

MOLECULAR ASSOCIATION¹

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INTRODUCTION

More than fifty years ago, Louis Henry first proposed the hypothesis of molecular polymerization, now called molecular association. Then successively, Vernon, Eötvös, Ramsay-Shields Trouton, Ph. A. Guye, Daniel Berthelot, Traube, Longinescu, Vaubel, Walden, Bingham and others published methods for determining the degree of molecular association, particularly for liquids. The experimental and theoretical material thus collected can not be disregarded but the question is far from the state of perfection now attained by the theory of electrolytic dissociation, founded in 1887, ten years after Henry's first paper, by Svante Arrhenius.

Solids, liquids and even certain gases are supposed to be composed of simple, double, triple, etc., molecules. So also water may be an extraordinarily complex liquid, formed by the accumulation of multiple molecules up to hextuples, and named dihydrone, trihydrone tetrahydrone, pentahydrone and hexahydrone, whose constitutional formulas have the form of a triangle, square, pentagon or hexagon, similar to the formulas of the saturated cyclic hydrocarbons, but with oxygen occupying the place of the carbon atom (Armstrong). Tamman has attempted to calculate the proportions of these complex molecules. In spite of all attempts, not a single type of these molecules has been isolated. To explain this failure, a new hypothesis has been added, namely, that associated molecules are in unstable equilibrium, so that they dissociate and come together again with great rapidity. To explain one hypothesis by another is hardly a method of finding the de-

¹ Translated from the French by Marion Hull.

sired truth. In recent years experimental proof that there is a molecular accumulation in crystals has been adduced with the aid of x-ray spectra (Bragg). Yet there is no satisfactory agreement between values for the degree of molecular association found by different methods. All this proves clearly that the hypothesis of molecular association, of molecules attached to each other, should be replaced by an idea which is nearer to reality.

For this reason G. G. Longinescu and G. Chaborski consider molecular association as a phenomenon of molar concentration. In place of molecular complexity they introduce the idea of molecular accumulation, and instead of degree of association that of degree of molecular accumulation. Water, the liquid which shows the highest degree of molecular association, has the greatest molar concentration, i.e., 55.5, and consequently the highest degree of accumulation. According to this point of view liquids, like gases, consist solely of simple molecules. The more a liquid is associated, the greater the number of these molecules in equal volumes. In numerous cases the degree of molecular association is approximately one-tenth of the molar concentration. The degree of accumulation X is equal to $100 \times D/M$. Thus for water the degree of accumulation is $100 \times 1/18 = 5.55$.

For thirty years I adhered to the general but erroneous theory of molecular association in spite of the vain attempts to harmonize the values for the degree of molecular association found by different methods. The credit for permanently changing my outlook belongs to my pupil and collaborator, Dr. Gabriela Chaborski, lecturer in inorganic chemistry at the University of Bucharest. It is significant that the great Dutch scientist, Van der Waals, combatted the theory of molecular association for more than thirty years and began to believe in it only towards the end of his life (Turner).

THE WORK OF LOUIS HENRY

Louis Henry, for fifty years professor of chemistry at the Catholic University of Louvain, published more than four hundred memoirs, a great number of which are on the relation between the volatility and the chemical constitution of organic compounds.

His first article on polymerization was published in 1878 (1). Twenty-seven years later he returned to these same ideas, "older really than 1878" (2). It is impossible, except by reprinting his work or by extensive quotation, to make amends to this Belgian chemist for the injustice done to him in the past, for scarcely an author mentions his work though it forms the basis of one of the most important chapters in modern physical chemistry. True, his ideas were primarily philosophical and qualitative, and he gave no precise values for the degree of molecular association. Yet they underlie modern progress in the same way that the work of Avogadro and the philosophic ideas of Crookes, Stokes and Lord Kelvin laid the foundations for our present knowledge of atomic structure. Henry deserves recognition for ideas which were prophetic half a century ago but are now universally accepted.

The starting point of his theory was the striking difference between the melting and boiling points of oxides and chlorides which are apparently similar in chemical composition. Even today a large proportion of the methods for determining molecular association are directly dependent on the differences between the melting and boiling points of normal and associated compounds, though numerous other physical constants, such as the surface tension, viscosity, molecular refraction and internal pressure, are also used. Henry explained the volatility of the chlorides, as compared with the oxides,—in the face of a greater volatility of oxygen as compared with chlorine,—on the assumption that the metallic oxides are in reality polymers of the unit MO . He assumes that the formulas of the chlorides are generally deduced from the vapor densities and are properly speaking molecular formulas, expressing the size and true weight of the molecules, while similar formulas for the oxides are minimal only. The following quotation presents the basis of his studies on oxides:

Most of the molecular formulas in use relate to the perfect gaseous state; they are insufficient for many compounds and inapplicable to the various states through which the same compound can pass artificially. Such are the formulas which are generally given to metallic oxides. They represent neither the true nature of these compounds, nor the true

size of their molecule. The metallic oxides RO_x , really similar to the chlorides, are for the most part unknown to us. We know only the very complex polymers $(RO_x)_n$ where n represents a high figure. As proof of this fact, can be cited the adding power of the oxides, their preparation by extremely complex progressive dehydration of hydroxides, occasioning a true molecular condensation, and finally their density in the solid state, which is abnormal in comparison with that of the corresponding hydroxides.

Shall we ever succeed in preparing or discovering the normal oxides, of which we know only such uncommon examples and which must be, in general, so different in properties from our present oxides? I do not know. All I can state is that in order to prepare them the conditions must be entirely different from those in which we are working today, for our present mode of preparing oxides is the sum total of all the circumstances under which these unknown compounds polymerize and escape us.

Twenty-seven years later, Louis Henry returned to these same ideas with more detail and precision, in his report, *L'État moléculaire de l'eau*, parts of which are quoted below:

Formed from two perfect gases, the one, H boiling at -253° under one atmosphere of pressure, the other O at -184° , uniting with a contraction of only a third of their volumes, liquid water boils at 100° and constitutes a truly exceptional case from the physical point of view. Its extraordinary characteristics are more easily recognized if we recall its congener, hydrogen sulfide, H_2S , which although containing sulfur, a solid boiling at 444° , is a gas boiling at about -61° . According to the best established analogies water should naturally be gaseous and should have a boiling point considerably below zero on the thermometric scale. According to Forcrand it should be in the neighborhood of -65° .

This anomaly Henry attributes to the metallic character of hydrogen which, as in other metallic oxides, produces polymerization, the latter being responsible for the values of the physical constants of liquid water. At the same time Henry considers water to be a symmetrical oxide, whose two hydrogens are identical, rather than an asymmetric hydroxyl compound, whose polymerization might be due to the hydroxyl radical as is presumably

the case in alcohols and acids, the most highly polymerized of organic compounds.

VERNON'S METHOD FOR DEGREE OF MOLECULAR ASSOCIATION

Early in 1891, Vernon published the first numerical data on the degree of molecular association (3). By comparing the boiling points of different organic compounds, Vernon found that doubling the molecular weight raises the temperature of boiling about 100°. Thus, while ethylene boils at -105° , butylene boils at -5° , octylene at $+126^{\circ}$, and hexadecylene at $+274^{\circ}$. The boiling point of water is 200° high because it is in reality four times associated. Hydrofluoric acid boils at 19.4° instead of -140° , hence its formula must be between $(\text{HF})_2$ and $(\text{HF})_4$. In the same way, liquid sulfur has the molecule, S_{12} . Sulfur dioxide, phosphorous trichloride and carbon tetrachloride are normal, nitric acid is twice polymerized and sulfuric acid four times. These values, determined by Vernon, are qualitative; sometimes they approximate the values found by other methods, but often they differ from them.

THE FORMULAS OF G. G. LONGINESCU

Ten years later, in 1901, we published our memoir "Observations sur les températures d'ébullition de quelques corps organiques liquides" (4). In this article, we showed the connection between the boiling points of organic liquids and their chemical composition. The principles which we followed in the investigation of this relationship were the ideas that the boiling point of a liquid must depend on its molecular weight, the number of molecules in unit volume, the number of atoms in a molecule and the nature of these atoms. To simplify the solution of such an involved problem, we divided it into four parts. In the first place, we compared the boiling point (on the absolute scale) of two liquids having the same number of molecules in unit volume ($D:D' = M:M'$) and the same number of atoms in a molecule, compounds containing C, H, O and N, elements having atomic weights up to 35.5. For these compounds the relation between

boiling points is almost equal to the ratio of their molecular weights.

