	18.029
40	1.17648	1.37529	39.180	214.2	18.004
60	1.22958	1.79671	34.124	215.5	17.959
60	1.28644	2.25575	28.562	216.8	17.890
70	1.34716	2.75594	22.432	218.0	17.790
50	1.28644	2.25575	28.562	217.7	17.818
65	1.31631	2.50047	25.572	218.3	17.760
70	1.34716	2.75594	22.432		

TABLE 4.

30.0°C.

%	$s$	$m_s$	$m_w$	$\varphi_s$	$\varphi_w$
0	0.995673	0	55.266		
5	1.01518	0.14834	53.530	211.7	18.094
10	1.03530	0.30257	51.719	212.4	18.092
20	1.07767	0.62990	47.854	213.5	18.087
30	1.12324	0.98479	43.643	214.4	18.074
40	1.17214	1.37018	39.036	215.7	18.045
50	1.22495	1.78982	33.996	216.4	18.018
60	1.28144	2.24699	28.451	217.8	17.955
70	1.34181	2.74499	22.348	219.0	17.855
60	1.28144	2.24699	28.451	218.7	17.883
65	1.31113	2.49063	25.471	219.3	17.823
70	1.34181	2.74499	22.343		

TABLE 5.

40.0°C.

%	$s$	$m_s$	$m_w$	$\varphi_s$	$\varphi_w$
0	0.992241	0	55.076	212.1	18.157
5	1.01169	0.14781	53.348	213.9	18.151
10	1.03165	0.30150	51.537	214.9	18.145
20	1.07366	0.62755	47.676	215.7	18.132
30	1.11888	0.98096	43.473	216.5	18.113
40	1.16759	1.36462	38.885	217.6	18.092
50	1.21996	1.78265	33.857	218.7	18.019
60	1.27615	2.23771	28.333	219.9	17.927
70	1.33625	2.73362	22.250		
69	1.27615	2.23771	28.333	219.6	17.953
65	1.30571	2.48034	25.366	220.2	17.895
70	1.33625	2.73362	22.250		

TABLE 6.

50.0°C.

%	$s$	$m_s$	$m_w$	$\varphi_s$	$\varphi_w$
0	0.98807	0	55.844	213.7	18.233
5	1.00735	0.14720	53.118	214.9	18.229
10	1.02720	0.30020	51.314	215.9	18.224
20	1.06898	0.62481	47.468	216.6	18.215
30	1.11398	0.97668	43.283	217.5	18.196
40	1.16248	1.35893	38.714	218.5	18.160
50	1.21465	1.77489	33.710	219.7	18.096
60	1.27058	2.22794	28.210	220.8	18.008
70	1.33047	2.72179	22.155		
60	1.27058	2.22794	28.210	220.5	18.031
65	1.30002	2.46952	25.256	221.0	17.980
70	1.33047	2.72179	22.155		



TABLE 7.

60.0°C.

%	$s$	$m_s$	$m_w$	$\varphi_s$	$\varphi_w$
0	0.98330	0	54.579	251.96 216.5 217.1 217.3 218.2 219.5 220.6 221.7 221.5 221.9	18.322
5	1.00231	0.14646	52.853		18.320
10	1.02198	0.29868	51.054		18.317
20	1.06358	0.62164	47.226		18.314
30	1.10850	0.97190	43.070		18.293
40	1.15693	1.35244	38.530		18.250
50	1.20891	1.76650	33.551		18.190
60	1.26468	2.21760	28.079		18.104
70	1.32447	2.70951	22.055		
60	1.26468	2.21760	28.079		221.5
65	1.29408	2.45825	25.140	221.9	18.078
70	1.32447	2.70951	22.055		

In the above tables, since the calculation of the molecular solution volumes was performed with data for one pair of solutions, they represent the molecular solution volumes for the solution of the mean concentration of the two which are chosen for the calculation.

In the above tables, for the molecular solution volumes of cane sugar, the calculations were carried out to four figures; and for those of water to five figures, taking the molecular weights<sup>1</sup> of cane sugar and water as 342.176 and 18.016 respectively. Such calculation may appear unreasonable, because the molecular weights used were not accurate in the third decimal figure; in the present case, however, the absolute values of molecular solution volumes are not needed but relative ones and therefore if a definite value be taken for the molecular weight, we could get accurate *relative* values of the molecular solution volumes.

When the solute is an easily weighable substance, we can determine the quite accurate value of weight percentage of the solute in the solution. In such a case, the accuracy of the calculated value of the molecular solution volume depends only on that of the specific gravity of the solution, and consequently the greatest error of  $\varphi_s$  and  $\varphi_w$  de-

<sup>1</sup> According to the international atomic weights for 1916, the molecular weight of cane sugar is 342.236, but this slight difference in the molecular weight does not bring any appreciable effect on the values of molecular solution volumes.

depends on the terms  $(100-a_1)s_1-(100-a_2)s_2$  and  $s_1a_1-s_2a_2$  respectively as seen in the equations (3) and (4).

#### 4. The Molecular Solution Volumes of Solute and Solvent in Aqueous Solutions of Alkali Halides.

The following four salts were taken: potassium chloride, sodium chloride, ammonium chloride and lithium chloride. As the materials, Merk's preparations of potassium chloride and ammonium chloride were used, after recrystallization; sodium chloride was purified by precipitation with hydrochloric acid gas from the solution; and lithium chloride was prepared in the following way: Commercial lithium chloride, after recrystallization, was fused in a platinum dish and then dissolved in water and again recrystallized. Lithium chloride is very hygroscopic and moreover it crystallizes with one or two molecules of water of crystallization<sup>1</sup> at room temperatures; therefore it is very difficult to weigh out a definite quantity of it, but it is more definite when fused. To avoid its decomposition, the fusion was accomplished in a combustion tube in a current of dry hydrochloric acid gas, according to Baxter<sup>2</sup>. For the preparation of a concentrated solution, a great quantity of the salt was required and in that case a platinum crucible was taken to the fusion. The crucible was set on a hollow on an asbestos plate and covered with a large inverted funnel through which a current of hydrochloric acid gas was conducted. By gentle heating of the crucible from the bottom, a fused salt was obtained which contained no trace of free alkali; but the cooling of the fused mass had to be very carefully conducted, lest a small quantity of lithium chloride should be decomposed, forming difficultly soluble lithium oxides. The fused salt thus formed could easily be detached from the crucible and it was quickly transferred into a tared weighing tube and, after cooling in a desiccator was weighed. As solvent water a conductivity water from which any dissolved gas was removed by boiling, was used.

<sup>1</sup> The transition temperature of hydrated lithium chlorides,  $\text{LiCl}\cdot 2\text{H}_2\text{O}$  and  $\text{LiCl}\cdot \text{H}_2\text{O}$ , is given as  $26^\circ$  or  $15.9^\circ\text{C}$ . in Abegg's Handbuch der anorganischen Chemie and Landolt-Börnstein's Tabellen respectively. By the determination of the author, the minimum values of the specific gravities of lithium chloride solutions (3%–40%) were always near  $23^\circ\text{C}$ , and this may be perhaps the transition temperature.

<sup>2</sup> *Loc. cit.*

The preparation of solutions: in the case of potassium chloride and ammonium chloride, a solution of a definite weight percentage was prepared by weighing water at first and then dissolving the calculated amount of salt in it. For the correction against the bouyancy in air, the specific gravities of potassium chloride and sodium chloride were taken as 2.00 and 2.14 after Baxter<sup>1</sup>, but as to ammonium chloride the literature gives several values and as any great accuracy was not required here, the value 1.52 was adopted. In the case of lithium chloride, as a definite amount of the salt could not be weighed out, the order of procedure was reversed; namely a calculated amount of water was added to a definite amount of salt. In this case the solution had to be weighed directly and the necessary data for the correction against the bouyancy in air were taken from those given by Gerlach<sup>2</sup>. In the preparation of a definite solution of lithium chloride, two solutions were prepared independent of each other and when the difference of specific gravities do not exceed 1/20000, it was assumed that the solutions had the correct percentage.

The method of determination of specific gravity: An Ostwald-Sprenger's pyknometer whose capacity is ca. 20 cc., was used. For the determination of specific gravities at several temperatures, it would have been convenient to use the dilatometric method, but in accuracy that is far inferior to the direct method. The pyknometer method was mostly used and in some cases the pyknometer itself was used as a dilatometer, one of the capillary limbs being calibrated.

For the thermostat of ordinary or higher temperature a toluene gas regulator was used; but for that below the room temperature an electric toluence regulator was used. A 2 volts current was used as the first circuit, shut or opened by a toluene regulator. By the aid of a small relay, this first current was used to shut or open a second circuit of 40 volts which, by the aid of a larger relay, shut or opened an ice water current to the thermostat. In this manner the temperature of the thermostat was automatically regulated to within 0.1°C.

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<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Zs. analy. Chem.*, 8, 281 (1869).

I. *The Molecular Solution Volumes of Solute and Solvent  
in Aqueous Solutions of Potassium Chloride.*

TABLE 8.

Specific Gravities of the Solutions.

