THE BOOK WAS DRENCHED

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ASSOCIATION THEORY OF SOLUTION

AND

INADEQUACY OF DISSOCIATION THEORY

BY

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PREFACE

The mechanism in the phenomenon of solution has been a subject of experiment and study for more than one generation. In these few pages interpretations of representative experimental observations on the subject have been done in ways not exactly recorded before. Much needful and relevant experimental verification with protracted discussion by many scientists will test their usefulness in time. It is my keenest ambition to take part in the discussions that may arise on account of this publication. The media through which a scientist may give publicity to his views are so vast that there are reasonable chances of escaping notice of some, even if I remain on the look out for all. I therefore draw attention of all scientists, who may be pleased to enlighten their fellow scientists by the publication of their own opinion, may kindly inform me also about the same.

Pointing out mistakes of any kind will be gratefully appreciated. Private criticisms and correspondences are also cordially invited.

Many figures have been taken and derived from Landolt Bronstein, Tabalen 5 Auflage 1923 published by Julius Springer, and a few quotations have also been made from 'Solubility' by Hilderbrand published by the Chemical Catalog Company, 'Physico-Chemical Tables' 2nd edition 1920 by Castell-Evans published by Charles Griffin & Co. Ltd., 'Theoritical Chemistry' by Nernst

and 'Physical Chemistry' by Walker published by Macmillan & Co. Ltd., 'Solutions' by Ostwald and 'Chemical Constitution' by Smiles published by Longmans Green & Co. Ltd., 'Chemists' Year book' by Atack published by Sherratt Hughes, 'Theories of solutions' by Arrhenius published by the Yale University Press, and Systematisk gennemforte termokemiske Undersogelsers numeriske og teoretiske Resultater, 1905, by Thomsen published by Det Kongelige Danske, Videnskabernes Selskab for which indebtedness is expressed to the authors and to the publishers for their kind permission.

It seemed suitable to write this book in English. It would have been happy if I had more control over this language. Readers may have an unavoidable additional inconvenience on account of the book being written in a language foreign to me. I shall always remain sorry for this.

I have great pleasure in expressing my best thanks to my friends who helped in many ways in this connection.

GHAZIPUR, U. P. }
INDIA, 1930. }

J. N. RAKSHIT.

CONTENTS

INTRODUCTION.

Respect for the gifted past and for the aged is religion, politeness to seniors and to fellow-scholars is good nature, but devotion to one's own subject and to truth is duty and therefore obligatory. Once one assumes a scholastic life duty towards his own subject must stand supreme. This sense of obligation and call of duty would give enough rsason to record the truth that he may discern inspite of many other influences, however powerful and dissuading they may be. Thus the assumption of a scientific life, some times has to be signalised by the production of what is practically a work done to order. It is true the choice of the subject of such a work is left to the aspirer, but one result of such work of compulsory interest is unavoidable. A book written from such sense and pressure is bound to lack the inspiration which may be expected when an author writes because the inner spirit compels him to do so. If, however, my readers will bear with patience the theme before them in the absence of such inner stimulus, may not tell too severely on them. With all respect for the mighty workers on the subject an honest and sincere attempt will be made to put forward my humble views with an expectation that the enterprise would not be wasteful.

I desire to consider what steps and what attitude should be taken with regard to the numerous publications

on the chemistry of solution that are presented before the scientists and I wish to make a few observations on what students and investigators should do for the preservation and promotion of the best interest of that great branch of science. I intend to proceed deliberately and cautiously on such lines as I find quite suitable and appropriate after mature consultation and discussion with many of my worthy friends who choose to have sympathy for my honest efforts. I will take the liberty of just indicating to my fellow scientists the broad and general lines on which it behoves them to follow, if they are solicitious of maintaining the status and rights, and the preivileges that a scientific mind and spirit should enjoy.

Scientists have always been on the side of free think-ing and the orderly progress of their dear subject on rational lines, and any biased movement should never have their countenance or support. It is only right and proper that a student of science should put forth all his efforts to maintain the full openness of mind and to adopt all measures that are conductive to the good and bene-ficent advance of the subject. In this connection I call upon all students of science who have an interest in the theory of solution to join together and make a common cause to make honest attempts to discover the truth in the way in which I desire to deal with experimental results of many illustrious past investigators. For the votaries of science the paramount consideration is the investigation of the secrets of nature. In the work of unlocking the secrets of nature, men are taught by tradition and training to bring to bear on the problems

before a mind free from bias, prejudice and preconceived ideas.

Probably many of my readers have noticed that in recent times there has grown a dangerous tendency among the young investigators and this is that of generalisation with quite insufficient data, and the worst of all this is that the unfortunate tendency is overlooked by many learned societies in publishing such communications.

Studies in the electrical properties of dilute aqueous solutions of salts, acids and bases gave results of conductivity measurements which afforded formation of several mathematical formulæ. Some of these experiments were done by very eminent scientists — by a batch of great physical chemists of the time, — such as Van't Hoff, Kohlrausch, Arrhenius, Ostwald and Nernst. These investigators being the leaders of the contemporary scientific opinion forced their views upon the dissociation of salts, acids and bases in aqueous solution, which unfortunately, however, had a further support by an agreement of some such electrical results with those of Pfeffer's Osmotic pressure determinations, as also those of the determinations of the lowering of freezing point and of elevation of boiling point of solutions.

Although electrolytes form only a fraction of the very vast general subject of solution yet basing on results obtained from them considerable calculations, and generalisations have been published which mostly are more contradictory than discordant amongst themselves. Mathematical treatment of a few sets of results have been so often used for the purpose of generalisation that any

open minded study on the subject is rendered far more
complicated than what would have been the case had these
results been published without any such misleading
generalisations so full of exceptions, and with mere state-
ment of broad experimental results.

In these few pages attempts are made to explain many
prominent facts observed during different investigations
with the assumption that the solvent and the solute
always form compounds in solution and the phenomena
of combination are attended by changes very much similar
to those of chemical change if not often indentical. This
association theory of solution has already been somewhat
conceived by Berthelot and Mendeleeff but unfortunately
during their life-time the complete establishment of theory
could not be achieved perhaps for want of sufficient ex-
perimental data.

In order to establish the complete association theory
of solution in this book all prominent phenomena are
dealt with and explained with simplicity, as far as possible,
in light of the present views.

Experiment of solutions with semi-permeable parti-
tion have been considerably developed in attempting to
explain many or rather all phenomena of solutions but
success so far achieved appears to be so insufficient that
other modes of explaining them became necessary. So
many varieties of experiments are done to tackle the
theory of solution that it would be beyond the scope of
this book to include many details of them ; besides it is
not necessary to deal with papers which could not produce
any results of sufficient importance. All important

experimental results on solutions have been explained on the assumption of the association theory of solution and thus ensuring its complete establishment.

In conclusion I take the opportunity of drawing the attention of the readers that science has gradually achieved the freedom of human mind from the domain of superstition and unquestioning belief. The history of science reveals the class between the impersonal attitude of the scientific mind and the pre-conceived notions of the age, to which belonged privileged votaries of science, who devoted themselves to win the victory for truth and reason. Facts were observed, investigated, catalogued, correlated and classified by me, and formed a bias upon which I raised a conception of association theory of solution and humbly place before such votaries of science.

CHAPTER I

SOLUBILITY

The term 'Solubility' indicates the quantity of a substance soluble with another substance at any particular condition. There is scarcely any distinction between the terms solvent and solute but, for the purpose of convenience the constituent present in larger quantity in the resultant mixture is called solvent. Sometimes the substance with lower melting point is called the solvent. The distinction between the terms solubility and miscibility is also not ordinarily made. Perhaps it would have been better to have distinguishing terms for two kinds of solutions or mixtures ;—the mechanical and the non-mechanical attended with changes of energy and property. Instances of the first type of solution yet remain to be properly established and those of the second type are all noticeable ordinarily.

Two or more gases mix in all proportions and their mixtures do not develop any appreciable simultaneous change in energy and property. But such phenomena may hardly be said to be instances of solutions.

When gases are suitably brought in contact with liquids, mixtures are formed with the occurrence of changes of energy and property, and such mixtures are easily called solutions. The formation of the law that the solubility of a gas at any given temperature in a definite volume of liquid is directly proportional to the pressure

was first done by Henry[1]. Several investigators[2] sub-sequently verified the law and established its general validity. Deviations, however, have also been observed when the gases are highly soluble.

Dalton[3] extended Henry's law by observing that when a mixture of two different gases is brought in contact with a liquid each dissolves proportionately to its partial pressure.

Determination of the solubility of a gas in a liquid may be carried out by bringing together known volumes of the gas and of the gas-free liquid, to shake them until no more diminution of gas is noticeable and then to determine the volume of the gas, by measuring the volume of gas expelled on exhausting and boiling out, by chemical process if any such suitable is applicable, or by finding out the partial pressure of a gas in its solutions. The last process[4] is useful in certain cases to give accurate results.

In the majority of cases, the solubility of a gas in a liquid decreases as the temperature rises. Irregularity in the change of solubility data of a gas in liquids with the temperature has been noticed in several cases. Existence of a minimum solubility at about 60° has been shown for hydrogen[5] and for rare gases[6] in water. Solubilities[7] of nitrogen, hydrogen and carbon-monoxide in a number of organic solvents are greater at 25° than those at 20°.

Attempts have been made to show a relationship between solubility of gases and other properties of solvent and solution. The phenomenon of the diminution of the solubility of a gas in a liquid with the rise of temperature

has been connected with its viscosity[8], the absorption coefficient for any temperature interval is approximately proportional to the corresponding diminution in the viscosity coefficient of the solvent. The maximum solubility of gases in mixed organic solvents has been compared with the occurrences[9] of minimum surface tension.

The introduction of one or more substances in a solution reduces the solubility of a gas in a liquid. A considerable number of measurements have been made to study the influence of salts and other substances on the solution of gases in water. It has also been proposed by numerous investigators that the diminished solvent power of a salt solution as compared with pure water is mainly determined, not merely by the specific nature of the dissolved gas, but by some factor involved in the relationship of the solvent and the solute. It has been suggested that the influence exerted by salts is a function of internal pressure[10] or the compressibility of the solution, that the interaction between the molecules or ions[11] of the dissolved substances cause the salts to lower the solubility, and that the lower solvent power of a salt solution as compared with water is connected with the hydration[12] of the salt.

The phenomenon of taking up of gases by solids can hardly be said to be an instance of solution, since it is influenced by the surface of the solid body, and changed by variation of temperature and pressure. Considerable studies on this subject are needed[13] from the technical stand-point, as the results on the absorption of gases by molten metals could be applied to regulate blow

holes in a casting and its subsequent other physical properties.

The mutual solubility of a pair of liquids may be divided into two classes :—(1) Soluble in all proportions and (2) soluble in limited proportions. Determination of solubility of one liquid in another when not soluble in all proportions, may be done by bringing together a large known volume of one with a small known volume of the other, shaking until saturation has been obtained and then finding the volume of the undissolved portion of the smaller liquid[14]. Several chemists[15] determined the solubility by shaking suitable quantities of two liquids together until they are mutually saturated and then analysing portions from each one of the layers. When mutual solubility is considerably influenced by variation of temperature it is often determined by the following method[16]. Weighed quantities of two liquids are put in a tube, which is then sealed and suspended in a bath of water or other suitable liquid The temperature of the bath is altered until the contents of the tube become uniform and determinations of this point are then repeatedly alternated with determinations of temperatures at which, as indicated by appearance of turbidity, the homogeneous contents of the tube begins to seperate into two layers.

There are some liquids the mutual solubilities of which vary with temperature, and which become soluble in all proportions at certain temperatures called "Critical solution temperatures". Fig. 1 represents the solubility rising with the temperature up to critical solution temperature of

phenol and water, benzoic acid and water, carbon disulphide and methyl alchol, and methylethyl ketone and water. The mutual solubility increasing with the fall of temperature up to lower critical solution temperature is represented by Fig. 2. for triethylamine and water, β-collidine and water, 1—methyl piperidine and water. The solubility curve becomes a closed ring when both upper and lower critical solution temperatures occur,—nicotine and water[17], 2—methyl piperidine and water[18] and guaicol[19] ; and such cases are represented by Fig. 3

High pressures[20] influence the mutual solubility of liquids. Introduction of a third substance generally interferes with the mutual solubility of two liquids ; and this phenomenon is utilised in everyday practice for "salting out" many organic compounds from their aqueous solutions by the introduction of a suitable quantity of salt.
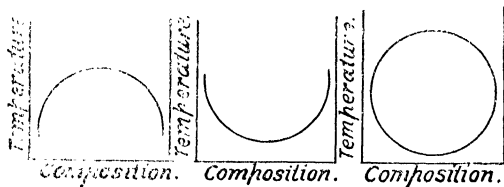

FIG. I.   FIG. 2.   FIG. 3.

It is rather difficult to know since when the solubility of solids in liquids has been studied but it is from the time of Davy[21] that the solubility of very common things in water, ordinarily appearing like in soluble, e.g., glass, clay, etc., has been established.

An accurate method of the determination of solubility has been described by Farrow[22] which may be conveniently used for special purposes. But ordinarily solubility of solids in liquids are determined in various other ways of which the following are the principal ones :—(1) preparation of a saturated solution at a fixed temperature and then determination of the amount of solute present in the known volume or weight of the solution, (2) finding out a temperature[23] at which a minute quantity of the solid in contact with its solution of known strength neither increases nor diminishes in amount, (3) in the case of sparingly soluble salts[24], comparison of electrical conductivity of the saturated solution of the substance with that of pure water, and (4) finding out potential difference[25] between the saturated solution of sparingly soluble salts, and a suitable electrode.

In the majority of cases, the solubility of solids in liquids increases as the temperature rises. Solubilities of a few substances[26] like sodium sulphate, calcium sulphate, calcium hydroxide, etc., do not vary in the same direction uniformly with the variation of temperature. Solubility of some salts in water reaches maximum or minimum with variation of temperature and these phenomena are very characteristic in the cases of calcium and barium salts of fatty acids.

Pressure[27] also slightly influences the solubility of solids in liquids. The solubility of a salt is increased by pressure if, during solution, a contraction occurs ; and conversely the solubility of a salt is decreased by pressure if an expansion occurs during solution. This subject need

more exhaustive investigation to disentangle the nature of solution.

The solubility of a solid in a liquid is considerably influenced by the introduction of a third substance in the solution. The increase or decrease of solubility in such cases entirely depends on the nature of the solute, the solvent and the third substance. The increase of solubility of iodine in potassium iodide and that of silver chloride in potassium cyanide is due to the formations of definite compounds. The solubility of salts in water is often diminished by the introduction of another salt containing one of the two radicales, negative or positive, common to the original solute ; and it is also often increased when none of the radicals of the third substance is common to any of the first salt. The solubility of a non-conducting solute in water is raised or lowered according to the respective individual nature of the solvent and two solutes. Considerable[s] studies have been on this subject but conclusions forthcoming from them are, unfortunately, unable to lead to any satisfactory generalisation.

Solubility phenomenon[29] has been stated to be encountered with substances which are closely allied chemically. The solubility of salts in water depends on the ability of the molecules or ions to surround themselves with a water mantle and thus to approximate in character to the solvent. When the molecule is capable of taking up the solvent, e.g., in the form of subsidiary balance compounds, it is then soluble even though undissociated. Thus compounds containing H_2O of crystallisation are usually soluble in water. If a connection exists between

the capacity of the solute to take up solvent and the solubility, the latter must be related to the structure of the molecule. Several applications of these considerations are dealt with briefly by Fritz Ephram, who also considered that the formation of precipitate is probably due to changes in constitution.

All the representative phenomena described in connection with the solubility of gases, liquids and solids in different liquid solvents could be explained by the assumption that in solution the solutes form compounds with solvents in proportion equal to the dilution. The nature of the solubility curve depends entirely on the stability and on other properties of such compounds under the conditions of the experiment. Assuming that all the solute molecules form compounds or associate with solvent molecules each other in proportion as their dilution considerable complication in explaining all phenomena connected with solubility could be obviated. It is advantageous to ignore the separate existence of any solvent molecule in a solution containing solute in any of its states of existence,—gas, liquid or solid. When a third substance is introduced in a binary solution a readjustment of formation of compounds takes place depending on the comparative affinity to form such associations under the conditions of the experiment. Maximum solubility indicates the limit of the ratio, for the formation of compound, of the solute and solvent molecules under the conditions of the experiment. The relationship[30] of some salts in dilute aqueous solutions has been determined by their influence on the critical solution temperature of the system phenol-

water and the results obtained could be only explained by admitting the association theory of solution and not by the dissociation theory. Combination of two solutes simultaneously with the solvent may be nicely illustrated from Van't Hoff's[31] results. He found that if a solution containing sodium sulphate and magnesium chloride in equivalent proportions is placed in a dilatometer, no anomalous expansion is observed at 5°, but if two molecules of sodium sulpuate are present for each molecule of the magnesium salt, there is a very considerable expansion if the liquid is heated above 5°, and a considerable contraction if it is cooled below this temperature. Although this experiment was not properly done yet the results show the difference of properties of the different compounds formed with solvent.

In studying the solubility of substances like sodium sulphate in water transition temperatures are noticed which have been erroneously explained by stating that a turning point in the solubility curve shows that the solid phase in the saturated solution is changing. The decrease[32] in the solubility of certain salts at higher temperatures may be explained by the assumption that the associations of solute and solvent in certain proportions are unstable beyond those conditions at which the curves cut or change directions, but some others having different molecular proportions are stable under the same circumstances.

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CHAPTER II

SPECIFIC GRAVITY OF SOLUTIONS

The terms specific gravity and density are often used in connection with solution practically conveying the same idea, although the density of a substance is defined as its mass per unit of volume and the specific gravity of a substance is defined as a ratio of the mass of a given volume to the mass of the same volume of water under the same conditions. For the purpose of this book the use of the term specific gravity would be suitable because most of the investigators on solution expressed their results in such terms. These terms are, however, interchangeable without committing much mistake on account of the fact that the unit volume of water at a standard temperature is taken as the standard unit of mass and the same volume of water at the same condition is taken as standard for the purpose of specific gravity determination.

Scientists at many laboratories have determined specific gravities of solutions by various methods and have expressed their results which widely differ in their modes of expression, the chief item being the temperature difference. Specific gravities were determined by knowing the weights of a fixed volume of solution at various temperatures and comparing these with the weight of the same volume of water at the same or different temperatures. These differences, in recording the results, are

so inconvenient that the figures of one can hardly be compared with those of the other. Although there may be ·reasons for working under conditions which varied so widely, yet it is only desirable to have such determinations done under uniform conditions, which could be fixed by international arrangement. There does not seem much difficulty in expressing specific gravity of solutions at any temperature compared with water at that very temperature. and such figures would be more helpful for theoretical considerations.

Determinations of specific gravity could be done by hydrometers, specific gravity bottles, pyknometers and plummets. Some of the observations on the subject like those recorded by Young and Forty[1] and Washburn and Mac Innes[2] should be studied by any beginner in such investigations.

Specific gravity determinations are not only made for the purpose of solving theoretical problems but for many important practical purposes, in connection with the manufacture of caustic soda, caustic potash, sugar, sulphuric acid, alcohol, etc. It is often necessary to know for commercial purposes the strength of the solute in solution ; and it is considered quite convenient to do so by the determination of specific gravities, if these figures could be converted into the actual amount of substance present in the solution. Accordingly many authors plotted their results into curves and by interpolation prepared tables by which, from the specific gravities of solutions of pure substance, strengths of these could be obtained. Such curves are, however, neither very regular nor could

be represented by simple equations on account of the fact that the molecular volumes of solute, solvent and their associations at different ratios are related by chemically allied phenomena which differ from one another.

Association theory of solution assumes that when a solute dissolves in a solvent a molecular combination takes place simultaneously as the formation of solution, in proportion same as their dilution, and when this proportion is disturbed or changed an immediate corresponding association of solvent and solute takes place uniformly. When this reaction takes place in solution along with the manifestation of disturbance of other properties, a change in volume is also accompanied, and this factor alone guides the alteration of specific gravity of solutions. The specific gravity curve of solutions is an expression of the force with which the molecules of solute and solvent are associated and ignorance of this led to the development of many equations to disentangle the theoretical nature of phenomenon of solution. It would be quite worth while to describe a few of them here, to show how the importance of the subject was felt by the earlier scientists.

Ostwald presumed that there are cases of concentrated aqueous solutions where no changes of volume on mixing occur and the specific gravity could be expressed by a complicated formula, which he said to be "somewhat obscure expression".[3]

$$\text{Specific gravity} = \frac{(m + m_0)SS_0}{mS_0 + m_0S.}$$

S = Specific gravity of the concentrated solution.

S_0 = Specific gravity of pure solvent.

m = weight of the concentrated solution.

m_0 = weight of the pure solvent.

Such equation, however, is useless as there is no solution known which does not undergo change in volume during dissolution.

Valson[4] determined a series of specific gravities of salt solutions at various dilutions and proposed a generalisation which is commonly known as "Valson's law of moduli" This paper attracted considerable attention of the scientists because quite a number of salt solutions gave agreeable results. When various salt solutions, each containing one gram equivalent per litre, are compared, it is found that the difference between the specific gravities of solutions which contain two specified metals in combination with same acid is equal, whatever be the acid, and similarly, that the difference between the specific gravities of the solutions of two salts of the same acid is independent of the nature of the metal of the salts. The specific gravity of the salt solution is obtained by adding, to a normal value, two numbers, one of which is determined by the metal and the other by the acid. These numbers are called *moduli*, Valson selected a low specific gravity solution of ammonium chloride, sp. gr. = 1.015, as the standard solution. Practically nothing has been said why water has not been chosen as standard, it appears however that water might have been a better standard, and then it would have been only necessary to alter the series of moduli by 15. The following Valson's figures are

multiplied by 1000, i.e. before using these should be divided by 1000.

Ammonium	.. 0		Barium	... 73
Potassium	.. 30		Maganese	... 37
Sodium	... 25		Zinc	... 43
Calcium	.. 26		Copper	... 42
Magnesium	... 20		Cadmium	... 61
Strontium	... 55		Lead	... 103
Chlorine	... 0		Silver	... 105
Bromine	... 34		Nitrate	... 15
Iodine	... 64		Carbonate	... 14
Sulphate	... 20		Bicarbonate	... 16

The specific gravity of a normal solution of sodium carbonate may be thus obtained :—

Standard number	1·015
Sodium	0·025
Carbonate............	0·014
Sp. gr. of N.Na$_2$CO$_3$ Solution ...	1·054

This figure very approximately agrees with that obtained by actual experiment.

Valson's numbers are referred to equivalent quantities $(H = 1)$ and the rule holds only for dilute solutions. This rule was extended to solution of any concentration by Bender[5] who divided the differences of specific gravities by the number of equivalents in a litre solution, the quotients agreed with Valson's moduli. The extended rule is illustrated by the following table, where M = number

of equivalents and Δ is the difference of specific gravities :—

M	NH$_4$Cl Sp. gr.	KCl Sp. gr.	KCl $\dfrac{\Delta}{M}$	NaCl $\dfrac{\Delta}{M}$	LiCl $\dfrac{\Delta}{M}$	$\frac{1}{2}$BaCl$_2$ $\dfrac{\Delta}{M}$
1	1·0157	1·0444	237	244	78	738
2	1·0308	1·0887	239	240	78	736
3	1·0451	1·1317	239	233	—	732
4	1·0587			234	79	
5	1·0728			232	76	

Figures under KCl$\dfrac{\Delta}{M}$, NaCl$\dfrac{\Delta}{M}$, LiCl$\dfrac{\Delta}{M}$, $\frac{1}{2}$BaCl$_2\dfrac{\Delta}{M}$ are the differences of specific gravities divided by the number of equivalents contained in a litre of solution. Moduli of Valson are obtained by $\dfrac{\Delta}{M}$, and the specific gravity of any solution containing M equivalents in a litre is obtained by adding Moduli of the salt multiplied by M, to the specific gravity of solution of sal-ammoniac which contains the same number of equivalents. Bender obtained the following *moduli* at 18°C in $\dfrac{1}{10,000}$ units :—

NH$_4$	...	O	$\frac{1}{2}$Zn	...	410
K	...	296	$\frac{1}{2}$Cd	...	606
Na	...	235	$\frac{1}{2}$Cu	...	413
Li	...	720	Ag	...	1069
$\frac{1}{2}$Ba	...	739	Cl	...	0
$\frac{1}{2}$Sr ·	...	522	Br	...	370

$\frac{1}{2}$Ca	...	282	I	...	733
$\frac{1}{2}$Mg	...	221	NO_3	...	160
			$\frac{1}{2}SO_4$	...	200

Thus the specific gravity of sodium nitrate containing 3 equivalents in a litre of solution may be calculated :—

Sp. gr. of NH_4Cl Solution (3N) ...   1·0451

| Na | ... | 0 0235 |
| NO_3 | ... | 0·0160 |

$0·0395 \times 3$ ... $= 0·1185$

Sp. gr. of 3N $NaNO_3$ ... $= 1·1636$

Groshams[6] investigated on the subject on a more rational method by regarding the phenomena on a molecular basis. He found that the difference between the molecular volume of a salt-solution decreases as the quantity of water increases in a decreasing rate. He proposed a formula,—

$$d = 1 + \frac{\alpha}{w + \beta}$$

where d = specific gravity

w = quantity of water referred to unit quantity of the salt,

α and β = Constants.

All these however may be considered useless in solving the theory of solution as it has not been set forth clearly how and on which stoichiometrical relationship they are based. Figures are also compared inspite of their obtaining under

dissimilar conditions ; gram equivalents of salts are taken and made up to one litre with varying quantities of water. The following table is prepared from their figures for normal solutions :—

Substance.	Sp. gr.	grams of salts per litre.	water per litre.	
			wt.	Mol.
KCl	1·0444	75·5	924·5	51·3
NH₄Cl	1·0157	53·5	946·5	52·6

It is thus very clear how absurd it is to compare data obtained by mixing one gram-molecule of ammonium chloride with 52·6 gram molecules of water with those obtained by mixing one gram molecule of potassium chloride with 51·3 gram molecules of water. The apparent agreement brought forward is entirely due to the taking of figures in unreasonably round numbers.

Walker[7] states "there is an undoubted regularity in the density of aqueous salt solutions. If we consider, for example, the density of normal solutions of a number of salts, we find that the difference in density between a chloride and a corresponding bromide is constant ; that the difference between a chloride and the corresponding sulphate is constant ; in short, that the difference between corresponding salts of two acids is approximately constant, no matter what the base is with which the acids are combined On the other hand we find that the difference in the densities of equivalent solutions corresponding salts of two bases are always the same and independent of the acid with which they are united. Examples are

given in the following table, where the densities are those
of normal solutions :—

	Cl	Br	I	$\frac{1}{2}SO_4$	$\cdot NO_3$
K	1·0444	1·0800	1·1135	1·0662	1·0591
NH_4	1·0157	1·0520	1·0847	1·0378	1·0307
Difference	0·0287	0·0280	0·0288	0·0284	0·0284

	K	Na	NH_4	$\frac{1}{2}Sr$	$\frac{1}{2}Ba$
NO_3	1·0591	1·0540	1·0307	1·0811	1·1028
Cl	1·0444	1·0396	1·0157	1·0667	1·0887
Difference	0·0147	0·0144	0·0150	0·0144	0·0141

From a consideration of this table, it is evident that
we can obtain the density of normal solution of any salt
by adding to the density of a salt chosen as standard two
numbers, or moduli, one of which is characteristic of the
base and the other characteristic of the acidic portion of the
salt. This regularity is known as *'Valson's Law of Moduli.'*

Text book writers attach full importance to Valson
without considering the rationality of his statement.
Using the above specific gravity figures and specific gravi-
ties of salts given in Kaye and Laby's tables, 1921, let
us calculate and consider (1) solution, (2) volumes of salts
used for the purpose, and (3) contraction occured during
the process of solution, on the following principle :—

wt. of 1000 cc. of $\dfrac{N}{1}$ KCl solution . ... = 1044·40

„   „   KCl. used for the purpose........... .. =   74·56

Gram or c.c. of water* used........ .... = 969·84 c.c.

* One gram of water taken to be one c.c. under the conditions of the
experiment.

Gram or c.c. of water used........ .... = 969·84 c.c.

Volume of KCl used $\dfrac{74\cdot56}{1\cdot99}$......... . ...• = 37·47 c c.

Sum of the volumes of solvent and solute... = 1007·31 c.c.

Actual volume of solution............... .... = 1000·00

Change in volume............................... = 7·31 c c.

contraction.

(1, Difference in quantities or volumes of water present.