In the second place, to determine the influence of the number of molecules in unit volume, we compared compounds for which the ratio of the densities is not proportional to the ratios of the molecular weight, but which always have the same number of atoms in each molecule. We found in this case that the ratio of the boiling points is equal to the ratio of the densities. Since the density of a compound is equal to the product of the molecular weight times the number of molecules in a unit volume, the boiling point of an organic substance is proportional both to the molecular weight and to the number of molecules.

In the third place, to establish the influence of the number of atoms contained in the molecule, we compared two compounds of different densities, having also a different number of atoms. In this case the ratio of the temperatures becomes equal to the ratio of the densities multiplied by the square root of the ratio of the number of atoms.

Denoting by T and T' the absolute boiling points, by M and M' the respective molecular weights, by N and N' the respective number of molecules in unit volume and by n and n' the number of atoms in these molecules, we can represent the above results by the formula:

$$\frac{T}{T'} = \frac{M}{M'} \frac{N}{N'} \sqrt{\frac{n}{n'}}$$

Since 1901, this formula has been mentioned in various physical and chemical treatises, of which we will mention the one by O. D. Chwolson (5).

THE DEGREE OF MOLECULAR ASSOCIATION OF ORGANIC COMPOUNDS IN THE LIQUID STATE

Two years later, in 1903, (6), we expressed this relation in the following form:

$$\frac{T}{D \sqrt{n}} = \frac{T'}{D' \sqrt{n'}} = \text{a constant}, \quad (1)$$

which is the starting point for a new method for the more exact determination of the degree of association of organic compounds in the liquid state. For a greater number of compounds the value for the constant is about 100. For compounds whose molecules are associated, like alcohols, acids, nitriles, etc., its value is much greater than 100, attaining the maximum value of 215 for water. From the relation (1) we can deduce:

$$\left(\frac{T}{100 \times D}\right)^2 = n \quad (2)$$

by placing the constant = 100. This relation permits the calculation of the number of atoms in a molecule of an organic liquid. In table 1, we give the number of atoms calculated in this way for a considerable number of compounds along with the known number of atoms in the same molecule. The table shows that the difference between these two figures is two units at the most. This insignificant difference shows us that the compounds considered are not polymerized. In table 2 are included the two numbers for compounds which are positively polymerized. According to our point of view, the degree of association is the ratio between n calculated and n known.

There is a remarkable agreement between the degree of association according to our method and that obtained by Ramsay-Shields and others. In particular, our value for the degree of association of water, 4.6, is close to that of Ramsay, 3.8, and that of Vernon, 4. Nitriles, alcohols and acids polymerize and appear to be wholly distinct from normal compounds.

THE DEGREE OF ASSOCIATION OF ORGANIC SUBSTANCES IN THE SOLID STATE

It is interesting to question whether a relation analogous to the preceding is possible for solid compounds. It would cast light on the obscure problem of physical chemistry as to whether solid compounds also exhibit the phenomenon of molecular polymerization.

TABLE I
The number of atoms in organic molecules

NAME OF COMPOUND	n		NAME OF COMPOUND	n	
	Calculated	Known		Calculated	Known
Methylene chloride.....	5	5	Benzyl chloride.....	16	15
Acetyl chloride.....	8	7	Ethyl hydroxyacetate.....	16	15
Methyl monochloroformate...	8	8	Dimethylfuran.....	16	15
Ethylene chloride.....	8	8	Anisole.....	18	16
Methyl formate.....	9	8	Butyl nitrate.....	15	17
Methyl nitrate.....	8	8	Ethyl monochloropropionate.	15	17
Ethyl chloride.....	9	8	Amyl chloride.....	18	17
Thiophene.....	10	9	Indene.....	18	17
Epichlorohydrin.....	10	10	Ethyl propionate.....	16	17
Ethyl nitrite.....	9	10	Methyl butyrate.....	17	17
Propionyl chloride.....	11	10	Propyl monochloroacetate....	16	17
Ethyl nitrate.....	10	11	Propyl acetate.....	17	17
Ethyl sulfonyl chloride.....	10	11	Butyl formate.....	17	17
Ethyl monochloroformate....	10	11	Piperidine.....	18	17
Methyl monochloroacetate....	10	11	Ethenylaminophenol.....	17	17
Methyl dichloroacetate.....	9	11	α -Chloronaphthalene.....	19	18
Furfural.....	12	11	Acetylphenol.....	18	18
Propyl chloride.....	12	11	Methyl propyl carbonate....	16	18
Methyl acetate.....	12	11	Hexahydrobenzene.....	18	18
Methyl carbonate.....	13	12	Ethyl carbonate.....	17	18
Chlorobenzene.....	12	12	Methyl benzoate.....	18	18
Allyl nitrate.....	12	12	Ethyl propyl ether.....	20	18
o-dichlorobenzene.....	12	12	Ethyl lactate.....	17	18
Methyl hydroxyacetate.....	13	12	Propyl hydroxyacetate.....	18	18
Butyryl chloride.....	14	13	Ethyl sulfocarbonate.....	18	18
Methyl sulfate.....	12	13	Ethyl sulfite.....	16	18
Methyl monochloropropion- ate.....	14	14	Ethyl sulfate.....	17	19
Ethyl monochloroacetate.....	14	14	Propionic anhydride.....	19	19
Methyl monochloroformate...	13	14	Cresol methyl ether.....	20	19
Benzol chloride.....	14	14	Ethyl phenyl ether.....	20	19
Ethyl acetate.....	14	14	Ethyl acetylacetate.....	18	19
Butyl chloride.....	14	14	α Methylpiperidine.....	20	20
Propyl nitrate.....	14	14	Ethyl butyrate.....	19	20
Methyl ethyl carbonate.....	14	15	Butyl acetate.....	19	20
Ethyl acrylate.....	15	15	Hexyl chloride.....	19	20
Methyl lactate.....	14	15	Methyl valerate.....	19	20
Ethyl ether.....	17	15	Ethyl benzoate.....	20	20
Chlorotoluene.....	16	15	Ethyl oxalate.....	18	20
			α Isopropylpyridine.....	21	20

TABLE 1—*Concluded*

NAME OF COMPOUND	n		NAME OF COMPOUND	n	
	Calculated	Known		Calculated	Known
n, Propylbenzene.....	23	21	Thymol methyl ether.....	26	27
Benzyl acetate.....	20	21	Butyl sulfide.....	28	27
Allylaniline.....	23	21	Heptyl methyl ether.....	28	27
Propyl ether.....	23	21	Methyldiphenylamine.....	28	27
Hexahydrotoluene.....	23	21	Decahydronaphthalene.....	29	28
Ethyl propyl carbonate.....	19	21	Methyl hexyl ketone.....	30	28
Ethyl methylacetoacetate....	21	22	Octylamine.....	30	28
Triethylamine.....	23	22	Tetraethylsilicane.....	27	29
Allyl benzoate.....	23	22	Amyl butyrate.....	27	29
Tetrahydronaphthalene.....	23	22	Methone.....	28	29
Phenyl sulfide.....	25	23	Heptyl acetate.....	28	29
Heptyl chloride.....	23	23	Hexahydrocymene.....	29	30
Butyl propionate.....	22	23	Octyl methyl ether.....	31	20
Paraconine.....	24	24	Methyl octyl ketone.....	33	31
Triethylsilicol.....	24	24	Octyl acetate.....	30	32
Triethylcarbinol.....	23	24	Heptyl propionate.....	30	32
Propyl carbonate.....	22	24	Decane.....	33	32
Acetylnaphthol.....	24	24	Triphenylamine.....	31	32
Pentyl ethyl ether.....	25	24	Amyl ether.....	31	33
Butylbenzene.....	26	24	Phenyltriethylsilicane.....	31	33
Carvacrol.....	26	24	Octyl ethyl ether.....	33	33
Butyric anhydride.....	23	25	Undecane.....	37	35
Butyl phenyl ether.....	26	25	Octyl propyl ether.....	36	36
Ethyl cinnamate.....	26	25	Dodecane.....	40	38
Terebene.....	25	26	Octyl butyl ether.....	38	39
Conine.....	27	26	Tributylamine.....	38	40
Propyl valerate.....	25	26	Tridecane.....	43	41
Ethyl naphthalene.....	24	26	Tetradecane.....	46	44
Diethylaniline.....	27	26	Octyl ether.....	49	51

The first point to settle is that relating to the value of the constant in the formula. As a result of comparisons, which we made, this constant may have a value of 50 or of 70.