%	0°	10°	20°	30°	40°	50°
0	0.999868	0.999727	0.99823	0.995673	0.992241	0.98807
5	1.03369	1.03262	1.02976	1.02728	1.02341	1.01912
10	1.06799	1.06605	1.06272	1.05975	1.05572	1.05108
15	1.10304	1.10039	1.09657	1.09331	1.08891	1.08410
20	1.13930	1.13615	1.13186	1.12826	1.12367	1.11877
25	—	1.17317	1.16835	1.16470	1.15999	1.15484
29	—	—	—	1.17970	1.17482	1.16969

TABLE 9.

0.0°C.

%	$s$	$m_s$	$m_w$	$\varphi_s$	$\varphi_w$
0	0.999868	0	55.499	25.81	18.019
5	1.03369	0.693818	54.500		17.989
10	1.06799	1.4324	53.352		17.941
15	1.10304	2.2191	52.041		17.894
20	1.13930	3.0561	50.591		

TABLE 10.

10.0°C.

%	$s$	$m_s$	$m_w$	$\varphi_s$	$\varphi_w$
0	0.999727	0	55.491	27.10	18.021
5	1.03262	0.69218	54.450		17.995
10	1.06605	2.4298	53.255		17.954
15	1.10039	2.2137	51.917		17.918
20	1.13615	3.0476	50.451		17.85
30	1.17317	3.9336	43.838		

TABLE 11.

20.0°C.

%	$s$	$m_s$	$m_w$	$\varphi_s$	$\varphi_w$
0	0.998230	0	55.408	28.95	18.048
5	1.02976	0.69056	54.300		18.038
10	1.06272	1.4253	53.089		18.000
15	1.09657	2.2061	51.736		17.966
20	1.13186	3.0361	50.260		17.92
25	1.16855	3.9181	78.646		

TABLE 12.

30.0°C.

%	$s$	$m_s$	$m_w$	$\varphi_s$	$\varphi_w$
0	0.995673	0	55.266	28.85 30.28 31.51 32.30 33.26 33.53	18.094 18.077 18.043 18.008 17.95 17.93
5	1.02728	0.68889	54.168		
10	1.05975	1.4214	52.941		
15	1.09331	2.1995	51.583		
20	1.12826	3.0254	50.100		
25	1.16470	3.9053	48.487		
27	1.17970	4.2713	47.800		

TABLE 13.

40.0°C.

%	$s$	$m_s$	$m_w$	$\varphi_s$	$\varphi_w$
0	0.992241	0	55.076	29.39 30.49 31.78 32.48 33.21 33.71	18.157 18.143 18.109 18.079 18.03 18.00
5	1.02341	0.6863	53.965		
10	1.05572	1.4159	52.739		
15	1.08891	2.1907	51.376		
20	1.12367	3.0141	49.897		
25	1.15999	3.8891	48.286		
27	1.17482	4.2542	47.602		

TABLE 14.

50.0°C.

%	$s$	$m_s$	$m_w$	$\varphi_s$	$\varphi_w$
0	0.98807	0	54.844	29.52 31.15 32.01 32.56 33.33 33.90	18.233 18.226 18.185 18.163 18.11 18.07
5	1.01912	0.6834	53.737		
10	1.05108	1.4097	52.507		
15	1.08410	2.1810	51.149		
20	1.11877	3.0009	49.679		
25	1.15484	3.8721	48.075		
27	1.16969	4.2621	47.394		

*II. The Molecular Solution Volumes of Solute and Solvent  
in Aqueous Solutions of Sodium Chloride.*

TABLE 15.

Specific Gravities of the Solutions.

%	0°	10°	20°	30°	40°	50°
0	0.999868	0.999727	0.99823	0.995673	0.992241	0.98807
5	1.03802	1.03656	1.03398	1.03071	1.02666	1.02210
10	1.07659	1.07394	1.07051	1.06664	1.06223	1.05729
15	1.11606	1.11235	1.10825	1.10386	1.09902	1.09381
20	1.15635	1.15206	1.14742	1.14258	1.13743	1.13198
23	1.18104	1.17634	1.17145	1.16632	1.16099	1.15551
26	1.20652	1.20151	1.19633	1.19099	1.18546	1.17980

TABLE 16.

0.0°C.

%	$s$	$m_s$	$m_w$	$\varphi_s$	$\varphi_w$
0	0.999868	0	55.499	15.51	18.019
5	1.03802	0.88782	54.735		
10	1.07659	1.8415	53.781	17.98	17.979
15	1.11601	2.8630	52.649	19.86	17.915
20	1.15635	3.9559	51.347	21.23	17.840
23	1.18104	4.6467	50.478	22.33	17.755
27	1.20652	5.3659	59.557	22.69	17.723

TABLE 17.

10.0°C.

%	$s$	$m_s$	$m_w$	$\varphi_s$	$\varphi_w$
0	0.999727	0	55.491	16.95	18.021
5	1.03656	0.88654	54.657		
10	1.07394	1.8370	53.648	19.08	17.988
15	1.11235	2.8541	52.481	22.58	17.935
20	1.15206	3.9419	51.157	21.76	17.871
23	1.17634	4.6281	50.276	22.82	17.82
26	1.20151	5.3435	49.351	22.98	17.77

TABLE 18.

20.0°C.

%	$s$	$m_s$	$m_w$	$\psi_s$	$\psi_w$
0	0.99823	0	55.408	18.14	18.048
5	1.03393	0.88429	54.519	19.83	18.022
10	1.07051	1.8311	53.476	21.52	17.955
15	1.10825	2.8433	52.284	22.09	17.925
20	1.14742	3.9254	50.950	23.05	17.850
23	1.17145	4.6088	50.067	23.27	17.831
26	1.19633	5.3206	49.136		

TABLE 19.

30.0°C.

%	$s$	$m_s$	$m_w$	$\psi_s$	$\psi_w$
0	0.995673	0	55.266	18.80	18.094
5	1.03071	0.88156	54.350	20.43	18.067
10	1.06664	1.8246	53.284	21.52	18.030
15	1.10386	2.8324	52.081	22.46	17.979
20	1.14258	3.9085	50.736	23.39	17.91
23	1.16632	4.5887	49.848	23.48	17.89
26	1.19099	5.2969	48.919		

TABLE 20.

40.0°C.

%	$s$	$m_s$	$m_w$	$\psi_s$	$\psi_w$
0	0.992241	0	55.076	19.42	18.157
5	1.02666	0.8781	54.137	20.75	18.135
10	1.06233	1.8170	53.063	21.85	18.097
15	1.09902	2.8200	51.852	22.67	18.053
20	1.13743	3.8913	50.507	23.58	17.98
23	1.16099	4.5677	49.620	23.68	17.97
26	1.18546	5.2722	48.692		

TABLE 21.

50.0°C.

%	$s$	$m_s$	$m_w$	$\varphi_s$	$\varphi_w$
0	0.98807	0	54.844	19.82 21.05 22.06 22.82 23.71 23.75	18.232 18.212 18.178 18.137 18.07 18.07
5	1.02210	0.8742	53.895		
10	1.05729	1.8085	52.815		
15	1.09381	2.8065	51.606		
20	1.13198	3.8726	50.265		
23	1.15551	4.5458	49.382		
26	1.17980	5.2471	48.460		

III. *The Molecular Solution Volumes of Solute and Solvent in Aqueous Solutions of Ammonium Chloride.*

TABLE 22.

Specific Gravities of the Solutions.

%	0°	10°	20°	30°	49°	50°
0	0.99987	0.999727	0.99823	0.995673	0.992241	0.98807
5	1.01672	1.01573	1.01377	1.01086	1.00731	1.00326
10	1.03250	1.03084	1.02840	1.02536	1.02170	1.01767
15	1.04763	1.04441	1.04264	1.03929	1.03558	1.03157
20	1.06220	1.05951	1.05642	1.05302	1.04919	1.04516
25	—	—	1.06997	1.06638	1.6250	1.05845
30	—	—	—	—	1.07584	1.07172

TABLE 23.

0.0°C.

%	$s$	$m_s$	$m_w$	$\varphi_s$	$\varphi_w$
0	0.99987	0	55.499	35.81 37.82 38.32 39.16	18.019 18.012 17.96 17.91
5	1.01672	0.9346	53.611		
10	1.03250	1.9299	51.579		
15	1.04763	2.9373	49.428		
20	1.06220	3.9708	47.167		



TABLE 24.  
10.0°C.

%	$s$	$m_s$	$m_w$	$\varphi_s$	$\varphi_w$
0	0.999727	0	55.491	36.66 38.22 38.88 39.59	18.021 17.988 17.95 17.93
5	1.01573	0.9493	53.560		
10	1.03084	1.9268	51.496		
15	1.04441	2.9310	49.323		
20	1.05951	3.9608	47.048		

TABLE 25.  
20.0°C.

%	$s$	$m_s$	$m_w$	$\varphi_s$	$\varphi_w$
0	0.998230	0	55.408	37.18 38.50 39.23 39.94 40.38	18.048 18.025 17.99 17.97 17.92
5	1.01377	0.9475	53.456		
10	1.02840	1.9223	51.374		
15	1.04264	2.9233	49.192		
20	1.05642	3.9492	46.910		
25	1.06997	4.9999	44.542		

TABLE 26.  
30.0°C.