	Cl.	Br.	I	½SO$_4$	NO$_3$
K	969·84	960·98	947·5	979·07	957·99
NH$_4$	962·20	954·04	939·7	971·73	950·65
Difference	7·64	6·94	7·8	7·34	7·34

	K	Na	NH$_4$
Cl	969·34	981·14	9(2·20
NO$_3$	957·99	968 99	950·65
Difference	11·35	12·15	11·55

(2) Difference in the volumes of salts used.

	Cl	Br	I	½SO$_4$	NO$_3$
K	37·47	43·11	54·61	32·80	48·14
NH$_4$	35·21	42·05	58·01	37·34	46 55
Difference	2·26	1·06	− 3·40	− 4 50	1·59

	K	Na	NH$_4$
NO$_3$	48·14	37·45	46·55
Cl	37 47	26·94	35·21
Difference	10·67	10·51	11 34

(3) Difference in contractions in solutions.

	Cl	Br.	I	$\frac{1}{2}SO_4$	NO_3
K	+7·31	+4·09	+2·11	+11·67	+6·13
NH_4	−2·60	−3·91	−2·29	− 9·07	−2·60
Difference	9·91	8·00	4·40	2·80	8·93

	K	Na	NH_4
Cl	7·31	8·08	−4·60
NO_3	6·13	6·44	−2·80
Difference	1·18	1·64	−0·20

These figures do not produce any similarity that may induce or support Valson's Law, on the contrary, they prove that for such calculations, disagreement is easily detectable if fourth place of decimals are considered. There does not seem to exist much justification in considering the figures in round numbers up to 3rd place of decimals where differences definitely perceptible on consideration of figures up to 4th place of decimals lead to some valuable conclusions.

Some of these densities of salt solutions have been wrongly applied the in light of the electrolytic dissocation of them in water by Nernst. He has introduced an irrational formula to represent the change of volume : —

$$V = \frac{M+W}{S} - \frac{W}{S_0}$$

Where   V = Change in volume in solution.

　　　　S = Density of solution.

　　　　W = Weight of water.

　　　　M = Molecular weight of the salt in grams.

　　　　S_0 = Density of the pure water at the same temperature.

This equation is erroneous in the sense that it dees not make any mention about the effects of dilution, since contraction varies quite widely when their solutions are equally diluted and on account of excluding the volumes of the salts used, which are neither the same for all salts, nor it is reasonable to presume that they occupy no volume in state of solution. The equation should be modified by the introduction of the volume of the salt used, as follows :—

$$V = \frac{M + W}{S} - \frac{W}{S_0} - \frac{M}{S_m}$$

where, S_m = the specific gravity of the salt. The changes in volume as recorded by Nernst would be then,

I	Diff.	II	Diff.	Diff. I–II
KCl = 7·31	3 22	NaCl = 8·08	1·61	− 0·77
K Br = 4·09		NaBr = 6·49		− 2·40
K I = 2·11	1 98	Na I = 5·92	0·57	− 3·81

Conclusions drawn from density figures to harmonise with dissociation theory of solution are thus exploded. These figures, however, fully support the association theory of solution,—all substances coming in solution combines with the solvent in ratio entirely dependent on dilution, forming

molecules, which differ in property from any one of those of the original solute or solvent, and from any of those associated ones that may be formed at any other dilutions. The properties of the resultant associated molecules will differ from those of the average of the components.

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CHAPTER III

CONTRACTIONS IN SOLUTION

The subject whether any change in volume occurs when a substance dissolves in a solvent has been under investigation from very early days. P. Gassend, A. Nollet, and M. Euller observed that salts dissolve in water without change in volume, but R. Watson seems to be the first to notice that a change in volume also takes place in some such cases[1]. Investigation on the subject was taken up by Dalton[2] with considerable seriousness. He found that contraction does occur in solution and confirmed the results of some of his earlier investigators, that the solid matters like the carbonates, the sulphates, the nitrates, the chlorides, the phosphates, the arsenates, the oxalates, the citrates, the acetates, etc., etc., add to the weight and the water adds to the bulk.

In those early days accurate methods of determination of volume changes in solution were neither known nor need for them much felt. When this matter was again taken up by a few other later investigators[1] it was found by Holker, Playfair, Joule, and Marignac,[1] that a certain amount of contraction does take place when substances pass into solution, and that the degree of contraction varies with different salts, and in some cases such as calcium hydrate, the volume of the solution is less than that of the water present in the solution.

Some study on the effect of dilution on the contraction which occurs during the process of solution
was made by Michel and Krafft and Kremers. They
noticed that contraction in solution of different substances
is differently influenced by change of dilution. Their
results, however, were not accurate and did not give
conclusions which could stand the test of modern accurate
methods. It would be interesting to compare the following remarks with the results that will be tabulated
hereafter. Wanklyn, Johnston and Cooper,[3] noted "the
venerable Dalton made the great discovery, about the
year 1840, that contraction occurs when salts dissolve
in water. This is strictly exemplified by lime water,
which occupies less space than the water which it
contains. On the other hand there are cases where the
volume of the solution of a mineral salt is almost as
great as the sum of the volume of the salt plus the
volume of the water in the solution. (The solution of
nitrate of silver is a case in point). There are even
instances where expansion takes place. This is exemplified
by some ammoniacal salts, where the volume of the
solution has been found to exceed the sum of the volumes
of water and dry salt." These three joint authors,[4] relying
on their inaccurate data remarked "Dalton also experimented upon sugar, but failed to notice that in that case there
is no contraction ; and it has been reserved for ourselves,
after a lapse of half a century, to record that there are
cases such as sugar where there is rigid maintenance of
volume."

Lumsden[5] found that organic compounds suffer change

in volume in passing into solution into hydrocarbons. But his assumption, that the change in volume which occurs on solution to depend only on the solute, is not reasonable. He found that the molecular solution volumes of solutes did not show any sudden change on passing through the melting point or boiling point of the solute which fact obviously leads to the conclusion that combination of solvent and solute taking place the original properties of both get altered. He has also found that change of volume in solution depends not only on the solute, but also on the solvent, and to a certain extent also on the concentration ; this subject, however, has been more thoroughly investigated afterwards.[6]

Contractions in solutions of halides of alkaline metals at certain conditions have been determined by Baxter and Wallace,[7] who tried to explain the phenomena by Richard's hypothesis of compressible atoms and by the assumption of hydration in solution. Their following figures are interesting because they have determined them with considerable accuracy, where C = change in volume during solution at 25° in c.c. per gram-molecule,—

C	C	C
LiCl $= -2\cdot03$	LiBr $= +0\cdot16$	LiI $= +3\cdot40$
NaCl $= -8\cdot48$	NaBr $= -6\cdot94$	NaI $= -4\cdot50$
KCl $= -8\cdot71$	KBr $= -7\cdot72$	KI $= -6\cdot31$
RbCl $= -9\cdot19$	RbBr $= -8\cdot70$	RbI $= -7\cdot86$
CsCl $= -1\cdot09$	CsBr $= -0\cdot00$	CsI $= +1\cdot77$

These investigators, however, did not properly consider the effects of dilution and variation of temperature.

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Besides they considered that during solution changes in the molecular volumes of the alkali halides take place, and did not much consider what happens to the molecules of the solvent in the state of solution. There are also a few other[8] investigators who determined changes in volume in solution, but their results are not quite free from experimental error and the range of variation is not wide enough to draw much attention. Favre and Valson thought that the change in volume during solution is the combined result of two opposing influences, (1) the contraction of the solvent under the influence of the solute, and (ii) an increase in the volume of the salt owing to its dissociation into its components.

The majority of the scientists, however, have attributed contraction in solution to be due to hydration of either of the salt molecules or of their ions. Tammann[9] argued that since the solutions behave in approximately the same manner when subjected to temperature and pressure, as the same bulk of water, at a higher pressure, there must be a compression of the water by the solute owing to an increase of internal pressure which he calls the *Binnendruck*.

Attempts have been made by some scientists to use this phenomenon of change of volume in generalising and correlating with other properties of solution. In the previous chapter it has already been mentioned about Valson's[10] remark that the differences between the specific gravities of solutions containing one gram-equivalent of various salts per litre of two specific metals with same acid radical are nearly identical and therefore independent of the nature of the acid, and conversely the differences

between the specific gravities of solutions of various salts of two specified acids with same metal are equal and therefore independent of the nature of the metal. He found that this law is true for dilute aqueous solutions of salts and he explained all irregularities by the assumption of volume changes during the formation of salts in solution. Bender[11] tried to extend this law to concentrated solutions. Observations of these investigators are true only empirically, and there is no reason why these results should be so. Some ordinary text-book writers[12] paid considerable attention to this Valson's law, which, however, does not appear to be rational. This subject has been critically dealt with in the previous chapter.

Traube[13] found that when a gram-molecule of a non-associated liquid is dissolved in water to form a dilute solution, a contraction amounting always to 12·2 c.c. occurs on account of an attractive force exerted by the solute on the solvent. Those substances which when prepared into a dilute solution in water are accompanied by a contraction in volume less than that of the above 12·2 cc. indicate to be associated substances according to Ramsay and Shield's method. Traube proposed that the diminution in contraction is proportional to the degree of association of the substance ; and on this assumption it is possible to ascertain the degree of association by observing its molecular contraction in aqueous solution. Thus,

$$\text{Degree of Association} = \frac{12 \cdot 2}{\text{molecular contraction in dilute aqueous solution}}.$$

Traube worked out a large number of figures by this method and also by another one by using Kopp's method

of finding out molecular volume of a liquid by the sum
of atomic volumes of the elements and radicals composing
the molecules. These results are, however, not important
in disentangling the nature of the relationship between
solvent and solute in the state of solution, because molecu-
lar contractions, as will be seen hereafter, are not constant
for the same solute and solvent at all dilutions and tempe-
ratures. In a few particular cases, under particular
conditions, Traube found that when some substances pass
into solution in water molecular contractions are approxi-
mately the same and calculations made on these limited
figures are hardly useful because the molecular contraction
is not the same if dilution or temperature is altered.

Before proceeding further, it would be better to
discuss the conception of volume in this connection. The
volume of a substance,—solid, liquid or gas, is really the
space occupied by it under a specific condition at which it
exists. An idea is to be formed if this volume indicates
any measure, or bears any relationship with the volume of
the molecules composing the mass. The volume of a
solid body may be imagined as a heap of molecules like
cubes or spheres having spaces or gaps between them. It
may have been noticed by many that if a piece of brick
which appeared to be a solid compact mass originally,
when placed under the wheels of a running railway train
is smashed and a small part is left behind on the railway
line with a more compact and denser composition than
it had before. A similar phenomenon is also observed if
any such piece of solid mass is hammered on the anvil.
Thus even a solid mass may assume a lesser volume when

subjected to a suitable pressure. It is also well known in the cases of liquids and gases that the volume is dependent on the pressure. Consequently it remains to be considered in this line of argument to what extent it is reasonable to think that the volume of a mass is an index of or proportional to the volume of its composing molecules. If the Kinetic theory is admitted the volume of a body is really a measure of the force with which the molecules composing the body is capable of bombarding the sides of the vessel in which it is kept.

Molecular volume or molar volume, as it is called now, is the volume occupied by a gram-molecule of a substance. And the figures for molar volumes are often compared as if they have something to do with the volumes of the actual molecules composing the body. Such measurements, however, do not seem to have much relationship with the actual volumes of the molecules. Molecular volume represents the pressure or the force with which the walls of the vessel containing the body is bombarded by its molecules present in a gram-molecule. Consequently, when a change in molecular volume is observed as a result of solution of a solute in a solvent it does not necessarily mean that the resultant associated or dissociated molecules, whatever they may be in solution, are correspondingly suffered in volume. It seems probable that the average space between the molecules are affected as a result of solution. This change in volume by solution may only mean that the bombarding capacity is changed without any reference to the volume of the particles themselves in their new state of solution. It is not

unreasonable that the volumes of the individual associated
or dissociated molecules and the average space between them
are simultaneously changed with the formation of solution
but the changed volume of a body, as will be shown below,
will probably have very little to do with volumes of
the molecules. The change in volume when a substance
is dissolved in a solvent would mean that the mass and
the Kinetic movements of resultant molecules are different
from those of the averages of the pure components.

Contraction in solution has been a subject of experi-
mental study by the author[14] basing on the determination
of specific gravities of solute, solvent and solution. The
volume relationship may be expressed by the following
formula—

$$C = Mv + Sv - S'v$$

where,

> C = Contraction occured during solution of a gram-
> molecule; when this figure is negative it
> means expansion.

Mv = Molecular volume of the solute

$$\frac{\text{Molecular weight.}}{\text{Specific gravity}}$$

> Sv = Volume of the solvent present in the solution
> containing one gram-molecule of solute.

> $S'v$ = Volume of the solution containing one gram-
> molecule of the solute.

By knowing the specific gravities of solute, solvent
and solution of known strength these figures may be
easily obtained for the purpose of determination of
molecular contractions in solution.

The following figures are interesting :—

(1) Molecular contraction increases with concentration.

Calcium oxide in water.

CaO. Sp. gr. = 3·08

% w/v	sp. gr. at 20°/20°C	Contraction per gram-molecule in c.c.
0·0133	1·00003	− 24·9
0·0399	1·00025	− 2·7
0·0665	1·00072	+ 22·8
0·1064	1·00142	+ 36·9
0·1330	1·00200	+ 46·4

Calcium hydroxide in water.

Ca(OH)$_2$ Sp. gr. = 2·078

0·0176	1·00003	− 25·8
0·0528	1·00025	− 3·3
0·0880	1·00072	+ 22·2
0·1408	1·00140	+ 35·2
0·1760	1·00200	+ 45·7

Carbon disulphide in benzene.

0	0·87250	—
1	0·87500	− 9·3
5	0·88920	− 3·5
10	0·90715	− 2·7
50	1·05780	− 1·0
80	1·17610	− 0·39
100	1·25770	—

Acetone in benzene.

0	0·87250	—
1	0·87102	− 5·7
5	0·86730	− 2·0
10	0·86350	− 0·8
50	0·83220	− 0·08
80	0·80855	− 0·03
100	0·79290	—

Methyl alcohol in benzene.

0	0·87250	—
1	0·87100	− 3·1
5	0·86762	− 0·75
10	0·86372	− 0·32
50	0·83210	− 0·04
80	0·80785	− 0 03
100	0·79105	—

Ethyl alcohol in benzene.

0	0·87250	—
1	0·87075	− 6·5
5	0·86682	− 2·0
10	0·86336	− 0·66
50	0·83542	+ 0·48
80	0·81455	+ 0·54
100	0·79100	—

Iso-propyl alcohol in benzene.

0	0·87250	—
1	0·87010	− 13·6
5	0·86661	− 2 9
10	0·86145	− 2·3
50	0·82776	− 1·7
80	0·80495	− 0·08
100	0·78900	—

Acetic acid in benzene.

0	0·87250	—
1	0·87230	− 13·1
5	0·87752	− 5·1
10	0·88448	− 3·8
50	0·94960	− 1·6
80	1·00810	− 0·06
100	1·05090	—

Acetic anlydride in benzene.

0	0·87250	—
1	0·87288	− 7·3
5	0·88056	− 1 7
10	0·89010	− 1·1
50	0·96816	− 1·0
80	1 03070	− 0·13
100	1·07318	—

Chloroform in benzene.

0	0·87250	—
5	0·90200	− 0·6
10	0·93178	− 0·4
50	1·17044	− 0·08
80	1·34922	− 0·09
100	1·46935	—

Nitrobenzene in benzene.

0	0 87250	—
1	0 87358	− 25·4
5	0·88675	− 4·6
10	0 90350	− 1·6
50	1·03520	+ 0·18
100	1·19654	—·

Narcotine in benzene.

0	0 87250	—
1	0·87350	− 113·2
2	0·87660	− 79·0
3	0·88048	− 56·5
4	0 88340	− 54·3
5	0·88762	− 44·0
100	1·3866	—

(2) Contraction decreases with concentration.

Calcium chloride in water.

CaCl$_2$. sp. gr. = 2·26.

1	1·00805	+ 27·5
5	1·04000	+ 26·9
10	1·07905	+ 25·8
30	1·22540	+ 21·5

Sodium iodate in water.

NaIO$_3$. sp. gr. = 3·56.

1	1·00825	+ 20·86
5	1·03990	+ 15·54
10	1·08970	+ 3·50

Silver nitrate in water.

AgNO$_3$. sp. gr. = 4·35

1	1·00850	+ 13·5
5	1·04140	+ 9·7
10	1·08255	+ 9·3
20	1·16308	+ 8·0

Toluene in benzene.

%V/v		
0	0 87250	—
1	0·87280	+5·0
5	0·87270	+1·9
10	0·87230	+1·2
50	0·86690	+1·2
80	0·86320	+0 05
100	0·86090	+0·003

Ethyl ether in Benzene.

0	0·87250	—
1	0·87150	+6·6
5	0 86635	+6·2
10	0·85890	+2·3
50	0·79930	+1·1
80	0·75115	0·48
100	0·71670	—

3) Contraction increases, reaches maximum and then decreases with increasing concentration.

Barium oxide in water.

BaO. sp. gr. = 5·10.

% w/v		
0·3875	1 00428	+45·9
1·1625	1 01325	+51·4
1·9375	1·02165	+47·9
3·1000	1·03445	+47 0

Potassium Bromate in water.

$KBrO_3$. sp. gr. $= 3\cdot271$.

1	1·00725	+5·1
2	1·01465	+6·5
3	1·02200	+6·5
4	1·02925	+6·2
5	1·03640	+5·6

(4) Contraction decreases, reaches minimum and then increases with increased concentration.

Ethyl acetate in benzene.

% v/v		
0	0·87250	—
1	0·87244	− 25·8
5	0·87200	− 29·2
10	0·87255	− 17·1
50	0·87882	− 13·4
80	0·88438	− 0·6
100	0·88820	—

(5) Contraction in solution varies with solvent.

Water in Methyl alcohol.

% w/w	sp. gr. at 0°/4°C	
	(By Ditmar and Fawsitt)	
0	0·8102	—
5	0·8240	+6·4
10	0·8375	+1·8
50	0·9287	+1·0
80	0·9723	+0·28
90	0·9843	+0·08

Water in Ethyl alcohol.
sp. gr. at 15·5°/15·5°C.
(By Hehner)

0	0·7938	—
5	0·8089	+2 4
10	0·8228	+1·9
50	0·9182	+1·0
80	0·9716	+0·36
90	0·9841	+1·1

Water in acetone.

% w/w	sp. gr. at 15°/15°C.	
	(by Squibb).	
0	0·7966	—
5	0·8113	+2·0
10	0·8260	+2 0
50	0·9247	+1·2
80	0·9755	+0·46

Water in Glycerine.
sp. gr. at 12-14°/12-14°C.
(by Lenz).

0	1·2691	—
10	1·2425	+0·044
50	1·1320	−0·072
80	1·0498	−0·071
90	1·0245	0·038

Water in acetic acid.

sp. gr. at 15°/4° C.

(By Oudemans)

0	1·0553	—
10	1·0713	+3·8
50	1·0615	+1·2
80	1·0284	+0·37
90	1·0142	+0·16

Water in nitric acid.

sp. gr. at 15°/4 °C.

(By Lunge and Ray).

0	1·5204	—
39·63	1·3754	+1·82
68·32	1·1953	+0·53
81 84	1·1065	+0·17
90·15	1·0554	+0·25

Water in sulphuric acid.

sp. gr. at 15°/4°C.

By Lunge and Ray.

0	1·8357	—
10	1·8198	+6·6
50	1·3990	−0·37
80	1·1424	−0·30
90	1·0681	−0 17

(6) Contraction in solution varies with temperature.

In these determinations densities of water at different temperatures were taken as follows :—

Temper-
ature. 10°C.   20°C.   30°C.   40°C.   50°C.   60°C.

Density
of
water. 1·00180 1·00000 0·99784 0·99489 0·99118 0·98650.

Potassium Chlorate.

KClO₃. Sp. Gr. = 2·307

20°/20°C.

% w/w.	Specific Gravity.	
1	1·00730	+ 19·4
2	1·01374	+ 13·6
3	1 02010	+ 11·0
4	1·02670	+ 10 3
5	1·03310	+ 9·1

30°/20°C.

1	1·00450	+ 14·1
2	1·01110	+ 11·3
3	1·01742	+ 10·1
4	1·02394	+ 9·4
5	1·03032	+ 8·2

40°/20°C.

1	1·00152	+10·3
2	1·00782	+ 8·1
3	1·01412	+ 8 0
4	1·02046	+ 6·9
5	1·02682	+ 6·3

50°/20°C.

2	1·00416	+ 7·9
3	1·00992	+ 5·8
4	1·01650	+ 6 3
5	1·02260	+ 5·0

Sodium Carbonate.

Na_2CO_3. Sp. gr. = 2·500.

10°/20°C.

% w/v.		
1	1·01245	+ 48·2
5	1·05308	+43·8
10	1·10500	+45·4

20°/20°C.

1	1·01030	+44·9
5	1·05038	+39·6
10	1·10100	+36·8
30	1·31800	+28·5

30°/20°C.

I	1·00820	+42·7
5	1·04718	+37·0
10	1·09718	+35·6
30	1·31325	+27·6

40°/20°C.

I	1·00455	+39·4
5	1·04320	+36·4
10	1·09274	+34·2
30	1·30708	+27·0

50°/20°C.

1	1·00062	+33·2
5	1·03880	+34·7
10	1·08778	+33·1
30	1·30125	+26·4

60°/20°C.

5	1·03500	+37·1
10	1·08350	+33·4
30	1·29632	+26·6

Sodium Sulphate.

Na_2SO_4. Sp. gr. $= 2{\cdot}670$.

10°/20°C.

% w/v.		
1	1·01140	+ 52·0
5	1·04880	+ 40·6
10	1·09840	+ 39·9

20°/20°C.

1	1·0090	+ 50·8
5	1·04672	+ 39·8
10	1·09350	+ 35·6

30°/20°C.

5	1·04350	+ 37·2
10	1·09018	+ 33·2
30	1·29920	+ 27·0

40°/20°C.

1	1·00372	+ 33·5
5	1·03940	+ 33·8
10	1·08578	+ 32·2
30	1·29340	+ 26·0

50°/20°C.

1	0·9980	+ 33·2
5	1·03523	+ 31·7
10	1·08080	+ 30·8
30	1·28780	+ 25·3

60°/20°C.

1	0·99525	+30·7
5	1·03058	+33·8
10	1·07550	+30·4
30	1·28220	+25·3

Calcium Sulphate (hydrated).

$CaSO_4.2H_2O.$ Sp. gr. $= 2·306.$

10°/20°C.

% w/w		
0·1	1·00288	+299·0
0·2	1·00330	+153·5

20°/20°C.

0·1	1·00125	+ 44·2
0·2	1·00210	+ 7·8

30°/20°C.

0·1	0·99860	+ 7 8
0·2	0·99920	+ 3·3

40°/20°C.

0·1	0·99530	− 4·9
0·2	0·99600	− 0·1

50°/20°C.

0·1	0·99160	− 4·9

Manganese Sulphate.

$MnSO_4$. Sp. gr. = 3·100.

60°/20°C.

% w/w		
20·31	1·20136	+ 32·3

Manganese Sulphate.   (Hydrated).

$MnSO_4, 4H_2O. = 2·388.$

10°/20°C.

% w/w		
1	1·00855	+16·0
5	1·03480	+13·7
10	1·06955	+ 7·3
30	1·21970	+ 3·2

20°/20°C.

1	1·00700	+25·4
5	1·03300	+12·9
10	1·06738	+11·4
30	1·21700	+ 3 0

30°/20°C.

1	1·00474	+26·8
5	1·03050	+11·9
10	1·06470	+10 7
30	1·21378	+ 2·7

40°/20°C.

1	1·00130	+11·0
5	1·02716	+10·4
10	1·06085	+ 8·5
30	1·20990	+ 1·8

50°/20°C.

1	0·99740	+ 6·2
5	1·02250	+ 6·1
10	1·05690	+ 8·1
30	1·20560	+ 1·6

60°/20°C.

30	1·20136	+ 2·2

Ferrous Sulphate (hydrated).

$FeSO_4$, $7H_2O$. Sp. gr. $= 1·899$.

10°/20°C.

% w/w		
1	1·00780	+34·3
5	1·02980	+19·8
10	1·05900	+20·4
20	1·11880	+16·3

20°/20°C.

1	1·00600	+35·1
5	1·02772	+19·6
10	1·05620	+18·0
20	1·11540	+14·3

30°/20°C.

1	1·00330	+ 19·7
5	1·02375	+ 11·7
10	1·05200	+ 13·3
20	1 11110	+ 11·7

40°/20°C.

1	0·99980	+ 5·3
5	1·02015	+ 4·5
10	1·04828	+ 10·2
20	1·10720	+ 10·1

50°/20°C.

5	1·01620	+ 3·8
10	1·04400	+ 8·9
20	1·10300	+ 9·7

60°/20°C.

5	1·01160	+ 4·3
10	1·03936	+ 8·9
20	1·09820	+ 9·4

Cadmium Sulphate (hydrated).

$CdSO_4, 8/3H_2O.$ Sp. gr.$=3·084$

10°/20°C.

% w/w		
1	1·01005	+ 37·4
10	1·03600	+ 25·7
30	1·29120	+ 18·4
50	1·56300	+ 12·0

20°/20°C.

1	1·00830	+37·8
10	1·08354	+24·3
30	1·28770	+17·6
50	1·36444	+11·7

30°/20°C.

1	1·00550	+24·4
10	1·08088	+24·3
30	1·28458	+17·5

40°/20°C.

1	1·00282	+24·3
10	1·07718	+21·9
30	1·28000	+18·1
50	1·55588	+11·6

50°/20°C.

1	0·99912	+24·1
10	1·07300	+21·0
30	1·27588	+16·3
50	1·55110	+11·1

60°/20°C.

1	0·99430	+29·0
10	1·06830	+21·9
30	1·27086	+16·3
50	1·54628	+11·4

Ethyl Alcohol

C_2H_6O. Sp. gr. at $20°/20°C = 0·79350$

20°/20°C.

% w/w		
1	0·99845	+ 4·8
10	0·98460	+ 4·8
25	0 96540	+ 5·3
50	0·92130	+ 4·1
70	0·87850	+ 2·9
90	0·83140	+ 1·7

30°/20°C.

1	0 99586	+ 3·0
10	0·98172	+ 3 4
25	0·96034	+ 4·8
50	0·91414	+ 3·4
70	0·87070	+ 2·2
90	0·82480	+ 1·1

40/°20°C.

1	0 99248	− 0·5
10	0·97800	+ 2·9
25	0·95494	+ 3·9
50	0·90660	+ 2·7
70	0 86185	+ 1·5
90	0·81592	+ 0·5

50°/20°C.

1	0·98866	− 0·6
10	0·97372	+ 3·1
25	0 94852	+ 3 2
50	0·89900	+ 2·0
70	0·85418	+ 0·9
90	0·80882	− 0·1

60°/20°C.

1	0·98440	− 0·4
10	0·96752	+ 2·1
25	0·94255	+ 2 6
50	0 89066	+ 1·3
70	0 84500	+ 0·2
90	0·79780	− 0·9

Some of the associations of solvent and solute permit isolation in a free solid state and amongst them hydrates of salts are very common. The following contractions, resulted by the combination of water with salt to form solid hydrates and concentrated solutions, are instructive to show that the molecular contractions in the solid hydrated crystals increase with hydration with diminishing rate of increase, which, however, are not always quite continuous up to solution. Or, in other words molecular contraction of a particular compound of solute and solvent is dependent on the particular ratio of the constituents and is not so much related to or bear necessarily any

similarity with any such compound of similar composition ; this is strikingly illustrated in the cases with manganese sulphate and sodium acetate, which, in contradistinction with others, produce larger contractions in solid hydrates than those in concentrated solutions.