Table 3 contains values of n for the solid state, calculated with the aid of the formula:

$$\left(\frac{T}{70 \times D}\right)^2 = n \quad (3)$$

TABLE 2
The number of atoms in polymerized organic molecules

NAME OF COMPOUND	<i>n</i>		NAME OF COMPOUND	<i>n</i>	
	Calculated	Known		Calculated	Known
Formic acid.....	9	5	Propylamine.....	20	13
Acetonitrile.....	19	6	Isopropylamine.....	21	13
Methyl alcohol.....	19	6	Trimethylene alcohol.....	21	13
Methylcarbylamine.....	13	6	Propylene alcohol.....	20	13
Acetaldehyde.....	14	7	Phenol.....	18	13
Thioacetic acid.....	13	8	Thiophenol.....	17	13
Propargyl alcohol.....	16	8	Trimethylamine.....	17	13
Acetic acid.....	14	8	Chlorhydrin.....	18	13
Propionitrile.....	21	9	Aniline.....	19	14
Ethyl alcohol.....	19	9	Butyric acid.....	19	14
Allyl cyanide.....	21	9	Benzaldehyde.....	18	14
Ethylcarbylamine.....	21	9	Butyl cyanide.....	26	15
Ethylene cyanohydrin.....	22	10	Ethylacetamide.....	26	15
Allyl alcohol.....	18	10	Butyl alcohol.....	22	15
Glycol.....	17	10	Benzyl cyanide.....	25	16
Acetone.....	16	10	Butylamine.....	21	16
Ethyl thiocyanate.....	16	10	Diethylamine.....	20	16
Dimethylamine.....	17	10	Diethyl ketone.....	20	16
Ethyl amine.....	16	10	Benzyl alcohol.....	20	16
Nitroethane.....	14	10	Methyl propyl ketone.....	20	16
Propyl aldehyde.....	14	10	Butyl thiocyanate.....	21	16
Allyl sulfocyanate.....	16	11	Methyl aniline.....	23	17
Pyridine.....	16	11	Valeric acid.....	23	17
Propionic acid.....	17	11	α Quinoline.....	22	17
Propyl cyanide.....	24	12	Benzylamine.....	21	17
Ethylformamide.....	23	12	Amyl cyanide.....	27	18
Propyl alcohol.....	20	12	Methyl butyl ketone.....	24	19
Phenyl cyanide.....	21	13			

in which T is the melting point of the solid organic compound and D its density in the solid state. The values of n thus calculated with $C = 70$, approximate those which are known. In the third column of this table are the values obtained for n in the liquid state, calculated with the help of the density in the solid state, the boiling point and the constant $C = 100$. By the close cor-

TABLE 3
The number of atoms in the molecules of organic solids

NAME OF COMPOUND	n KNOWN	n CALCULATED		NAME OF COMPOUND	n KNOWN	n CALCULATED	
		Solid	Liquid			Solid	Liquid
m-aminobenzoic acid.....	17	17	—	Cinnamyl methyl ketone.	21	19	26
Anisic acid.....	19	21	—	Cumidine.....	23	25	28
Acetopropionic acid.....	16	15	20	p-Chlorophenol.....	13	12	15
Camphoric acid.....	30	29	—	β -Chloronaphthalene.....	18	14	18
Cinnamic acid.....	19	20	20	+ Camphor.....	26	28	24
Citric acid.....	21	21	—	Dimethylaniline.....	20	17	23
Citramalic acid.....	18	15	—	Erythritol.....	18	15	15
Cumic acid.....	24	23	—	p-phenylquinoline.....	26	22	—
Phthalic acid.....	18	18	—	Guyaiacol.....	17	17	16
Phenylacetic acid.....	18	17	18	α Naphthol.....	19	18	21
Gallic acid.....	18	17	—	β Naphthol.....	19	23	—
Hippuric acid.....	23	25	—	Nitrobenzene.....	14	11	16
Itaconic acid.....	15	15	—	σ -Nitrophenol.....	15	15	17
Maleic acid.....	12	13	—	p-Nitrophenol.....	15	15	—
Amygdalic acid.....	19	17	—	Naphthalene.....	18	18	18
Malic acid.....	15	12	—	σ -Nitroaniline.....	16	15	15
Methylsuccinic acid.....	17	15	—	p-Nitroaniline.....	16	17	—
m-nitrobenzoic acid.....	17	17	—	o-Nitrochlorobenzene.....	14	10	14
Oxalic acid.....	8	10	—	m-Nitrochlorobenzene.....	14	10	14
Protocatechuic acid.....	17	18	—	p-Nitrochlorobenzene.....	14	14	14
Salicylic acid.....	16	18	—	+ m-Nitrotoluene.....	17	12	18
Succinic acid.....	14	16	—	+ p-Nitrotoluene.....	17	18	20
Tetrahydrobenzoic acid..	19	16	22	+ 1, 2, 4, Nitroxylene....	20	15	22
Trichloroacetic acid.....	8	9	8	Orcinol.....	17	16	18
Tartaric acid.....	16	14	—	Methyl oxalate.....	14	16	14
Phthalic anhydride.....	14	14	14	Phenanthraquinone.....	24	24	—
Acetanilide.....	19	20	21	Pyrogallol.....	15	15	14
Acetocinnamone.....	21	20	—	Pyrocatechol.....	14	15	14
Acetophenone.....	17	18	—	Saligenin.....	17	19	—
Aniline.....	14	13	18	p-toluidine.....	17	18	19
Benzamide.....	16	18	17	Thymol.....	25	22	—
Benzanilide.....	26	23	—	Terpineol.....	26	30	27
α -Benzaldoxime.....	14	16	18	1, 3, 4, Xylenol.....	17	21	—

respondence the relation (3) is verified for a considerable number of compounds.

TABLE 4
The number of atoms in the molecules of polymerized solids

NAME OF COMPOUND	n KNOWN	n CALCULATED		NAME OF COMPOUND	n KNOWN	n CALCULATED	
		Solid	Liquid			Solid	Liquid
Acetic acid.....	8	16	14	Ethylene cyanide.....	10	21	—
Benzoic acid.....	15	21	19	α Diethylurea.....	20	28	26
α Crotonic acid.....	12	24	24	Phenol.....	13	17	18
Formic acid.....	5	11	9	Hydroquinone.....	14	23	—
+ Trimethylacetic acid..	17	24	23	Quinone.....	12	18	—
Anisic alcohol.....	20	27	23	Resorcinol.....	14	18	—
Acetamide.....	9	18	18	Thiourea.....	8	19	—
Propionamide.....	12	23	—	Trimethylcarbinol.....	15	32	21
Anthraquinone.....	24	31	22	Urea.....	8	18	—
Benzene.....	12	20	15				

TABLE 5
Number of atoms for C = 70

NAME OF COMPOUND	n KNOWN	n CALCULATED		NAME OF COMPOUND	n KNOWN	n CALCULATED	
		Solid	Liquid			Solid	Liquid
Benzoic anhydride.....	27	14	26	Hexadecane.....	50	34	56
Azobenzene.....	24	16	22	Levulose.....	24	11	—
+ Cetyl alcohol.....	51	31	56	Mannitol.....	26	14	—
Benzyl-naphthalene.....	31	16	29	+ Nonadecane.....	59	31	59
Codeine.....	43	21	—	+ Octadecane.....	56	30	56
Ethyl cinnamate.....	25	14	25	+ Octadecylene.....	54	27	56
Diphenylamine.....	24	16	25	s Octadecylene.....	54	27	56
Glucose.....	24	11	—	Picric acid.....	19	10	—

Table 4 includes compounds which show the phenomenon of molecular polymerization in the solid state. Formic acid, acetic acid, acetamide, propamide, ethylene cyanide, urea, etc. appear with double molecules.

Table 5 shows that the values n calculated on the basis of the constant $C = 70$ are much lower than the known values, most of

them being exactly half the first. With the constant $C = 50$, we obtain for n values equal to those of the first column. In this last case, $C = 50$, these compounds are not more polymerized in the solid state than in the liquid state. In changing the value of the constant for these compounds, we must also make $C = 50$ for the compounds in the preceding tables. We must then also modify the conclusions. The fact that these compounds are polymerized in the solid state remains correct, yet the degree of polymerization must be doubled. Formic acid and the other compounds which we mentioned above have molecules four times polymerized in the solid state, that is, twice as much as in the liquid state. It is known that for liquids the degree of polymerization decreases as the temperature is raised. Since it is natural that when the temperature is lowered, polymerization increases it is logical that we should find a greater degree of polymerization in the solid state. The compounds in table 3 present the phenomenon of polymerization, having for the most part double molecules for they tend to polymerize in the liquid state. Molecules of water in the solid state will, in this case, be 10 times polymerized, while they would be only 6 times polymerized with the constant $C = 70$.

The values of the constant C as a function of the atomic weights of constituent elements. For compounds containing bromine, iodine, etc., elements with high atomic weights, the results do not agree. The reason for this difference is the dissimilarity of the respective atomic weights.