%	$s$	$m_s$	$m_w$	$\varphi_s$	$\varphi_w$
0	0.995673	0	55.266	37.69 38.69 39.59 40.05 40.62	18.094 18.075 18.040 18.01 17.96
5	1.01086	0.94473	53.303		
10	1.02536	1.9166	51.222		
15	1.03929	2.9139	49.034		
20	1.05302	3.9366	46.760		
25	1.06638	4.9831	44.393		

TABLE 27.  
40.0°C.

%	$s$	$m_s$	$m_w$	$\varphi_s$	$\varphi_w$
0	0.992241	0	55.076	37.83 38.90 39.75 40.25 40.79 40.98	18.157 18.137 18.108 18.07 18.03 18.00
5	1.00731	0.94141	53.115		
10	1.02170	1.9097	51.039		
15	1.03558	2.9035	48.858		
20	1.04919	3.9222	46.589		
25	1.06250	4.9650	44.231		
30	1.07584	6.0328	41.801		

TABLE 28.

50.0°C.

%	$s$	$m_s$	$m_w$	$\varphi_s$	$\varphi_w$
0	0.98807	0	54.844	37.79	18.231
5	1.00326	0.93763	52.902		18.213
10	1.01767	1.9022	50.839		18.177
15	1.03157	2.8923	48.670		18.14
20	1.04516	3.9072	46.410		18.09
25	1.05845	4.9461	44.127		18.07
30	1.07172	6.0097	41.545		

IV. *The Molecular Solution Volumes of Solute and Solvent in Aqueous Solutions of Lithium Chloride.*

TABLE 29.

Specific Gravities of the Solutions.

%	0°	10°	20°	30°	40°	50°
0	0.996868	0.999727	0.998230	0.995673	0.992241	0.98807
3	(1.0185)*	1.0178	1.0176	1.0175	1.0176	1.0177
6	(1.0357)*	1.0351	1.0349	1.0347	1.0348	1.0350
10	1.0598	1.0584	1.0579	1.0577	1.0554	1.0584
20	1.1199	1.1178	1.1170	1.1169	1.1174	1.1185
30	1.1860	1.1833	1.1823	1.1821	1.1828	1.1843
35	1.2218	1.2176	1.2189	1.2175	1.2180	1.2197
40	1.2601	1.2568	1.2554	1.2551	1.2556	1.2573

TABLE 30.

10.0°C.

%	$s$	$m_s$	$m_w$	$\varphi_s$	$\varphi_w$
0	0.99973	0	55.491	17.30	18.021
3	1.0178	0.72016	54.800		17.996
6	1.0351	1.4647	54.006		18.001
10	1.0584	2.4963	52.875		17.93
20	1.1178	5.2726	49.637		17.90
30	1.1833	8.3720	45.975		17.89
35	1.2189	1.0063	43.976		17.89
40	1.2568	1.1857	41.855		

\* The values were obtained by extrapolation.

0	0.99973	0	5.5491	} 18.27	18.021
6	1.0351	1.4647	5.4006		

TABLE 31.

30.0°C.

%	$s$	$m_s$	$m_w$	$\varphi_s$	$\psi_w$
0	0.995673	0	55.266	} 12.08	18.094
3	1.0175	0.71996	54.785		
6	1.0347	1.4642	53.989	19.26	18.000
10	1.0577	2.4646	52.840	20.05	17.979
20	1.1167	5.2686	49.597	20.97	17.94
30	1.1821	8.3540	45.931	21.17	17.92
35	1.2175	1.0050	43.925	21.28	17.89
40	1.7551	1.1840	41.797	21.28	17.89
0	0.995673	0	55.266	} 15.78	18.094
6	1.0347	1.4642	53.989		

TABLE 32.

50.0°C.

%	$s$	$m_s$	$m_m$	$\varphi_s$	$\psi_w$
0	0.98807	0	54.844	} 12.4	18.232
3	1.0177	0.72006	54.795		
6	1.0350	1.4646	54.004	19.12	17.999
10	1.0584	2.4963	52.873	19.72	17.983
20	1.1185	5.2760	49.667	20.68	17.94
30	1.1843	8.3793	46.015	21.06	17.89
35	1.2197	10.068	44.004	21.27	17.86
40	1.2573	11.861	41.872	21.23	17.86
0	0.98807	0	54.844	} 10.5	18.202
6	1.0350	1.4646	54.004		

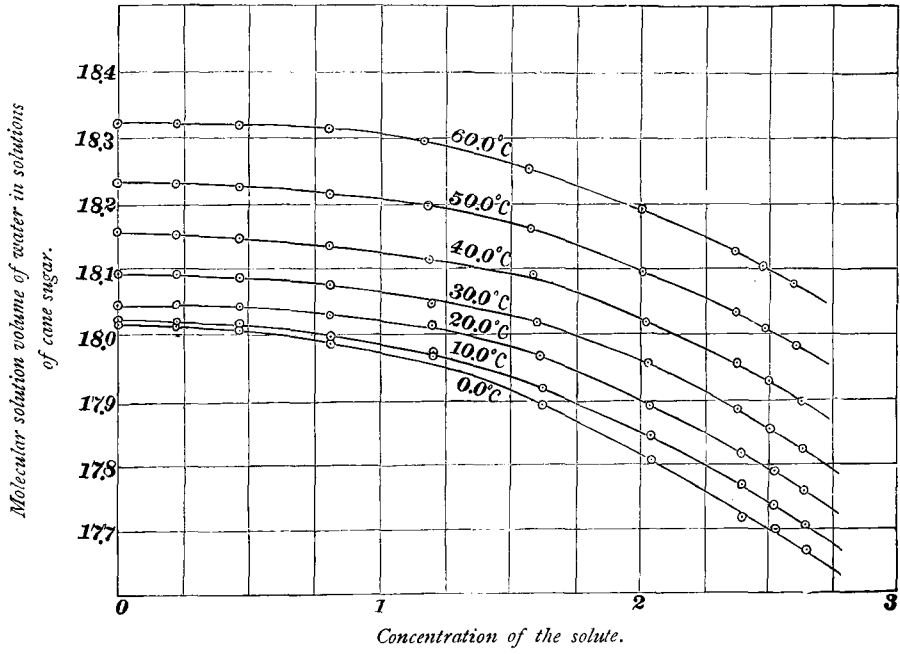


Fig. 1.

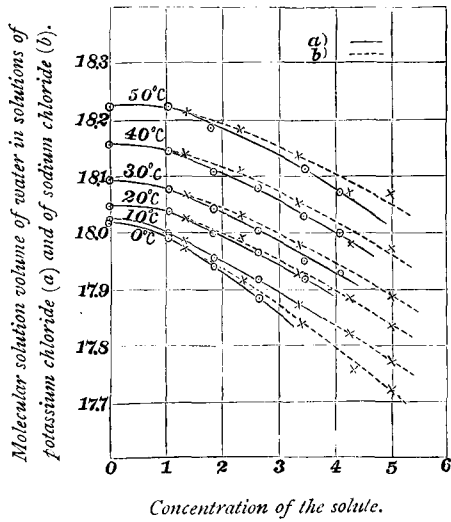


Fig. 2.

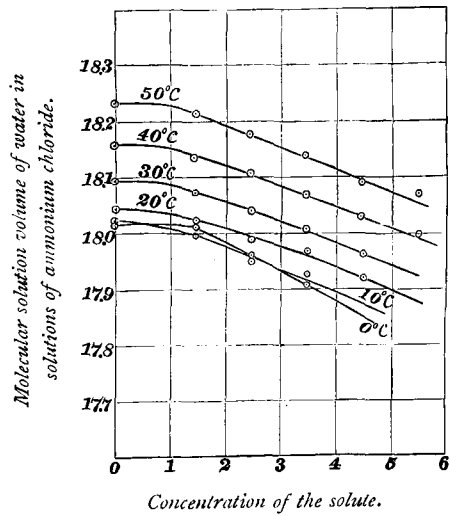


Fig. 3.

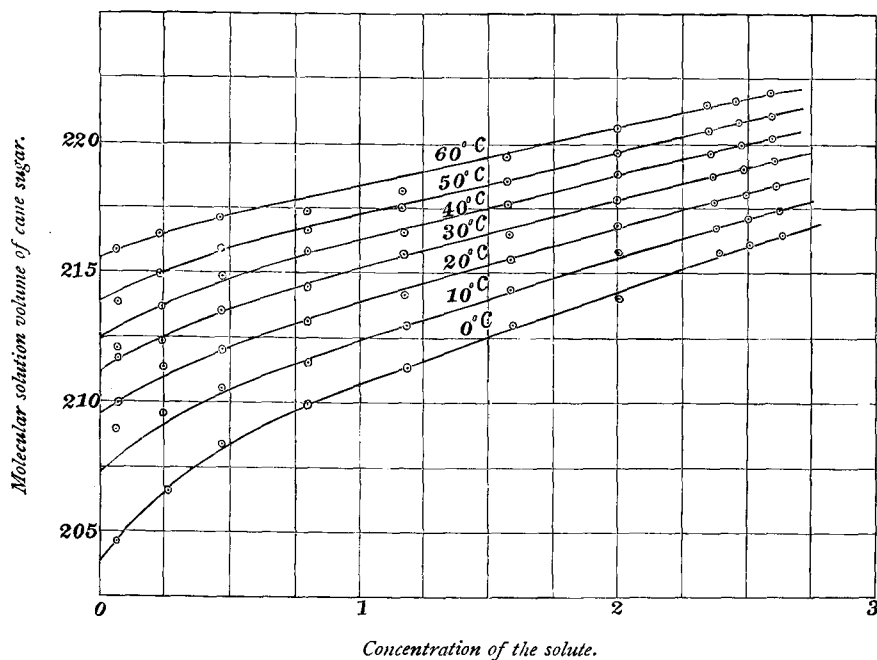


Fig. 4.