Substance.	Sp. gr.	Mol. Vol.	Mol. Contraction.
$CuSO_4$	3·606	44·4	
, H_2O	3·2289	54·3	8·1
, $2H_2O$	2·953	67·0	13·4
, $3H_2O$	2·663	80·0	18·4
, $4H_2O$	2·645	83·9	23·5
, $5H_2O$	2·284	109·1	25·3
,$40H_2O$	1·20809		35·6
,$48H_2O$	1·1855		40·1
$MgSO_4$	2·709	44·8	
, H_2O	2·445	55·6	7·2
, $2H_2O$	2·373	67·0	13·8
, $5H_2O$	1·869	112·4	22·4
, $6H_2O$	1·751	130·8	22·0
, $7H_2O$	1·676	146·6	24·2
,$48H_2O$	1·13026		34·2
,$64H_2O$	1·0017		43·3

ZnSO$_4$	3·624	45·6	
, H$_2$O	3·280	54·7	8·9
, 2H$_2$O	3·958	66·6	15·0
, 5H$_2$O	2·208	113·7	21·9
, 6H$_2$O	2·072	130·2	23·4
, 7H$_2$O	1·965	146·8	23·8
,17·7H$_2$O	1·4740		31·3
,20H$_2$O	1·40175		32·6
NiSO$_4$	3·418	44·6	
, H$_2$O	—	65·5	6·1
, 6H$_2$O	2·931	129·9	23·6
, 7H$_2$O	1·949	144·6	26·0
, 60H$_2$O	1·14068		42·3
,100H$_2$O	1·08603		44·9
CoSO$_4$	3·444	44·7	
, H$_2$O	3·125	55·2	7·5
, 2H$_2$O	2·712	70·9	9·8
, 3H$_2$O	2·327	97·4	19·3
, 5H$_2$O	2·134	114·6	20·1
, 6H$_2$O	2·019	130·1	22·6
, 7H$_2$O	1·918	146·0	24·7
, 60H$_2$O	1·13989		41·4
,100H$_2$O	1·08554		47·5

$FeSO_4$	3·346	44·5	
, H_2O	3·047	56·2	6·3
, $2H_2O$	2·773	67·7	12·8
, $4H_2O$	2·227	100·5	16·0
, $7H_2O$	1·900	145·7	23·8
, $80H_2O$	1·10597		49·8
,$100H_2O$	1·10937		60·8
$MnSO_4$	3·282	45·0	
, H_2O	2·845	55·7	7·3
, $2H_2O$	2·526	73·6	7·4
, $3H_2O$	2·356	86 6	12·4
, $4H_2O$	2·261	98·0	18·8
, $5H_2O$	2·103	114·4	20·6
, $32H_2O$	1·16917		0·8
, $42H_2O$	1·13615		− 0·07
$NaO_2H_3C_2$	1·3970	58·69	
, $3H_2O$	1·4442	94·32	18·4
, $6·4H_2O$	(Supersaturated solution)		14·6
, $7·0H_2O$	(Supersaturated solution)		16·3
, $10·2H_2O$	1·16822		17·6

Ostwald[15] noted that the break in the solubility curve of sodium sulphate at 32-33°C is exclusively due to the change of the solid phase in solution at this temperature. But he also experimented with saturated solution of this salt in a dilatometer and observed no break at this temperature. Water of hydrated sodium sulphate is differently

bound with the salt in the solid state and in the state of aqueous solution. In the solid state the force of union is overbalanced at 32-33°C and it has been shown that in solution it does not do so even at a higher temperature than this. Ordinary text book writers often erroneously considered that at the temperature of the break in the solubility curves of salts, whose solid hydrates lose water of hydration at transition temperatures (below 100°C) when heated in the solid state would part with the same amount of water at higher temperature even in solution. The break in the solubility curve takes place on account of the fact that the associations of solvent and solute at that ratio is unstable at that temperature. The relationship between water and salt gets altered as soon as the hydrated solid substance is dissolved in water.

The relationship of water with sodium sulphate, sodium carbonate and sodium acetate in solid hydrated crystals and in solutions have been very conclusively established by dilatometric experiments. The changes in volume, when they were heated above their respective transition temperatures, in saturated solution, in ordinary solution or in dilute solution, are nominal and negligible. If, however the hydrates of these salts behave likewise in solution or in supersaturated solution as they do in the solid state there would have been corresponding changes in volume owing to the separation of water molecules from the hydrated salts.

Molecular contractions in aqueous solutions of varying dilutions of sodium sulphate and sodium carbonate are

given below to show that the state of combination is quite stable up to temperatures much above those of their transition temperatures of the solid hydrated salts. These determinations were made by observing the expansion of fixed weights of solutions by means of a dilatometer composed of a 100 cc. flask fitted with a ground hollow glass stopper with a graduated glass tube of accurately measured bore. The flask was placed in the waterbath fitted with electric stirrer. The temperature of the bath was raised at the rate of 1ºC per minute, approximately, to the boiling point of water, and when the solution in the dilatometer reached constant volume it was cooled down at the same rate. The volumes given in the following tables are the means of two readings at the same temperature of rising and falling :—

$Na_2SO_4, 50H_2O.$
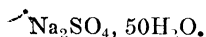
Solution $= 107 \cdot 5500$ gms.

Temp. °C	Total Volume c.c.	Mol. Contraction c.c.
15	95·26	30·3
30	95·70	29·1
40	96·11	28·5
50	96·56	28·0
60	97·05	27·8
70	97·65	27·2
80	98·23	27·4
90	98·77	28·5

Na_2SO_4, $100H_2O$.
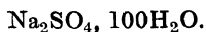
Solution = 102·3130, gms.

15	95·76	32·7
30	96·18	31 0
40	96·58	30·1
50	97·01	29·4
60	97·49	29·5
70	98·11	28·1
80	98·58	30·3
90	99·18	31·1

Na_2SO_4, $150H_2O$.
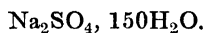
Solution = 99·6840 gms.

15	95·24	35·9
30	95·60	34·8
40	95·99	33·4
50	96·40	33·2
60	96·88	33·0
70	97·37	31·5
80	98·01	32·4
90	98·62	34·3

Na_2SO_4, $200H_2O$.
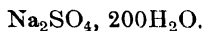
Solution = 98·8155 gms.

15	95·31	43·91
30	95·66	42·8
40	96·00	42 8

Temp.	Total Volume c.c.	Mol. Contraction c.c.
50	96·49	39·6
60	96·91	37·8
70	97·38	44·0
80	97·98	44·0
90	98·56	47·0

Na_2CO_3, $50H_2O$.

Solution = 105·9430 gms.
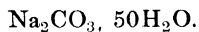
Temp.	Total Volume	Mol. Contraction
15	95·15	39·2
30	95·75	36·5
40	96·20	34·5
50	96·62	35·3
60	97·01	36·1
70	97·51	36·4
90	98·61	37·9

Na_2CO_3, $100H_2O$.

Solution = 100·8242 gms.
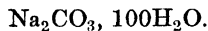
Temp.	Total Volume	Mol. Contraction
15	95·50	42·4
30	95·90	39·9
40	96·05	39·0
50	96·49	38·3
60	97·04	36·9
70	97·30	42·3
90	98·42	44·6

$$Na_2CO_3, 150H_2O.$$
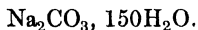
Solution = 99·2494 gms.

15	95·50	42·4
30	95·90	39·9
40	96·28	38·8
50	96·72	37·8
60	97·18	38·1
70	97·73	37·8
80	98·32	37·9
90	98·82	42·4

$$Na_2CO_3, 200H_2O.$$
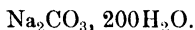
Solution = 98·0740 gms.

15	95·18	45·0
30	95·53	42·8
40	95·89	43·1
50	96·32	42·1
60	96·81	41·5
70	97·33	42·1
80	97·92	42·4
90	98·60	46·1

It is seen in these figures that although the molecular contractions are not widely changed with increase of temperature still, each solution has a minimum. If molecular contraction is an index of the force with which the associated molecules bombard the sides of the wall of its

container then it would conclude that its variation in composition is attended with corresponding some other intramolecular change.

Large number of experiments have been done by different investigators with aqueous solutions of substances to find out to what extent the solutes keep up the solvent in state of combination. They may be discussed in the following way :—

(1) Armstrong and his colaborators determined hydration by the precipitation of solutes from solution by the introduction of another solute, by the change of velocity of reactions such as inversion of cane sugar, and by the hydrolysis of methyl acetate by dilute acids with or without addition of salts. These methods presume that the molecules of the two solutes or their molecular associations with the solvent do not react with each other in any way but only remain there as physical mixtures ; the position as regards how the two solutes remain in solution does not seem to be quite clear now and more statements on them are needed. In any case the hydration figures obtained by these methods indicate more what happend when two solutes are introduced in a solvent than what is the case with a solution of any one of them. It has been argued that on the introduction of calcium chloride in a solution of sucrose, the hygroscopic property and higher solubility of salt operate, resulting the dehydration with regard to the effect of dilution on the velocity of the rate of inversion by hydrochloric acid ; but for the very same reason, however, it would follow that the hydrations would be more or less proportional to the comparative solubilities

and hygroscopic properties. The following figures may be considered in this connection :—

Molecular hydration by Armstrong	Solubility in 100gms. of water at 15° (from Comey).	Calculated molecules of water required to dissolve one molecule of substance.	Other properties.
$NH_4Cl,10H_2O$	35·2	8·4	Non-hygroscopic.
$KCl,10H_2O$	33·4	12·5	,,
$NaCl,13H_2O$	35·9	9·0	,,
$BaCl_2,19H_2O$	34·4	33·6	,,
$CaCl_2,22H_2O$	66·0	9·2	Hygroscopic.

It is quite clear from this table, when figures are properly compared, that the solubility and hygroscopic property could not allow full support to the following inference by Armstrong, "in view of the general character of the effect produced by salts, bearing in mind that easily soluble hygroscopic salts, such as calcium chloride, have far greater influence than sodium chloride, for example, it appears justifiable to regard the acceleration as concentrated effect due to the withdrawal by the dissolved substance of a certain proportion of water molecules, which thus became removed from the sphere of the action of the acid." The above table shows that the molecules of water required to dissolve one molecule of substance do not bear any proportion with the molecular hydrations found by Armstrong when figures for calcium chloride are compared.

with those of other salts. These investigators seemed to have made no clear and good case, so far, to find out any relationship amongst each other of the properties of solubility, association with solvent, deliquescence and efflorescence. The formation of high hydrate in solution of efflorescent hydrates of sodium carbonate and sodium sulphate goes much against the above presumption.

(2) The method of Jones and his coworkers based on abnormal lowering of freezing points of solutions, assumes that the solutes "must take up a part of the water forming complex compound with it, and thus removing it from the field of action so far as freezing point lowering is concerned." If molecular contraction indicates the molecular association of solvent and solute, then such phenomena of abnormal lowering of freezing points should have been observed in cases of many non-electrolytes whose solutions gave contraction in the same direction. Since contraction in solution is general to many electrolytes and non-electrolytes it is reasonable to think that their conception of association of solvent and solute may not be the only cause to abnormally affect the freezing point of aqueous solutions.

(3) The method based on the solubility of gases, liquids and solids in water, produced by the addition of electrolytes and certain non-electrolytes, considers that the solute molecules get associated with some of those of the solvents, leaving others free to behave and act as if they have nothing to do with the associated ones ; but such assumption could be considered hardly justified since when the free solvent molecules are removed from the field the

original ratio of molecular association will be disturbed and changed. The presence of some surplus of molecules of solvent is required to retain the determined ratio of hydration. It is more probable that such experiments would give the indications for only relative associations of solvent molecules with those of the two solutes present in the field than what happens when only one of them is present. When more than one solute is introduced in a solvent the molecular association of any one of them may not represent what happens when the other is absent from the field. In a solution of mixture of two substances the molecular association of any one of them with the solvent is a function of their masses present and of their comparative chemical properties with reference to the solvent. Thus the results obtained by the above method might not represent with certainty what the case is when one solute is present. Herzog and Bergen-Thun[17] found that the addition of a small quantity of sucrose to a solution of calcium chloride of about 7 N-concentration causes an increase in the boiling point which is less than that calculated by Raoult's equation. The boiling point of a more concentrated solution is, however, decreased, whilst for certain concentrations there is no effect. A depression of the boiling point is observed when lactose or mannitol is added to a 8·09 N-calcium chloride, or when dextrose is added to a 8·09 solution ; also by the addition of sucrose to solutions of lithium chloride or calcium thiocyanate. Very little departure from the calculated increase in boiling point is observed when sugar is adeed to 5·3 N-sodium chloride solution.

(4) The merit of the determination of hydration of ions by the measurement of change of concentration at electrodes caused by the transport of solvents with the ions during electrolysis has been questioned[18] ; these results could only give association of solvents with ions taking part in the electric current and might not possibly represent what the case is with others.

(5) Although there is not enough data to arrive at a definite conclusion about the method of determination of hydration by the measurement of relative migration velocities of ions, yet it may be stated that the results obtained by this method would represent only the condition of the ions taking active part in the passage of electric current and might not give any idea about those molecules or ions who do not take part in the conduction of electricity.

(6) The distribution method or the one by determination of variation of partition coefficient of a neutral indicating substance between water and an immiscible solvent with the addition of substances in water hydrations of which have to be determined, assumed that some of the water was attached to the solute as water of hydration and thereby was removed from its role of solvent, and that the lowering of solubility afforded a direct measure of this "fixed" water, and it also assumed that the indicating substance was insoluble in the hydrated salt. Sugden[19] had a few results which agreed with those determined by other methods, but there were several others which gave disagreeing results probably indicating the merit of the general assumption that the associated molecules of solvent and solute do not dissolve the indicating substance under

the conditions of the experiment. If molecular contraction is a function of association of solvent and solute, the proposal of Sugden—that the figures obtained by this distribution process as hydration of some particular salts may be regarded as fixed values for all dilutions—becomes inconsistent. The molecular contraction varies with dilution indicating the change of association of solvent and solute. The abnormal behaviour of chlorates and nitrates of potassium was explained by stating that the solution of these salts exert a greater solvent power upon acetic acid than does pure water. If this explanation is to be accepted then it may just suit the reverse one for the other salts, that is, the solutions of other salts exert a lesser solvent power upon acetic acid, and are not free from action at all.

Jablczynski[20] tried to measure the dimensions of ions in aqueous solutions from measurements of densities of solution. It is rather difficult to accept his figures on account of want of reliable proof regarding the relationship between the volumes of ions and that of unit weight of solution. Even if ions are present in solution the volume of an unit of mass of solution will also partially depend on the mean free space in which each one of them are moving by dint of kinetic movements and not so much on the volume of each individual compoment of solution.

It would be interesting to raise in this connection, how these results of determination of molecular contraction of substances in solution, reflect on the studies of other physical properties of solution which have been so long presumed to have revealed the real nature in which a

solute remains in the state of solution. The real study of combination of two components as such or in a state of solution in a third substance- the solvent- has been a very exhaustive, laborious and searching investigation during a course of long period by Kendall and his coworkers.[21] He started with the determination of viscosity, and preparation of additive compounds of organic acids and other organic substances in pairs, and subsequently prepared another set of additive compounds of aldehydes, ketones, phenols, esters with organic acids. He measured the viscosity of solutions of solids in liquids to establish a connection between the viscosity and the composition of ideal binary mixtures by experiments with mixtures of benzene and benzyl-benzonate, of benzene and ethyl benzoate, of toluene and ethyl benzoate, of toluene and benzyl-benzoate, of benzene and p-napthalene, of benzene and diphenyl, of toluene and naphthalene, and of toluene and diphenyl. Results obtained in these determinations were used in a formula which seem lacking in rationality. Freezing point determinations of aqueous solutions lead to the establishment of identity of a few interesting additive compounds of organic acids with water of hydration. Discovery of these additive compounds in aqueous solutions is quite useful in organic and inorganic chemistry but has misled the investigator and his co-workers to think that water can function both as a weak acid and weak base, and that the extent of hydration in aqueous solutions should be found to increase the increasing acidity or basicity of the solute. Among the reasons why such hypothesis cannot be accepted:two of

them seem to be very clear,— the experiments conducted
with rather a limited number of samples should not lead
to any such generalisation and even admitting there are
no mistakes in his experiments adequate proof is wanting
that those compounds which separated at freezing point
are really what were present in the solution. When a
substance is subjected to extreme cold, the kinetic
movements of the particles manifestable in terms of
thermal effects gradually decrease and ultimately come to
a point when the solute molecules, in a state of combination
with solvent molecules in proportion the same as their
dilution, become unstable, and the formation of a
stable compound sets in causing the separation of a
frozen mass. If it is presumed that the substance present
in solution could be separated by freezing, then the
molecular contractions of some of the hydrated substances
given in the foregoing pages would have been different.
If the substances were present in solution in a state of
combination with solvent the same as they could be
separated by freezing, the relationship between these
hydrated substances and the rest of the solvent molecules
present in the solution should have been properly
interpreted. It does not seem rational to think that the
two classes of molecules, combinations of solute and
solvent, and pure solvent are present as a mechanical
mixture.

Proving the identity of additive compounds between
100% sulphuric acid and the normal sulphates of the
alkali metals and the acid metal sulphates by the freezing
point determinations, Kendall postulated that the

formation of solvent—solute complex is a prerequisite to ionisation in solution. On this assumption it should be possible to predict the degree of dissociation in any given solution from (a) the stability of the complexes with respect to their components, and (b) the instability of the complexes with respect to their ionisation products. Attempts have been made to substantiate this hypothesis with figures available on influences on freezing points and osmotic preasures. Since influences on freezing points and osmotic pressures have been differently explained on the basis of association theory of solution, the support sought naturally *ultra-vires*. Kendall pointed out that the hypothesis of Milner, Ghosh and others, failed to explain the anomaly of the ionisation of strong electrolytes, because they, like the older hypothesis, ignored the role of the solvent in ionisation. Argument like this could not be more useless and irrational, since he accuses others for not taking into consideration the effect of the bulk of the solvent present in the solution whereas he himself, has used in his calculation only a portion of the molecules of the solvent which could be separated with the solute by means of application of extreme cold. There may be truth in the assumption of the formation of $Hg (NO_3)_2, 8H_2O$; $Hg (Cl_4)_2, 6H_2O$; and $HgF_2, 2H_2O$; but he failed to establish that these are the very compounds that are present in solution in an unchanged condition at all dilutions and at any other changed condition. Substantial support is needed why salts, acids, or bases should ionise at all, if solute and solvent associate why would it ionise afterwards, and why one should

take it for granted that if anything conducts electricity it is due to the presence of ions. All kinds of electrolytic dissociation theories presume that there are some molecules of solvents present in an electrolyte which do not take part in the conduction of electricity, or in other words these are non-conductors. There are salts, acids and bases, and their hydrates which conduct electricity in the pure states, and it seems irrational to think that when they are brought in a solution some molecules of each substance retain or increase their property of electrical conductivity while the remaining lose it altogether. It may be argued that there are some ions present in the solid substance which cause the conduction of electric current but the assumption of a mixture of ionised and non-ionised molecules can hardly be conceived without their mutual influence on each other, since, if one is removed the other can not exist as such and therefore it is convenient to consider that there is only one kind of molecule present. At any rate these points should have been made quite clear before the putting forward of theories by Kendall. A great deal of argument has been based on comparative results of strong acids, weak acids, strong bases, and weak bases, without properly defining these terms or clearly establishing lines of demarcation or gradation in this connection[22]. While studying the problem of weak or strong acids and bases subtances like borax[23] might have formed some part on account of their high molecular depression of freezing points. It appears, however, that weak or strong acids and bases are more or less relative terms, before applying them in such connection it is

essential to establish lines of demarcation with a number of samples which should be far more representative than what Kendall and his co-workers have done. A relationship that would take place between solvent and solute depends entirely on the chemical nature of the substances, as, (a) some are perfectly neutral and perfectly stable in solution[24], (b) the other class instantly decompose when it is attempted to dissolve them in water. As the type of the first class may be taken the alkaline salts, of the second, mercuric sulphate, nitrate and stannous chloride offer examples, as also thallic salts of all three.

Attempts have been made to correlate contractions of volume and refractive index of liquid mixtures[25] but results could not be said to be satisfactory for want of consideration of other changes of property that simultaneously attend the phenomena.

All the observed facts may be easily explained by the following assumptions. When a solute dissolves in a solvent all the molecules of both combine with each other in proportion to the dilution and when the number of solute molecules are increased or decreased corresponding association of solvent and solute takes place uniformly. All the molecules of the solvent and the solute being influenced by identical conditions it is unreasonable to presume that there should be a mixture of different kinds of combinations e. g. the ionised or the non-ionised. The process of association of the solvent and the solute is reversible at all conditions. The associated molecules of the solute and the solvent need not bear similarity to those of either component, in respect of chemical,

electrical, optical, osmotic, etc., properties.   Dilution, temperature and pressure influence the properties acquired by the associations of solvent and solute.

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CHAPTER IV.

SURFACE TENSIONS OF SOLUTIONS.

The terms surface tension and capillarity are used in chemistry apparently indicating the same property of matter. Surface tension is the property of matter acquired by virtue of the molecular attractions which tend to draw the molecules as close together as possible. Capillarity is that property of matter which causes the rise of liquids in narrow tubes, the spheriodal shape of falling drops and soap bubles, the spreading of oil on the surface of water, etc. The phenomenon of surface tension was under observation by scientists from the very early days. Quantitative measurements seem to have commenced by Jurin[1], who showed that the difference of the levels of liquids inside and outside a capillarly tube is inversely proportional to the diameter of the bore. Young[2], and finally Ramsay and Shields[3] established the following formula for ordinary practical determinations :—

$$Y = \tfrac{1}{2}rhd \text{ in grams, per centimeter.}$$

where,   Y = Surface tension, that is the force which acts normally along a line of unit length on the surface of the liquid on account of the existence of mutual attraction amongst the component particles ;

     r = radius of the tube in centimetres ;

     h = height in centimetres of the liquid column ;

     d = density of the liquid.

Besides the determination of surface tension by means of measuring the rise of liquids in the capillary tube the weight of falling drops from a tube of known bore may be measured and utilised for the purpose. Several investigators[4] used the following formula in determining surface tensions of a large number or samples :—

$$Y = \frac{W}{2 \pi r}$$

where, Y and r are the same as before ;

W = weight of the drop of the liquid.

Both these methods have been criticised by some authors and several other methods have been proposed for the determination of surface tension, but since the bulk of the data are obtained by these two methods it does not seem so much necessary to consider the latter ones here. Moreover the critcisms are not impressive enough.

The progress of the determination of surface tension of solutions was followed almost simultaneously with that of the pure liquids. The chief difficulty seemed to have been noticed by the investigators is that of a suitable general formula which would express the relationship between the surface tension of a mixture and those of its components. Formulas[5] proposed for the purpose have been found useless on account of. the ignorance of the fact that the solvent and the solute remain in solution in a state of combination so that the property of the resultant product will differ from that of either components and from that of the avarage of the components. Attempts have also been made to improve the formula by

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introducing a factor to counteract the effect of contraction or expansion on mixing ; but this also did not afford any satisfactory result. The following pairs on mixing give surface tension values which lie between those of the components :—

Benzene and toluene   Chloroform and ether
   ,,   ,, acetone   ,,   ,, acetone
Ethyl iodide and methyl iodide   ,,   ,, carbontetra
Methyl and isobutyl acetate   chloride.

The following pairs give values of surface tension on mixing which fall below those of either components[7]:—

Acetic acid and benzene   Fatty acids and water
            ,, chloroform   Carbondisulphide and
Benzene and chloroform   ethelene dichloride
   ,,   ,, carbondisulphide   ,, and ether
   ,,   ,, ethyl iodide   ,,   ,, chloroform.
   ,,   ,, ether

In the former class of mixtures the compounds formed in solution acquire a property of surface tension which is close to the average of those of the components but in the latter cases this property of the resultant product is definitely lower than those of their average and those of any one of the components.

Considerable experiments[8] have been done with mixtures at different temparatures basing on Eotvos's[9] following formula :—

$$Y (MV)^{\frac{2}{3}} = (T' - T K$$

where, $Y =$ Surface tension.

                $MV =$ Volume of a gram molecule.

$T =$ Critical temperature or the temperature at which surface energy becomes zero. (Surface energy $=$ Surface tension $\times$ area)

$T =$ the temperature of observation.

$K =$ Constant.

Results obtained by these experiments have been utilised to establish a relationship between the surface tensions of mixtures and their molecular complexity but no satisfactory generalisations were obtained because the compounds formed as a result of solution may differ in all properties from either of the components and from any other compound formed at any other dilution.

Surface tensions of binary mixtures may be classified under three main groups : —

(a) Surface tensions decrease with increasing concentration : —

HCl in water at 20°C.		Ethyl alcohol in water at 15°C.	
% HCl	$\dfrac{dyn}{cm.}$	% C_2H_6O.	$\dfrac{dyn}{cm.}$
0	73·03	0	72·2
5	72·46	10	51·2
10	72·25	20	40·6
15	71 96	30	34·7
20	71·44	40	31·2
25	70·74	50	29·1
		60	27·7
		70	26·6
		80	25·4
		90	24·1
		100	22·5

HNO$_3$ in water at 20°C.		NH$_4$OH in water at 18°C.	
$^0/_0$ HNO$_3$		$^0/_0$ NH$_4$OH	
7·25	73·10	0	73·0
9·00	72·70	5	66·5
22·00	71·48	10	63·6
37·00	68·10	15	61·3
50·00	65·43	20	59·3
70·00	59·36	25	57·7

(b) Surface tensions increase with increase concentration :—

KCl in water at 18°C.		CaCl$_2$ in water.		
$^0/_0$ KCl	$\dfrac{dyn}{cm.}$	$^0/_0$ CaCl$_2$	$\dfrac{dyn}{cm.}$ at 10°C.	$\dfrac{dyn}{cm.}$ at 30°C.
0·00	72·41	0·00	74·12	71·12
6·73	74·16	3·56	74·28	72·35
12·65	75·11	6·05	76·18	73·25
21·06	77·67	12·34	78·63	75·72
		22·57	83·83	80·38
		25·90	85·74	82·76
		31·90	89·60	86·44

KNO$_3$ in water at 18°C.		CuSO$_4$ in water		
$^0/_0$ KNO$_3$		$^0/_0$ CuSO$_4$	at 10°C.	at 30°C.
0·00	72·59	0·00	74·12	71·12
5·75	73·07	6·43	74·83	71·87
		12·33	75·66	72·72
15·19	74·46	14·69	76·10	—
21·46	75·41	25·4	—	74·12

NaOH in water at 20°C.

% NaOH		Cane sugar in water at 18°C.	
0·00	72·8	% $C_{12}H_{22}O_{11}$	
5	74·6	0·00	72·28
10	77·3	8·71	72·76
15	80·8	10·73	73·13
20	85·8	23·63	73·47
25	90·6		
30	95·1		
35	99·7		

Na_2SO_4 in water at 18°C.

% Na_2SO_4	
0·00	72·47
4·91	73·79
9·22	74·99
12·73	75·52

(c) Surface tensions increase, reach maximum, and then decrease with concentration.

H_2SO_4 in water at 18°C.

% H_2SO_4	$\dfrac{dyn}{cm.}$	% H_2SO_4	$\dfrac{dyn}{cm.}$
0·00	72·82	80·33	71·20
6·57	72 88	84·49	68·53
12·70	73·48	90·0	63·56
35·76	76·14	92·7	60·30
47·58	76·70	95·4	57·59
62·37	75·42	97·1	55·31
76·56	72·56	98·7	53·66

The variation of surface tensions with dilution of solutions of electrolytes and non-electrolytes suits well with the association theory of solution but does not do so with the dissociation theory of solution. The latter, however, practically proposes no theory regarding the existence of solvent and solute in non-electrolyte solution, and assumes in the case of electrolyte that the acidic and basic radicals composing the molecules get gradually separated with increasing dilution. The variation of surface tension with dilution is not synchronous with that of electrical conductivity. The association theory of solution assumes formation of different compounds at each dilution in molecular ratio, whose properties differ from those of the components and from any such compound formed at any other dilution. This property of a solution also differs from that of the average of the components. Increase of temperature has a decreasing effect on surface tension as may be seen in the cases of solutions of calcium chloride and copper sulphate. If surface tension is a function of attraction between the molecules of a liquid, compounds formed between the solvent and the solute in solution do not decompose with rise of temperature, and the molecules of the solute and the solvent do not undergo any change of aggregation or depolymorisation with rise of temperature then the associated molecules get further away with the rise of temperature only on account of increase of their kinetic movements. The actual increase of the distance between two particles would bear a function with the co-efficient of expansion of the substances. The increase in volume bears a relation to the distance between

the particles, and this distance influences the attraction between themselves or, in other words the surface tension. It seems desirable to find out properly if there is any relationship between co-effiicients of expansion and co-efficient of change of surface tension of solutions with variation of temperature in order to establish the validity of the above assumptions.

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CHAPTER V

VISCOSITIES OF SOLUTIONS

The existence of the property of internal friction causing some work done in the relative displacement of the particles of a solid, liquid or gas is called its viscosity. It is ordinarily measured by observing the rate of flow through capillary tubes. The phenomenon was under observation by a few earlier[1] investigators and the subject was systematically undertaken by Hagenback.[2] Quantitative determination of this property of matter is based on the assumption (1) that when a liquid moves through a tube its particles move parallel to the axis of the tube and (2) that the layer of the particles next the wall of the tube remain stationary and those in the centre move at the maximum speed. The formula worked out for the purpose is

$$\eta = \frac{\pi \, r^4 \, P \, T}{\pi \, L \, V} - \frac{V \, d}{8\pi \, L}$$

where, $\eta =$ force needed to move a layer of the substance of unit area through a distance of unit length past an adjacent layer unit distance away. This value is called the coefficient of viscosity.