In fact, the compounds C_2H_5Cl , C_2H_5Br , and C_2H_5I always contain the same number of atoms, but the mass of the atom chlorine, bromine and iodine is not in the same ration with respect to the mass of the other atoms. The mass of the atom of bromine is almost 3 times and that of the atom of iodine is 4 times the mass of the other seven atoms taken together. To obtain concordant results in this last case, it is sufficient to give to the constant a value which is a function of the atomic weights of the constituent elements. The determination of these values is very easy for organic compounds of bromine, iodine and some other elements.

TABLE 6
The number of atoms for halides, with C corrected

NAME OF COMPOUND	TEMPERATURE OF		DENSITY	n CALCULATED		n KNOWN
	Fusion	Boil- ing		Solid	Liquid	
Ethyl bromide.....	—	428	1.52	—	12	12
Propyl bromide.....	—	456	1.4	—	17	15
Allyl bromide.....	—	493	1.57	—	15	14
Amyl bromide.....	—	311	1.47	—	7	8
Monobromobenzene.....	—	402	1.25	—	16	17
Benzoyl bromide.....	—	344	1.38	—	10	11
Monobromotoluene.....	—	343	1.46	—	9	9
α monobromonaphthalene.....	—	550	1.5	—	21	18
Phosphorus bromide.....	—	448	2.93	—	4	4
Phosphorus oxybromide.....	319	468	2.82	10	6	5
Phosphorus thiobromide.....	311	—	2.85	10	—	5
Hydrobromic acid.....	—	204	1.78	—	2	2
Boron bromide.....	—	364	2.69	—	3	4
Sulfur bromide.....	—	473	2.63	—	5	6
Silicobromoform.....	—	390	2.7	—	4	5
Methyl iodide.....	—	317	2.2	—	5	5
Ethyl iodide.....	—	346	1.98	—	7	8
Propyl iodide.....	—	376	1.78	—	10	11
Amyl iodide.....	—	428	1.54	—	17	17
Hexyl iodide.....	—	450	1.47	—	21	20
Heptyl iodide.....	—	477	1.40	—	25	23
Octyl iodide.....	—	499	1.35	—	31	26
Acetyl iodide.....	—	381	1.98	—	8	7
Phenyl iodide.....	—	468	1.83	—	15	12
Hydriodic acid.....	—	239	2.27	—	2	2
Iodine chloride.....	298	—	3.2	12	—	2
Iodic acid.....	443	—	4.63	12	—	5
Potassium iodide.....	896	—	3.06	108	—	2
Potassium iodate.....	833	—	3.98	57	—	5
Siliciodoform.....	—	439	3.4	—	5	5
Lead ethyl.....	—	383	2.03	—	18	17
Mercury ethyl.....	—	432	2.44	—	15	15
Mercury methyl.....	—	369	3.07	—	7	9
Tetraethylstannane.....	—	454	1.19	—	31	29
Tetramethylstannane.....	—	351	1.31	—	15	15
Triethylstannane.....	—	533	1.41	—	22	22
Antimony ethyl.....	—	431	1.3	—	23	22
Trimethylbismuthine.....	—	385	2.3	—	15	13
Triethylarsine.....	—	413	1.15	—	20	22
Zinc ethyl.....	—	391	1.18	—	16	15

TABLE 6—Concluded

NAME OF COMPOUND	TEMPERATURE OF		DENSITY	n CALCULATED		n KNOWN
	Fusion	Boiling		Solid	Liquid	
Zinc methyl.....	—	319	1.39	—	8	9
Antimony chloride.....	344	503	3.06	15	6	4
Antimony bromide.....	363	556	4.15	9	4	4
Silver fluoride.....	708	—	5.8	7	—	2
Silver chloride.....	533	—	5.5	10	—	2
Silver bromide.....	693	—	6.4	14	—	1
Silver iodide.....	813	—	5.6	27	—	2
Silver chlorate.....	503	—	4.4	14	—	5
Silver nitrate.....	471	—	4.35	12	—	5
Arsenic chloride.....	—	407	2.21	—	5	4
Arsenic bromide.....	298	—	3.66	5	—	4
Cobalt chloride (6H ₂ O).....	360	—	1.84	24	—	3 or 21
Chromyl chloride.....	—	389	1.96	—	5	5
Chromic anhydride.....	453	—	2.8	—	16	4
Cuprous chloride.....	683	—	3.7	22	—	2
Cuprous bromide.....	777	—	4.7	13	—	2
Cadmium chloride.....	814	1,179	3.63	53	21	3
Cadmium bromide.....	844	1,079	4.8	32	10	3
Cadmium iodide.....	677	—	4.6	22	—	3
Cadmium nitrate (4H ₂ O).....	453	—	2.9	26	—	9 or 21
Ferric nitrate (18H ₂ O).....	320	—	1.68	23	—	26
Germanium chloride.....	—	359	1.89	—	6	5
Manganous chloride (4H ₂ O).....	361	—	1.56	34	—	3 or 15
Nickel carbonyl.....	—	316	1.84	—	8	9
Lead chloride.....	758	2,173	5.8	90	72	3
Lead tetrachloride.....	258	378	3.18	33	8	5
Lead iodide.....	656	1,173	6.07	60	19	3
Selenium oxychloride.....	283	453	2.44	10	6	4
Stannous chloride.....	523	879	2.7	31	22	3
Stannic chloride.....	—	593	2.3	—	14	5

In fact, these elements produce numerous organic compounds whose densities and boiling points are very well known. By introducing these data into the preceding formula, it is easy to obtain the respective values for the constant. This was the way in which we found the values 79 for bromine, 66 for iodine, and 46 for mercury (7).

Table 6 contains a number of examples showing the evident

agreement of the results obtained. The constants of other elements can be determined with the aid of the following equation:

$$C_{\text{liquid}} = 100 - \frac{A}{3.7} \quad \text{and} \quad C_{\text{solid}} = 50 - \frac{A}{5.7},$$

in which A signifies the atomic weight of the respective elements.

These formulas have a double importance. First, they permit us to generalize our relation and to find valuable indications on the molecular constitution of a great number of organic compounds. In addition, these formulas prove to us that the atomic weight also must be taken into account in our fundamental relation.

We finally arrive at this important conclusion that the known quantities for our relation are: melting or boiling point of a compound, its density (which represents its molecular weight and the number of molecules in a unit volume), the number of atoms, and the weight of these atoms.

This formula for the liquid state can therefore be written in the form:

$$A = 3.7 \left[100 - \frac{T}{D n} \right] \quad (4)$$

which gives for lead ethyl, mercury ethyl, ethyl bromide, ethyl iodide, tetramethyl stannane, bismuth trimethyl and antimony ethyl values 196; 203; 133; 76; 122; 199; 111 close to the atomic weights of lead 206, of mercury 200, of iodine 127, of bromine 80, of tin 118, of bismuth 208 and of antimony 120. The conclusion drawn from these examples is that organic compounds, which contain an element with a high atomic weight are governed by this atomic weight.

The value of the constant C for different pressures of boiling. We have used above the boiling points of compounds at normal pressure, 760 mm. It is necessary, as Ph. A. Guye showed in 1903, to determine the numerical values of the constant for lower pressures in order to calculate n for compounds which boil only

under vacuum. This determination does not present any difficulty. The relation (2) can be written in the form:

$$T_{760} = 100 \times D \sqrt{n};$$

$$T_p = C_p \times D \sqrt{n}$$

whence

$$C_p = 100 \frac{T_p}{T_{760}}$$

The question is reduced then to a calculation of the ratio of the temperatures of boiling under pressure p and at normal pressure. The calculation of n thus becomes possible even for pressures lower than normal (8).

THE DEGREE OF ASSOCIATION OF INORGANIC COMPOUNDS IN THE LIQUID AND THE SOLID STATE

For inorganic compounds, the degree of association can be calculated with the same exactness as for organic compounds. The melting and boiling points of oxides, acids, salts, bases and elements are much higher than those of organic compounds. We found, as did Vernon, that hydrofluoric acid is four times polymerized. Liquid sulfur has the molecule S_{12} . Oxides of chlorine and of nitrogen, phosphorus trichloride, and the halogen compounds of carbon and of silicon are normal, as found by Ramsay and Traube. Nitric acid we found normal, while it is doubly polymerized according to Vernon and Ramsay. Sulfuric acid, normal according to us, would be four times polymerized according to Vernon but only twice according to Vaubel. Carbon disulfide is doubly polymerized according to Vaubel and us. Sulfur dioxide, normal according to Vernon and us, would be twice polymerized according to Vaubel. Phosphorus would have, according to us, nine atoms in the liquid molecule, while according to Vaubel and Ramsay, it would have only four (9),

The degree of association for elements and salts in the solid state is entirely unexpected and large. Thus carbon, silicon,

lithium, and calcium have a degree of polymerization greater than 200. Beryllium, magnesium, and strontium have more than 100 atoms in a molecule in the solid state. For sodium, aluminum, and potassium the number of atoms in a molecule is greater than 50. Chromium, manganese, iron, cobalt and nickel are polymerized without their degree of polymerization exceeding thirty.