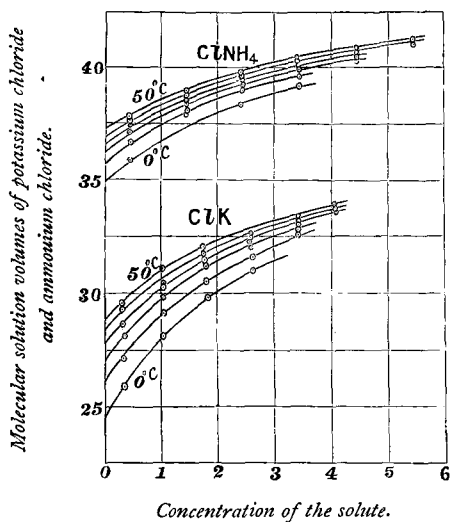


Fig. 5.

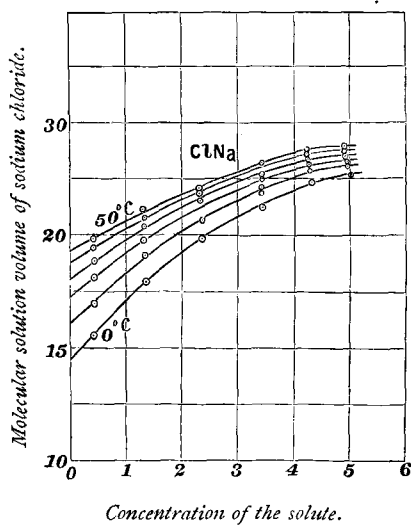


Fig. 6.

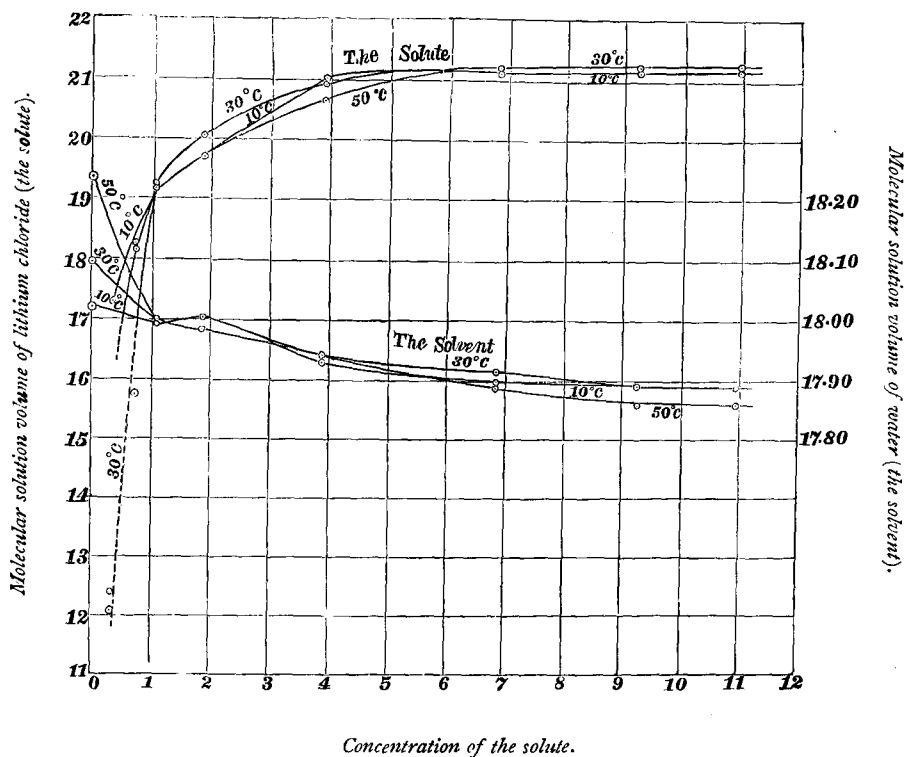


Fig. 7.

### 5. Discussion of the Results.

Representing graphically the above results, taking the molecular solution volume as ordinates and the number of mols of solute in one litre of solution as abscissa, Figg. 1-7 were obtained. As seen from these figures, the volume change of solution is the total sum of the volume changes of the solute and solvent; and, in general, the volume of solvent contracted by an increase of the concentration of the solute, while the volume of solute dilated.

*The volume of the solvent in solution.* As seen from Figg. 1-3, in all the solutions above examined, except those of lithium chloride, the molecular solution volume-concentration curves for the solvent are of the same form. So far as the concentration of solute is lower than one mol per litre, the contraction of solvent is very small, but in higher concentrations it becomes greater until at last it becomes a linear function of the concentration.

Now, the cause of the change of volume in solution appears to depend on the molecular cohesion or physico-chemical affinity between solute and solvent. If the solution is dilute the sphere of action of solute molecules does not extend to all the solvent molecules in the solution, and the greater part of solvent molecules, which are not affected by solute molecules, would be in the same state of aggregation as in the pure state; thus the change of volume of solvent in dilute solutions is very small. In more concentrated solutions, however, the sphere of action of solute extends to all the solvent molecules, and the volume of solvent would change linearly with the concentration of the solute.

The amount of volume change of solvent, as above described, is seen to be one of the measures of the physico-chemical affinity between solute and solvent. The following table represents the amount of volume contraction which takes place when the concentration varies from 1.5 molars to 2.5.

TABLE 33.

Compressibility of the Solvent (Water).

	0°C.		10°C.		20°C.	
	in cc.	%	in cc.	%	in cc.	%
C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	0.20	1.11	0.19	1.05	0.18	1.0
ClK	0.06	0.33	0.05	0.28	0.048	0.27
ClNa	0.06	0.33	0.055	0.31	0.058	0.32
ClNH <sub>4</sub>	0.045	0.25	0.040	0.22	0.035	0.19
	30°C.		40°C.		50°C.	
	in cc.	%	in cc.	%	in cc.	%
C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	0.17	0.94	0.17	0.94	0.17	0.94
ClK	0.048	0.27	0.044	0.24	0.045	0.25
ClNa	0.05	0.28	0.035	0.19	0.04	0.21
ClNH <sub>4</sub>	0.030	0.17	0.035	0.19	0.030	0.16

In spite of the fact that the above values are merely approximate, it is clear that the amount of volume change of solvent depends on the nature of the solutes. In the above data, the compression of the solvent is greatest in the case of cane sugar as solute; it is less and nearly equal in the case of potassium chloride and sodium chloride,

and least in the case of ammonium chloride. In all the cases the degree of compression becomes smaller and smaller as the temperature rises. From this record of the compressibility of solvents, any quantitative relation can not be found with certainty, but it may be supposed that the compressibility is a function of the molecular weight,  $M$ , and the molecular volume,  $V$ , something like  $\frac{\varphi(M)}{f(V^{\frac{2}{3}})}$ .

*The volume change of the solute in solution.* In solution, as the solute and solvent are only relative terms, what has been said about solvent may equally well be applied to the case of solute. As seen in Figg. 4-6, the molecular solution volume of solute increases with the increase of concentration while its rate of increase decreases with the increase of the concentration.

The dilatation of the solute with concentration is as follows:

TABLE 34.