$r =$ radius of the tube,

$P =$ pressure under which discharge of liquid takes place.

$T =$ time.

$L =$ length of the tube.

V = volume of the liquid discharged.

d = density of the liquid.

If all these could be measured at any temperature then the absolute viscosity of the substance is known under those conditions. Practical determinations, however, of all of them are not only difficult but are not often very accurate. Consequently it has become useful to know the result by comparing the time of flow of a given volume of the liquid with that of some standard one under the same conditions and the results may be applied to the following formula :—

$$\eta = \frac{\eta s \times T}{Ts}$$

Where η = viscosity of the liquid.

ηs =   ,,   ,,   ,,   standard liquid.

T = time of the flow of the liquid.

Ts = ,, ,, ,, ,, ,, ,, standard liquid.

Ordinarily water is taken as a standard because its viscosity has been very accurately measured at varying conditions. Mention may be made in this connection of the popular apparatus devised by Ostwald for the purpose of comporative measurements. It is a very simple instrument but gives quite accurate and considerable amount of data on this subject have been recorded by the use of this ; and such figures are called specific viscosities. Amongst the investigators who took part in the determinations of viscosity in absolute units the names of Thorpe and Roger[3] may be mentioned, a reference to their original paper gives an idea as to their satisfactory methods of determination including the apparatus used

for the purpose which undoubtedly ensures considerable accuracy.

Smiles[4] has made a very fair, collection of all representative data how intra-molecular relationship of atoms or groups of atoms in a molecule could influence the viscosity. In the case of platinum and gold, Ray[5] found the following variation of valency in different molecules. bi-, ter-, quadri-, and quinque-valent gold compounds have been prepared. Potassium dithioethelene glycol was reacted on platinic chloride under varying conditions of temperature and dilutions to yield ter-, quadri-, quinque-, sexa-, and octa-valent platinum compounds. Dilution remaining same the higher the temperature of reaction the lower the valency of platinum. Influence of temperature and other conditions at which a reaction is allowed to take place on the valency of the compounds formed has been shown in the case of action of platinic chloride on ethyl sulphide. The products of such reactions contained tri-, tetra-, and pentavalent platinum compounds.

In the case of mixtures or solutions the viscosities do not represent those of the calculated average of the compounds. Had there been no reaction between solvent and solute—the viscosity of the solution would have been an average of the componants or would bear a relationship with the average : but since they do not do so it is not unreasonable to presume that whenever a deviation from average is found a combination between solute and solvent is suspected. Thus the determination of viscosity may be employed to establish the probable existence in a solution,

of compounds which cannot be isolated by the usual laboratory processes. The converse, however, may not be true ; if a solution gives a viscosity which is more or less equal to the calculated average of the components it need not be concluded that no reaction has taken place because the resultant associated molecules of solvent and solute may assume a property, in such cases, the same as the sum of those of the pure components.

It is worthwhile discussing what the effect would be on the viscosity of the resultant product if any reaction has taken place between the solvent and the solute. Smiles (loc. cit.) has shown how atoms or groups of atoms produce varying effects on the viscosity of a substance depending on the nature how they are linked to the mole cule, and Ray's researches have given an idea how the valency of an element can change according to its state of combination with the remaining part of the molecule. When a molecule of a solute is suitably brought in contact with one or more molecules of solvent a combination takes place ; the rearrangement inside such final compound depends on the condition at which such reaction takes place as also on the ratio of the molecules of the solvent available for the purpose. It is not necessary that each time a solvent is added the property of the resultant product will be proportionately increased, because at each dilution an intramolecular rearrangement takes place. Whenever a considerable deviation is noticed from the average of the components of the mixture or from those formed at other dilutions it is concluded that a change in the constitution has taken place. But the converse,

however, need not be taken to be true. If a solution does not show any or much deviation from the average of the components it may mean that the compounds formed under such conditions have a property the same as that of the average of the components.

Viscosities of some mixtures are very interesting to show how association of solvents and solutes take place at varying conditions.

(1) Viscosity increases with increased concentration : —

Aqueous solution of sucrose. Aqueous solutions of glucose.

%w/w	Specific viscosity at 25°C.	%w/w	Specific viscosity at 25° C.
20·10	1·917	24·03	2·216
14 78	1·570	20·14	1 901
9·98	1·329	15·70	1·619
4·85	1·141	10·20	1·316
2·00	1·054	4·63	1·131
1·00	1 026	2·11	1·062
		1·00	1·027

Solution of Benzene and ethyl alcohol.

%w/w alcohol.	Temp.	Viscosity.
0	79·3	0·00317
1·30	74·8	0 00327
4·30	70·6	0 00334
6·90	69·2	0 00336
15·20	67·4	0·00341
22·4	66·9	0·00344

%w/w alchohol.	Temp.	Viscosity.
37·3	66·9	0·00361
47·4	67·1	0·00377
70·3	69·1	0·00416
88·0	72·7	0·00438
100·0	77·1	0·00442

Aqueous solutions of potassium Chloride.

Gram equivalent per litre solution.	Specific viscosity at 25°C.
4·174	1·097
3·757	1·067
8·818	1·023
1·879	0·998

(2) Viscosity decreases with increased concentration.

Aqueous solution of caesium nitrate at 25°C.

Gram equivalent per litre solution.	Viscosity.	Gram equivalent per litre solution.	Viscosity.
0·02314	0·008899	0·3173	0·008697
0·0511	0 008883	0·4520	0·008617
0·1076	0·008844	0·5652	0·008557
0·1557	0·008804		
0·2475	0·008742	0·7321	0·008480

Aqueous solution of potassium chlorate.		Aqueous solution of Rubidium chloride.	
Gram equivalent per litre solution.	Specific viscosity. at 18°C.	Gram equivalent per litre solution.	Specific viscosity. at 18°C.
0·5	0·9848	2·0	0·9405
0·2	0·9948	1·0	0·9645
0·1	0·9990	0·5	0·9790
0·05	1·0008	0·204	0·9915
		0·101	0·9969

Aqueous solution of ammonium chloride.		Aqueous solution of caesium chloride.	
Gram equivalent per litre solution.	Specific viscosity at 18°C.	Gram equivalent per litre solution	Specific Viscosity at 18°C.
4	0·9677	2·0	0·9230
2	0·9626	1·0	0·9510
1	0·9766	0·5	0·9731
0·5	0·9367	0·2	0·9883
0·2	0·9944	0·1	0·9940
0·1	0·9961		

(3) Viscosity increases, reaches maximum and then decreases with increased concentration.

Aqueous solution of nitric acid.

Gram equivalent per 100 gms. of solution.	η 0°C.	η 10°C.
53·90	0·02945	0·02324
58·10	0·03295	0·02470
61·56	0·03459	0·02604
64·30	0·03560	0·02676
66·60	0·03475	0·02584
67·82	0·03422	0·02579
71·24	0·03288	0·02465
72·85	0·03276	0·02456

Aqueous solution of Acetic Acid.

Grams of acid per 100 gms. of solution.	η 13°C.	η 20°C.	η 30°C.	η 40°C.	η 80°C.
2·1	0·01906	0·01640	0·01353	0·01128	0·00967
5·7	0·02671	0·02222	0·01752	0·011421	...
10·8	0·03105	0·02540	0·01981	0·01575	0·01287
13·0	0·03187	0·02601	0·02009	0·01595	0·01304
13·3	0·03003	0·02632	0·02069	0·01626	0·01327
17·2	0·03330	0·02694	0·02070	0·01643	0·01324
19·6	0·03354	0·02726	0·02093	0·01635	0·01327
21·6	0·03360	0·62727	0·02079	0·01640	0·01327
23·3	0·03388	0·02739	0·02091	0·01643	0·01316
23·9	0·03322	0·02701	0·02052	0·01618	0·01314
24·4	0·03355	0·02708	0·02073	0·01628	0·01287
27·7	0·03314	0·02664	0·02038	0·01603	0·01297

Aqueous solution of methyl alcohol.		Aqueous solution of ethyl alcohol.	
%	η 25°C.	%	η 25°C.
100·0	0·005525	99·20	0·0115
79·64	0·01003	78·09	0·01804
58·61	0·01399	61·85	0·02173
37·82	0 01567	45·57	0·02351
19·74	0·01378	39·65	0·02343
0·00	0·00891	20·71	0·02343
		0·00	0·00891

Aqueous solution of n-propyl alcohol.		Aqueous solution of allyl alcohol.	
%	η 25°C.	%	η 25°C.
100·00	0·01936	100·00	0·01232
73·13	0·02509	83·20	0·01537
59·38	0·02652	69·56	0·01750
28·62	0·02118	65·00	0·01790
17·40	0·01697	56·63	0·01891
0·00	0·00891	48·56	0·01892
		47·82	0·01891
		47·31	0·01867
		46·88	0·01895
		45·21	0·01888
		36·53	0·01346
		35·53	0·01834
		33·70	0·01789
		25·98	0 01632
		14·06	0·01349
		0·0	0·01891

Solution of benzene in methyl alcohol.

% w/w Benzene	Temp.	Viscosity.
0·0	63·7	0·00326
18·14	59·9	0·00347
31·60	58·2	0·00354
41·60	57·6	0·00359
50·10	57·6	0·00359
63·3	57·2	0·00361
70·4	57·3	0·00360
78·5	57·6	0·00362
90·4	59·0	0·00362
91·9	59·6	0·00357
100·0	79·3	0·00317

Solution of ethyl alcohol in carbontetra chloride.

% w/w ethyl alcohol.	Temp.	Viscosity.
0·0	75·6	0·00499
4·58	65·1	0 00518
6·71	64·6	0·00521
9·65	64·0	0·00520
20·95	63·8	0·00530
30·2	64·2	0·00530
36·6	64·8	0·00526
58·8	67·7	0·00310
73·0	70·5	0·00490
100·0	77·1	0·00442

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Solution of aniline in acetic acid.

% aniline.	$\eta 25°C$.	$\eta 50°C$.
0·0	0·0134	—
15·5	0·0729	0·0296
24·7	0·123	—
37·9	0·219	0·0565
40·9	0·214	0·0558
44·5	0·203	0·0523
49·6	0·181	—
62·3	0·118	0·0382
100·0	0·0362	0·0201

(4) Viscosity decreases, reaches minimum and then increases with increased concentration.

Aqueous solution of potassium bromide.

Gram equivalent per litre.	Specific viscosity at 18°C.
4·032	0·9599
1·973	0·9285
0·9333	0·9533
0·503	0·9738
0·01976	0·9887
0·0992	0·9924

Aqueous solution of Potassium thiocyanide.

Gram equivalent per litre.	Specific viscosity at 18°C.
3 95	1·0332
1·975	0·9499
1·005	0·9587
0·5025	0·9768
0·201	0·9915
0·1005	0·9974

Aqueous solution of ammonium nitrate.

%	$\eta 10$°C.	$\eta 30$°C.	$\eta 50$°C.
49·83	0·015898	0·011423	0·008824
37·22	0 012939	0·009239	0·007002
27·08	0·012091	0·008608	0·006298
12·19	0·012054	0·007994	0·005756
5·975	0·012559	0·007994	0·005702

A comparative examination of the above figures will show that the viscosity of a solution deviates from that of the average of its components. This deviation from the average indicates that the components, in order to lose their respective property must have lost their separate existence or identity. The components of the solution must have *combined* to acquire a property of the solution different from that of the average.

The effect of temperature on the viscosity of solution is just as it is on its other physical properties. It may be seen from the viscosities of solutions of acetic acid and

ammonium nitrate that maximum and minimum points occur at different dilutions at different temperatures. This is probably due to interference of other properties which may be maintaining a balance with this property. While viscosity is increased or decreased some property or properties like those of thermal, optical etc., are correspondingly and sisultaneously changed.

In attempting to find out reasons for the influence of temperature on the viscosity of solutions it may be considered that kinetic theory applies to the increased movement of molecules. Now does this mean that the increase of motion alone influence this property, or any other assumption is needed ? It has been primarily assumed that a layer of molecules inmediately in contact with the surface of the vessel is motionless and the central portion moves away causing a friction which is a function of viscosity. In the following diagram let the particle A represent those in contact with the wall of the tube and B_t, B_t, $B_{t'}$, and $B_{t'}$, be the positions of moving particles at temperatures t and t' respectively ; the latter temperature being the higher of the two. The diagram only shows the vertical component movements of the particle B but it may have other motions which, however, need not be considered in connection with viscosity determination as they are not likely to influence such phenomena.
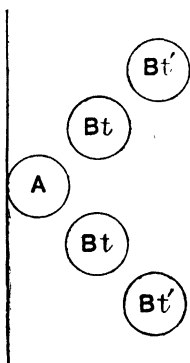
On account of movements, the particle B assumes the positions as represented in the diagram and no work is done against the attraction on the vertical line between A and B so long as B is not removed from these positions but if the moving particle is removed from B_t or B_t' positions some work is done. Less work is done in removing B_t' than that is done by removing the other, the former being further away. Thus, at the higher temperature t' less viscosity is found. If, however, the effect of increase of temperature is to increase only the vertical movements of the particles then the coefficient of expansion would have been inversely proportional to the same viscosity. But actually this is not the case which means that with the rise of temperature the molecules may suffer some movements other than that which influences the viscosity ; and probably there are some intra-molecular changes leading to the development of other properties.

The dissociation theory of solution postulates that molecules like KCI break up in water into K and CI ; that the quantity of this decomposition is influenced by dilution, and that these dissociated ions receive a coating of solvent forming outter shells which preserve them against the action of other kinds of ions present in the same field. It has also been said that the molecules of chemically similar substances undergo similar dissociation under similar conditions. Some[8] authors declared that these ions do not move alone but do so being surrounded by clusters of solvent molecules, the frictional resistance to their motion with the particles of the solvent being

thus eliminated. Keeping these views in mind a study of viscosity figures of compounds of chemically similar cations with same anions is useful in examining the validity of the dissociation theory to explain the plenomena. Compounds of potassium and sodium gave the following results on the determination of their specific viscosity at different temperatures :—

	$\frac{N}{1}$	$\frac{N}{2}$	$\frac{N}{4}$	$\frac{N}{3}$
NaOH (25°)	1·2535	1·1087	1·0560	1·0302
KOH (25°)	1·1294	1·0637	1·0313	1·0130
Difference.	0·1061	0·0450	0·0247	0·0172
NaCI (25°)	1·0973	1·0471	1·0239	1·0126
KCI (25°)	0·9872	0·9874	0·9903	0·9928
Difference.	0·1101	0·0597	0·0236	0·0198
NaNO₃(25°)	1·0655	1·0259	1·0122	1·0069
KNO₃ (25°)	0·9733	0·9822	0·9870	0·9921
Difference.	0·0902	0·0437	0·0352	0·0148
Na₂CO₃(25°)	1·2847	1·1367	1·0610	1·0310
K₂CO₃(25°)	1·1667	1·0784	1·6391	1·0192
Difference.	0·1180	0·0583	0·0219	0·0118
Na₂SO₄(25°)	1·2291	1·1058	1·0522	1·0235
K₂SO₄(25°)	1·1051	1·0486	1·0206	1·0078
Difference.	0·1240	0·0572	0·0316	0·0157

The dissociation theory also presumes that some of the molecules are dissociated and the rest undissociated, and

that these undissociated molecules interfere with the property of the components of the dissociated ones. Reasonably assuming that the influence of the undecomposed molecules of sodium and potassium compounds is the same or nearly, so under the same conditions, the difference of viscosities of solution of the same normality of hydroxides, chlorides, mitrates, carbonates and sulphates would have been equal, the effects due to anions being eliminated by subtraction. The figures, however, as shown above do not support either as they are, or, even when they are manipulated by some factor. Agreement of these differences would have secured a great support to the dissociation theory but unfortunately, the experimental results being untoward, the inadequacy of the theory gets established here also. Occurrence of maximum and minimum viscosities at suitable concentrations of some electrolytes, and of decrease and increase of viscosity with increased concentration with those of others have not also been properly explained by the dissociation theory.

The association theory of solution, however, finds no difficulty in explaining all such phenomena, because the compounds formed at different dilutions assume properties which differ from those of the components and of such compounds at any other dilution.

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CHAPTER VI

OSMOTIC PRESSURES OF SOLUTIONS.

When solid or liquid substances are brought in contact with a liquid solvent, taking precaution so that the mixing due to agitation is the minimum the process of solution will immediately commence and continue till a homogeneous mixture is obtained This process is called osmotic phenomenon and the tendency to form such solution is known as osmotic pressure. Attempts to find out the existence of such a property of solutions were first made by Abbe Nollet[1], who found that if a glass vessel be filled with alcohol, the opening covered with a bladder, and the vessel immersed in water, then the volume of the contents of the vessel gradually increases. Parrot[2] in 1815 repeated the same experiment and came to the conclusion that miscible liquids show a tendency to move on their own accord when they are just brought in contact with, but not agitated in any way, with another so as to form a homogeneous mixture ultimately. Butrochet[3] and Vierordt[4] performed some quantitative measurements and concluded that, if there be a partition of a membrane of pig's bladder between water and aqueous solution of salt the water passes through the membrane more rapidly than the salt. They also found that the difference between the rates of osmosis of pure water and of salt solution depends on the nature of the salt, on the concentration of the solution and on the nature of the

membrane or the permeable partition used for the purpose.
The influence of the nature of the partition was studied
subsequently by Thomas Graham[5] and Traube[6]. Graham
used animal membranes for all his researches and Traube
was the first investigator to use chemical membranes-
prepared in his laboratory by precipitation. He prepared
precipitation membranes of non-setting glue and tannic
acid, lead tannate, copper tannate, lead silicate, copper
silicate, tin silicate, copper ferrocyanide and copper
ferricyanide. He found that these membranes differed in
their permeability to dissolved crystalloids. Ammonium
sulphate and barium nitrate can permeate through glue-
tannic acid membrane but cannot do so through copper
ferrocyanide membrane. Traube thus proved that the
membranes were selective in such action and the phenome-
non was divided into two kinds.

When a vessel containing a solution is closely covered
with a partition placed in another vessel containing pure
solvent the pressure inside the vessel will depend on the
rate with which the solute and solvent molecules enter and
exit through the membrane. In one case the membrane is
permeable both to solvent and solute and in another case
the membrane is permeable to only one component of a
binary solution. The second one attracted considerable
interest and such membranes for a binary solution were
called *semi-permeable membranes* by Van't Hoff[7]. By the
use of semi-permeable membranes in a solution many
quantitative properties of solutions have been studied.
Absolute permeability and semi-permeability to many
solutes have been studied by several investigators and it

has been asserted that no membrane is absolutely im-
permeable to a solute. But several cases have been found
which would easily allow quantitative measurement, being
practically semipermeable. A very specific instance of the
semipermeability has been strikingly established in the
case of cane-sugar solution. Pfeffer[9] made some simple
experiments with sugar solutions by means of an apparatus
which consisted of a small cylindrical pot of porous ware
in the walls of which a precipitate of copper ferrocyanide
was allowed to form by diffusion of 0·25 per cent solution
of copper sulphate and 0·21 per cent solution of potassium
ferrocyanide from opposite sides of the cell walls. The
pot was previously carefully washed, soaked in water for
sometime, filled with solutions of copper sulphate, and
dipped upto the neck in the solution of potassium ferro-
cyanide. This pot was suitably fitted with a closed
manometer and a tube for filling the cell with the solution,
the osmotic pressure of which was to be determined.
His applications of this simple instrument for determina-
tion of osmotic pressure of sugar solution is considered
as classical experiments. Morse[10], however, lately per-
formed a most important research on cause-sugar solution
proving the true semi-permeable character of copper
ferrocyanide membrane towards such solutions; his experi-
ment extended over a period of sixty days, at the constant
temperature of 15°C, which showed that a pressure of
over 12 atmospheres was kept practically constant all
along.

A considerable number of measurements of osmotic
pressure were carried out by Pfeffer, which received very

valuable support from Van't Hoff. These experiments, however, were repeated very liberally by Morse[11], by means of an apparatus devised by himself and his co-workers. Frazer and Myrick[12] have considerably modified this apparatus and performed several experiments. Lord Berkeley and Hartley[13] used another type of apparatus. All these various investigators worked very keenly on the line directed by Pfeffer and obtained results which only confirmed the first three fundamental laws laid by him. Solutions are said to obey the following osmotic laws:

(1) Osmotic pressure is directly proportional to the concentration, provided the solution is not too strong.

(2) Osmotic pressure is directly proportional to absolute temperature.

(3) Equimolecular nonelectolyte solutions of different substances have equal osmotic pressure.

(4) Osmotic pressure is independent of the nature[14] of the solvent, provided the dissolved substance has the same molecular weight in two solvents. Some solutions, like acetic acid in benzene and acetic acid in water, indicate difference of osmotic pressure of solution of same strength on account of the solute behaving as double molecules in benzene solution.

Analogy very often helps understanding even in science, and it is therefore generally applied very conveniently but in the case of analogy between gas laws and laws of osmotic pressure of solutions, it is apt to confuse the fundamental conception of solution. Gas molecules remain in a space in a state of combination with nothing whereas the solute molecules in solution remain in a state

of combination with the solvent molecules. According to association theory of solution the solute molecules remain in a state of solution in association or in combination with solvent molecules in proportion to the same as their dilution. It would seem erroneous to think that the solute molecules move in solution in the same way as gas molecules in space. Solute molecules while moving carry with them all the molecules of the solvent with which it is combined.

It is useful to mention here that the effect of analogy in this case has furnished some valuable arguments to Van't Hoff. The celebrated · investigator dealt with the results of Pfeffer in 1887 and elucidated many important facts which might not have been discovered had he not compared Pfeffer's results with those of gases. He presumed that solute melecules in a sufficiently dilute solution behave like an "ideal gas" molecules ; in an "ideal solution" the action of the dissolved molecules upon one another, as well as their actual volume compared with that of the space they inhabit, are so small as may be considered negligible. It was thought that the osmotic pressure of solution is due either to a kinetic cause or to an attraction of the solute molecules for the solvent molecules. In both the cases the osmotic pressure should be proportional to the number of impacts of solute molecules ; and the attraction for solvent molecules should be also proportional to the number of the solute molecules. According to the dissocia-tion theory of solution, however, some of the molecules of the solute in an electrolyte break up into ions and then behave as two molecules and bombard separately on the

walls of the membrane thus causing increase of pressure than that obtainable from a non-electrolyte solution of the same molecular concentration.

It has not been properly discussed how the hypothesis of attraction, of solute molecules for solvent molecules as the cause of osmotic pressure, is affected in the case of solutions which are electrolytes and which have partly or completely dissociated molecules of the solute. Like the other hypothesis it would be also necessary to presume that each of the ions, split up from the solute molecules, acquires the same property, so far as the osmotic pressure is concerned, as an entire undissociated original molecule. And if osmotic pressure of solution is due to the attraction of solutes inside the cell for the pure solvent outside the membrane then this attraction is proportional to the number of molecules consisting of entire and broken up individual ions.

Abnormality of electrolytes has been explained by the assumption of Arrhenius's dissociation theory. Solute molecules gradually split up into ions each of which separately acquires properties pertaining to osmotic phenomena the same or similar to the original molecule. Thus it has been presumed that the osmotic pressure in an electrolyte is due to undissociated and dissociated molecules. If, there are 100 molecules of sodium chloride in one litre, of which 25 are dissociated, the osmotic pressure will be due to 75 molecules of NaCl, 25 of Na-or NaOH and 25 of—Cl or HCl, or, in other words the action will be due to 125 (= 75 + 25 + 25) molecules in the place of 100. It has thus been assumed that the osmotic

pressure of an electrolyte will be due to three different kinds of solutes, NaCl, Na, and Cl, in a salt solution. These differ widely in chemical properties from each other and the dilution of the first one does not agree with that of the other two. In view of the analogy of osmotic laws with gas laws and particularly in the application of Dalton's law for pressure of mixed gases it is reasonable to presume that each of the particles of NaCl, Na, and Cl will behave with respect to osmotic pressure as if the other two are absent in the field. Now, if the first law of osmotic pressure be applied, it would follow that the osmotic pressure due to NaCl molecules is not the same as Na or Cl, since their concentrations are not always the same but would be the same only when the dissociation is 50 per cent. Had the problem been taken up in this light and necessary calculations made the validity of such assumption would have been better or rather correctly recorded.

Osmotic pressure is assumed to be due the bombardment of solute molecules on the walls of the membrane and the abnormal osmotic pressure of electrolytes is explained by the help of Arrhenius's electrolytic dissociation theory. Each ion formed by splitting up of the solute acquires osmotic properties the same as the original undissocisted molecule ; thus, in the case of NaCl the osmotic effect in an aqueous solution will be not due to NaCl alone but due to NaCl, Na, and Cl. It is also necessary to presume in this connection that the osmotic properties of Na, and Cl are either same or similar as those of unbroken NaCl.

Bates[15] did a number of experiments on osmotic pressure of electrolytes of varying concentration and calculated the degrees of ionisation. His results have brought about considerable confusion on the relationship between the theory of osmotic pressure and that of ionic dissociation of Arrhenius. Views have been expressed that osmotic pressure is not regarded as due to bombardment of the membrane by the molecules of the solute and it is thought very doubtful whether any very large number of the solute molecules ever reach the semi-permeable membrane at all. It has also beee proposed by Schay[16] that the osmotic pressure is primarily connected with the solvent, and only secondarily with the solute. It has been concluded that the divergence from Oswald's dilution law exhibited by strong electrolytes may be due to the behaviour of either of the ions, of the non-dissociated moleeules, or of the both and that Van't Hoff's law $\pi V = RT$, (where π = Osmotic pressure) does not hold either for one or both of these molecular species. The osmotic pressures of the ions and of the non-dissociated molecules in solutions of electrolytes have been calcqlated by means of conductivity data, together with measurements of one of the collegative properties, such as lowering of the freezing point and the electromotive force of concentration cells. The osmotic pressure of the univalent ion is, in ganeral, a little below that calculated from Van't Hoff's law, whilst that of the non-dissociated molecules of a strong univalent electrolyte is considernbly groater, the deviation being about 15 per cent. in a concentration of 0·0001 N. The bivalent ions deviate much more than univalent ions,

whereas non-dissociated molecules of bivalent salts obey the law fairly closely.

Bates's[15] results are extremely interesting and useful in proving the failure of the electrolytic dissociation theory as his figures decidedly establish the uselessness of the hypothesis that the abnormality of osmotic pressure of electrolytes is explained by the assumption of occurrence of ionisation, and this fact has unfortunately been formed to be one of the pillars on which Arrhenius based his theory. Bates, however, took a round about method of explaining all these discrepancies,—instead of pointing out the uselessness of the dissociation theory on this basis he tried to meet the irregularities by the assumption that the dissociated and undissociated molecules are hydrated in solution. It is true that the solute molecules are hydrated in solution as electrolyte or non-electrolyte but not necessarily in the way in which he has taken them to be.

Mendeleeff[17] has regarded solutions as strictly definite chemical combinations which may be formed at temperatures higher than their dissociation temperatures and at ordinary temperatures, and stated that results of determinations of osmotic pressure, isotonic coefficients, vapour pressure of weak solutions, molecular depressions and electrical conductivities could not show the methods of hydration of the substance dissolved in water. Bates's results give indirect support to the above. Hydration is usually considered as a cause of increasing the osmotic pressure of the freezing point lowering of a solution largely by lessening the amount of "free" water in the

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solution but his figures show that hydration has some effect besides that due to the removal of "free" water in a solution ; his results are in harmony with the assumption that any water or solvent present in the field must be in a state of combination with solute molecules in a ratio identical with the dilution.

In a solution the solute and solvent molecules are all combined and none of them are free. The ratio of their combination is same as their dilution. If any one portion of them are removed different compounds are formed with different properties. No dissociation takes place in electrolytes as professed by advocates of electrolytic dissociation theory. Solutes have a tendency to increase their combination, if possible, with more molecules of solvent and similarly, solvents have a tendency to combine with those of the other. The solution in an osmotic cell consists of uniform compounds of solvent and solute, and each such associated molecule tries to unite with an additional molecule of solvent through the membrane ; the pure solvent in the outside also tries to combine with solute molecules. If the membrane is semipermeable the solute molecules will not pass out whereas the solvent molecules will permeate through and increase the volume or increase the pressure inside the cell in the case of restricted volume. Such pressure is called osmotic pressure.