This enormous polymerization of metals, given by our method, is in marked opposition to the idea generally accepted that metals are monoatomic even in the solid state. This is the reason we believe that the constant C must have values much greater than 100 and 50 respectively for compounds whose melting and boiling points are greater than 800°.

On the other hand the value of the constant is less than 100 for liquefied gases such as He (23.8) Ne (16) Ar (44.1) O (56.3) and N (67.8) considering the molecules of these elements as diatomic in the liquid state. As an exception, liquid hydrogen has the constant C = 208, which signifies that liquid hydrogen is strongly polymerized (10).

THE SECOND METHOD OF G. G. LONGINESCU

We established, in 1908, (11) the relation:

$$\frac{T}{M} \frac{1000}{T} = 64,$$

in which T signifies the boiling point and M the molecular weight of the compound. This relation provided us with the simplest and surest method for differentiating between a polymerized and a normal compound. The hydrocarbons, ethers, esters, organic halogens, and organometallic compounds appear absolutely normal, having for the constant a value between 63 and 65. Yet all the polymerized compounds give values greater than 64, reaching a value of 99.2 for water, which appears once more as the most polymerized liquid.

We mention only the values of the constant for the first members of each polymerizing series. Thus, we have for formic acid the value 72, methyl alcohol 76.8, aldehyde 67, methyl amine 69,

nitrile methane 73.4 and nitrobenzene 66.4. Among inorganic compounds we found the following normal in the liquid state: Cl_2 64.8, Br_2 64, HCl 63.5, HBr 66.7, SOCl_2 63.2, SO_2Cl_2 63.3, Cl_2O 64, NOBr 64.5, PCl_3 63.3, AsCl_3 63.2, AsF_3 63.3, POCl_3 63.1, PSCl_3 63.3, S_2Cl_2 63.6, CrO_2Cl_2 63.2, SnCl_4 65.5, SiCl_4 64.6, GeCl_4 65.1, GeHCl_3 64.5, TiCl_4 63, VCl_4 63.2, VOCl_3 63.2, SO_2 63.2, SO_3 65.2, SO_3HCl 65, $(\text{CN})_2$ 63.4, CS_2 64.1, H_2S 63.7, $\text{Fe}(\text{CO})_5$ 64, N_2O 63.1, Hg_2 63.1. Among inorganic compounds polymerized in the liquid state we found water 99.2, HF 78.8, CNH 74.8, NH_3 75.8, NO 67.4, N_2H_4 83.4.

It can be seen that this method is superior to the first one indicated above. In fact, it gives exact results for all the elements, it permits a distinct separation of normal from associated compounds, and is unexpectedly sure and simple for inorganic compounds. On the contrary, this method is inferior to the first in determining the degree of association. It shows only whether a compound is more or less associated than another, for example that methyl alcohol 76.8 is more associated than formic acid 72.

Liquified gases, considered as diatomic, give the following values for the constant: He_2 701.4, Ne_2 258, Ar_2 111.7, H_2 83, N_2 82, O_2 78. They then will be polymerized in the liquid state and the rare gases, enormously polymerized.

Because of the fact that this relation is an equation of the second degree, it admits two values for the molecular weights. The result is a strange phenomenon, it is true, but a very important one, namely, that a liquid compound is a molecular complex of polymerized and dissociated molecules.

A GLANCE AT OTHER METHODS

A complete analysis of all the known methods is not needed since we have three substantial works on this problem, those of W. E. S. Turner, *Molecular Association*, London, 1915; of P. Walden, *Molekulargrößen von Elektrolyten in Nicht-wässrigen Lünsgsmitteln*, Leipzig, 1923; and of S. Smiles, *The Relations between Chemical Constitution and some Physical Properties*, Longmans, Green and Co. (1910). Among the well established methods are those of Ramsay and Shields, Morgan, Bratschinski,

Mitchell and Bennett, Walden, Bingham, Traube, Guye, and Holmes. These methods are not only complicated but inexact in their results.

Vaubel (12) determines the molecular weight in the solid state by the use of new relations between the osmotic pressure, the lowering of the freezing point and the elevation of the boiling point in equimolecular solutions. Jorissen uses the formula

$$n = \frac{193 M^2}{T_T d_e}$$

where d_e represents the density at the boiling point and T the boiling temperature, the formula being verified for forty substances. W. Herz (13) established the relation

$$\frac{M_k}{d_k} = \frac{M_e}{d_e} = \text{a constant}$$

where M is the molecular weight and d the density, while k and e refer to the critical temperature and the boiling point respectively. This ratio must be unity for normal compounds but not for associated compounds. He also established the relation

$$\frac{M_k}{M_e} = 2.69 \frac{d_k}{d_e}$$

This ratio has a value of 0.98 for esters, 0.97 for methyl, ethyl and propyl alcohols, and 0.99 for acetic acid.

Ph.A. Guye (14) has criticized methods of determining molecular size as follows:

All formulas using as experimental data the surface tension, i.e., a property of the surface layer separating the liquid phase from the vapor phase (including those of Ramsay and Shields, Ramsay and Ross Innes, Kistiakowski, Walden, Dutoit and others) cannot give an indication of the molecular complexity except in this surface film. This complexity is doubtless very often the same as in the mass of liquid, but it is not always and necessarily so.

Neither can certain other relations, apparently independent of surface tension, be accepted as really giving the molecular size in the

liquid phase. These are those which are a function of the boiling point (or what amounts to the same thing, the critical temperature) such as, for example, Trouton's relation and Longinescu's formula. It is easy to demonstrate that relations of this class give a value for molecular size which must generally lie between that which characterizes the inner liquid mass and that of the surface layer.

In fact, the boiling point is that at which, under a pressure of one atmosphere, the number of molecules passing through the surface layer in both directions, i.e., from the liquid phase to the vapor phase and vice versa, is strictly the same in unit time. Now it is clear, that if the surface layer is polymerized in comparison with the liquid mass, the boiling point thus defined will be raised above its normal value. If this layer is partially dissociated, this temperature will be lowered.

Consequently, in the case of Trouton's formula, for example, the denominator T will be too large if the surface layer is polymerized. On the other hand, in the numerator the term λ will include not only the heat of physical vaporization, but also the heat of chemical depolymerization of associated molecules. According to the relative import of these two terms, it will be possible to produce a sort of compensation which explains why in certain cases, with nitriles for example, the Trouton formula indicates as normal, liquids that are clearly polymerized in the surface layer. This almost amounts to saying that when a liquid has not the same complexity in the surface layer as in the inner liquid mass, the use of Trouton's formula is no longer possible.

As for Longinescu's formula, one of his terms, T , depends on the surface layer, the other, d , depends on the liquid mass and is independent of the surface layer. If there is polymerization in the surface layer, T will be too large and consequently n (or, what amounts to the same, the molecular weight) will be too large also. If there is dissociation in the surface layer, T will be too small and also n . Consequently, the Longinescu formula will give results of the same kind as formulas based on surface tension, with this difference, however, that the degree of association or dissociation indicated by this relation will be generally intermediate between that which exists in the surface layer and that in the mass of the liquid. This is generally known to be so.

The most rational physical properties to use in the exact determination of the molecular size in the liquid phase must be completely independent of the properties of the surface layer. In this case, then, it is necessary to exclude surface tension, boiling point, vapor tension, and latent heat of vaporization. These constants can lead only to approxi-

mate results which must be considered only as indications and not as determinations, especially when they are abnormal. Among the properties of liquids, on which research must be carried to obtain exact values for molecular weight in the liquid phase there may be mentioned density, coefficients of expansion and compressibility and viscosity as leading to most reliable conclusions. In this direction some very interesting experiments have already been done by Traube, Walden, Duclau and others.

RECENT WORK ON MOLECULAR ASSOCIATION

It is beyond our scope to analyze in detail the large amount of work on this subject published up to the present. We shall, however, summarize the work which has appeared since 1922.

Frederick G. Keyes (15) calculates the association of CO_2 from the Joule-Thomson effect. He finds that for -53° , there is one double molecule of CO_2 for 500 simple molecules and at 127° one double molecule for 20,000 simple molecules.