	0.0°C.		Difference.	Percentage.
	<i>a</i> in cc.	<i>b</i> in cc.		
$C_{12}H_{22}O_{11}$	212.5	216.1	3.6	1.68
ClK	29.	30.8	1.8	6.02
ClNa	18.2	20.0	1.8	9.43
$ClNH_4$	37.5	38.5	1.0	2.6
	10.0°C.			
$C_{12}H_{22}O_{11}$	214.0	217.1	3.1	1.44
ClK	30.0	31.6	1.6	5.2
ClNa	19.2	20.7	1.5	7.9
$ClNH_4$	38.2	39.0	0.8	2.1
	20.0°C.			
$C_{12}H_{22}O_{11}$	215.3	218.0	2.7	1.25
ClK	30.6	32.0	1.4	4.4
ClNa	19.2	20.7	1.5	7.5
$ClNH_4$	38.6	49.3	0.7	1.8
	30.0°C.			
$C_{12}H_{22}O_{11}$	216.4	219.0	2.6	1.2
ClK	31.0	32.2	1.2	3.8
ClNa	20.6	21.8	1.2	5.6
$ClNH_4$	38.8	40.1	1.3	3.4



40.0°C.				
$C_{12}H_{22}O_{11}$	217.3	219.9	2.6	1.2
ClK	31.4	32.4	0.0	3.1
ClN <sub>2</sub>	20.9	22.0	1.1	5.2
ClNH <sub>4</sub>	39.0	40.3	1.3	3.3
50.0°C.				
$C_{12}H_{22}O_{11}$	218.3	220.8	2.5	1.1
ClK	31.6	32.6	1.0	3.1
ClNa	21.2	22.5	1.0	4.6
ClNH <sub>4</sub>	39.0	40.4	1.4	3.5
60.0°C.				
$C_{12}H_{22}O_{11}$	219.3	221.7	2.4	1.1

In the above table  $a$  and  $b$  are the molecular solution volumes of the solute at 1.5 and 2.5 molar concentration respectively, and percentages of dilatation are the percentage values of  $a - b$  in  $\frac{a+b}{2}$ . The compressibility of the solvent expressed in the terms of pressure is tolerably great, but not so great that we can not admit it as an inner pressure<sup>1</sup> of solution; but, if solutes are in the same state of aggregation in solutions as in the pure state, the dilatation of the solutes, in the terms of pressure becomes so great that it can not be admitted as inner pressure of solution. According to the research of T. R. Richards,<sup>2</sup> the compressibility of the following salts in 100–500 megbars are as follows:

	Compressibilities $\times 10^6$ at 20.0°C°.		
	Kgm/cm <sup>2</sup> .	Megbars.	Atmosphere.
ClK	4.93	5.03	5.09
ClNa	4.03	4.11	4.17

Therefore, to produce such volume change as is represented in the table 34, the inner pressure must be of the order of  $10^4$  atm., but it is not reasonable to assume the existence of such a great pressure in solution. To explain this contradiction, it may be supposed that the molecular state of aggregation of a solute in solution is different

<sup>1</sup> See the following paragraph.

<sup>2</sup> J. Amer. Chem. Soc., **31**, 158 (1909).

from that in its pure state. It is generally accepted that the phenomena "dissolution" is nothing but the disintegration of the solute in the solvent to its molecular order by the mutual affinity of the solute and solvent. Then solute molecules, occluded by solvent molecules, are compressed and diminish their volumes. But this kind of compression is not the only cause of the change of volume of solute in solution; the volume changes due to ionisation or polymerisation would perhaps play a great rôle for volume change of solute in solution. This supposition explains why the dilatation of cane sugar, which is a non-electrolyte, is less than that of electrolytes.

The change of molecular solution volume in lithium chloride solution is represented in Fig. 7. It is well known that lithium chloride polymerizes in solution; and, since ionisation and polymerization take place in its solution at the same time the matter becomes somewhat more complicated in this case. As seen in the figure the volume changes of both of solute and solvent are great in dilute solutions and become less with the increase of concentration.

From the above point of view about the change of molecular solution volumes in solution, arise certain interesting problems, such as the inner pressure of solution by the mutual compression of solute and solvent and the molecular solution volume of its solute in a saturated solution. These will be considered in the following paragraphs.

## 6. Inner Forces of Solution and Molecular Pressure.

Tammann,<sup>1</sup> who assumed some inner force acting in solution studied the problem of solution from a standpoint entirely different from that of van't Hoff and Arrhenius. The change of specific volume of solution by temperature proceeds in quite the same way as that of the pure solvent by some external pressure, and then the concentration of solution is comparable to external pressure on solvent as to its influence on volume. Now, the change of specific volume of solution with the change of temperature in several concentration is first determined and then the external pressure is calculated under which the pure solvent undergoes the same change of volume as the solution; these pressures as the inner pressure forces of solution are denoted by  $\Delta K$  in the terms of pressure. By dividing these terms by the concentrations of the corresponding solutions  $m$ , we get values which are con-

stant and independent of concentration for solutions of the same solute. Tammann used this expression,  $\Delta K/m$ , for comparison of several solutions of different solutes.

The idea of some inner force acting in solution is of value in the study of solution; but the inner force defined by Tammann can not be considered a real existing force, because, while the volume of solute is tolerably great with respect to the total volume in concentrated solutions, Tammann's inner force is also estimated by a direct comparison of the total volume of solution to that of the pure solvent; and this is the same as to neglect the volume of solute in solution.

In the present study, the volume of solute in solution has already been estimated, therefore it is possible to calculate the amount of external work required to effect such a volume change on the pure solute as that in solution: and it is more reasonable than Tammann's method to consider this pressure as the inner pressure acting in solution.

In the following table, the molecular volume of water at  $0^{\circ}\text{C}$ . being taken as unity, those in solution in different concentrations at different temperatures were calculated and denoted by  $v$ ; and then the external pressure  $P$ , required to effect such volume change as  $v$ , were calculated from the data of dilatation and compressibility of water given by Amagat.<sup>1</sup> Theoretically the value  $P$  diminished by one atmosphere must be taken as the inner pressure of the solution, but such correction is not necessary as it is within the uncertainty of calculated results.

TABLE 35.

The solution of Cane Sugar at  $0.0^{\circ}\text{C}$ .

Mean conc.	$\phi_w$	$v$	$P$ , atm.
0.075	18.019	1.0000	1
0.227	18.015	0.99977	4.5
0.469	18.004	0.99917	16.0
0.814	17.986	0.99816	36.0
1.188	17.968	0.99717	55.0
1.596	17.891	0.99289	141.5
2.040	17.804	0.98808	241.2
2.395	17.719	0.98334	342.5
2.524	17.700	0.98229	365.
2.648	17.665	0.98037	407.5

<sup>1</sup> C. R., 116, 41 (1893).

TABLE 36.

The Solution of Cane Sugar at 10.0°C.

Mean conc.	$\varphi_m$	$\nu$	<i>P.</i> atm.
0.075	18.021	1.00014	1
0.226	18.019	1.00000	3
0.469	18.018	0.99995	4.5
0.812	17.998	0.99883	27
1.165	17.970	0.99728	59.5
1.591	17.920	0.99450	119
2.0335	17.844	0.99039	208
2.387	17.767	0.98624	301
2.515	17.737	0.98435	345
2.638	17.701	0.98235	391

TABLE 37.

The Solution of Cane Sugar at 20.0°C.

Mean conc.	$\varphi_m$	$\nu$	<i>P.</i> atm.
0.074	18.048	1.00164	1
0.226	18.047	1.0016	1.5
0.467	18.042	1.0013	7
0.810	18.029	1.0006	21
1.162	18.004	0.99920	51.5
1.582	17.959	0.99671	106.5
2.026	17.890	0.99286	193.5
2.378	17.818	0.98887	286
2.506	17.790	0.98732	323
2.628	17.760	0.98562	263

TABLE 38.

The Solution of Cane Sugar at 30.0°C.

Mean conc.	$\varphi_m$	$\nu$	<i>P.</i> atm.
0.074	18.094	1.00421	1
0.225	18.092	1.0041	3
0.466	18.087	1.0038	9.5
0.807	18.074	1.0031	24
1.177	18.045	1.0015	58

Mean conc.	$\varphi_m$	$v$	<i>P.</i> atm.
1.580	18.018	0.99996	93
2.018	17.955	0.99651	172.5
2.369	17.883	0.99248	267
2.496	17.855	0.99092	304.6
2.618	17.823	0.98919	346.5

TABLE 39.

The Solution of Cane Sugar at 40.0°C.

Mean conc.	$\varphi_m$	$v$	<i>P.</i> atm.
0.074	18.157	1.00757	1
2.250	18.151	1.0073	6
0.465	18.145	1.0069	15
0.804	18.132	1.0062	28
1.173	18.113	1.0047	63.5
1.574	18.092	1.0040	79
2.010	18.019	0.99993	173
2.359	17.953	0.99628	260
2.486	17.927	0.99485	295
2.607	17.895	0.99307	339

TABLE 40.

The Solution of Cane Sugar at 50.0°C.

Mean conc.	$\varphi_m$	$v$	<i>P.</i> atm.
0.074	18.233	1.01182	1
0.386	18.229	1.0116	6
0.463	18.224	1.0113	12
0.801	18.215	1.0108	23
1.168	18.196	1.0097	46
1.567	18.160	1.0078	78
2.001	18.096	1.0042	172
2.349	18.031	1.0006	257
2.475	18.008	0.99931	289
2.596	17.980	0.99774	328

TABLE 41.

The Solution of Cane Sugar at 60.0°C.

Mean conc.	$\varphi_m$	$v$	<i>P.</i> atm.
0.073	18.322	1.01678	1
0.223	18.320	1.0167	3
0.460	18.317	1.01655	6
0.797	18.314	1.0164	9
1.162	18.293	1.0152	35
1.559	18.250	1.0128	87
1.992	18.190	1.0095	161
2.338	18.125	1.0052	263
2.464	18.104	1.0047	275
2.584	18.078	1.0033	309

TABLE 42.

The Solution of Potassium Chloride at 0.0°C.