Osmotic pressure is directly proportional to the concentration because this phenomenon depends on the number of associated molecules that come in contact per unit of area of membrane and attract the solvent

molecules from its outside. The irregularities that are observed occasionally in concentrated or dilute solutions are due to the difference in affinity for pure solvent molecules of different associated molecules of solute with solvent. Affinity for combination with another molecule of water by $CuSO_4,10H_2O$ and by $CuSO_4,11H_2O$ may not be the same. Irregularity of the first law of osmotic pressure is due to this cause and may not be due to anything else.

It has also been found in many cases that the osmotic pressure is directly proportional to the absolute temperature. It is commonly known that the rate of chemical reaction is greatly increased by the rise of temperature and it is also similarly known that the solvent or solution property is also considerably increased similarly. Osmotic pressure being an index of the affinity between solvent and solute for their combination it is quite rational that this property would also increase with temperature. The increase of osmotic pressure consequent on the rise of temperature has been ascribed by Van't Hoff to the increased kinetic movement of the solute molecules only. This, however, need not be admitted by the association theory of solution, because Van't Hoff's law indirectly presumes that the solute and solvent molecules are not in a state of combination but exist separately somewhat like a mechanical mixture in solution.

Solutions of equimolecular concentrations have almost the same osmotic pressure in the case of non-electrolytes, —the affinity of a molecule of cane sugar for a certain number of water molecules is almost the same as that of

any other non-electrolyte producing solute for the same number of molecules, so long as other conditions of the solutes are the same. In the case of electrolytes, however, such corresponding affinities differ from any non-electrolytes but will agree amongst themselves in many cases. Irregular osmotic pressure of electrolytes has been ascribed to the splitting up of the molecules into ions with dilution thereby changing the number of impacts on the walls of the vessel. The association theory of solution ignores such explanations and considers that the variation of osmotic pressure with dilution in the case of electrolytes is due to the variation of affinity of the solute molecules to combine with various number of solvent molecules.

The evil effect of analogy of osmotic laws with the gas laws reached its climax when Nernst[18] stated that the osmotic pressure is independent of the nature of the solvent. He mathematically treated the problem and concluded that by dissolving the "same quantity of iodine in a litre of water as in a litre of carbon disulphide", the osmotic pressure obtainable would be the same in two solutions Unfortunately he did not quote any experimental figures to support this view. It would have been very convenient if reliable figures were available to deal with in this connection. The association theory of solution does not consider it necessary that a fixed quantity of solute will have the same osmotic pressure when dissolved in different solvents to produce solutions of the same volume. Osmotic pressure in each case will depend on the affinity of the associated molecules inside the cell, for the

pure solvent kept outside. In any case, however, Nernst's above statement needs modification as the concentration will be different if a definite weight of the substance be dissolved in a litre of each of the solvent since the contractions in solution are not the same under the circumstances. Besides, if the osmostic pressure becomes independent of the nature of the solvent it becomes inconsistent with other properties of a solution, -electrical conductivity[19], viscosity, specific rotation etc., are dependent on the nature of the solvent. Walden obtained the following variation in molecular conductivities of extremely dilute solutions of tetraethyl ammonium iodide for 23 different solvents at 25°C.

Acetone	225	Nitromethane	120
Acetonitrile	200	Methyl rhodanide	96
Acetyl chloride	172	Ethyl rhodanide	84·5
Propionitrile	165	Acetyl acetone	82
Ethyl nitrate	138	Acetic acid hydride	76
Epichlorohydrine	66·8	Benzylcyanide	36
Ethyl alcohol	60	Asymmetric ethyl	
Benzenitrile	56·5	sulphate	26·4
Furfurol	56	Ethyl cyanacetate	28·2
Diethyl sulphate	43	Salicylaldelyde	25
Nitrobenzole	40	Anisaldehyde	16·5
Methyl Alcohol	124	Water	112·5

Instances of the influence of solvents on the rotation of optically active compounds have been worked out by

Patterson[20] and specific rotations of oil of turpentine and ethyl tartrate are very interesting in this connection.

Considerable confusion has been introduced by the topics of ideal and non-ideal solutions in connection with osmotic phenomenon of solutions and it seems worth while discouraging any such analogy with gas laws because no advantage could be gained now. Bancroft[21] has shown that even when the solutions are very dilute gas laws are not nearly obeyed, if marked heat effects accompany the admixture. When heat is evolved on mixing, the osmotic pressure is considerably greater than that calculated on the basis of the gas laws ; when heat is absorbed, the osmotic pressure is considerably less than that calculated as before. No one has been able to explain this statement on the basis of the bombardment view of osmotic pressure, the bombardment being due to the molecules of the solute.

Several theories have been put forward to explain the osmotic phenomenon, merits and demerits of which have been carefully discussed by A. F. Findlay[22] and it is not necessary to repeat them here. Evidences[23] seem to be more in favour of the theory which directly, indirectly, or partially accepts the association of the solvent and the solute in a solution.

Attempts have been made to establish relationship[24] between osmotic pressure, reduction of the freezing point and electrical conductivity ; and it has been found that the amount of dissociation of different salts into their ions in dilute solutions when calculated from these different methods, did not always compare well. The numbers

obtained by these methods are in fair agreement in the cases of potassium and ammonium chlorides, calcium nitrate and potassium ferrocyanide. With magnesium sulphate, and the chlorides of calcium, lithium, strontium, and magnesium, the agreement is by far no means a satis· factory one. Thus these results do not help the dissociation theory in any way and the phenomena seem to have nothing to do with the theory ; on the contrary, however, all these facts may be easily explained by the association theory of solution.

For the purpose of comparison of osmotic properties of substances, data with solutions in molecular ratios of solvent and solute are not available. Unfortunately, investigators determined osmotic pressures of solutions, containing varying weights of solutes in a litre of solution. Such figures are not, however, very useful in a comparative study in establishing relationship between the solvent and the solute. But, if the osmotic pressures of aqueous solutions of potassium nitrate and cane sugar (Landolt-page 1422) be compared, it will be of interest to find that while the sugar solution increases in osmotic pressure proportionately with increased concentration, that of potassium nitrate behave in an entirely different way. Column 4 of the following table shows the difference of osmotic pressure of the two substances of same molecular dilution. Admitting the accuracy of determinations, the difference would have been highest at the highest dilution, according to the dissociation theory of breaking up of $KNO_3 = K + NO_3$. Thus the figures do not support the hypothesis very much.

1 Molecules per litre.	2 KNO$_3$ (Pressure in atmospheres)	3 Sugar (Pressure in atmospheres)	4 Difference of cols. 2 and 3.
0·0125	0·466	0·3176	+0·1484
0·0250	0·890	0·6350	+0·2550
0·0500	1·560	1·2700	+0·2900
0·1000	2·390	2·5400	−0·1500
0·1330	2·870	3·3790	−0·5090
0·2000	4·500	5·0820	−0·5820

Association theory of solution would explain the phenomenon in its own way as being due to the compounds formed with potassium nitrate at those dilutions, which have their affinities to form compounds with larger number of molecules of water and such affinities are partially expressed in terms of those pressures.

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CHAPTER VII

THERMAL EFFECTS OF SOLUTIONS

Studies in the disturbance of thermal equilibrium by the solution of a substance in a solvent have been thought to be more carefully applied than that is ordinarily done in disentangling theories of solutions. Being carried away by the electrolytic dissociation theory of solution the most valuable results of Thomson have not been sufficiently treated by the ordinary text-book writers to impress on juvenile minds the correct nature of solutions as could be deduced from the classical researches of the celebrated Danish Chemist. In a short treatise like this it would not be possible to discuss his entire results but it is desired to take up enough data which would be fairly helpful in explaining the following phenomena in the light of the association theory of solution : —

(1) Heats of solutions and dilutions or hydrations.

(2) Speciffic heats of solutions.

(3) Freezing points of solutions.

(4) Vapour tensions and boiling points of solutions.

As early as 1840, Hess[1] declared the law of thermo-neutrality for all chemical processes by clearly stating

that when the same chemical change takes place between definite amounts of substances under the same conditions, the same amount of heat is always given out, provided that the ultimate products are the same; and this law gradually helped a good deal in the formation of the "*Law of Conservation of Energy.*" In studying thermal effects of solutions the law will always be applied and it will be necessary to remember that the differences of energies between two identical conditions of the system must be the same, irrespective of the method by which the system is transferred from one condition to the other.

In measuring the thermal effects of solution, calories (cal.) are used as units but sometimes larger units are used, $K = 100$ calories and $Cal. = 1000$ calories. The last one is now considerably used. The terms used in this connection may be defined as below :—

(1) *Heat of solution* of a substance is the thermal effect produced by dissolving one gram molecule of a substance in a given number of molecules of solvent

(2) *Heat of dilution* of a solution is the thermal effect produced when the quantity of solution containing one grammolecule of a solute is further diluted by a given number of molecules of solvent.

(3) *Heat of hydration* is the thermal effect produced by the combination of one grammolecule of substance with a definite number of molecules of water to form a definite hydrate.

Thomson determined heats of solutions of several substances from which the following figures[2] are taken, which are true at about 18°C.

Heats of Solution.

(a) Compounds of non-metals.

1. Gases.

Substance. (Gaseous).	Molecular formula.	Molecules of water in the solution.	Heats of solution in colories of one gram molecule of the substances.
Hydrogen chloride	HCl	300	17,315
Hydrogen Bromide	HBr	400	19,940
Hydrogen Iodide	HI	500	19,210
Ammonia	NH_3	200	8,430
Sulphur Dioxide	SO_2	250	7,700
Carbon Dioxide	CO_2	1500	5,880

2. Liquids.

(Liquid)			
Sulphur Dioxide	SO_2	300	1,500
Sulphuric Acid	H_2SO_4	1600	17,850
Sulphuric Acid hydrate	H_2SO_4,H_2O	1600	11,470
Nitric Acid	HNO_3	300	7,480
Phosphoric Acid	H_3PO_4	200	5,350
Phosphorous Acid	H_3PO_3	120	2,940
Hypophosphorous Acid	H_3PO_2	200	2,140
Formic Acid	CH_2O_2	200	150
Acetic Acid	$C_2H_4O_2$	200	375·

3. Solids.

(Solid)	Molecular formula.	Molecules of water in the solution.	Heats of solution in calories of one gram molocule of the substances.
Phosphoric Acid	H_3PO_4	120	+ 2,690
Phosphorous Acid	H_3PO_3	120	− 130
Hypophosphorous Acid.	H_3PO_2	200	− 170
Boracic Acid	$B_2O_3,3H_2O$	800	− 10,790
Ammonium Chloride	NH_4Cl	200	− 3,880
Ammonium Bromide	NH_4Br	200	− 4,380
Ammonium Iodine	NH_4I	200	− 3,550
Ammonium Sulphate	$(NH_4)_2SO_4$	400	− 2,370
Ammonium Nitrate	NH_4NO_3	200	− 6,320
Ammonium Hydrogen Sulphate	$(NH_4)HSO_4$	200	− 20
Oxalic Acid	$C_2H_2O_4$	300	− 2,260
Oxalic Acid (cryst)	$C_2H_2O_4,2H_2O$	530	− 8,590
Citric Acid	$C_6H_8O_7$	600	− 3,600
	$C_6H_8O_7,H_2O$	400	− 6,430

(b) Compounds of the metals ; bases and salts.

KCl	200	− 4,440
KBr	200	− 5,080
KI	200	− 5,110
$KClO_3$	400	− 10,040
$KBrO_3$	200	− 9,760

(Solid)	Molecular formula.	Molecules of water in the solution.	Heats of solution in calories of one gram molecule of the substances.
	KIO_3	500	− 6,780
	KNO_3	200	− 8 520
	K_2CO_3	400	+ 6,490
	KOH	250	+13,290
	$NaCl$	100	− 1,180
	$NaBr$	200	− 190
	NaI	200	+ 1,220
	$NaNO_3$	200	− 5,030
	Na_2CO_3	400	+ 5,640
	$NaOH$	200	+ 9,940
	$LiCl$	230	+ 8,440
	$LiNO_3$	100	+ 300
	$BaCl_2$	400	+ 2,070
	$BaBr_2$	400	+ 4,980
	$BaI_2, 7H_2O$	500	− 6,850
	$Ba(NO_3)_2$	400	− 9,400
	BaO	...	+34,520
	$Ba(OH)_2$	...	+12,260
	$Ba(OH)_2, 8H_2O$	400	−15,210
	$SrCl_2$	400	+11,140
	$SrBr_2$	400	+16,110
	$Sr(NO_3)_2$	400	− 4,620
	SrO	. .	+29,340
	$Sr(OH)_2$	...	+11,640
	$Sr(OH)_2, 4H_2O$	...	−14,640
	$CaCl_2$	300	+17,410

(Solid)	Molecular formula.	Molecules of water in the solution.	Heats of solution in calories of one gram molecule of the substances.
	$CaBr_2$	400	+ 24,510
	CaI_2	400	+ 27,690
	$Ca(NO_3)_2$	400	+ 3,950
	CaO	2,500	+ 18,330
	$Ca(OH)_2$	2,500	+ 2,790
	$MgCl_2$	800	+ 35,920
	$MgSO_4$	400	+ 20,280
	Al_2Cl_6	2,500	+ 153,690
	$ZnCl_2$	300	15,630
	$ZnBr_2$	400	15,030
	ZnI_2	400	11,310
	$Zn(NO_3)_2, 6H_2O$	400	− 5,840
	$ZnSO_4$	400	+ 18,430
	$CdCl_2$	400	+ 3,010
	$CdBr_2$	400	+ 440
	CdI_2	400	− 960
	$Cd(NO_3)_2 H_2O$	400	+ 4,180
	$CdSO_4$	400	+ 6,050
	$MnCl_2$	350	+ 16,010
	$Mn(NO_3)_2 6H_2O$	400	− 6,150
	$MnSO_4$	400	+ 13,790
	$FeCl_2$	350	+ 17,200
	Fe_2Cl_6	2,000	+ 63,360
	$CoCl_2$	400	+ 18,340
	$NiCl_2$	400	+ 19,170
	$CuCl_2$	600	+ 11,080

(Solid)	Molecular formula.	Molecules of water in the solution.	Heats of solution in calories of one gram molecule of the substances.
	$CuSO_4$	400	$+15,800$
	Tl_2Cl_2	9,000	$-20,2000$
	$Tl_2(NO_3)_2$	600	$-19,940$
	Tl_2SO_4	1,600	$-8,280$
	Tl_2O	570	$-3,080$
	$Tl_2(OH)_2$	470	$-6,310$
	$PbCl_2$	1,800	$-6,800$
	$PbBr_2$	2,500	$-10,040$
	$Pb(NO_3)_2$	400	$-7,610$
	$SnCl_2$	300	300
	$SnCl_4$	300	$29,920$
	$HgCl_2$	300	$-3,300$
	$Ag_2(NO_3)_2$	400	$-10,880$
	Ag_2SO_4	1,400	$-4,480$
	$AuCl_3$	900	$4,450$
	$AuBr_3$	2,000	$-3,760$

From such results Thomsen concluded along with others that : —

(a) The heats of absorption of gaseous substances are always positive, on account of the gases changing their states to liquids in addition to any, often occuring secondary reactions.

(b) The heats of solution of liquids are positive.

(c) The heats of solution of solids very widely depending on the nature and compsition of each.

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It has been said[3] that the molecules of the solvent and the solute form a homogeneous solution where the molecules acquire an uniform motion ; but such an equalisation of molecular motions, retaining the acquired momentum, must result in a development of heat.

There seems to be no sufficient reason why heat should be produced as a result of the equalisation of molecular velocities since no work is done in any way according to this assumption. Only two energies are added to form an average. On the contrary it could be concluded that the evolution of heat is an indication that the solvent and the solute react to produce solution, which naturally forms a support of the association theory of solution.

Thomsen[4] showed some regularity in heats of solutions of halide salts but that is not very reasonable since figures of different dilutions have been used for the purpose of comparison and such salts produce heats of dilution.

Thomsen also tried to show the dependence of the heat of solution on the molecular weight of the substance but no mention has been made about heats of ammonium salts (AmCl = - 3880 ;   AmBr = - 4,380 ;   AmI = - 3,550), which go against any such ganeralisation.

Heats of solution of sparingly soluble or insoluble substances have been determined by Thomsen[5] by an ingenious method. He found that the heats of neutralisation of equivalent quantities of aqueous solutions of bases of alkalies, alkaline earths and other oxides were constant for the same acid, but there was very much bigger thermal effect when the salt formed is partly or

wholly precipitated from the solution simultaneously. He presumed that the degree of solubility of the compound would not influence the true heat of neutralisation and that the increased evolution of heat is due to the heat of precipitation of the substance. His results of a number of specially devised experiments are given below :—

Substance,	Heats of solution
$PbCl_2$	− 6,800 c
$PbBr_2$	− 10,040
PbI_2	− 15,970
$TlCl$	− 10,100
$TlBr$	− 13,750
TlI	− 17,850
$AgCl$	− 15,740
$AgBr$	− 20,100
AgI	− 26,410

The figures for heats of solution have been utilised for the estimation of heat of hydration of salts. The difference between the heats of solution of the anhydrous salt and hydrated salt gave the heat of hydration. The heat of hydration may be due partly to the affinity of the salt for water and partly to the latent heat of water, since water molecules change their state of liquid aggregation to become the constituents of a solid body. The heat of hydration varies with the nature of the salt and with the number of molecules of combined water. The following figures of heats of hydration of hydrated crystals are due to Thomsen and refer to a temperature of about 18⁰C.

Heats of total Hydration.

$MgCl_2, 6H_2O$	32,970 c	$BaBr_2, 2H_2O$	9,110 c
$SrBr_2, 6H_2O$	23,330	$BaCl_2, 2H_2O$	7,000
$SrCl_2, 6H_2O$	18,640	$CuCl_2, 2H_2O$	6,670
$CaCl_2, 6H_2O$	21,750	$AuCl_3, 2H_2O$	6,140
$CoCl_2, 6H_2O$	21,190	$SnCl_2, 2H_2O$	5,720
$NiCl_2, 6H_2O$	20,330	$NaI, 2H_2O$	5,230
$Na_2PtCl_6, 6H_2O$	10,170	$NaBr.2H_2O$	4,520
$Na_2PtBr_6, 6H_2O$	18,540	$CdCl_2, 2H_2O$	5,290
$K_2Mg(SO_4)_2 6H_2O$	20,620	$Na_2HPO_4, 12H_2O$	28,470
$K_2Zn(SO_4)_2, 6H_2O$	19,810	$Na_4P_2O_7.10H_2O$	23,520
$K_2Cu(SO_4)_2, 6H_2O$	22,970	$Na_2CO_3, 10H_2O$	21,800
$MnCl_2, 4H_2O$	14,470	$Na_2SO_4 10H_2O$	19,220
$FeCl_2, 4H_2O$	15,150	$MgSO_4.7H_2O$	24,080
$CdBr_2, 4H_2O$	7,730	$ZnSO_4, 7H_2O$	22,690
$K_2Mn(SO_4)_2, 4H_2O$	12,820	$CuSO_4, 5H_2O$	18,550
$Ca(NO_3)_2, 4H_2O$	11,200	$MnSO_4, 5H_2O$	13,750
$Sr(NO_3)_2, 4H_2O$	7,680	$Na_2S_2O_6, 2H_2O$	6,280
		Li_2SO_4, H_2O	2,640

The above numbers give the heats of total hydration and Thomsen also measured heats of hydration of partially hydrated salts of salts hydrated with lesser number of molecules of water than it can form at other conditions. He placed the finally powdered weighed salt upon a flat platinum plate continued drying for a considerable period at a constant temperature, weighed from time to time to control the progress of dehydration, then removed from the drying apparatus when the weight showed that the required number of molecules of water had been driven

off, the salt analysed, and then the heat of solution per
gram molecule in 400 gram-molecules of water measured
at the usual temperature of about 18°c. Although it is
difficult to suggest what other better method there could
be to perform such elaborate experiments, yet it is quite
clear that the samples of salts hydrated with varying
numbers of molecules of water may contain an admixture
of the same salt hydrated with different numbers of mole-
cules of water, keeping of course the average water content
correct. Heats of solution of salts, whose various
hydrated crystals are definitely known and of a few others
of interest are given below :—

Heats of Solution.

$CuSO_4$	+ 15,800 C	$ZnSO_4$	+ 18,430 C
$,H_2O$	+ 9,330	$,H_2O$	+ 9,950
$,2H_2O$	+ 6,160	$,2H_2O$	+ 7,670
$,3H_2O$	+ 2,810	$,3H_2O$	+ 5,270
$,4H_2O$	+ 630	$,4H_2O$	+ 3,500
$,5H_2O$	− 2,730	$,5H_2O$	+ 1,300
		$,6H_2O$	− 840
		$,7H_2O$	− 4,260
$MgSO_4$	+ 20,280	$MnSO_4$	+ 13,790
$,H_2O$	+ 13,300	$,H_2O$	+ 7,810
$,2H_2O$	+ 11,050	$,2H_2O$	+ 6,240
$,3H_2O$	+ 7,490	$,3H_2O$	+ 4,150
$,4H_2O$	+ 4,240	$,4H_2O$	+ 2,240
$,5H_2O$	+ 2,010	$,5H_2O$	+ 40
$,6H_2O$	− 100		
$,7H_2O$	− 3,800		

$CaCl_2$	$+17,410$ C.	$2K_2CO_3$	$+12,980$
$,1{\cdot}67H_2O$	$+10,800$	$,H_2O$	$+\ 8,560$
$,1{\cdot}98H_2O$	$+10,036$	$,3H_2O$	$-\ \ \ 760$
$,2{\cdot}75H_2O$	$+\ 6,927$		
$,3{\cdot}49H_2O$	$+\ 3,752$		
$,3{\cdot}76H_2O$	$+\ 2,971$		
$,6{\cdot}07H_2O$	$+\ 4,340$		
$MgCl_2$	$+35,920$ C		
$,3{\cdot}03H_2O$	$+14,871$		
$,4{\cdot}51H_2O$	$+\ 8,360$		
$,4{\cdot}61H_2O$	$+\ 7,731$		
$,5{\cdot}05H_2O$	$+\ 6,181$		
$,6{\cdot}11H_2O$	$+\ 2,950$		

Na_2CO_3	$+\ 5,636$
$,H_2O$	$+\ 2,254$
$,2H_2O$	$+\ \ \ \ 43$
$,3H_2O$	$-\ 2,067$
$,4H_2O$	$-\ 4,202$
$,5H_2O$	$-\ 6,638$
$,6H_2O$	$-\ 8,412$
$,7H_2O$	$-10,765$
$,8H_2O$	$-12,623$
$,9H_2O$	$-14,387$
$,10H_2O$	$-16,160$

$Na_4P_2O_7$	$+11,850$	
$,H_2O$	$+\ 9,380$	$2,470 = 1 \times 2,470$
$,2H_2O$	$+\ 7,030$	$2,350 = 1 \times 2,350$
$,5H_2O$	$+\ \ \ \ 50$	$6,980 = 3 \times 2,327$
$,10H_2O$	$-11,670$	$11,720 = 5 \times 2,344$

In reviewing the results of determination of heats of hydration of salts with an even number of molecules of water Thomsen[6] considered that the thermal effects corresponding to the addition of the individual molecules of water are far more uniform on account of molecules of water symetrically arranged around the nucleus of the salt, and in the case with others containing an uneven number of molecules of water the addition of the first molecule of it being attended with a considerable thermal effect, produces a disturbance in the symmetry of the molecule. It is rather difficult to give full support to this view because there is nothing to show that the thermal effect is the only indication how each of the individual molecules of water is linked with the molecule of the substance. It is also not possible to say that the thermal effect is a measure of strength of the linkage between the water and the substance, since there are some hydrates or partial hydrates which on addition of the last molecule produces a negative thermal effect. This negative effect would then mean that the final molecule of water would reduce the force of linkage between the substance and the other water molecules or the final molecule could not be attracted on account of this having a negative thermal effect, the force of linkage would be negative or in other words there would be repulsion.

According to Thomsen's figures it is evident that the individual molecules of water in the hydrated salts are bound with unequal strength if thermal effect is a function of the binding force. Sodium phospate is the only exception to have all 10 molecules of water bound in the same

manner with a strength corresponding to about 2352 c
for each gram-molecule of water. Unfortunately,
however, the process by which the hydrates of
substances were prepared are not beyond doubt and it
is not improbable that the different hydrates with which
he experimented were not free from contamination with
other hydrates.

Hydrate formation does not seem to be quite allied to
the chemical property of a substance. Sodium carbonate
and potassium carbonate, though extremely chemically
alike, do not combine with similar number of water
molecules. Heats of hydration do not indicate the capacity
of the salt for combining with water since potassium
carbonate though liberates more heat (8,560 c) in combin-
ing with the first molecule of water than that does sodium
carbonate (2,254 c) under the same circumstances, the
former could not combine with correspondingly higher
number of molecules of water. The chlorides of calcium
and magnesium have very large heats of hydration, 21,750
c and 32,970 c respectively. But these can only combine
with 6 molecules of water whereas there are many others
which have much lower heats of hydration yet they could
easily retain much larger number of molecules of water in
solid crystalline state.

It is thus seen that the similarily in chemical nature
has neither much relationship with the heats of formation
of hydrates nor does it suggest much about the number of
water molecules with which combination would take place :
there is also hardly much justification in drawing generali-
sations about hydrated substances from their heats of

hydration. On the contrary, however, it is undeniable that as the salts gradually get hydrated, many other properties along with the thermal effects get changed. The force with which the substance and water are combined is not only expressed in terms of thermal effects but also in terms of several other forms of energy which may manifest simultaneously. When a substance combines with water the resultant product differs from the original two in volume, general, thermal, optical, electrical, etc., properties. Assuming energy is indestructible it may be concluded that when heats of formation of hydrate is negative the energy is getting transformed into some other form to an equivalent amount. It is unnecessarily thought by several authors that the magnitude of thermal effect is the sole index of the force with which the water molecule is bound with the molecule of the substance.

Although it is not quite within the scope of this book to discuss the inner structure of the anhydrous or the hydrated molecule, yet, it may not be out of place to say that the different water molecules may be differently placed with respect to the different atoms of the substance, and manifestation of variation of different properties with variation of hydration is a result of the position of water with respect to the different atoms composing the molecule. It may be possible that by gradual addition of different water molecules to a substance for the purpose of hydration a readjustment in equilibrium of all kinds of energy takes place to establish final equilibrium in the last stage of the compound. Or in other words thermal effects of hydration may be positive or negative, according as the sum total of

other properties, optical, electrical etc., taking place simultaneously.

Heat of solution is unavoidably connected with heat of dilution and it is impracticable to determine heat of solution alone. But considerable light could be thrown on the subject also if heats of dilutions were known. As will be seen, heat of dilution depends (1) on the nature of the dissolved substance, (2) on the amount of water present and (3) on the temperature of the experiment. Thomsen[7] considered that when different hydrates are formed in aqueous solutions the change of thermal effect with the amount of added water must show certain fixed points indicating their formation, and otherwise the thermal effect must vary as a regular and continuous function of the amount of water. This, however, does not seem to be a reasonable argument since fixed points are not always found in cases with even solid definite hydrates which are well isolated. Absence of fixed points in the heats of dilution is not, therefore, a proof of the absence of hydrates in solution because more than one hydrate may occur in a solution according as water is available for the purpose.

Variation in heats of dilution supports the idea of reaction taking place at each dilution. The solvent and the solute do not form a mechanical mixture; dilution is attended with changes in different forms of energies which would ordinarily take place when a chemical reaction takes place. The following figures of heats of dilution determined by Thomsen would give considerable support to the association theory of solution :—

Molecules of water	H_2SO_4 C	HNO_3 C	H_3PO_4 C	HCl C	HBr C	HI C	Formic CH_2O_2 C	Acetic $C_2H_4O_2$ C	Tartaric $C_4H_6O_6$ Solid.
1	6,379	3,285	1,741	(5,375)	—	—	172	-152	—
2	9,418	—	—	11,365	(13,860)	(12,540)	167	-156	—
3	11,137	5,710	3,298	13,362	15,910	14,180	- -	—	—
4	—	—	—	—	—	—	—	-111	—
5	13,108	6,655	—	14,959	17,620	17,380	—	—	—
8	—	—	—	—	—	—	—	-2	—
10	—	7,318	—	16,157	19,100	18,580	—	—	—
19	16,256	—	—	—	—	—	—	—	—
20	—	7,458	4,938	16,756	19,470	18,990	—	+173	-3307
49	16,684	—	—	—	—	—	—	—	—
50		—	5,169	17,115	19,820	19,140	126	+278	-3452
99	16,858	—	—	—	—	—	—	—	—
100	—	7,439	5,269	17,235	19,910	19,180	148	+335	-3516
199	17,065	—	—	—	—	—	—	—	—
200	—	—	5,355	—	—	—	149	+375	-3566
300	—	—	—	—	—	—	—	—	—
320		7,493	—	—	—	—	—	—	—
400	—	—	—	—	—	—	—	—	-3600
500	—	—	—	—	19,940	19,210	—	—	

For the determination of the following heats of dilution of caustic alkalis Thomsen used their solutions in 3 molecules of water originally and finally diluted them up to 200 gram-molecules of water ; m = water of dilution.