E. E. Walker (16) studies the molecular association of compressed gases and proves that only substances the molecules of which are of the same length are truly corresponding substances. For associated compounds an associated factor must be introduced into the critical constants.

N. Vasilescu Karpen (17) establishes a new relation for the calculation of internal pressure of liquids and a criterion for molecular association. He calculates the total work produced by isothermal expansion from the increase in volume, the mechanical equivalent of heat, the heat absorbed and the latent heat of expansion. Deviations prove a molecular association.

J. A. Müller (18) calculates the degree of polymerization at the critical point,

$$x = \frac{3}{8} \frac{RT_e}{P_e V_e}$$

He shows that all except helium, having $x = 0.923$, are polymerized. For normal gases, x is very slightly raised, H = 1.22, O = 1.283, N = 1.285, A = 1.285, Cl = 1.363. Hydrocarbons

have $x = 1.4$, ethers the same, ethyl alcohol 1.5, acetic acid 1.8, acetonitrile 2, and water 1.84.

A. Leduc (19) calculates the degree of polymerization from the equation of state for CO_2 as four percent in saturated vapors.

Carl Wagner (20) uses Trouton's rule as a criterion for association. Among other values, he finds water 26, ethyl alcohol 27.1 and propyl alcohol 26.9.

K. Stachorskii (21) calculates the degree of association at the boiling point with the aid of the molecular weight, the boiling point, surface tension and specific volume.

Luise Lange (22) studies the relation between the dielectric constant and the degree of association of liquids. According to Debye's theory the polar moment is influenced by association. The author finds the following polar moments, multiplied by 10^{-18} , nitrobenzene 3.84, pyridine 2.11, ether 1.22, propyl alcohol 1.53, butyl alcohol 1.65, isobutyl alcohol 1.75, and iso-amyl alcohol 1.76.

M. F. Carrol (23) starts with the hypothesis that association is a general property of all substances, normal ones included. He modifies the equation of state by replacing the constants a and b of Van der Waal's equation by the functions of the degree of association. According to his experiments, the heat of association increases with temperature for associated substances, while it is constant for normal ones.

Louis Harris (24) deduces from the absorption spectrum of vapors, that formic acid has simple molecules at room temperature. On increasing the temperature, the associated molecules become more numerous.

F. Schuster (25) establishes a relation between internal pressure and the covolume and determines the degree of association of a molecular volume, by a modification of Traube's method. He obtains values at the boiling point agreeing with values found by other methods.

C. P. Zahn (26) studies the variation of the dielectric constant of water vapor with pressure and temperature. By interpreting results obtained with the aid of Debye's formula, he explains the anomaly observed at 47° by the formation of an absorption layer

on the condenser plates and not by molecular association as has been proposed by Jona.

D. B. MacLeod (27) establishes a linear relation which shows that the viscosity of a liquid is proportional to the molecular weight, the degree of association and the space unoccupied by molecules. The degree of association can be calculated at any temperature, if it is known at one temperature.

G. Bredig and L. Teichmann (28) established the degree of association for hydrocyanic acid as 2.04, deduced from newly determined critical constants.

Kwantaro Endo (29) determines from the distribution coefficient that phenol in benzene is in great part tripolymerized and with the aid of cryoscopy, that phenol in water is similarly tripolymerized.

Frederick Stanley Brown and Charles R. Bury (30) in determinations by cryoscopic methods with solvents dried by phosphorus pentoxide or partially saturated with water, find that alcohols and phenols are more associated in wet solvents and that their degree of association increases with concentration, while organic acids are more associated in dry solvents.

Jacques Duclaux (31) considers water, according to Röntgen's hypothesis, as an ice solution, containing polymerized molecules identical with those present in ice and accordingly lighter than water. With Sutherland, he calls hydrol "that which remains when the dissolved ice is removed from the real water; real water is a solution of ice in hydrol." The conclusions of Duclaux are as follows:

The study of the variation in the coefficient of expansion of water with pressure leads to the assigning of a formula intermediate between $(\text{H}_2\text{O})_9$ and $(\text{H}_2\text{O})_{12}$ to the molecules of ice.

The study of the variation of compressibility with temperature shows that the relative change per degree of the quantity of ice dissolved in water at 0° is greater than 0.02. . . . The heat of depolymerization of a molecule of dissolved ice is greater than 3000 calories. . . . The heating of water produces both the expansion of the non-polymerized part and the melting of a part of the ice, whence a contraction results, which decreases the coefficient of expansion of water.

The following values are the most probable: The molecule of ice is $(\text{H}_2\text{O})_9$ or $(\text{H}_2\text{O})_{12}$. The heat of depolymerization of a molecule of dissolved ice is about 4000 calories. A liter of water contains at 0° about 200 g. of ice. In the neighborhood of 0° , this quantity diminishes about 4 g. per degree. The specific heat of dissolved ice is 0.62, that of non-polymerized water 0.99.

The compressibility of depolymerized water at 0° is about 360×10^{-7} and increases about $\frac{1}{317}$ per degree. Pressure diminishes the quantity of dissolved ice by about 0.14 g. per atmosphere. Under a pressure of 3000 atmospheres water contains only about 10 g. of ice. . . . It should be said that most of the methods assume that the molecules of non-associated normal liquids are simple. This hypothesis is perhaps not necessary since the disagreement would disappear entirely if normal liquids were formed of double and triple molecules.

G. Tammann (32) studied the molecular complexity of water in detail basing his work on the existence of a type of molecule characterized by large volume and possessing the reticular structure of ice I. At 0° water contains 0.22 molecules of the ice I while at 50° the concentration of it is very small. The other types of molecules of water are not as easy to recognize and distinguish. On the assumption that molecules of the four kinds of ice can also be found in water, there must exist four types of water molecules, polymerized or isomeric with each other. As pressure is increased the molecules of type I diminish in number and at above 2500 kgm. cm^2 ice III crystallizes, heavier than water. The existence of type I is proved by different physical phenomena which vary with pressure and temperature. At high temperatures and low pressures, water contains molecules of $(\text{H}_2\text{O})_2$ which were recognized by W. Nernst. As to the other types of molecules and their weights, we know little about them.

Tammann next studied the concentration of molecules of type I at 0°C ., the relation between type I and others, the change of volume with the transformation of molecules of type I, the degree of polymerization of type I, the heat of transformation of molecules of type I, the variation of specific heat of water with temperature, the influence of molecules of type I on the viscosity of water in relation to pressure and temperature, and the variation

of the surface tension of water with pressure and temperature. The refractive index of ice is greater than that of water, for the number of molecules of type I increases by crystallization. The article closes with the following conclusion: "The determination of the concentration of molecules of type I permits the thermodynamic calculation of their molecular weights, $(\text{H}_2\text{O})_9$, in case these molecules dissociate into 9 H_2O , and $(\text{H}_2\text{O})_6$, in case they dissociate into $2(\text{H}_2\text{O})_3$."

G. Antonoff (33) commences his article "Sur la structure moléculaire des liquides et des solides" as follows:

Present ideas on the nature of liquids are somewhat lacking in coordination and in general no one of the recent theories is of a sufficiently comprehensive character to solve the enigma of the liquid state. It has been considered that liquids can be divided into "normal liquids" and "abnormal liquids." The first have been so named because they obey some empirical laws devoid of all theoretical basis. If a phenomenon appears abnormal from the point of view of a law based on a limited number of facts, this signifies that the true law has not been found. This is sufficiently demonstrated with liquids. Researches have resulted based on purely empirical points of view in the minds of most investigators, with an accumulation of detailed facts but without a satisfactory theory or even a fruitful hypothesis. A great amount of work has been done on the study of solutions, i.e., on mixtures of different liquids, and the results is that the problem of liquids, already a difficult one, has been further complicated through the mutual action of two liquids, whose individual nature has not yet been defined. . . . of two liquids, whose individual nature had not yet been defined. . . . In the present state of our knowledge there is no method, direct or indirect, which permits the determination of the molecular weight of liquids . . . , and no theory indicates where and when the phenomenon of association is produced.

Antonoff passes next to the study of solutions and continues:

Van't Hoff has shown that dissolved materials obey the laws of the gaseous state. These laws can be verified for dilute solutions. But in more concentrated solutions appreciable deviations are encountered. As in the case of gases, it is natural to assume that if simple laws are not applicable, this is due to molecular forces which cannot be neglected

at high concentrations where the distance between molecules becomes small and the field of molecular forces distinctly appreciable. I have, nevertheless, reason to believe that molecular forces have no effect on the above properties.

Antonoff's conclusions are:

The fact that at the critical point separation occurs into two phases of equal volume, indicates that one-third of the molecules attach themselves to another third to form double molecules. Thus at the critical point, the system will contain an equal number of double and simple molecules, which after separation occupy equal volumes. The different phases in equilibrium with each other contain the same number of molecules per unit volume.