Mean conc.	$\varphi_w$	$v$	<i>P.</i> atm.
0.347	18.019	1.0000	1
1.063	17.989	0.99837	32
1.826	17.941	0.99559	87
2.638	17.894	0.99307	138

TABLE 43.

The Solution of Potassium Chloride at 50.0°C.

Mean conc.	$\varphi_m$	$v$	<i>P.</i> atm.
0.342	18.233	1.01182	1
1.047	18.226	1.0114	9
1.795	18.185	1.0091	60
2.591	18.163	1.0079	87
3.437	18.11	1.0050	154
4.067	18.07	1.0027	207

TABLE 44.

The Solution of Sodium Chloride at 0.0°C.

Mean conc.	$\varphi_m$	$v$	$P$ . atm.
0.444	18.019	1.00000	1
1.365	17.979	0.99779	45
2.352	17.915	0.99426	113.5
3.400	17.840	0.99008	198
4.301	17.755	0.98533	295
5.006	17.723	0.98360	337

TABLE 45.

The Solution of Sodium Chloride at 50.0°C.

Mean conc.	$\varphi_m$	$v$	$P$ . atm.
0.437	18.233	1.01182	1
1.342	18.212	1.0103	33
2.308	18.178	1.0078	90
3.330	18.137	1.0065	119
4.209	18.07	1.0027	207

TABLE 46.

The Solution of Ammonium Chloride at 0.0°C.

Mean conc.	$\varphi_m$	$v$	$P$ . atm.
0.467	18.019	1.00000	1
1.429	18.012	0.99960	8.5
2.434	17.96	0.9970	59
3.454	17.91	0.9940	119

TABLE 47.

The Solution of Ammonium Chloride at 50.0°C.

Mean conc.	$\varphi_w$	$v$	$P$ . atm.
0.469	18.232	1.01182	1
1.420	18.213	1.0107	24
2.397	18.177	1.0087	69
3.399	18.14	1.0053	149.5
4.427	18.09	1.0037	185
5.478	18.07	1.0027	207

The inner pressures as calculated above as a function of concentration were represented graphically in Figg. 8-9. When the solution is dilute, the increase of inner pressure by the increase of concentration is slow, but at the vicinity of 1.5 molar concentration the pressure suddenly increases and thereafter nearly as a linear function of concentration. The increase of inner pressure corresponding to the increase in concentration by one molal in the range of the inner pressure which is directly proportional to the concentration may be termed "*molecular pressure in solution*". This is a factor of physico-chemical affinity of solution.

TABLE 48.

Solution.	Temperature.	Mol. pressure in atm.
$C_{12}H_{22}O_{11}$	0°-60°	220.
ClK	0°-50°	130.
ClNa	0°-50°	130.
ClNH <sub>4</sub>	0°-50°	150.

*A comparison of the kinds of pressures, that is, osmotic pressure, Tammann's inner force and the author's inner pressure.*

TABLE 49.

## Tammann's Inner Forces of Solutions.

A) *Cane Sugar Solution.*

Temperature 10°-30°.

<i>m</i>	4.75	9.50	19.00	38.00	76.00
$\Delta K$	105.	218.	408.	700.	1217.
$\frac{\Delta K}{m}$	22.	23.	22.	23.	16.

B) *Potassium Chloride Solution.*

Temperature 10°-30°.

<i>m</i>	5.2	11.2	16.8	17.9	22.5	23.2	33.4	33.7
$\Delta K$	312.	607.	850.	916.	1080.	1126.	1345.	1380.
$\frac{\Delta K}{m}$	60.	55.	55.	51.	48.	49.	40.	41.



C) Sodium Chloride Solution.

Temperature 10°-30°.

<i>m</i>	1.61	3.24	6.48	12.96	25.93
$\Delta K$	182.	336.	665.	1217.	2145.
$\frac{\Delta K}{m}$	113.	104.	103.	94.	83.

D) Ammonium Chloride Solution.

Temperature 10°-40°.

<i>m</i>	11.1	25.0
$\Delta K$	628.	1018.
$\frac{\Delta K}{m}$	57.	36.

*Tabulation of the osmotic pressure of aqueous solutions of cane sugar determined by Morse and Lord Berkeley and Hartley.*

TABLE 50.<sup>1</sup>

No. of mols in litre.	Osmotic pressure at 0°C.	
	(Morse.)	(Lord Berkeley and Hartley.)
0.527	—	13.95
0.534	14.38	—
0.646	19.48	—
0.828	24.83	—
0.877	—	26.77
1.228	—	43.97
1.579	—	67.51
1.930	—	100.78
2.194	—	133.74

These values of the three kinds of pressures are represented in Figg. 8-9. The inner pressure determined by the author is less than Tammann's inner force but is greater than osmotic pressure directly determined. In dilute solutions the inner pressure is nearly equal to the osmotic pressure. The relation between this inner pressure and osmotic pressure will be considered in the next article of this study.

<sup>1</sup> Findlay: Osmotic Pressure, p. 23.

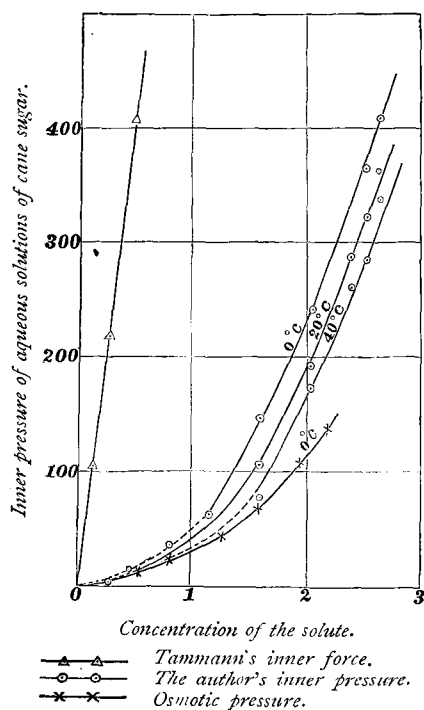


Fig. 8.

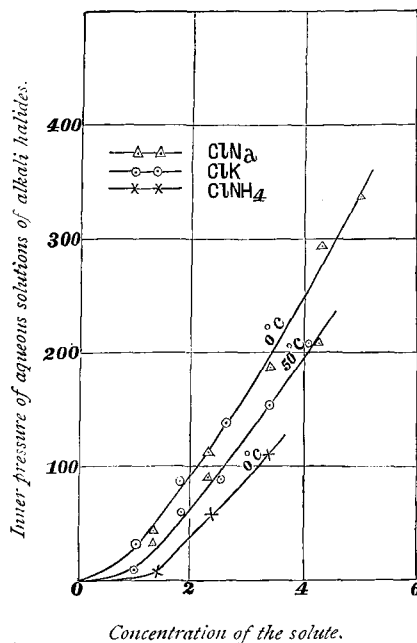


Fig. 9.

## 7. The Relation between the Solubility and the Molecular volumes of Solutes.

The solubility of a solute in a given solvent is one of the physico-chemical properties which is characteristic of that solute. But solubility depends on many factors and is of very complex nature; therefore at present there is no simple relation established between it and the other properties of said solute or solvent; in other words, there is no quantitative theory of solubility.

Hardman and Partington<sup>1</sup> have found a relation of solubility to temperature applying Kirchhoff's law, as follows:

$$\log S = A - \frac{B}{T} - C \log T,$$

where  $S$  is the solubility and  $A$ ,  $B$ , and  $C$  are constants characteristic of the solute. But, since this equation contains three constants, there is no difference in value from the empirical formula:  $S = A + BT + CT^2$

<sup>1</sup> J. Chem. Soc., 99, 1769 (1911).

as Tyrer<sup>1</sup> remarked. From the study of solubilities at critical temperatures, Tyrer has found the following relation :

$$S^n = a \left( \frac{V}{v} \right)^n - b,$$

where  $n$  is a certain constant,  $V$  the total volume of solution,  $v$  the specific volume of solute and  $a$  and  $b$  are constants characteristic of a given solute and solvent. But there are no sufficient data to verify this equation.

Under the supposition that there would be some definite relations between the molecular volumes of substances and their solubilities in water, the author examined the solubilities of sparingly soluble organic liquids in water. For such substances, it may be assumed that their molecular volumes in saturated solution are not greatly different from those in the pure state and therefore that they may be put equal to each other. But in literature, the determination of the solubilities of such substances are infrequent, and only the data on alkyl halides by A. Rex<sup>2</sup> are appropriate. The solubilities and molecular volumes of alkyl halides are tabulated as follows :

TABLE 5 I.

0.0°C.