Heats of dilution of caustic alkalis.

Gram molecules of total water present in solution $(m+3)$	Heats of dilution in c.	
	$KOH,(m+3)H_2O$	$NaOH(m+3)H_2O$
5	$+1,496$	$+2,131$
7	$+2,095$	$+2,889$
9	$+2,364$	$+3,091$
20	$+2,678$	$+3,283$
25	–	$+3,286$
50	$+2,738$	$+3,113$
100	$+2,748$	$+3,000$
200	$+2,781$	$+2,940$

A concentrated solution of ammonia, $NH_3,3·2H_2O$ developes respectively $+324$, $+350$, and $+380$ c on dilution with 15, 25, and 50 gram molecules of water.

Heats of dilution of the following salts of representative nature were studied by Thomsen, which already contained n molecules of water, with the addition of m molecules of water,—

Heats of salt solutions.

(a) Heats of solution and dilution are positive.

$n+m$	$Mg(NO_3)_2$ $n=12$	$Cu(NO_3)_2$ $n=10$	$2(NH_4C_2H_3O_2)$ $n=4$	$ZnCl_2$ $n=5$	$CuCl_2$ $n=10$
10	–	–	$+1,088$	$+1,849$	–
15	$+262$	$+744$	–	–	–

$n+m$	$Mg(NO_3)_2$ $n=12$	$Cu(NO_3)_2$ $n=10$	$2(NH_4C_2H_3O_2)$ $n=4$	$ZnCl_2$ $n=5$	$CuCl_2$ $n=10$
20	+412	+940	+1,800	+3,152	+1,630
30	—	—	—	—	+2,458
50	404	+904	+2,584	+5,317	+3,336
100	+364	+776	+2,988	+6,809	+4,052
200	+370	+729	+3,250	+7,632	+4 510
400	+421	—	+3,432	+8,020	—

(b) Heats of solution and dilution are negative.

$n+m$	$2NaCl$ $n=20$	$2NaNO_3$ $n=12$	$2NH_4NO_3$ $n=5$	$(NH_4)_2C_4H_4O_6$
10	—	—	−1,282	—
15	—	—	—	—
20	—	—	−2,518	—
30	—	—	—	−296
50	—	−2,262	—	−648
100	−1,056	−3,288	−4,584	−1,014
200	−1,310	−3,860	−5,018	−1,242
40	−1,410	−4,192	−5,288	−1,358

(c) Heats of solution and of dilution are of opposite sign.

$n+m$	Na_2SO_4 $n=50$	Na_2CO_3 $n=30$	K_2CO_3 $n=10$	$KHSO_4$ $n=20$
50	—	−566	−122	−64
100	−655	−1,190	−406	−30
200	−1,132	−1,601	−598	+108
400	−1,383	—	−749	+382
800	−1,483	—	—	+766

Thomsen tried to apply these figures only in putting forward suppositions regarding the formation or existence or non-existence of hydrates in solution. It has already been pointed out that there is poor justification in making such suppositions. If hydrates are formed by the association of solvent and solute the reaction would naturally be followed by manifestations of readjustment of all forms of energies that remained latent in the components before the reaction. Thermal form of energy is not the only one that gets disturbed. The algebraic sum of all the the energies must be the same all along. These figures however clearly prove that each time a solvent is introduced or withdrawn a redistribution of heat energy takes place thus indicating a reaction between solvent and solute.

According to the association theory of solution, the combination of solvent and solute is dependent on the molecular ratio in which they are present in solution and each such reaction is frequently complete simultaneously as the solution is complete. Manifestations of different forms of energy that follow each reaction are dependent on the nature of each particular compound or association of solute and solvent. It is not necessary that manifestation of any particular energy measurable after any such particular reaction should always be followed or preceded by mathematically proportionate liberation or absorption of the same energy as a result of a similar reaction. The distribution of energy consequent on the formation of an association of solute and solvent depends on the position of the lastly added solvent molecule with respect to the

components of the solute and vice-versa, keeping, of course finally the sum of energies in all forms present in the latent form constant before and after the reaction.

The evolution of heat due to mixing up of one gram-molecule of sulphuric acid with increasing amounts of water shows the rate of increase of thermal effect much higher up to 19 molecules of water than that with more water. Thermal effect on dilution of nitric acid with water reaches its maximum when there are 20 molecules of water to 1 molecule of acid, and then it falls to rise again when 320 molecules of water are added. The thermal effect of dilution does neither bear any striking similarity with other chemical properties nor with the molecular weights. In the cases of the halogen acids the thermal effects of hydrobromic acid are the highest instead of being an intermediate one. In reviewing the thermal effects of acetic acid Thomsen[8] on the ground of rise of the figures from negative to positive considered that the formation of hydrate in solution is improbable. There is absolutely no reason to consider such deduction to be correct, since such variation suits well with the associa-tion theory of solution.

It is obvious that the solid salts melt and simultaneou-ously or subsequently pass into solution including the heat of fusion in the heat of solution in the first stage. By extrapolating the curve of molecules of water used in dilution an imaginary figure for heat liberated in calories may be obtained when there is no water and such points would indicate the apparent heat of fusion. The following

results were obtained by extrapolating Thomsen's figures :—

Substance.			Heat of fusion.
NH_4NO_3	...	...	+ 450 c
$Mg(NO_3)_2$	...	...	− 500
$Cu(NO_3)_2$	...	...	−1400
$NH_4C_2H_3O_2$	...	...	+ 150
$CuCl_2$	...	...	− 700
$ZnCl_2$	...	...	+ 300

It would be of considerable interest to know how such figures compare with those that could be actually obtained. A solid passing into the liquid state suffers change in molocular vibration and it is quite important to settle if the solid must become liquid in order to mix with a solvent to form a solution. It has not been properly dealt with whether the solid molecules become liquid before passing into solution or only get covered with layers of solvent molecules, and remain still solid in the centre of the outter sphere of the solvent. Some of Thomsen's figures may be utilised for the purpose of elucidating whether the solute molecules in solution are present as liquid or as any other state, gas or solid, at which the pure substance would have been, under the same conditions. He[9] determined the following heats of solution of the same substance at different states :—

	SO_2	NH_3
Heats of solution of gas	7,700c	8,430
Heats of solution of liquid	1,500	3,400
Heats of liquefaction of gas	6,200	5,030

	H_3PO_4	H_3PO_3	H_3PO_2
Heats of solution of liquid ⋯	5,210c	2,940c	2,140c
Heats of solution of solid ⋯	2,690	−130	−170
Heats of liquefaction of solids	2,520	3,070	2,310

Although these results are in support of the assumption that solute molecules remain in a liquid state in solution yet more investigation on the subject is very much welcome.

Thomsen in Chapter VII of his book on thermochemistry dealt with the influence of temperature on the magnitude of the thermal effect of chemical process. He considered that "the thermal effect of a chemical reaction is not a consistant magnitude, since it is dependent not only upon the temperature, but also upon the state of aggregation and other conditions under which the substance re-act, as, for instance upon the degree of dilution." He is only partially true in interpreting his results in this way, the correct method of explaining his results would be different. The thermal effect due to a particular chemical reaction is always the same no matter how the phenomenon is brought about but if, however, such reaction takes place in a medium (of solvent) then the thermal effects due to the interaction between solvent and solute would operate both before and after the reaction whose thermal effects are under observation. The thermal effects due to the reactions between a solvent and a solute vary always with dilution and temperature. These two factors control formation and stability of the associations formed between a solvent and a solute. Such

thermal effects are unavoidably added, to those of the original chemical reactions ; consequently the thermal effects due to chemical reaction taking place in solution are not due to the primary chemical reaction only but also due to other simultaneous actions between solvent and solutes before and after the reaction.

Double salts have heats of formation as chemical reaction as well as heats of solution. Thomsen (ibid 327) obtained the following figures :—

Reaction	Heat of formation	Heat of solution.
$MgSO_4, K_2SO_4$	3,300 c	10,600 c
$ZnSO_4, K_2SO_4$	4,140	7,910
$CuSO_4, K_2SO_4$	20	9,400
$MnSO_4, K_2SO_4$	950	6,380
$MgSO_4, K_2SO_4, 6H_2O$	23,920	$-10,020$
$ZnSO_4, K_2SO_4, 6H_2O$	23,950	$-11,020$
$CuSO_4, K_2SO_4, 6H_2O$	22,990	$-13,570$
$MnSO_4\ K_2SO_4, 4H_2O$	13,810	$-\ 6,440$
$HgCl_2, 2KCl, H_2O$	6,130	$-16,390$
$HgBr_2, 2KBr$	1,230	$-\ 9,750$
$HgI_2 2KI$	3,040	$-\ 9,810$
$SnCl_4, 2KCl$	24,160	$-\ 3,380$
$SnCl_2, 2KCl, H_2O$	4,890	$-13,420$
$AuCl_3, HCl, 4H_2O$	32,130	$-\ 5,830$
$AuBr_3, HBr, 5H_2O$	35,280	$-11,400$

When anhydrous sulphates are mixed to form double sulphates the reaction is attended with considerable evolution of heat but when their aqueous solutions are mixed no thermal effect is noticed. Halides, however, interact under

the latter circumstances with considerable evolution of heat :—

$$HgCl_2Aq, 2KClAq \qquad = 1,920 \text{ c}$$
$$AuCl_2Aq, HClAq \qquad = 4,530$$
$$AuBr_3Aq, HBrAq \qquad = 7,700$$
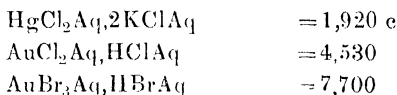
On the ground that when two sulphates capable of forming double salts mixed in their aqueous solutions do not show any heat effect, Thomsen concluded that such salts do not exist in aqueous solution as double salts.

Tammann[10] tried to show from a knowledge of the heat of solution of one substance in another that it is possible to decide whether or not a chemical reaction has taken place during solution. The heat of solution is made up of quantities of heat brought about by (i) the conversion of an anisotropic substance into an iso-tropic condition, (ii) the mixture of the isotropic substance with solvent, and (iii) the chimical process, such as formation of compounds, change in molecular weights, and ionisations. He considered that dimensions of the first two quantities can be calculated theoretically, hence from experimentally determined heat of solution it is possible to see whether any heat change due to third cause is contained in the experimental value, and so ascertain whether chemical processes have taken place. This paper, though does not assume any antagonistic view towards the association theory of solution which propounds invariable reaction between solvent and solute to effect solution, does not properly consider the manifestations of all phenomena attended by solution. When a substance passes into solution thermometric measurements indicate the thermal

changes in equilibrium but if optical, electrical, etc., measurements are done before and after the solution, it would be possible to know other work done during the process of solution.

Thus studies in thermal change alone would neither indicate the nature nor the magnitude of the chemical reaction attended by the process of solution.

Tammann's[11] theory of concentrated solution is rather based on conclusions drawn from studies of most of the physical properties, specific heat, viscosity, electrical conductivity, and optical rotatary power,—that ordinarily attend any chemical change. But he realised the material support from the fact that the specific heat of a solution is usually smaller than that of water it contains on account of diminution of the specific heat of water under pressure. The theory is mainly on the behaviour of solutions towards pressure and temperature. The condition of a solvent under a certain pressure is the same as that of a solution of a certain concentration. This result lead to the conclusion that the solution of a substance keeps the solvent under a certain pressure thereby causing the solution to behave in a similar manner to the solvent under corresponding pressure which varies with the nature and concentration of the dissolved substance.

Among the many examples that Tammann brought forward in support of his theory, Nernst considered that the expansion by heat of water and alcohol under pressure, and of certain concentrated solutions of calcium chloride in these two solvents are useful for the purpose

of illustration in his text book. Increase of volume due to increase of temperature from 0^0 to 50^0 of pure water under pressures of 1, 1000, and 3000 atmospheres, and of aqueous solutions containing 10,20, and 30 per cent calcium chloride are shown in groups of curves. Similar expansion curves of pure alcohol under pressures of 1,500, and 1000 atmospheres and those of alcoholic solutions 8.6, 25. 1 per cent calcium chloride are shown. In these groups of curves considerable similarity has been established between expansion by heat of pure solvent under pressure, and of solution of certain strengths. The internal pressure, of the solution to which the pure solvent must be subjected in order to make its coefficient of expansion equal to that of a solution under pressure, is practically proportional to the concentration of the solution up to high concentrations, but varies with the nature of the dissolved substance. Like expansion by heat measurements of compressibility agreed with the value of the internal pressure of a solution. Deviations, however, have been found in cases of very concentrated solutions ; and the theory does not apply in cases with dilute solutions.

Tammann's remarkable results suit well with the association theory of solution ; and association theory would explain the phenomena in its own way which is of course slightly different. Dissociation theory assumes that a considerable portion of calcium chloride breaks up in aqueous solution into calcium hydrate and hydrochloric acid, thus if there is any truth in the dissociation theory of solution the internal pressure of solvent must be due

to a mixture of $CaCl_2$, $Ca(OH)_2$ and HCl and not due to $CaCl_2$ molecules alone.

It has not been shown why it would be rational that a solvent would similarly behave with respect to volume variation under the influence of heat or pressure when alone or in a state of solution with some solute. In studying changes in volume of solution it has been often presumed that the solutes maintain fixed volume, but whatever may be the state of solute before solution under otherwise the same conditions than that as solution, while present in solution they may be reasonably considered to remain there as liquid and therefore liable to be influenced by pressure or heat in the same way as the solvent. The volume of the solute need not be considered uninfluenced while that of the solvent undergoing change, unless very definite proofs are available.

When a gram molecule of calcium chloride is mixed with successively increasing quantitives of solvents like water or alcohol the volumes of the solute in association with varying molecules of solvent are not equal to the sum of the volumes of solvent and solute before the solution. The changes of volumes consequent on solution, which in this case of aqueous solution of calcium chloride are contractions might be according to Tammann's theory of solution equal to diminution of volumes of water under the pressures like what Nernst compared in graphs. The following figures[12] have been calculated from the molecular contractions of calcium chloride solutions, using coefficients of compressibility of water at 20^0 from Landolt.

% w/w	sp. fr.@20/20°	Molecular contraction.	Contraction per 100 cc. of water.	Coef. of compressibilty, atmosphere × 10.	Pressure in solution in atmosphere.
1	1·00805	27·5	0·248	45·8	54
5	1·04000	26·9	1·22	42·4	288
10	1·07905	25 8	2·37	39·9	594
30	1·22540	21·5	6·28	39·9	1,574

If, however, change in volume by heat or pressure is due to change in the molecular vibration with respect to its amplitude or frequency then the increasing quantity of solvent molecules being associated with a solute molecule can always alter the volume of the final associated molecule of the solvent and the solute, the associated molecule acquiring new properties.

It is also necessary to consider in this connection how the solute and solvent molecules remain associated with respect to their inter-molecular relationship, whether the solvent molecules come in between any of the atoms or groups of atoms or simply form a spherical sheath round the solute molecule one after another in proportion to the dilution. Tammann's theory is not only inapplicable in the case of very concentrated or dilute solution but it needs its applicability properly considered when the solutions are attended with expansions and when the contractions rising to maximum decrease with increasing dilution. Although from the observed contractions in solution pressures could be calculated which would produce such

change in volume of solvent assuming the solute present remain unaltered with the change of condition, yet it is not proposed to entertain usefulness of such figures for want of rationality in comparing them with those obtainable by changing pressure or thermal conditions of the pure solvent. The condition of the solvent in a state of combination with solute may not be the same as that in uncombined state.

Association theory assumes that solvent and solute remain in solution always in state of combination and as soon as they are brought to a condition of unstability they begin to form stabler compounds with different proportions of the one with the other and this phenomenon is nicely illustrated in the following experiments.[13] Bodlander was the first to observe that on dissolving amonium sulphate in mixtures of alcohol and water. at certain concentrations, the liquid divides into two well defined layers. Traube and Neuberg found a similar behaviour with potassium and sodium hydroxides and carbonates, sodium phosphate and zinc and magnesium sulphates and other salts. They therefore examined this change in the case of ammonium sulphate under varying conditions of temperature and concentration.

With a solution containing 340 grams of salt per litre, 750 cc. of which is mixed with 250 cc. of alcohol (99·6 per cent.) it is found that with increasing temperature there is in the upper layer a decrease in the relative amounts of water and salt, and an increase in that of the alcohol ; in the lower layer, there is an increase of water, but a decrease of salt and alcohol. The change in the

composition of the lower layer is, however, so small, that within tolerably wide limits of temperature it may be looked upon as constant. Keeping the temperature constant, and increasing either the amount of alcohol or salt in solution, it was found that in the upper layer there is a decrease in the relative amounts of water and salt and an increase in that of alcohol, in the lower layer there is a decrease in the alcohol and an increase in the salt, the water first increasing and then decreasing. In this way the addition of 40 grams of salt to a litre produce about the same effect as addition of 100 grams of alcohol.

Experiments with K_2CO_3 led to similar conclusions as those above quoted. It was not possible in either case to determine whether the components of the layers are present in definite molecular proportions, but this appeared to them to be likely, especially in the case of the lower layer, the percentage composition of which has a great tendency to remain constant.

Similar separation of layers have been found by the author while an excess of codeine powder is heated in flasks containing aqueous alcohol of different strengths.

Specific heat of solutions.

Equal weights of different substances experience very different elevation of temperature with the same quantity of heat; the term specific heat is applied to the thermal capacity referred to the unit of weight, which is as a rule different for different substances. Ordinarily the specific

heat of a substance is the quantity of heat absorbed by 1 gram of the substance when its temperature is raised 1°C.

The specific heat of liquids often vary very much with the temperature at which it is determined and those of water is particularly instructive in this sense.

Specific heat of water at 15°C.

0	1·0093	35	0·9973	70	1·0000
5	1·0049	40	0·9973	75	1·0008
10	1·0019	45	0·9975	80	1·0017
15	1·0000	50	0·9978	85	1·0026
20	0·9988	55	0·9982	90	1 0036
25	0·9980	60	0 9987	95	1·0046
30	0·9976	65	0·9993	100	1·0057

Specific heats of many substances have been determined by several authors and it would not be possible to tabulate them all here. Only a few typical instances will be briefly quoted below from Landolt, Castell-Evans, and Thomsen.

$CuSO_4$

Substance.	Temperature.	Specific heat.	Molecular heat.
$CuSO_4$	0-20	0 1509	24·09
$CuSO_4,H_2O$	,,	0·1761	31·28
,$3H_2O$	,,	0·2293	49·00
,$5H_2O$	,,	0·2690	67·17
,$50H_2O$	12-15	0·848	
,$75·4H_2O$	15-49	0·849	

Substance.	Temperature.	Specific heat.	Molecular heat.
,75·4H$_2$O	19-89	0·871	
,150H$_2$O	15 49	0·904	
,150H$_2$O	18 89	0·941	
,200H$_2$O	12 14	0·951	
,200H$_2$O	18-53	0·9516	
,400H$_2$O	13-17	0·975	

MgSO$_4$

MgSO$_4$,	25-100	0·225	27·1
,H$_2$O	9	0·2400	33·21
,6H$_2$O	9	0·3482	79·66
,7H$_2$O	9	0·3610	89 97
,7H$_2$O	20-42	0·3615	89·11
,20H$_2$O	19-24	0·755	
,24·1H$_2$O	16-48	0·751	
,24·1H$_2$O	18-90	0·796	
,50H$_2$O	14-18	0 862	
,50H$_2$O	19-52	0·8672	
,157·8H$_2$O	15-48	0·843	
,157·8H$_2$O	19-89	0·897	
,200H$_2$O	18	0·952	

ZnSO$_4$

ZnSO$_4$	22-100	0·174	28·1
,H$_2$O	9	0·1935	34·73
,6H$_2$O	9	0·2996	80·75
,7H$_2$O	9	0·3257	93·66

Substance.	Temperature.	Specific heat.	Molecular heat.
,$18\cdot05H_2O$	15-48	0·685	
,$18\cdot05H_2O$	18-90	0·738	
,$45\cdot1H_2O$	15-50	0·814	
,$45\cdot1H_2O$	19-90	0·828	
,$50H_2O$	20-52	0·8420	
,$200H_2O$	20-52	0·9523	

$NiSO_4$

$NiSO_4$	15-100	0·216	33·4
,$6H_2O$	18-52	0·313	82·3
,$50H_2O$	25-56	0·8371	
,$200H_2O$	25-56	0·9510	

$FeSO_4$

$FeSO_4$			
,$3H_2O$	-	0·247	
,$7H_2O$	19-16	0·346	96·2
,$7H_2O$	46-100	0·357	
,$200H_2O$	18	0·951	

$MnSO_4$

$MnSO_4$	21-100	0·182	27·5
,$5H_2O$	17-46	0·323	77·8
,$5H_2O$	22-100	0·407	
,$50H_2O$	19-51	0·8440	
,$200H_2O$	19 51	0·9529	

$NaO_2C_2H_3$

Substance.	Temperature.	Specific heat.	Molecular heat.
$NaO_2C_2H_3$ (Solid)	14-59	0·350	28·7
,,$3H_2O$ (Solid)	0-46	0·510	69·4
,,$25H_2O$	19-52	0·9037	
,,$50H_2O$		0·938	
,,$100H_2O$	19-52	0·9687	
,,		0·965	

Na_2SO_4

Na_2SO_4	17-98	0·2312	32 84
,,$18H_2O$	24-100	0·731	
,,$40H_2O$	20-23	0·843	
,,$50H_2O$		0·894	
,,$65H_2O$	18	0·892	
,,$100H_2O$	18	0·920	
,,$200H_2O$	18	0·955	
,,$400H_2O$	12-15	0·977	

Na_2CO_3

Na_2CO_3	16·98	0·2728	28·92
,,$25H_2O$	21-52	0·8649	
,,$50H_2O$	18	0·896	
,,$100H_2O$	18	0·933	
,,$200H_2O$	18	0·958	

CH_4O (Methyl alcohol)

Substance.	Temperature.	Specific heat.	Molecular heat.
CH_4O	5-10	0·5901	18 9
12%	6-10	1·073	
20%	7-11	1·073	
31%	3-7	0·980	
50%	0-5	0·818	
50%	21-27	0·861	

Ethyl alcohol.

C_2H_6O	16-30	0·602	27·7
10%	18-40	1·0324	
20%	,,	1·0456	
30%	,,	1·0260	
40%	,,	0·9806	
50%	0-5	0·863	
50%	0-15	0·992	
50%	20-26	0·912	
50%	0-98	0·950	

Great caution is needed in utilising the above figures in disentangling the nature of the relation between solvent and solute in solution. For the purpose of comparison it seems more rational and convenient to consider molecular heats than specific heats. The following points require study in this connection :—

(1) Whether the physical condition of the solute and solvent remain the same (solid, liquid or gas) as they

would have been had they remain mixed under the same conditions.

(2) Specific heat or molecular heat of a substance depends on its state of existence, as well as the intervals of temperatures and pressures between which the observations are made.

(3) Influence of the ratio of the quantities of solvent and solute on the specific heat or molecular heat of the either.

(4) If solvent and solute are not associated in solution the molecular heats of the solution would have been the average of those of the pure substances under the same condition. Basing on a very limited number of figures of densities and specific heats of solution, Thomsen[14] concluded that there is a close relation between these two properties of solution ; but the corresponding figures for methyl alcohol or ethyl alcohol would not support this view besides it is quite rational to think that dilution and specific heat are simultaneously connected to density. along with other properties of solution,— optical, electrical etc. And therefore Thomsen's conclusion could not be considered as general, though favourable figures were obtained in a few cases by him.

Specific heat of substances had been found to vary with the range at which such measurements were taken ; different quantities of heat energy will be required to raise 1°C temperature of substances starting from different temperatures. In ordinary text books it has not been properly discussed how far the thermometer liquid could give correct measurement in this reepect. Whether the

expansion of the thermometer substance, which is mercury in the case of mercury thermometers is regular enough to indicate the correct measurement of specific heats at all temperatures. Often variation in the specific heat is considered to be the indication of change in the inter-molecular region. Addition of successive instalments of heat increases the molecular movements of the substance, but sometimes portions of heat are utilised in breaking up the molecules. In this connection it may be argued that the unaccounted for heat may have been utilised in producing other effects, e.g. electrical, optical, etc. of the substance; more investigation on this line is needed.

Freezing points of Solution

It is known from time immemorial that suitable withdrawal of heat from a liquid would render it a solid and that this solidification takes place at a reasonably fixed temperature. If the temperature remains constant from the commencement of solidification till the whole of the liquid is solid then the substance is considered pure. Glacial acetic acid solidifies at 17° but when a small quantity of water is introduced it must be cooled down to about 10° before the freezing starts and the same is the case with phenol and many other substances. The tem-perature at which solidification starts is called the freezing point. Solutions have different freezing points than any of its components. The effect of the presence of solute in a solvent is to produce a depression of freezing point,—a fact first noticed and studied by Elagden[15], who found in

the case of several substances, that the depressions of
freezing points of acqueous solutions were proportional to
the quantity of solute. Blagden found when two solutes
are present together in a solution the depression of
freezing point was equal to the sum of the effects which
would be exerted as if each of them were present by
itself. Much credit should be given to this investigator
for the accuracy of his experiments considering the time
when he performed them. In persuance of his law,
the depression of freezing point is proportional to the
concentration, he performed a number of experiments, and
found out that the law is not absolutely true : the lowering
of freezing points of solution containing large quantities
of solute is increased more rapidly than the quantity of
substance present in solution, and sometimes increased
more slowly than that expected from the contents of
solution.

It was known from early times that in freezing, solvents
leave behind solutes in the rest of the solution and this
problem was properly raised by Rudorff[16] and Dufour,
who performed quite a large number of experiments ; the
subject was further investigated by some subsequent
experiments by a few others.[17] Rudorff performed quite a
large number of experiments with potassium chloride,
sodium nitrate and potassium carbonate, and came to the
conclusion that the lowering of the freezing-point is
proportional to the quantity of salt present in solution.
He also found that this is not the case with several other
salts, e.g. calcium chloride, barium chloride, sodium chloride
etc. The ratio of lowering of freezing point and the

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quantity of salt in 100 parts of water which is constant in
the cases with former classes of salts, increases with in-
creased concentration in the cases with the latter class of
salts. Rudorff tried to explain this abnormality by the
assumption that such salts are present in a state of com-
bination with the solvent and on this hypothesis he made
several calculations as to the magnitude of hydration of
salts in solution. Experiments of Coppet[18] brought addi-
tional light on the subject. His conclusions were :

(1) Blagden's law of proportionality also holds good
for supersaturated solutions.

(2) The lowering of freezing point is proportional to
the number of molecules of solute present in solution and
not to its quantity in gross weight. Solutions containing
equimolecular concentrations of salts approximately freeze
at the same temperature.

(3) Substance which lower the freezing points of
solutions, in a decreasing degree exist in solution as
several partially decomposed hydrates by the action of
water or by the lowering of temperature.

Coppet's results showed that the molecular depressions
of the freezing points are nearly equal in groups of
similar compounds, which differ from group to group
though practically of the same dimensions. He, however,
devoted most of his labour to investigate the deviations
from the law of proportionality exhibited by certain
substances. The following figures of aqueous solutions
of earlier investigators seem still quite interesting, where
t=lowering of freezing point and m=salt content of the
solution.

m	CaCl₂ Rudorff t/m	NaCl Rudorff t/m	NH₄C Coppet t/m
1	− 0·400	− 0·600	—
2	− 0·450	− 0·600	− 0·415
4	− 0·462	− 0·600	—
6	− 0·476	− 0·600	− 0·400
8	− 0·487	− 0·600	—
10	− 0·490	—	− 0·385
14	− 0·490	− 0·600	—
18	− 0 528	− 0·633	—
20	− 0·555	− 0·647	− 0·345

The ratio of $\dfrac{t}{m}$ increases with concentration of chlorides of calcium and sodium but decreases with increased concentration of ammonium nitrate. The nitrates of sodium, barium, calcium, strontium, silver and lead, sulphate and carbonate of sodium, amonium sulphocyanide, and acetic acid lower the freezing points of their aqueous solutions in a decreasing degree.