In his article, "Propriétés physiques des liquides fonctions de la température" (34) Antonoff establishes the fact that the properties of liquids vary discontinuously as a function of temperature. The discontinuities are distinctly greater than the experimental error. He concludes that the facts are perfectly explained by the hypothesis that matter is subject to molecular changes such that at relatively low temperatures only very complex aggregates of molecules are present as elementary constituents.

H. Brereton Baker (35) studied the change of properties of substances under prolonged drying during years or even decades. We propose the term ultra-drying for this kind of drying. Entirely unexpected changes in properties were found under this treatment. The boiling points of ten liquids ultra-dried with P_2O_5 show a considerable rise. The melting points of sulfur and iodine show rises of 5.5° and 2° respectively after nine years of ultra-drying. The melting points of sulfur trioxide ultra-dried for twenty years and of bromine and benzene so dried for ten years were found to be 61° , -45° , 6° respectively. The vapor density of ether, ultra-dried for ten years, was found to be 81.7, twice the normal value, and that of methyl alcohol, ultra-dried also for ten years, to be 45, while the normal is 15. Baker explains these transformations by the polymerization of the respective molecules after the removal of water. Even benzene and hexane, considered as normal hydrocarbons, appear to be asso-

ciated. In an ordinary liquid, there would be a continual combination and separation of molecules.

In other experiments, Baker (36) used catalysts, wood charcoal, platinum black, or thorium oxide, and measured the vapor pressure and surface tension, before and after the action of the catalyst. In general, vapor pressure was found to be greater in the presence of the catalyst. The longer the time of contact with the catalyst, the greater was the molecular weight found to be. Thus acetic acid, after a day's contact with wood charcoal, had a molecular weight of 1.5×60 , after three weeks 2.5×60 , and after 12 months 2.49×60 . In contact with platinum black it had a molecular weight of 2.4×60 after two weeks and of 2.97×60 after eight months. Water in contact with platinum had a molecular weight of 3.352×18 on the first day and of 4.442×18 after six months. Slightly lower values were obtained with thorium oxide.

According to Baker liquids can be compared to dissociable gases such as N_2O_4 . At low temperatures the heavy molecules predominate, at higher temperatures light ones. Association, like dissociation of molecules, takes place much more slowly for liquids than for gases. In liquids, the equilibrium can be easily disturbed by even a slight change of temperature and the return to normal conditions takes a long time, sometimes even months. In the same way the effect of the catalyst is produced much more slowly in a liquid than in a gas.

Roland Herbert Purcell (37) studied the action of ultra-drying on certain chemical reactions. Thus the reduction of copper oxide by carbon monoxide without drying takes place in 90 minutes at 100° , and after a drying of ten days in twenty hours. In the same way, Bi_2O_3 is reduced by CO without drying in a few minutes at 250° and after ten weeks drying, the reduction is produced only at 450° . On the other hand, HgO is easily reduced by CO at 180° , even after a drying of eight months.

The Earl of Berkeley (38) proposes an experimental method for the investigation of molecular association which is based on an optical measurement of the density of the various portions of a liquid confined in a centrifuge tube which can be rotated at a

velocity which may prove sufficient to separate the constituents of a liquid into fractions of different densities. If this proves feasible valuable information can be obtained. While the proposal includes the separation of isotopes by this method, several million times the force of gravity would have to be attained, for Svedberg's latest model of the ultra-centrifuge, which multiplies gravity by 42,000 has effected separations of molecular types only when the difference in molecular weight was some ten thousand fold.

THE NEW THEORY OF MOLAR CONCENTRATION OF G. G. LONGINESCU
AND GABRIELA CHABORSKI

The present state of knowledge of molecular association is, as has been shown, entirely chaotic. The idea of molecular association has not even led to concordant results. In fact, the degree of association determined for the same compound very often differs greatly from one method to another. On the other hand, since the degree of association is never an integer, there are present some simple molecules as well as associated ones, i.e., double, triple, and even more complex ones. This lack of homogeneity in the constitution of the liquids as well as in the results obtained fails to give sufficient basis for a good theory. It is necessary to abandon the paths followed in the past. The idea of molar concentration has opened a new and promising approach.

Dr. Gabriela Chaborski has expressed the opinion that the phenomenon of molecular association, or more exactly the phenomena which distinguish associated liquids from normal ones, are not due to simple molecular association, but to the accumulation or crowding of the molecules into a given volume of pure compound Molecular association is reduced, according to her, to a question of concentration of gram molecules in a given volume. This new conception has been very fruitful in its results.

The molar concentration C_m , of a pure liquid or solid is the number of gram-molecules contained in a liter of the solid or liquid compound and is given by the expression:

$$C_m = \frac{1000d}{m}$$

Thus the molar concentration of ether, whose density is 0.714 and molecular weight 74.08, is 9.6, which means that in a liter of pure ether there are 9.6 gram-molecules of ether. Similarly the molar concentration of carbon tetrachloride is 10.4, that of toluene 9.4, that of benzene 11.2, and that of water, the largest of all, 55.5.

For 350 compounds studied by us the values for the molar concentration all lie between 55.5 for water and 0.09 for tristearin.

TABLE 7
Comparison of molecular association with molar concentration

SUBSTANCE	DEGREE OF ASSOCIATION X	$\frac{C_m}{10} = 100 \frac{d}{m}$ (Longinescu-Chaborski)
1. Toluene.....	0.94 (Ramsay-Shields)	0.94
2. Carbon tetrachloride.....	1.01 (Ramsay-Shields)	1.04
3. Monochlorobenzene.....	0.99 (Walden)	0.98
4. Monobromobenzene.....	0.94 (Longinescu)	0.95
5. Ethyl alcohol.....	1.8 (Walden; Bingham)	1.71
6. Phenol.....	1.13 (Walden)	1.13
7. Propanol.....	1.4 (Longinescu)	1.39
8. Chloral.....	1.02 (Ramsay-Shields)	1.02
9. Acetic acid.....	1.75 (Longinescu)	1.75
10. Acetic anhydride.....	1.04 (Ramsay-Shields)	1.06
11. Nitroethane.....	1.40 (Longinescu)	1.39
12. Aniline.....	1.05 (Ramsay-Shields)	1.10
13. Benzotrile.....	0.97 (Ramsay-Shields)	0.97
14. Ethyl ether.....	0.99 (Ramsay-Shields)	0.99
15. Methyl formate.....	1.62 (Traube)	1.60
16. Ethyl acetate.....	1.08 (Walden)	1.05

All organic liquids which are considered associated have a molar concentration greater than 10. For normal liquids, whose degree of association x approaches 1, the molar concentration is 10 or very close to 10. Therefore, for all liquids, the degree of association is equal to a tenth of the molar concentration, that is:

$$x = \frac{100d}{m}$$

In many cases, the agreement between the degree of molecular accumulation and the degree of molecular association is perfect, as is shown in table 7. This indicates that molar concentration

is the common point of contact of the various physical constants with the help of which the degree of association has been determined.

For instance the lowering of the freezing point of liquids gives values which are often either larger or smaller than those which correspond to the simple molecule. When Δ is found to be smaller, the variation is explained on the hypothesis of molecular association, i.e., by a molecular weight greater than that of the gaseous state. When, on the contrary, values found for Δ are larger than they should be, the explanation is found in the hypothesis of a non-electrolytic dissociation.

The values of Δ would no longer appear as abnormal and all the discrepancies are easily explained, if Δ is expressed as:

$$\Delta = C \frac{g}{MG}$$

i.e., as a function of molar concentration. The degree of association x is expressed by the ratio between molecular weight M' calculated from cryoscopic data and the simple molecular weight:

$$\frac{M'}{M} = x.$$

on the other hand, the degree of association is approximately equal to a tenth of the molar concentration.

$$\frac{C_m}{10} = x,$$

from which we obtain:

$$\frac{M'}{M} = \frac{C_m}{10} \text{ or } M' = M \frac{C_m}{10}$$

By introducing this value of M' into the formula which gives Δ we have:

$$\Delta = C \frac{g}{M \frac{C_m}{10} G}$$

a relation which shows that Δ is inversely proportional to the molar concentration.

All the exceptions, where Δ is larger or smaller than that which corresponds to the simple molecule, are easily and directly explained, without the need of resorting to two contrary hypotheses, that of molecular association and especially that of non-electrolytic dissociation. According to this point of view all these differences are due exclusively to the molar concentration of the substance considered. For instance, in cases where Δ is smaller than the normal value, it is usually assumed that the difference is due to association, which implies an increase of molecular weight and therefore a decrease in the number of free particles. The formula above shows, on the contrary, that the molecular weight remains normal, but that the number of free particles is increased.