Substance.	Mol. wt. M	Solubility. S	Sp. gr.	Mol. vol. V
1. Methylene chloride	84.9	2.363	1.37777 <sup>B</sup>	61.6
2. Chloroform	119.4	1.062	1.52637 <sup>B</sup>	73.3
3. Tetrachlormethane	153.8	0.097	1.63195 <sup>B</sup>	94.4
4. Methylene bromide	173.9	1.173	—	—
5. Methyl iodide	141.9	1.565	2.3346 <sup>B</sup>	60.8
6. Ethylene chloride	98.9	0.922	1.28032 <sup>B</sup>	77.2
7. Ethylidene chloride	98.9	0.656	1.2044 <sup>B</sup>	82.0
8. Ethyl bromide	109.0	1.067	1.496439 <sup>B</sup>	73.0
9. Ethyl iodide	155.9	0.441	1.9845 <sup>C</sup>	78.4*
10. Propyl chloride	78.5	0.376	0.9156 <sup>B</sup>	85.8
11. Isopropyl chloride	78.5	0.440	—	—
12. Propyl bromide	123.0	0.298	1.383 <sup>B</sup>	88.6

<sup>1</sup> J. Chem. Soc., **97**, 621, 1778 (1910); J. phys. Chem., **16**, 69 (1912).

<sup>2</sup> Z. physik. Chem., **55**, 355 (1906).

<sup>B</sup> From Beilstein's Organische Chemie.

<sup>C</sup> From Tables annuelles internationales de Constantes, Vols. I-III.

	Substance.	Mol. wt. M	Solubility. S	Sp. gr.	Mol. vol. V
13.	Isopropyl bromide	123.0	0.418	1.3583 <sup>B</sup>	90.5
14.	Propyl iodide	170.0	0.114	1.784 <sup>B</sup>	95.4
15.	Isopropyl iodide	170.0	0.167	—	—
16.	Carbon disulphide	76.1	0.248	1.2905 <sup>B</sup>	58.9*

TABLE 52.

20.0°C.

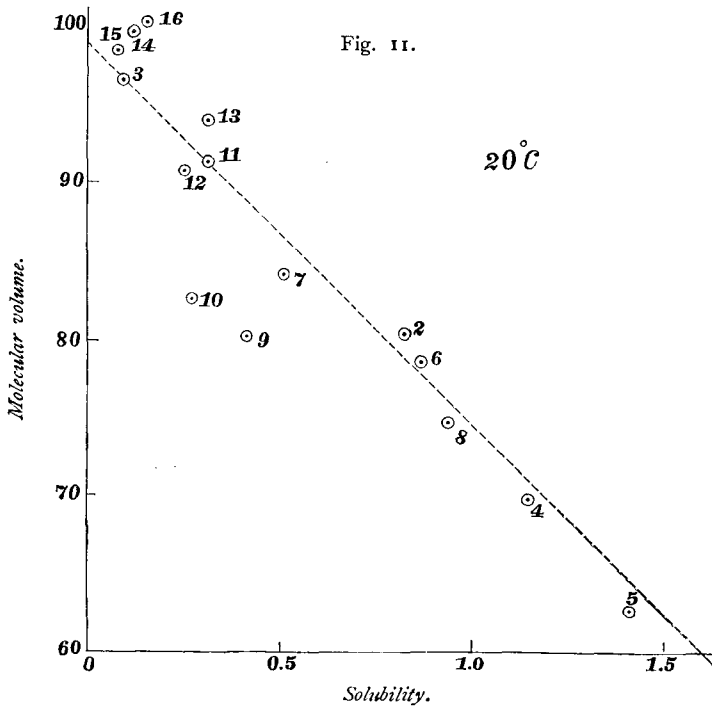
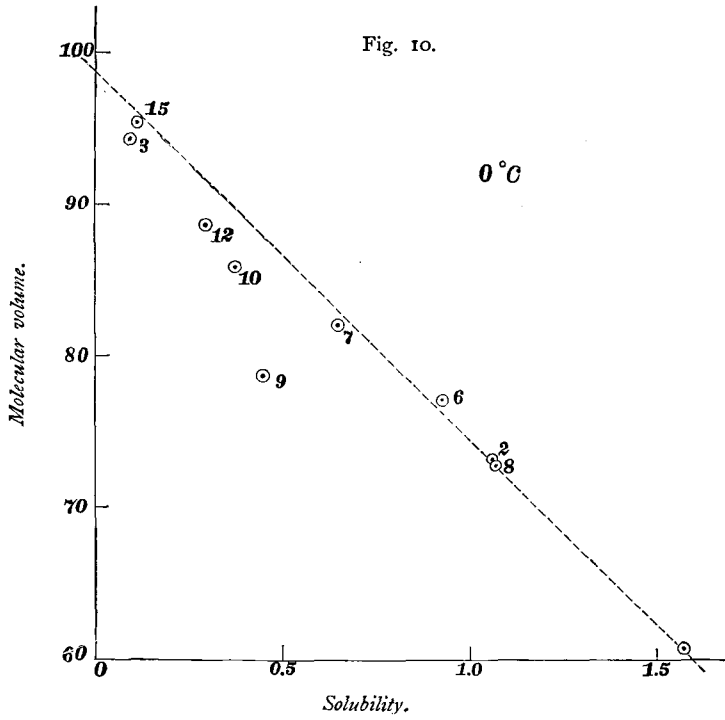
	Substance.	Mol. wt.	Solubility. S.	Sp. gr.	Mol. vol. V.
1.	Methylene chloride	84.9	2.000	—	—
2.	Chloroform	119.4	0.822	1.4868 <sup>1</sup>	80.4
3.	Tetrachlormethane	153.8	0.080	1.5930 <sup>1</sup>	96.5
4.	Methylene bromide	173.9	1.148	2.488 <sup>B</sup> <sub>Extrap.</sub>	69.8
5.	Methyl iodide	141.9	1.419	2.269 <sup>B</sup> <sub>Extrap.</sub>	62.5
6.	Ethylene chloride	98.9	0.869	1.254 <sup>B</sup> <sub>Mean</sub>	78.8
7.	Ethylidene chloride	98.9	0.550	1.1743 <sup>B</sup>	84.2
8.	Ethyl bromide	109.0	0.914	1.4580 <sup>1</sup>	74.7
9.	Ethyl iodide	155.9	0.403	1.9387 <sup>1</sup>	80.4*
10.	Propyl chloride	78.5	0.272	ca. 0.892 <sup>B</sup>	82.6
11.	Isopropyl chloride	78.5	0.305	0.8588 <sup>B</sup>	91.4
12.	Propyl bromide	123.0	0.245	1.3520 <sup>B</sup>	90.8
13.	Isopropyl bromide	123.0	0.318	1.3097 <sup>B</sup>	93.8
14.	Propyl iodide	170.0	0.107	1.7427 <sup>B</sup>	98.6
15.	Isopropyl iodide	170.0	0.140	1.7033 <sup>B</sup>	99.8

TABLE 53.

30.0°C.

	Substance.	Mol. wt. M	Solubility. S	Sp. gr.	Mol. vol. V
2.	Chloroform	119.4	0.776	1.4680 <sup>1</sup>	81.4
3.	Tetrachlormethane	153.8	0.085	1.5757 <sup>1</sup>	97.7
4.	Methylene bromide	173.9	1.176	ca. 2.466 <sup>B</sup> <sub>Extrap.</sub>	70.5
5.	Methyl iodide	141.9	1.429	ca. 2.237 <sup>B</sup> <sub>Extrap.</sub>	63.5
9.	Ethyl iodide	155.9	0.415	1.911 <sup>1</sup> <sub>Extrap.</sub>	81.5

<sup>B</sup> From Beilstein's Organische Chemie.<sup>1</sup> From Tablas annuelles internationales de Constantes, Vols. I-III.



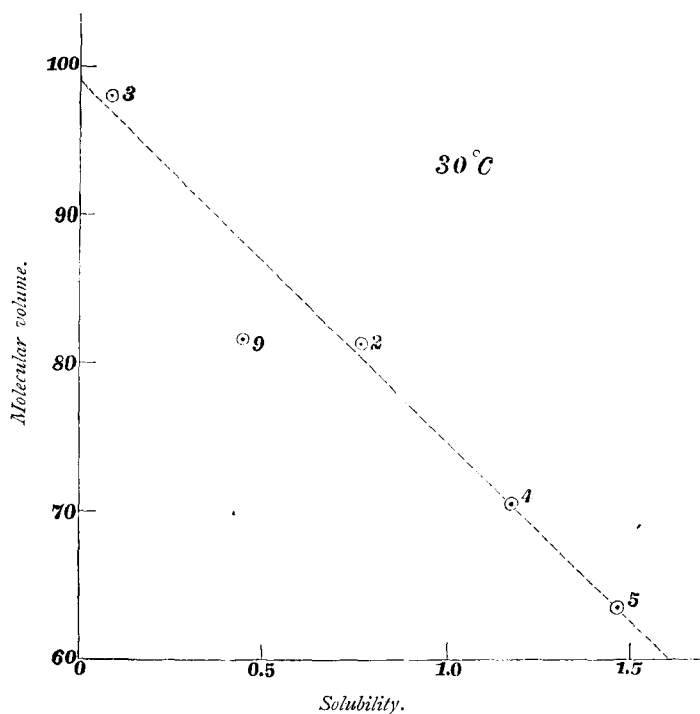


Fig. 12.