The most useful results on the determination of freezing points of solution have been obtained by Raoult. The extension of his investigations[19] to substances other than salts won proper value to his work. He determined molecular depressions of freezing point of many organic substances basing his calculations for solutions of one gram molecular weight of substance in 100 grams of water. Generally he made experiments with solutions containing one gram molecule of substance in one litre of water. He examined more than 200 solutions of fairly

representative nature. In very few cases[20] his solution, contained 1/2 grammolecule or lesser quantity of solute in 1000 grams of solution. From the results of his experiments he laid down the following law :—

"One molecule of any component, when dissolved in 100 molecules of a liquid, lowers the freezing-point of the liquid by an amount which is nearly constant, viz., 0·62⁰ or its simple multiple."

Raoult was a man of considerable reputation and declaration of such a law from him created material interest amongst the contemporary investigators. He and several other scientists subsequently tried to find out the constant molecular depression of freezing points by solutes in several solvents. Much accuracy of such investigation is due to Beckmen[21], the apparatus invented by him is now in use in most laboratories and his thermometer is almost indispensable. Numerous determinations were made for finding out depression of freezing points of many solvents assuming the law of proportionality and results calculated for one gram molecular weight of solute in 100 grams of solvent.

Van't Hoff[22] worked out a theoretical method for the determination of depression of freezing points of solutions assuming its existence of a corresponding connection with osmotic phenomena. The cryoscopic[23] constant, **K**, would be the depression of the freezing-point of a solvent when gram molecule of any substance (which does not dissociate or associate) is dissolved in 100 grams of the solvent, supposing the laws for dilute solution hold good for such a concentration. Raoult (1882) and Van't Hoff (1887)

howed that $K = \dfrac{R\,T^2}{100\,L}$

vhere, R = gas constant = 0·02 (approximately),

   T = absolute freezing point of the solvent,

   L = latent heat of fusion of the solvent.

\ few typical figures may be quoted as an illustration in his connection.

Solvent.	M.P.	Latent heat cal.	K calc.	K obs.
Water, H_2O	0·0	80·025	18·57	18·5
Antimony chloride, $SbCl_3$	—	13·37	177	18·4
Formic acid, $HCOOH$	−7·5	57 38	28·4	27·4
Acetic acid, CH_3COOH	16·5	43·2	33·8	39
Benzene, C_6H_6	5·5	3·0	51	49
Phenol, C_6H_6O	39·6	26·9	70	74
Nitrobenzene, $C_6H_5NO_2$	−9 21	22·3	69·5	70·7
Aniline, C_6H_7N	−6·0	—	—	58·7
).Xylol	16	39·3	42·5	43
Ethelene bromide, $(CH_2Br)_2$	7·9	13	119	118

Following figures show the variation of cryoscopic onstant "K" with the nature of the solute :—

Solvent.	Solute.	K
Water	Methyl Alcohol, CH_4O	17·3
	Ethyl Alcohol, C_2H_6O	17·3
	Cane sugar, $C_{12}H_{22}O_{11}$	18·5
Water	Phenol, C_6H_6O	15·5
	Acetone, $CH_3CO\,CH_3$	17·1
	Ammonia, NH_3	19·9

Solvent.	Solute.	K
	Aniline, $C_6H_5NH_2$	15·3
	Acetic Acid, CH_3COOH	19·0
	Hydrochloric Acid, HCl	39 1
	Nitric Acid, HNO_3	35·8
	Sulphuric Acid, H_2SO_4	38·2
	Barium Oxide, BaO	49·7
	Calcium Oxide, CaO	48·0
	Sodium Hydroxide, NaOH	36·2
	Potassium Hydroxide, KOH	35·3
	Sodium Chloride, NaCl	35·1
	Potassium Chloride, KCl	33 6
	Sodium Nitrate, $NaNO_3$	34·0
	Ammonium Nitrate, NH_4NO_3	32·0
	Sodium Acetate, $NaOOCCH_3$	32·0
	Boric Acid, B_2O_3	20·5
	Borax, $Na_2B_4O_7$	66·0
	Magnesium Acetate, $Mg(CH_3CO_2)$	47·8
	Magnesium Sulphate, $MgSO_4$	19·2
Water	Copper Sulphate, $CuSO_4$	18·0
	Zinc Sulphate, $ZnSO_4$	18·2
Acetic Acid	Chloroform, $CHCl_3$	38·6
	Hexane, C_6H_{14}	40·1
	Camphor, $C_{10}H_{16}O$	39·0
	Acetone, CH_3COCH_3	38·1
	Methyl Alcohol, CH_3OH	35·7
	Ethyl Alcohol, C_2H_5OH	36·4
	Phenol, C_6H_6O	36·2
	Ammonium Acetate, CH_3COONH_4	35·0
	Potassium Acetate, CH_3COOK	39·0

Solvent.	Solute.	K
	Stannic chloride, $SnCl_4$	41·3
	Sulphuric Acid, H_2SO_4	18·6
	Hydrochloric Acid, HCl	17·2
	Magnesium Acetate, $Mg(CH_3COO)_2$	18·2
Formic Acid	Chloroform, $CHCl_3$	26·5
	Benzene, C_6H_6	29·5
	Acetone, CH_3COCH_3	27·8
	Acetic Acid, CH_3COOH	26·5
Ethylene-Bromide	Chloroform, $CHCl_3$	118
	Benzene, C_6H_6	119
	Acetic Acid, CH_3COOH	58
	Ethyl Alcohol, C_2H_5OH	57
Benzene	Hexane, C_6H_{14}	51·3
	Chloroform, $CHCl_3$	51·1
	Nitrobenzene, $C_6H_5NO_2$	48·0
	Camphor, $C_{10}H_{16}O$	51·4
	Acetone, CH_3COCH_3	49·3
	Aniline, $C_6H_5NH_2$	46·3
	Stannic chloride, $SnCl_4$	48·8
	Methyl Alcohol, CH_4O	25.3
	Ethyl Alcohol, C_2H_6O	28·2
	Acetic Acid, CH_3COOH	25·3
Nitrobenzene	Benzene, C_6H_6	70·6
	Acetone, CH_3COCH_3	69·2
	Methyl Alcohol, CH_3OH	35·4
	Ethyl Alcohol, C_2H_6O	35·6
	Acetic Acid, CH_3COOH	36·1

It is thus seen that a solvent is differently influenced

by different solutes with regard to its freezing point. An abstract of a few representative figures are tabulated to show how differently a solute is influenced by solvents when experimented with for the same purpose :—

Solute	"K" in different solvents					
	Water	Acetic Acid	Formic Acid	Ethelene Bromide	Benzene	Nitro-benzene
Methyl alcohol	17·3	35·7	—	—	25·3	35·4
Ethyl alcohol	17·3	36·4	—	57	28·2	35·6
Acetone	17·1	38·1	27·8	—	49·3	69·2
Acetic acid	19·0	—	26·5	58	25·3	36·1
Hydrochloric acid	39·1	17·2	—	—	—	—
Chloroform	—	38·6	26·5	118	51·1	69·9
Hexane	—	40·1	—	—	51·3	—
Camphor	—	39·0	—	—	51·4	—
Naphthalene	—	39·2	—	—	50·0	73·6

Solute and solvent remaining the same, dilution has a fundamental influence on the cryoscopic constant 'K'. A large number of figures on this subject was recorded by numerous investigators from time to time, the bulk of which, however, have been included in Landold—Bornstein Tabellen, 1923 pp. 1424-1460, from which a few representative ones are given below. These were determined by Beckman's method by dissolving about 0·1 to 0·2 gms. of substance in about 15·20 gms. of solvent, the depression of freezing point observed and results calculated for the molecular depression by use of the formula.

$$K = \frac{T.L.M.}{100.g}$$

where,—

> M = molecular weight
> G = grams of solute
> L = grams of solvent
> T = depression of the freezing point of the solvent
> K = molecular depression of freezing point when one gram-molecule of solute dissolved in 100 grams of solvent.

(a) Molecular depressions of freezing points remain practically unchanged at varying concentrations :—

Potassium chloride in water.			Potassium carbonate in water.		
Cencentration in grams per 100 gms. of solvent.	T	K	Concentration in grams per 100 gms. of solvent.	T	K
1	− 0·45	33·3	1·41	− 4·5	44·11
2	− 0·9	33·3	3·06	− 0·95	42·90
4	− 1·8	33·3	5·29	− 1·7	44·40
1	− 3·55	33·4	12·20	− 3·9	44·18
12	− 5·33	32·99	14·86	− 4·7	43·70

(b) Molecular depression of freezing points increases with increasing concentration.

Calcium chloride in water.			Camphor in benzene.	
1	− 0·4	44·40	0·411	48·7
2	− 0·9	49·95	1·253	48·37

Calcium chloride in water.			Camphor in benzene.	
8	− 3·9	54·12	2·791	49·05
10	− 4·9	54·39	5 897	49·61
14	− 7·4	58·66	12·11	50·40
18	− 10·0	61·66	23·12	51·40
			26·59	52·08

Sodium chloride in water.

1	− 0·6	35·08
15	− 9·2	35·85
18	− 11·4	37 01
20	− 12·8	37·41

(c) Molecular depression of freezing points decreases with increasing concentration.

Ammonium nitrate in water.			Barium nitrate in water.		
2	−0·83	33·21	0·01002	− 0·00214	56·0
10	−3 853	0·80	0·2236	− 0·04311	50·4
20	−6·90	27·60	2·175	− 0·363	43·5
30	−9·35	24·90	4·375	− 0 654	39·1
40	−11·75	23·50			
50	−13·60	21·76			
60	−15·60	20·80			
70·24	−17·40	19·82			

(d) Molecular depression of freezing points increases

passes through maximum and then decreases with increasing concentration.

Ethyl alcohol in water.			Methyl acetate in water.		
T	K		T	K	
0·001851	− 0·000670	16·7	2·288	− 0·566	18·3
0·1332	− 0·04936	17·07	7·198	− 1·794	18·5
2·418	− 0·9645	18·34	12·65	− 3·123	18 28
17·96	− 7·49	19·2			
51·06	− 23·6	21·2			
86·22	− 33·9	18·2			

d-Potassium tartrate in water.

2·428	− 0·40	37·0
4·855	− 0·83	39·0
9·710	− 1·64	38·0
19·42	− 3·18	37 0

(e) Molecular depression of freezing points decreases passes through minimum and then increases with increasing concentration

Sulphuric acid in water.			d-Tartaric acid in water.		
0·00299	− 0·00161	52·75	0·1504	− 0·0234	23·3
0·04095	− 0·02102	50·3	1·522	− 0·209	20·6
0·6364	− 0 265	40 9	7·633	− 1·000	19·7
1·989	− 0 765	37·7	34·66	−·4·79	20·7
3·618	− 1·37	37·0			
9·397	− 3·80	39 7			
22·685	− 11·83	51·1			

Barium chloride in water.

0·00446	− 0·00119	55·7
0·2379	− 0·0577	50·5
2·3659	− 0·5319	46·83
20·52	− 5·10	52·0
25·1	− 7·85	65·1

Citric acid in water.

0·1924	− 0·0226	23·0
3·929	− 0·3978	19·4
13·45	− 1·350	19·1
27·85	− 2·849	19·6
52·24	− 5·792	21·3

Aluminium sulphate in water.

0·4474	− 0·073	56·0
2·520	− 0·260	34·6
12·600	− 1·531	41·2

Maganese sulphate in water.

1·941	− 0·293	22·8
5·120	− 0·687	20·3
18·572	− 2·591	21·1

Maganese nitrate in water.*

1·611	− 0·46	51·5
3·222	− 0·88	49·0
9·670	− 2·98	55·2
56·41	− 38·50	122·2

Cobalt chloride in water.

0·0225	− 0·0093	53·8
0·1159	− 0·0457	51·3
1·0342	− 0·2930	49·1
1·6314	− 0·6134	48·8
3·601	− 1·3934	50·3
5·477	− 2·1900	51·93

A critical examination of all the figures quoted above on the depressions of freezing points will show that all kinds of variation are noticeable in them ; although it is true that there is a certain amount of constancy in the

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* Concentrations given are in the volume.

sense that they do not vary in any large extent ; the minimum is almost always more than half that of the maximum for the same solute and solvent. This low range of variation made such figures accepted as constants and largely employed as such in the determination of molecular weights of substances by means of the formula given above by many investigators.

Many figures are not available on the influence of temperature and solvent on the constant "K" and investigation on such line are needed. Beckmann and Maxim[24], however, found by using phenol as solute and carbontetra chloride as solvent that the freezing point data give values for the molecular weight of phenol which increases from 90 in a 0.019% solution to 313 in a 2.31% solution ; and the same substance in bromoform, m.p. 8^0, gave molecular weight rising from 97 in 0.296% solution to 190 in 4.33% solution. These authors have explained the fact in a different way but they may be due to the difference in the formation of compounds between solvent and solute.

According to the association theory a solution is a compound of solute and solvent in molecular ratio identical as dilution. On cooling a solution below the temperature of freezing of the solvent, the molecules of the solution may get vibration similar as the molecules of pure solvent at the same conditions but its solidification could not take place on account of the solute molecules keeping them in association with a certain amount of force and thereby maintaining them in a state of solution. To displace their force to effect separation of the solvent in a solid state a corresponding amount of energy is needed. And this

negative counterbalancing energy can be imparted to a
solution by the application of cold, under which circums-
tances the freezing of solvent would take place. The
difference of temperature' and the total quantity of heat
needed for the solidification of the solvent from the solution
are functions of the force with which solute and solvent
are kept attracted in solution. Evidently then the "solu-
tion force" is dependent on the nature of solvent and
solute, and on their proportion of combination.

The behaviour of aqueous solutions of salts or electro-
lytes is somewhat different from other solutions or non-
electrolytes which is due to the difference in properties of
solution molecules of two kinds of solutions and not due
to the dissociation of solutes into ions as has been
assumed by the dissociation theory.

Mention has already been made about the assumptions
of Van't Hoff in working out his formula for the deter-
mation of molecular weight in solution which are only
true as long as the solutions are dilute enough to obey
osmotic pressure laws within certain limits. Explanation
of results of osmotic pressure determinations on the light
of association theory has been given already. This theory
is against any such assumption that solute molecules could
remain in solution as gas molecules in space, the former
are bound with solvent molecules and are not as free to
move about as the latter. In a solution the movements
of molecules of solute and solvent are in their state of
combination and therefore Van't Hoff's assumptions are
not supported on the grounds of rationality.

Variation of "K" has been explained by many

scientists by basing multitudes of assumptions but only three principal ones may be tabulated here ;—

(1) Solute forms complex molecules amongst themselves

(2) Solute gets partially associated with the solvent.

(3) Solute gets dissociated.

In explaining all variations of "K" association theory does not require the help of such assumptions.

Considerable difficulty is experienced in the comparative study of variation of "K" of a solute in different solvents on account of recording such figures after calculating for 100 grams of solvent containing one gram molecule of solute. 100 grams of all solvents neither contain the same number of molecules nor occupy the same volume. It would be very convenient or rather correct to work out the constants in terms of one gram-molecule of solute dissolved in 100 gram-molecules of solvent or any such fixed number of molecules.

Comparative study of many figures becomes also irrational on account of the fact that they are mostly obtained by performing the experiment at some dilution and then mathematically calculating the same for another dilution, one gram molecule of solute for 100 grams of solvent. "K" varies with dilution and the figures quoted cannot in such cases represent the actual fact. In order to perform comparative study of "K" it would be only rational to have the figures determined with proper consideration to concentration in molecular proportions of solute and solvent.

Van't Hoff in working out his formula for the lowering

of the freezing point of solution assumed that the frozen solvent of sufficient quantity to keep one gram-molecule of solute in solution, melts at the normal freezing point of the solvent and passes into solution just as solvent passes through a semipermeable membrane in an osmotic pressure determination experiment. In doing this, Van't Hoff assumed, the solvent does the osmotic work, which is equal to the osmotic pressure of the solution under the same conditions. Now the question arises when the pure solvent passes into solution does it only 'work' which could be measured by osmotic pressure, or which could correctly be represented by the sum of all kinds of changed properties of solution,—electrical, thermal, optical, etc. It seems reasonable that when any solute or solvent is introduced or withdrawn from a solution the actual amount of work done may not be measured by the measurement of one of the simultaneous change of properties of solution but may be done by determining all such accompanying changes.

Some interesting results were obtained in studying thermal effects of binary mixtures by Madgin[25] and his coworkers but these being obtained by cryscopic methods, though very useful otherwise could not be used as a direct evidence in establishing the association theory of solution. Because the compounds separated by extreme cold may not be the same that are present in solution before freezing. On the whole their results are very helpful in connection with the association theory of solution and further developments are anxiously awaited.

Vapour pressures and boiling points of solutions.

It was known from very early days that the presence of foreign matter in solution affects the temperature of boiling of water. Experiments on the subject were started by Faraday[26] and others[27] since 1822 with non-volatile salts with the object of studying their influence on boiling point of water. These early investigators performed quite a number of experiments but did not succeed in arriving at any generalisation and their work was restricted in the determination of the temperature at which solutions of different strengths boiled, or in other words, the temperature at which the vapour pressure of the solution becomes equal to that of the atmosphere. The pressure remaining practically constant, the variation of temperature with the strength of the solution was recorded.

Determination of vapour pressure at a fixed temperature of solution containing varying quantities of solute was started by Gay-Lussac and Prinsep[28], and conducted to a fair extent by Von Babo[29]. Wullner's[30] experiments on this subject afforded a generalisation. From his results he concluded that the lowering of vapour pressure of water due to the existence of solutes, having no appreciable pressure at the temperature of the experiments, in solution is proportional to the quantity of the solute. He also noted that it would not matter if the solute be composed of one salt only or a mixture of more than one. This view however did not stand long, Pauchon[31], and afterwards Tammann showed that Wullner's law of

proportionality is not strictly accurate so far as aqueous solutions of salts are concerned :—

(1) Sodium sulphate, ammonium sulphate, magnesium sulphate, ($MgSO_4,6H_2O$), and ammonium bromide agree fairly with the law of proportionality of lowering of vapour pressure with proportionate increase of concentration.

(2) Sodium nitrate, potassium nitrate and chlorate of potash cause relatively decrease of vapour pressure as the concentration increases.

(3) Instances have also been found by Tammann where vapour pressure increases at first, reaches maximum and then decreases with increased concentration.

(4) Most other salts gave increase of the relative diminution of vapour pressure as the concentration increased.

Effects on vapour pressure by a molecule of non-volatile solute present in solution in different concentrations have been subsequently studied by several other investigators. A few figures of Emden[32] and Walker[33] are very interesting in this connection as a fair representation of the most instances of effects of dilution or concentration :—

Substance.	% Present in solution.	Relative lowering of vapour pressure caused by one molecule of solute dissolved in 100 molecules of water.	
		By Walker.	By Emden.
NaCl	5.96	2.07	2.12
,,	18.60	2·18	2·14
,,	32.265	2·29	2·25
$CO(NH_2)_2$	6 667	1·11	
,,	13·333	1·07	
,,	26·667	0·91	

From the results of Caven and Ferguson[34] it may be easily concluded that water in the solid hydrated salts is differently bound with different salts, and Sidgwick[34] has shown that same is the case with aqueous solutions by means of determinations of vapour pressures. The binding force is influenced by the chemical nature of salt. Tammann made an extended series of experiments on the determination of lowering of vapour pressures of aqueous salt solutions of different concentrations at a fixed temperature of 100°C. His figures seem to be very systematic and some of which are quoted below; where N = number of grammolecules of salt dissolved in 1000 grams of water, and figures = lowering of vapour pressures in mm. at different concentrations ÷ diminutions of vapour pressures in mm. when $N = 0.5$.

(a) Molecular lowering of vapour pressure remains constant at all dilutions :—

Substance	N = 0.5	1	2	3	4	5	6	8	10
KCl	1 0	1 0	1·0	1·01	1·03	1 05	1·04	—	—
KSCN	1·0	1·05	1·11	1·17	1·16	1·19	1·17	1·16	1·11
KBr	1·0	1·08 ·	1·06	1 07	1·10	1 11	1·10	—	—
KI	1 0	1·01	1 04	1·10	1·12	1·13	1·14	1·13	1·11

(b) Molecular lowering of vapour pressure increases with increased concentration.

	N = 0.5	1	2	3	4	5	6	8	10
KF	1·0	1·05	1·08	1·18	1·25	1·29	1 31	1·37	—
NaI	1·0	1 06	1·24	1·37	1·41	1·47	1·52	1·55	1 53
LiBr	1 0	1·07	1·23	1·32	1·43	1·53	1·65	1 75	1·79

(c) Molecular lowering of vapour pressure decreases with concentration.

N = 0·5	1	2	3	4	5	6	8	10
NH_4NO_3 1·0	0·860	0·822	0 816	0·81	0·81	0·79	0·74	0·70
KNO_3 1·0	0·02	0·97	0·93	0·90	0·86	0·83	0·77	0 72

(d) Molecular lowering of vapour pressure increases, reaches maximum and then decreases with increased concentration.

N = 0·5	1	2	3	4	5	6	8	10
NaSCN 1 0	1·06	1·20	1·28	1·81	1·35	1 40	1 38	1·35
NH_4Br 1·0	1·004	1·025	1·038	1·044	1·021	1·019	0·999	0·96

(e) Molecular lowering of vapour pressure decreases, reaches minimum and then increases again with increased concentration.

N = 0·5	1	2	3	4	5	5	8	10
$N(C_2H_5)H_8Cl$. 1·0	0 80	0·38	1·105	1·107	1·119	1·109	—	—
$K_2S_2O_3$ 1·0	0·95	0 98	1·00	1·04	1 05	1·07	1·7	—
Na_2W_4O13 1·0	0·84	3·84	1·07	1·05	—	—	—	—
$CdCl_2$ 1·0	0 98	0·96	c 99	1 01	1 03	—	—	—

More investigation under each of the following heads seem still quite welcome :—

(1) Influence of temperature.—Molecular lowering of vapour pressure of solutions at rising temperatures.

(2) Influence of concentration.—Molecular lowering of vapour pressure of solutes at different concentrations.

(3) Influence of nature of solute.—Molecular lowering of vapour pressure of different solutes in same solvent under similar temperatures, pressures and concentrations.

(4) Influence of nature of solvent —Molecular lowering of vapour pressure of the same solute in different solvents under similar temperatures, pressures and concentrations.

It has already been mentioned that some experiments on these lines have been made by Von Babo and Wullner, and Raoult[35] tried to do elaborate experiments on the subject. Unfortunately, however, he rushed into generalisation with quite insufficient data. It does not seem worth while to discuss much on his figures specially as they are more or less repetitions of his previous workers. The rapidity with which he started generalisation throws considerable doubt on the interpretations of his results. He also admitted that he had some difficulty in obtaining accurate results.

Elevation of boiling point.

Some of the above mentioned results created considerable interest in the subject and attention was drawn to perform experiments in a different[36] way. Atmospheric pressure was kept constant at 760 mm. and elevations of boiling point of solutions were studied by Beckmann[37]. Difficulties were experienced in obtaining concordant and accurate results in such determinations by Raoult, Tammann, and Beckmann for the purpose of finding out molecular weights of solutes on the basis of elevation of B. P. produced. Beckmann, however, over-come the difficulty by the discovery of his method and his thermometer, which are now applied in almost all laboratories as his freezing point method. Constant

"K" the molecular elevation of boiling point for different solvents have been determined by numerous investigators by taking solutes of known molecular weights. The following formula is used ; –

$$K = \frac{M \times t \times L}{10 \times g}$$

Where, K = Molecular elevation of boiling point at 760 mm.

M = Molecular weight of the solute.

t = Elevation of boiling point observed.

L = Weight of the solvent in grams.

g = Weight of the solute in grams.

Thus the constant "K" represents the elevation of boiling point of a solvent that could be produced by the solution of 100 grams of solvent with one gram-molecule of solute. Actual experiments are to be done in a very dilute solution and by calculation figures are to be obtained as above. A few typical instances of "K" are given below :— .

Substance.	B. P.	Latent heat of Vapourisation.	"K"
HCl	−82·9	105·5	6·4
HBr	−68·7	51·4	15·0
HI	−35·7	38·7	28·3
H.OH	100·0	535·7	5·2
$CH_3.OH$	6·7	267·5	8·4
C_2H_5OH	78·4	207·0	12·0
C_3H_7OH (Normal)	97·3	162·6	17·3
C_6H_5OH	182·1	114·3	36·0

Substance.	B. P.	Latent Heat of Vapourisation.	"K"
$C_5H_{11}{\cdot}OH$ (iso-amyl alcohol)	131·5	125·1	25·8
$C_5H_{11}{\cdot}OH$ (tertiary amyl alcohol)	102·0	106·1	22·6
C_2H_5Cl	12·0	83·1	19·5
C_2H_5Br	37·7	61·65	25·3
C_2H_5I	72·2	47·6	50·1

These figures indicate probable relationship inherent on the chemical nature on account of their gradation with change of radical in the molecule.

The two sets of figures given above for two amyl alcohols are instructive amongst themselves and show how intra-molecular or atomic adjustment in a molecule could influence such properties.

These so called constants "K" of solvents have been determined under special conditions of dilute solutions and are not really constants when strictly examined. These are only approximately true for dilute solutions and do not hold good for concentrated solutions. For practical purposes, however, they are extremely useful in rough determination of molecular weights of substances.

This constant "K" not only varies with the nature of the solvent and solute but may do in 5 different ways with variation of concentration as was the case vapour pressure. Beckmann[38] and his coworkers have done a large number of determinations of molecular weights by observing elevation of boiling point of solutions, amongst which his work on the influence of temperature and solvent on the

molecular weights of the dissolved substances seems very interesting in this connection. Although his figures are too few to afford any generalisation yet they show how further investigation is needed on such line. The influence of temperature on the molecular weight determination of phenol by the elevation of boiling points of carbon tetra-chloride at temperatures of 75⁰, 60⁰ and 54⁰ has been examined. The results of such investigation show that the variation of temperature of determination has no appreciable influence on the molecular weight or on "K" at a given concentration. But the same constant varies with concentration of solute. Following tables show the influence of concentration in aqueous solutions :—

(*a*) Molecular elevation of boiling point does not appreciably change with concentration.

Concentration in gms. per 100 gms. of solvent.	t	"K"	Concentration in gms. per 100 gms. of solvent.	t	"K"
Cadmium iodide. $CdI_2 = 36.1$			Boric acid. $H_3BO_3 = 63$		
4·54	0 068	5·4	2·35	0·186	4 9
14·31	0 212	5·4	2·99	0·241	5·0
22·53	0 328	5·3	5·02	0·450	5·0
			7·69	0 610	4·9
			10·92	0·900	5·1
			17·27	1·390	5 0
			26·50	2·130	5·0
			36·41	3·010	5·1

(*b*) Molecular elevation of boiling point increases with increased concentration.

Barium chloride. $BaCl_2 = 208\cdot3$			Potassium chloride $KCl = 74\cdot6$		
3·397	0·208	12·8	0·376	0·050	10·0
8 777	0·525	12·5	0·752	0·091	9·0
18·619	1·174	13·1	2·279	0·288	9·4
35·036	2·517	14·9	6·191	0·768	9·3
54·191	4·157	16·0	18·44	2·376	9·6
			27·17	3·75	10·3
			48·94	7·60	11·6

Cobalt sulphate.
$CoSO_4 = 15\cdot51$

4·446	0·110	3·8
9·596	0·262	4·2
20·60	0·568	4·28
32·84	1·055	4·98

Potassium iodide $KI = 166\cdot0$			Cane sugar. $C_{12}H_{22}O_{11} = 342\cdot2$		
4·32	2·256	9·8	4·316	0·1964	5·1
11·22	0·656	9·7	7·25	0·212	4·9
18·20	1·076	9·8	11·02	0·322	5·1
29·24	1·812	10·8	21·66	0·633	5·3
47·61	3·159	11·0	36·15	1·056	6·2
104·80	8·02	12·0	65·97	1·93	5·9
			100·95	2·95	6·3
.			175·1	5·12	7·5
			276·2	8·07	8·3

Sodium chloride.

NaCl = 58·5

0·4388	0·074	9·9
2·158	0·351	9·5
4·386	0·717	9·6
12·17	2·182	10·5
18·77	3·866	12·0
31·242	6·82	12·8

(c) Molecular elevation of boiling point decreases with increased concentration.

Silver nitrate.