The interpretation on the basis of molar concentration has the advantage of employing only a single concept. In the case of liquids for which

$$x = \frac{100d}{m} = \frac{C_m}{10} = \text{approximately } 1,$$

Δ will have a normal value. In the case of compounds for which $x = \frac{C_m}{10}$ is larger than 1, Δ will have a smaller value than normal.

Finally if $x = \frac{C_m}{10}$ is smaller than 1, Δ will have a larger value than normal. This last case is that of substances for which a non-electrolytic dissociation is timidly assumed.

It should be noted that recently the existence of agglomerations of molecules in certain liquids has been ascertained by Röntgen-spectrography. If this is confirmed it will contribute experimental proof of these accumulations in liquids with high molar concentration.

The same simple and single interpretation can be applied to all the exceptional cases of capillary rise. Ramsay and Shields have accepted a temperature coefficient $K = 2.12$ for normal liquids. For associated liquids K is smaller than 2.12 and for those which are supposedly dissociated K is larger than 2.12 and attains a value of 6.21 for tristearin, as determined by P. Walden. Gabriela Chaborski (39) has modified the formula of Ramsay and Shields

by replacing the molecular volumes by their values in molar concentrations:

$$\frac{\gamma_1 \left(\frac{1000}{C_m}\right)^{\frac{2}{3}} \gamma_2 \left(\frac{1000}{C_m}\right)^{\frac{2}{3}}}{t_2 - t_1} = K.$$

This formula shows that all compounds with high molar concentration have a small temperature coefficient. Those with small molar concentration have a large temperature coefficient. There is a satisfactory parallelism between the values of K and those of molar concentration. The agreement goes as far as the value of $K = 6.21$ (tristearin) for which Walden calculated $x = 0.200$ and of which the molar concentration is 0.9.

As for special case of compounds having a degree of association smaller than 1, it seems to us that the idea of molar concentration shows clearly the insufficiency and lack of generality of the idea of molecular association, which has not succeeded in giving a satisfactory explanation of these deviations from the normal value of K . In fact, it can hardly be assumed that these substances undergo a non-electrolytic dissociation, and especially to a degree as high as would be required for tristearin, when we are dealing with pure and stable compounds which can largely be distilled without decomposition at atmospheric pressure. The idea of molar concentration, on the other hand, explains these special cases easily and without any constraint, replacing molecular association by an accumulation of simple molecules and the non-electrolytic dissociation by a depletion of simple molecules.

A NEW EXPRESSION OF AVOGADRO'S LAW

Under the concept of molar concentration there is no molecular complexity; only the number of simple molecules in unit volume varies from one compound to another. When this number exceeds a certain value the phenomenon of molecular accumulation appears. The degree of accumulation is a tenth part of molar concentration and is expressed by $x = \frac{100d}{m}$. All liquids for which the product $100d$ is greater than the molecular weight

in the gaseous state, are polymerized. It is the simplest way of separating associated compounds from non-associated ones. Molar concentration, in its turn, is caused by molecular attraction. Associated liquids, therefore, are compounds in the interior of which the molecular attraction is greater than in non-associated liquids. Associated liquids are really comparable to compressed gases, in which the diminution of volume is greater than that which corresponds to the outside pressure. In the same way that Van der Waals explained the difference in compressibility of gases by molecular attraction we wish to explain molecular association by the internal compression of molecules. Liquids with large molar concentrations are compounds subject to a large internal pressure. We thus achieve a new expression for Avogadro's law. *Equal volumes of fluids, and possibly of solids, at the same temperature and under the same external pressure, contain numbers of simple molecules proportional to the internal pressure.* Associated compounds, non-associated ones, and those considered as dissociated are compounds in which the internal pressure varies from one end of the scale of internal pressures to the other. There must be a proportionality between degrees of molecular accumulation and internal pressures of the respective compounds. This new expression of Avogadro's law is applicable to both the gaseous and the liquid state. Instead of considering acetic acid, water and other compounds as associated in the vapor state, it is simpler to assume that they contain different numbers of molecules in equal volumes. Instead of explaining differences in compressibility of vapors by the formation of associated molecules, it is more natural to attribute these differences to internal attraction and to consider the molecules as remaining simple and non-associated.

Instead of generalizing Avogadro's law, we transform it completely. Instead of modifying the nature of the molecules by their association, we modify their number in unit volume, while preserving their simplicity.

The degree of molecular accumulation comes to the support of these conceptions. In fact, we have $100d = mx$, an analogous expression to $28.9d = m$, which gives the molecular weight in

the gaseous state. This last relation can also be expressed in the general form $28.9d = mx$, applicable to associated compounds like acetic acid in the vapor state. Given that the second relation is the result of Avogadro's law, the first relation, applicable to liquids, is also a result of Avogadro's law. In the same way, the number 28.9 can be considered as the molecular weight of air, the number 100 can be considered as the molecular weight of water in the liquid state by giving the value 5.55 to its degree of molecular association. The molecular weight of a compound in the liquid state is then the product $100d$. On the other hand, as the degree of accumulation is proportional to the molar concentration and as this in turn is proportional to the internal pressure p , it follows that the second relation must take the form:

$$100d = kpm$$

To verify this result it is necessary to know the exact value of the internal pressure p . But that is lacking at present, for the values obtained vary from one method to another just as in the case of the degree of association.

EXPERIMENTS OF I. N. LONGINESCU ON THE INTERNAL PRESSURE OF A FLUID

Based on the works of Amagat, Leduc, Born and especially of Van Laar, I. N. Longinescu (40) determined that the totality of molecular forces of a fluid can be represented by the relation:

$$K \frac{m^2}{d^5}$$

In this formula K is a constant, d is the distance between the centers of two gram-molecules, and m a physical quantity called mass attraction, which plays the same rôle as does Newtonian mass in the phenomena of gravitation and as the electric charge in electrostatic forces. For various reasons the repelling forces are neglected but the results are satisfactory without being absolute. The molecules attract each other according to the 5th

power of the distance, as in the formulas of Tyrrer and Boltzmann. The essential property of the mass attraction is that it is additive.

$$m = c_1 + c_2 + c_3 + \dots\dots\dots$$

In reality the atomic constants c_1, c_2, c_3 are valence constants and one atom is capable of having several constants depending on the combination involved.

As for associated substances, agreement between calculated values and known values is obtained by assuming a certain increase of the mass attraction for the respective radicals. The degree of association in each organic series diminishes with the number of carbon atoms because the relative effect of the characteristic radical diminishes also. The advantage of the new theory is that it predicts the degree of association solely on the basis of the chemical formula.

By successive transformations the relation:

$$\frac{T_c}{d_c \sqrt{n}} = 450 \text{ is established,}$$

which is the formula of G. G. Longinescu at the critical point. This is the first time that this relation has been obtained theoretically.

The expression

$$\frac{T_c}{d_c \sqrt{n}} = \frac{6000 (c_1 + c_2 + c_3 + \dots\dots\dots)^2}{m \sqrt{n}}$$

is also established by I. N. Longinescu and is the most simplified expression of the generalized formula of G. G. Longinescu. According to I. N. Longinescu the degree of accumulation of Longinescu Chaborski is proportional to the critical temperature and inversely proportional to the number of atoms in the molecule. Thus, CH_3OH has a larger degree of accumulation and a smaller number of atoms in the molecule than $\text{C}_2\text{H}_5\text{OH}$.

The work of this young Roumanian scientist is of great importance. By introducing the concept of mass attraction he has shown that molecular association can be explained solely by the

attraction of simple molecules which varies with the fifth power of the distance.

CONCLUSION

We have now come to the end of the trail made by science during the past fifty years. The ideas of Louis Henry enriched science through the addition of a most important chapter, that of molecular association. If the explanation of this phenomenon "so strange in its nature and so important in its generality" is now based on molecular complexity, the phenomenon itself is interesting and Louis Henry deserves much credit for having called attention to it. With the aid of the concept of molar concentration we have shown that the phenomenon of molecular association is in reality only a phenomenon of simple molecular accumulation. Hence the hypotheses of molecular complexity and of non-electrolytic dissociation are both unnecessary. Molar concentration explains logically, directly and simply all the deviations observed in cryoscopic and capillary measurements. Solids and liquids are composed of simple molecules just as gases are. Associated molecules do not exist; only the concentration of simple molecules varies from one substance to another and is much greater for "associated" than for normal compounds. Avogadro's law must receive a new expression: equal volumes of fluids and possibly of solids, at the same temperature and under the same external pressure, contain numbers of simple molecules proportional to the internal pressure.

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