Representing the above relations graphically in Figg. 10-12 as usual, it appears that solubility and molecular volume are in a simple linear relation and moreover that this relation holds at different temperatures, as 0°, 20°, and 30°C. This may be expressed by the following equation:

$$S = -\frac{1.60}{99.0} + 160,$$

or

$$\frac{S}{M} = N = -\frac{1.70}{99.0} \cdot \frac{V}{M} + \frac{1.60}{M},$$

where  $S$  denotes the solubility and  $M$  the molecular weight of solute; and in dilute solutions,  $N$  will be proportional to the number of mols in solution. Methylene chloride and ethyl iodide show great deviation from this formula; and carbon disulfide also shows a great deviation, and perhaps for the reason that the latter is of a different class from alkyl halides and wherefore has a different affinity to water.

The relation of solubility here set forth may be the first quantitative one ever proposed, and is too regular to appear accidental. It seems very desirable to continue the research concerning this relation

in other homologous series; and such is the writer's intention; but for the present it is impossible to procure the necessary materials. Certain experiments have been made on hydrocarbons of benzene series; and the solubilities and molecular volumes obtained are given in the following table.

TABLE 54.

Temperature: 20.0°C.

Substance.	Mol. weight.	Solubility.	Sp. volume.	Mol. volume.
Benzene	78.1	0.181	0.87873	88.9
Toluene	92.1	0.063	0.86675	106.3
Xylene	106.1	0.018	0.86081	123.2
Mesitylene	120.1	ca. 0.002	0.8558	140.2

In the case of hydrocarbons of benzene series also, the solubility decreases with the increase of molecular volume; but it does not show such an interesting result as in the case with alkyl halides, because, in the latter case quite independent of the magnitude of the molecular weight, the solubilities are always in the reverse order of molecular volumes, while in the former case, the molecular weight and molecular volume are, from the first, in the same order.

Considering what relation may exist with a substance that has great solubility, the molecular solution volume in saturated solution of cane sugar and alkali chlorides may easily be estimated by graphical extrapolation from the data already found.

TABLE 55.

A) *Aqueous Solution of Cane Sugar.*

Temperature.	Solubility. No. of grs. of solute in 100 grs. of solution.	Sp. gravity of saturated solution.	Mol. concentration of saturated solution.	Mol. sol. vol. estim. by extrapolation.
0°	64.18	1.321	2.477	216.
10°	65.58	1.325	2.539	217.
20°	67.09	1.329	2.605	218.3
30°	68.70	1.334	2.679	219.5
40°	70.42	1.339	2.755	220.5
50°	72.25	1.344	2.837	221.5
60°	77.18	1.350	2.926	222.5

B) *Aqueous Solution of Potassium Chloride.*

Temperature.	No. of grs. of solute in 100 grm. of solubility, solution.	Sp. gravity of saturated solution.	Mol. concentration of saturated solution.	Mol. sol. vol. estim. by extrapola- tion.
0°	21.6	1.151	3.33	32.
10°	23.7	1.1635	3.70	32.8
20°	25.4	1.171	3.99	33.5
30°	27.1	1.180	4.28	33.5
40°	28.6	1.186	4.55	34.
50°	29.9	1.190	4.77	34.

C) *Aqueous Solution of Sodium Chloride.*

0°	26.28	1.209	5.434	23.
10°	26.29	1.204	5.416	23.
20°	26.37	1.200	5.414	23.5
30°	26.49	1.195	5.417	23.5
40°	26.65	1.191	5.430	24.
50°	26.83	1.186	5.445	24.

D) *Aqueous Solution of Ammonium Chloride.*

0°	22.7	1.072	4.54	40.
10°	24.9	1.074	5.00	40.
20°	27.1	1.076	5.44	41.
30°	29.3	1.078	5.91	41.
40°	31.4	1.080	6.34	41.
50°	33.5	1.081	6.77	41.

E) *Aqueous Solution of Lithium Chloride.*

0°	40.1	1.261	11.90	ca. 21.4
10°	41.9	1.271	12.56	21.4
30°	45.8	1.298	14.03	21.4
50°	49.2	1.33	15.44	21.4

As seen from the above table, the molecular solution volume of the solute in saturated solutions, at different temperatures do not differ much from each other, and are almost independent of temperature.

*A comparison of the molecular volumes of solute in solid states and the molecular solution volumes in saturated solutions.* At present, the



molecular condition of substance in a solid state is not so exactly defined as in a gaseous state or in solution; and here the molecular volume of a solid substance is calculated under the assumption of the existence of normal molecules, as suggested from the chemical formula.

	Mol. wt.	Sp. gr.	Mol. vol.
ClK	74.55	2.00	37.3
ClNa	58.46	2.14	27.3
ClNH <sub>4</sub>	53.50	1.51	35.4
ClLi	42.40	2.07	20.5

In the case of cane sugar, as its coefficient of expansion is comparatively great, its specific gravities at different temperatures were determined in a specific gravity bottle using xylene (boil. pt. 159°C.) as the filling liquid.

Temperature.	Sp. gr. of xylene.	Sp. gr. of cane sugar.
20°	0.86122	1.5869
30°	0.85260	1.5885
40°	0.84418	1.5833
50°	0.83521	1.5810

By the help of Morse's value of the specific gravity 1.59231 at 0°C., the specific gravity at 10°C. has been estimated by graphical interpolation, to be 1.590, and from these data the molecular volumes of cane sugar in solid state has been calculated as follows:

Temperature.	Mol. vol.	Temperature.	Mol. vol.
0°	214.4	30°	215.8
10°	215.2	40°	216.2
20°	215.6	50°	216.4

Now on comparing the molecular volumes of solutes in solid state with molecular solution volumes in solutions, it may be clearly seen that in all cases, the molecular solution volumes in saturated solutions are very far nearer to molecular volumes in solid state than molecular solution volumes in dilute solutions. The molecular solution volumes in saturated solutions are less than the molecular volumes in solid state in the cases of potassium chloride and sodium chloride, and are little larger in ammonium chloride and cane sugar, and are equal to in lithium chloride.

From the above few experimental results, it is not desirable to build up any hypothesis, but perhaps it may be said that, in solutions, the molecular solution volume of the solute approaches to molecular volume in solid state by the increase of concentration.

If the molecular solution volumes in solution determine the state of saturation, then the saturation or solubility is also determined by physico-chemical affinity between solute and solvent, as the change of molecular solution volume is caused by that physico-chemical affinity.

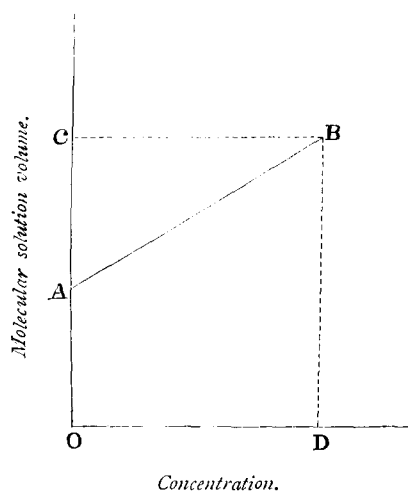


Fig. 13.

To illustrate the relation between them, Fig. 13 was constructed, measuring the molecular solution volume of the solute along the axis of ordinates and the concentration along the axis of abscissa. Thus  $AB$  represents the change of the molecular solution volume of the solute as the concentration increases,  $DB$  and  $OD$  being respectively the molecular volume in and concentration of the saturated solution. Now, if the molecular volume of solute in a saturated solution has a definite value  $DB$ , the concentration of the saturated solution would be determined only by the two factors, the inclination of  $AB$  and the length of  $CA$ ,  $CB$  being a parallel to  $OD$ , and these two also depend on the physico-chemical affinity between the solute and solvent. Then the solubility of any substance would depend on its physico-chemical affinity to the solvent and it is difficult to represent its solubility as a single function of another physical constant of the solute or solvent. But in the case of halogen alkyls, whose affinities to the solvent would

not much differ among themselves, a simple relation between solubility and molecular volume as above described will be expected.

### **8. A Conception on the State of Solution.**

From what has been said above, the following conclusion has been drawn as to the state of solution.

When a substance is dissolved in a solvent, change in molecular solution volumes of the solute and solvent generally takes place by the physico-chemical affinity between the solute and solvent; the molecular solution volume of the solute increases with the increase of its concentration, while the molecular solution volume of the solvent decreases as the concentration increases. When the molecular solution volume of the solute reaches a certain definite value, the solution becomes saturated and this molecular solution volume in the saturated solution is almost equal to the molecular volume of the solute in a pure state.

### **9. Summary.**

1. The method of determination of the molecular solution volumes of solute and solvent in solution has been described.
2. By this method of determination, the molecular solution volumes of cane sugar, potassium chloride, sodium chloride, ammonium chloride, and lithium chloride in aqueous solutions in several temperatures have been determined.
3. The compression of molecular solution volume of solvent by the action of solute molecules has been represented in pressure terms and it was compared with osmotic pressure directly determined and Tammann's inner force of solution.
4. Some relations between the molecular volume of a solute and its solubility have been pointed out.
5. As the conclusion of the above experimental results, a conception on the state of solution has been proposed.

I desire to express my cordial thanks to Prof. Osaka for the interest he has taken in my work and for his valuable advice.

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