AgNO$_3$ = 169·97

0·804	0·044	9·3
1·543	0·087	9·6
3·893	0·197	8·6
7·495	0·382	8·7
15·545	0·741	8·1
35·08	1·526	7·39
86·43	3·143	6·18
136·36	4·415	5·50

Potassium nitrate,

KNO$_3$ = 101·1

0·505	0·051	10·0
1·010	0·095	9·5
2·789	0·248	9·0
9·22	0·797	8·7
19·74	1·603	8·22
53·37	3·795	7·2
70·76	4·677	6·69

Barium nitrate.

Ba(NO$_3$)$_2$ = 261·5

1·205	0·065	14·0
2·270	0·104	12·0
23·25	0·911	10·2

Lead nitrate.

Pb(NO$_3$)$_2$ = 331·0

1·569	0·070	15·0
13·816	0·418	10·0
29·10	0·824	9·4

Sodium nitrate. $NaNO_3 = 85$			Rubidium chloride. $RbCl = 120\ 9$		
0·3931	0·044	9·5	0·4943	0·039	10 0
0·7250	0·080	9·4	1·1420	0 089	9·4
3·785	0·398	9·0	2·502	0·190	9·2
7·343	0·771	8·9	6·385	0·478	9·1
			11·383	0·860	9·1

(*d,* Molecular elevation of boiling point increases, attains maximum and then decreases with increased concentration—

Mercuric chloride. $HgCl_2 = 270·9$			Mannite. $C_6H_{14}O_6 = 182\ 1$		
3·341	0·056	4·5	2·38	0 065	5·0
8·68	0·159	5·0	4·298	0·121	5·1
16·54	0·268	4·4	6·501	0 192	5·4
34·90	0 496	3·8	12 67	0·360	5·2
52·59	0·645	3·3	19·67	0·535	5·06

Magnesium sulphate. $MgSO_4 = 120·4$			Fructose. $C_6H_{12}O_6 = 180·1$		
2·733	0·097	4·3	10 16	0·294	5·2
7·236	0·281	4·7	16·12	0 488	5·5
43·47	1·455	4 03	27·52	0 807	5·28

Iodic Acid $HIO_3 = 175·9$			Urea. $CO(NH_2)_2 = 60·1$		
3·39	0·116	6 0	1·118	0·090	4·8
5·51	0·190	6·1	3·361	0·269	4·8
10·74	0·385	6·3	6·60	0·549	4·99
29·94	0·772	4·53	16·59	1·169	4·23

(e) Molecular elevation of boiling point decreases, attains minimum and then increases with increased concentration.

Calcium chloride.		
$CaCl_2 = 111{\cdot}0$		
0·585	0·091	1 7
2·405	0·302	1·39
5·35	0·643	1·34
10·89	1·481	1·51

Lithium nitrate.		
$LiNO_3 = 69{\cdot}1$		
1·96*	0·278	9·8
6·36*	0·830	· 9·0
13·99*	1·516	7·49
23·29*	2·916	8·66
31·91*	4·428	9·58
45·03*	8·496	13 03

Copper sulphate		
$CuSO_4 = 159{\cdot}7$		
3 356	0·091	4·3
7·811	0·189	3 9
15·952	0·374	3·7
32·36	0·874	4·3
56·95	2·283	6·37
73·77	3·768	8·16

Manganese sulphate		
$MnSO_4 = 151{\cdot}1$		
3·713	0·114	4·6
14·46	0·373	3·9
24·21	0·678	4 23

Nickel sulphate		
$NiSO_4 = 154{\cdot}8$		
2·766	0·096	5·4
11 196	0·396	4·6
23·143	0 738	4·94
34·461	1·389	6·24
37·735	1·734	7 11

Volatile solvent and solute.—Vapour pressure of solution containing both solvent and solute—as volatile substances has neither been much determined nor

* Concentrations are in gms. per 100 c.c. solvent.

available data properly interpreted so well as they should be. I could only try to deal with a few useful figures to show how their study may disentangle the nature of the phenonrenon of solution.

Planck[32] worked out a formula establishing a relationship between lowering of vapour pressure with concentration of the dissolved substance in the liquid and in the vapour, which was subjected to some experimental test by Winkelmann[40] who found considerable deviations in several cases. It is not worth while establishing much importance on such formula for want of its testing with sufficient experimental data.

Vapour pressures of some binary mixtures of volatile solvents and solute have been determined but they are also not comprehensive enough to allow much discussion. Amongst these a few only are given below which may be good enough to show that the solute and solvent remain in solution in a state of combination. Variation of vapour pressure with concentration of any of the constituents of the solution always do not depend on their quantity only but also on the particular association they form at that condition.

(a) Increase or decrease of vapour pressure with concentration depends on the temperature of determinations :—

Acetic Acid and Benzene.

Molecular percentage of acetic acid.	Pressure in milimetres of mercury.	
	at 49·99°	at 85·05°
10	26·0	31·9
20	24·6	32·9

	Pressure in milimetres of mercury.	
	at 49·99°	at 85·05°
30	23·6	33·4
40	21·9	33·1
50	—	32·7
60	18·6	31 7
70	16·5	—
80	13·8	—
90	8·7	25·5

(*b*) Vapour pressure increases or decreases passes through maximum or minimum, and then decreases or increases with concentration.

Acetone and chloroform.

Chloroform.	Pressure in milimetres of mercury.		
	at 28·15°	at 40·40°	at 35·10
0	25 88	42·50	74·18
10	24·5	40·6	69 9
20	33·1	38·6	66·2
30	21·9	35·6	63·1
40	20·8	34·9	60·3
50	19·8	33·2	60·0
60	19·0	32·1	56·4
70	18·9	32·2	56·8
80	19·6	33·4	58 6
90	20·7	35·2	60·7
100	22·18	37·18	63·28

Carbon disulphide and acetone.

Pressures in mm. of mercury.

CS₂	at 24·78°	at 35·17°
0	23·16	34 38
10	32·1	48·2
20	38·0	56·1
30	41 3	60·6
40	43·3	63 3
50	44·8	64·7
60	45·2	65·3
70	45·5	65·5
80	44·7	64 2
90	43 9	61·5
100	35·85	51·23

Nitric acid and water.

% w/w Nitric acid.	at 75°	at 85°	at 95°	at 100°
0	289	434	634	760
20	260	390	554	663
30	230	350	497	583
40	195	300	435	510
50	155	250	375	450
60	135	225	330	405
70	115	195	300	370
80	170	250	375	450
90	295	440	625	745
100	524	725	—	—

Pressures in mm. of mercury.

Ethyl alcohol and water.

% w/w Alcohol.	Pressure in mm. of mercury at 39·76°.	% w/w Alcohol	Pressure in mm. of Mercury at 74·79°
100	129·8	100	653·0
99·13	131 1	99·00	653 2
98·20	131 4	97·93	654·0
97·52	131·5	95·68	654 3
96·37	130·9	94·57	652·8
90·04	129·2	90·88	651·0
80·00	125 5	82·46	640·5
40·85	107·6	41·80	549·0
22·00	90·5	30·25	515·2
15·92	81·4	20·0	468·8
0 0	54·7	0·00	286·7

Propyl alcohol in water.

% w/w Propyl alcohol.	Pressure in mm. of mercury at 49·92°.	% w/w Propyl alcohol.	Pressure in mm. of mercury at 79·80°
100	. 90	100	374·6
93·83	121·3	93·83	479·2
90 42	129·3	90·42	506·6
80·65	138·4	80·65	541·7
75·34	138·9	75·34	545·7
69·98	140·4	71·46	549·7
69·51	139·7	70·72	548·5
39·36	139·1	69·98	548·5
38·79	138·7	58·96	547·0
24 88	136·4	38·09	539·6
0·00	92·05	23·79	530·0
		0·00	352·2

Cryohydrates :—In attempting to separate solvent from aqueous solutions of certain substances it has been found that practically pure ice separates out till a certain concentration is reached when separated solid water becomes a mixture of solvent and solute in a ratio practically same as the mother liquor from which the solidification has taken place. On further application of cold the rest of the solution solidifies gradually containing the solute and solvent in the same ratio as the solution. When such solids of constant composition separate out the temperature of the solution remains practically constant. For the reason that the solution behaves like a pure liquid, and has a definite freezing point the separated substance was supposed to be a definite compound of salt and water and called a CRYOHYDRATE. Similar phenomena of freezing of a mixed binary liquid at constant temperature and conversely melting of mixed solid at the same temperature were noted by Guthrie[41]. This investigator called such combinations an "eutectic mixture." He found that a mixture of $Pb(NO_3)_2 = 46.86$ and $KNO_3 = 53.14$, melts at constant temperature of about 207° and that by altering this proportion in any way a mixture of higher melting point is obtained. Laterly several such mixtures were discovered. Cryohydrates are also instances of eutectic mixtures and those of NaCl, NaI, NH_4Cl, $NaNO_3$, $FeCl_3$ have formed subjects of investigation by Guthrie[42], Mazotto[43], and Roozeboom[44].

Constant boiling points :—Boiling points of solutions containing volatile liquids only have also been much less investigated and formerly whatever experimental facts

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were available have been rather improperly applied in connection with the theory of solutions. The following aqueous solutions have approximately constant boiling points at 760 mm. pressure :—

Approximate strength of solute.			Boiling point.
96% ethyl alcohol	...	...	78°C
75% propyl alcohol	...	...	88°
68% nitric acid	...	...	86°
20·2% hydrochloric acid	...	...	110°
75% formic acid	..	...	107°

These do not mean that these mixtures are definite compounds but only indicate the magnitude of vapour pressures relative to each other under those conditions.

Subjecting a binary solution to the action of gradually decreasing or increasing heat the combination between solvents and solute is broken at respective temperatures. At such conditions, solvent, solute, or mixture of solvent and solute may separate out in the form of matter other than liquid, i.e , solid or gaseous state. The difference of thermal condition needed for such separation is to work against the force with which the solute and solvent are bound together in order to remain in a state of solution and to convert solute, solvent or mixture of both solute and solvent into solid or gaseous state. Each of the molecules of solvent and solute after becoming released from the tie of solution forces as a result of corresponding thermal action, higher or lower than the limits of existence in a state of solution, subjects themselves simultaneously

to the action of the temperature of existence and to the rest of the solution. If they are not sufficiently attracted by the rest of the solution they leave it as a solid or gas totally or partially according as the case may be. The cases when both the ingredients of the binary liquid mixture separate out in the same proportion as the composition of the solution they do so at a fixed temperature as has been said already. Interesting instances of this phenomenon could be found in the following pairs of mixtures[45] :—

Substance.	M.P.
{ Hexachloro-cyclopentenone	97·7°C
Penta chloro-monobromo-cyclopentenone	87·5°
{ Mercuric bromide.	236·5°
Mercuric iodide.	255·4°

Mixtures of given definite ratio of these two pairs will separate from their liquid states as a solid mixture, having the same composition as the solution, at fixed unchanged temperatures In majority of cases, however, such constant freezing point mixtures are obtained in limited ratios of the components of the solution. One of the components gaining concentration as a result of the separation of the other by the application of cold, and it would do so having more affinity for passing into solution than the tendency created for separating out by the application of cold.

Some of the binary mixtures composed of both volatile components could vaporise as has been stated already in the same rate as they are in a quantitative ratio in solution at 760 mm pressure. Lecat in his book "La Tension de

Vapeur des Melanges de liuides : L'Azeotropisme", Lamer-
tin 1918, Brussels, gave instances of some cases of binary
mixtures which boil at constant temperatures producing a
distillate of same composition as a the original solution.
Following are a few interesting examples[46] :—

(a) Minimum boiling point of the binary mixture is
lower than that of the pure substance of low boiling point.

	B.P.			B.P.	Minimum B.P. of mixture.
Cyclohexane	80·8°	and	Carbontetra chloride.	76·8°	76·5°
,,	,,	,,	Benzene	80·2°	77·5°
,,	,,	,,	Methylethyl ketone.	79·6°	72·0°
Carbontetra Chloride	76·8°	,,	Ethyl acetate	77 2°	74·8°
Mesitylene	164·0°	,,	Chlorotoluene	161·3°	160·5°
,, .	,,	,,	Propionic acid	140·7°	139·3°

(b) Maximum constant boiling point of the binary
mixture is higher than that of any of the pure substance
of high boiling point.

	B.P.			B.P.	Maximum B.P. of mixture.
Chloroform	61·0°	and	Acetone	56·3°	63·4°
Water	100°	,,	Hydrochloric acid	80·0°	110°
,,	,,	,,	Nitric acid	86 0°	120·5°

	B.P.			B.P.	Maximum B.P. of mixture.
Pyridine	115·5°	and	Propionic acid	140·7°	105·8°
Phenol	181·5°	,,	Glycol	197·4°	199°
,,	,,	,,	Benzaldehyde	179·2°	185·6°
,,	,,	,,	Aniline	184·4°	186·2°
,,	,,	,,	Ethylbutyrate	178·6°	185·6°
,,	,,	,,	Benzyl alcohol	205·5°	206°
Formic acid	100·8°	,,	Diethyl ketone	102·2°	105·0°

The magnitude or the degree of the lowering or the elevation of boiling point depends on the force needed to work against the energy binding the substance present in solution. Ternary mixtures, known to give constant boiling points,[46] come under this law also.

General Remarks :—Having described the representative experimental facts regarding the removal of solvent or solute from solution by the presentation of suitable thermal conditions it behoves now to consider to what extent such phenomena of their removal from solution could tell the secrecy of the mechanism of formation and state of existence of solution. Van't Hoff and numerous other physical chemists have indirectly or directly stated that the relation-ship between solute and solvent in dilute solutions is not identical in nature with that in the concentrated solutions without making or establishing a clear line of demarcation between the two kinds of solutions. Properties of solutions vary considerably with concentrations and it is easy to find out ranges of

concentrations where data of one solution agree with those of another of different ranges of concentration. For the purpose of comparison, it is therefore necessary to have similarity in molecular concentrations of both solvent and solute. Apart from the irrationality of distinguishing electrolytes from non-electrolytes by considering that solutes of electrolytes break up into its components in solution Arrhenius[47] as well as several other scientists have no justification in accepting Kirchhoff's and Von Babo's results that at high dilutions of salts a further addition of water has no thermal effect. This assumption has unfortunately, been utilised in explaining many phenomena of dilute solutions and sometimes extended towards concentrated ones also. It is quite worth while repeating the experiments of the earlier investigators who had neither sufficiently accurate methods of measurements nor quite sensitive instruments. Even admitting that no thermal work is done by the introduction of additional solvent to a a dilute solution it remains to be proved whether any work is done against other properties of it, e.g. optical, electrical, etc., under the circumstances.

Van't Hoff in establishing gas laws for dilute solutions and in its application to explain phenomena connected with deviations from boiling points and freezing points of solution assumed that the solution is so diluted that relationship between the solvent and solute to remain in a state of solution continue to exist uninterfered with the change of dilution. Throughout his calculation he never considered fully what work is done in removing solvent from the solution against the force by which solvent and

solute are kept in state of solution. The association theory of solution puts forward that in solution any changes in the ratio between solute and solvent always accompany corresponding changes in energy which may express itself in terms of thermal, optical, electrical, etc., alterations. Ignorance of this fact renders Van't Hoff's theory useless in elucidating any thing about the phenomenon of solution. Some of the text book writers[48] paid much importance in spreading out this erroneous idea about solution without properly ascertaining if any work, other than that of thermal, is done in changing dilution of a dilute solution. There does not seem much justification in accepting, Van't Hoff's mathematical calculations and deductions in connection with theories of solutions because he only drew similarity of some figures with those of gases but did not mean to express any mechanism between solute and solvent in dilute solutions. "Van't Hoff's theory of solution" becomes a misnomer after the author has said[49] in this connection "simply leave the question of mechanism alone altogether."

The association theory of solution assumes that solute and solvent always remain in solution in state of combination and in attempting to remove one of them from solution by freezing, vaporising or boiling work must be done first to separate them and then to change the condition from liquid to solid or to gas. This work may be perceptible in, thermal, electrical, etc., forms of energy. Deviations from boiling points vapour tensions and freezing points of a solvent containing a solute in solution is due to additional work that must be done to

separate the components of the mixture. Magnitudes of deviations somewhat apparently indicate the strength of binding force between solute and solvent in solution, and this, however, needs experimental confirmation.

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CHAPTER VIII.

OPTICAL PROPERTIES OF SOLUTIONS.

Measurement of work done in changing optical properties of a substance has not been done in such a way as to render its application in this book. It would have been convenient if such data were available regarding the measurement of changes in potential energy by the alteration of optical properties of substances. Such re-searches would have been useful in forming accurate inferences regarding the relationship between solvent and solute in solution, and in changing their dilution.

Experimental results on optical properties of solutions may be taken in this book under the following branches :—

    (1) Refraction.
    (2) Polarisation.
    (3) Absorption.
    (4) Fluorescence.

Each one of these branches is very comprehensive and it is beyond the scope of this book to give any full treat-ment of them. Only those portions will be considered which will help expressing any knowledge of the relation-ship between solvent and solute in solution.

1. *Refraction.*

The velocity of propagation of light through different substances depends on the nature of the medium including its compositon, temperature, pressure etc. This variation

of propogation of light through a medium is ordinarily measured basing on the fact that when a ray of light passes through a substance in an inclined angle, the sine of the angle gets changed. The velocity of light through a medium has been taken to be proportional to the sine of the angle between the normal and the refracted ray. The velocity of light through a medium may be expressed in terms of comparison with that through a standard medium. Light attains its maximum velocity in vacuum which decreases when it passes through matter. Vacuum or air is ordinarily taken as standard. The index of refraction is the ratio of the velocity of light in the two media and is known by the ratio of the sine of the angle of incidence to the sine of the angle of refraction and often expressed by the symbol n.

$$n = \frac{\text{Sin } i}{\text{Sin } r} = \frac{V_1}{V_2}$$

where i = angle of incidence ; r = angle of refraction ; V_1 = velocity of light in a standard medium, ordinarily vacuum or air ; V_2 = Velocity of light in medium under observation. The speed of light through space containing matter depends on the wave length of vibration, the angle of incidence remaining constant, rays of different wave lengths will be refracted differently in the same medium. Thus a composite ray of light gets differently refracted and the phenomenon is known as dispersion. To obtain comparative values of the refractive indices of substances, they are usually measured with lights of standard wave lengths, and often A or D lines in the solar spectrum are chosen for the purpose.

The refractive index has been found to vary with the density of the medium and these two properties of matter have been connected by different authors by means of the following formula :—

(1) by Laplace[1],

$$\frac{n^2-1}{d} = R' = \text{Constant},$$

(2) Gladstone and Dale[2],

$$\frac{n-1}{d} = R'' = \text{Constant},$$

and (3) by Lorentz[3] and Lorentz[4].

$$\frac{n^2-1}{n^2-2} \times \frac{1}{d} = R = \text{Constant}.$$

Although it is desirable to have 'n' and 'd' determined at a standard temperature for the purpose of accurate measurements yet variation due to variation of temperature does not seem to affect these formulae appreciably. The constants R', R'' R''' are called " specific refractive power" and the product of this with molecular weight of the substance is called the "molecular refractive power".

Refractivity of solutions has been determined by many investigators and references on which have been fairly collected by Smiles[5]. Specific refractive power of any of the components of a binary mixture in liquid state has been determined in numerous cases by the following formula derived from that of Gladstone and Dale :—

$$\frac{n_3-1}{d_3} = \frac{n_1-1}{d_1} \times \frac{p}{100} + \frac{n_2-1}{d_2} \times \frac{100-p}{100}$$

where, n_1, n_2 and n_3 are the refractive indices of solute, solvent and solution respectively and d_1, d_2 and d_3 the

corresponding densities at the same temperature, and p is the percentage by weight of the solute in solution.

Using Lorentz and Lorenz's formula the following is obtained :—

$$\frac{n^2_3 - 1}{n^2_3 + 2} \times \frac{1}{d_3} = \frac{n^2_1 - 1}{n^2_1 - 2} \times \frac{p}{100 - d_1} + \frac{n^2_2 - 1}{n^2_2 + 2} \times \frac{100 - p}{100 \cdot d_2}$$

In determining refractivity of solutes by means of these formulae it has been found in some cases that the refractivity varies with the solvent used. Although this method is not so valuable in determining refractivity of solutes yet results obtained by them are quite useful in establishing fundamental principles of association theory of solution especially in view of the fact that more divergency is noticeable in cases where more alteration in volume takes place on mixing the components. Pulfrich[6] proposed a correction for the change in volume but this part of the subject needs more investigation to show how solvent and solute are related in a state of solution so far as this property is concerned.

It has not been considered properly in working out the above formulae if any reaction sets in between solvent and solute in solution. If the following figures of refractivity of acetic acid in benzene, toluene, and pyridine at different dilutions are studied it will be at once seen without any doubt that the relationship between acetic acid and pyridine in solution is not the same as that the acetic acid forms with benzene or toluene, the relationship of acetic acid in solutions with benzene or with toluene seem to be nearly the same. The following table is prepared from Zawidzki's[7] figures taken from Landolt, 1923, 994.

Approximate w/w% Acetic Acid.	Difference of refractive indices (n_D) at 25·2° of acetic acid solutions in different solvents.		
	Benzene Toluene.	Pyridine Toluene.	Pyridine Benzene.
0	0·00428	0·01329	0·00901
10	0·00213	0·01299	0·01086
20	0·00697	0·01489	0·00792
30	0·00060	0·01617	0·01557
40	0·00076	0·01875	0·01799
50	−0·00015	0·02111	0·02126
70	−0·00070	0·02620	0·02690
80	−0·00087	0·02582	0·02669
90	−0·0066	0·01649	0·01715
100	−0·00009	0 00012	0·00021

It is seen in the figures of columns 3 and 4 that the maximum differences are in the mixtures when acetic acid in the solutions is about 70% ; the compounds formed with two components of the solution at this dilution differ in refractivity most widely. Had there been no such formation of compounds between solute and solvent in the case with pyridine and acetic acid solutions, the differences given in columns 3 and 4 would have been more or less uniform. The compounds of acetic acid with benzene or toluene in solution are very much alike in refractive properties.

A few typical instances are given below to show the variation of refractive indices of solutions with dilution.

(a) Refractive index increases or decreases practically uniformly with concentration of solute or solvent.

%	Aqueous solution of HCl $n_D^{17 \cdot 5}$ By Wagner.	Aqueous solution of KCl, $n_D^{17 \cdot 5}$ By Wagner.
0	1·33320	1·33320
1	3551	3455
2	3779	3589
5	4449	3980
10	5528	4598
15	6565	4616
20	—	5032

Aqueous solutions of glycerine ; By Henkel and Roth.

% Glycerine =	1·226	6·320	9·308	12·746	14·178	19·843
$n_D^{17 \cdot 5}$ =	1·33463	1·34075	1·34000	1·34868	1·35041	1·35765.

Solution of ethelene dibromide and propyl alcohol.

$C_3H_4Br_2$% =	10·0084	20·9516	40·7320	60·0940	
$n_D^{18 \cdot 07}$ =	1·386161	1·391892	1·399136	1·415815	1·439013.
$C_3H_4Br_2$% =	80·0893	90·01912	100·0000		
$n_D^{18 \cdot 07}$ =	1·475796	1·503227	1·540399		

Solution of acetone and benzene.

C_3H_6O% =	0	9·8	20·0	31·0	40·0
n_D^{16} =	1·5036	1·4885	1·4723	1·4558	1·4426.
C_3H_6O% =	49·5	69·4	84·7	100·0	
n_D^{16} =	1·4284	1·4011	1·3803	13609	

(b) Refractive index increases, reaches maximum and then decreases with increased concentration.

%	Methyl alcohol in water. $n_D^{17\cdot5}$ By Wagner.	Ethyl alcohol in water. $n_D^{17\cdot5}$ By Wagner.	Acetone in water. $n_D^{17\cdot5}$ By Drude.
1	1·3339	1·33379	1·3335
2	1·33359	1·33444	—
4	1·33404	1·33571	—
10	1·33565	1·33997	—
20	1·33858	—	—
25	—	1·35132	1·35135
40	1·34292	1·35968	—
42·25	1·34313	—	—
49·8	1·34313	—	—
50	1·34311	1·36318	1 3637
60	1·34154	1·36525	—
65	1·33990	1·36577	—
66·9	—	—	1·3671
69	—	1·36584	—
70	1·32748	1·36572	—
89·9	—	—	1·3649
100	—	—	1·3606

Aqueous solution of sulphuric acid. By Hess.

H_2SO_4 %w/w = 0	19 981	39 757	59 980	80 096	100
n_D^{15} = 1·33364	1·35782	1·38169	1·40653	1·43083	1·42772

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Aqueous solution of acetic acid in water.

By Buchkmeiner.

$CH_3CCOH\% w/w$

	$=0$	14.339	44.431	71.194	83.828	100
n_D^{20}	$=1.33313$	1.34380	1.36362	1.37496	1.37722	1.37265

Refractive indices of mixtures of sulphuric acid and water in various proportions for all principle lines of solar spectrum from A to H inclusive have been determined by Van der Willigen[8], who has shown that a progressive increase in refraction and dispersion takes place with every addition of H_2SO_4 molecule until a maximum is reached at a point. Some of his results are given below :—

$SO_3\%$	$=$	71.27	81.41	85.93	86.97	91.43	94.72
$n_D^{18.3}$	$=$	1.42466	1.43595	1.43806	1.43669	1.43426	1.43163
Sp gr. at $0°/0°$	$=$	1.64925	1.76065	1.80676	1.83123	1.84485	1.84995

Although the specific gravity steadily increases with concentration of the acid yet the specific refractive index remains maximum at a concentration of 85.93% SO_3. Van der Willigen concluded that the formulae connecting refractive indices of solvent, solute and solution are not applicable to mixtures of sulphuric acid and water.

Cheneveau[9] in studying the variation of specific refraction of salts in dilute aqueous solutions has shown that specific refraction $\dfrac{n_D - 1}{d}$ of a dissolved salt is constant for solutions down to a dilution equal to $\dfrac{N}{10}$. He[10]

however, subsequently found that at extreme dilutions the refractive power may diminish or increase, with the decreased concentration according to the nature of salt used. Results are plotted for magnesium nitrate, potassium chloride and ammonium nitrate and it is seen, in very dilute solutions, the value of $\frac{n-1}{d}$ decreases with the pressure of the dissolved substance for the two substances first named but increases, as the pressure decreases in the case of ammonium nitrate.

Studies in the refractive properties of substances in solution with increasing quantities of solvent, show that compounds are formed at each stage of dilution refractive properties of which are not necessarily always gradual with the ratio of increased solvent. Association of solute and solvent takes place at each dilution producing compounds which may differ considerably in refractive properties from the compounds formed at any other dilution. Proper attempts have not been made by the followers of the dissociation theory of solution to explain these phenomena in light of their assumptions that electrolytes like KCl breaks up into KOH and HCl in aqueous solution. It seems almost impossible to explain reasonably by the dissociation theory of solution the mechanism taking place in cases of solutions stated above, which are easily explained by the assumption that the solvent and the solute remain in a state of combination at all dilutions.

Gladstone and Hibbert[11] carried out a large number of experiments and found that the influence of solution on

the salt is a very complex. The behaviour of different
salts is not uniform ; some increase and other decrease in
refractivity on passing into solution. These facts also
could not be reasonably explained[12] by the electrolytic
dissociation theory. Although in many cases the
refractive index of a substance, can be calculated from the
refractive power of its solutions, other cases, not a few in
number, have also been met with where the refractive
index so obtained, not only differs from that obtained
with the solid substance, but depends also on the solvent.
At first this behaviour was considered to be due to
ionisation, but it was found later that many cases can not
be explained on this view. Recently, the subject has
again been studied by Walden, in pursuance of his
previous work on non-aqueous solutions. This author has
determined the refractive indices of tetraethylammonium
iodide, tetrapropylammonium iodide. and phenyldimethyl-
ethylammonium iodide in a large number of different
solvents. Whilst the refractive indies of these substances,
calculated by the mixture formula, have been found to
vary only slightly with the concentration of the solution,
the values calculated from solutions in different solvents
have been found to differ considerably from one another.
These differences cannot be ascribed to variation in the
degree of ionisation, because it has been found that they
occur even in solutions in which the degree of ionisation is
the same, and further in solution in which the degree of
ionisation is different, the same value for the refractivity
has been obtained. In considering other physical
properties of the solute and solvent, however, the author

shows that the molecular volume of a substance in solution is a variable quantity according to the solvent employed. Thus for tetraethylammonium iodide in aqueous solution, the molecular volume is 186·9, whereas in acetonitrile solution it is only 157·1. The molecular volume, however, varies only slightly with the concentration in any given solvent On comparing the values of the molecular refractivity with those of the molecular volume in different solvents, it is found that the greatest value of the refractivity is found in that solvent in which the molecular volume of the solute is the least, and vice versa. Moreover, it is found that the solute has the highest value, of molecular volume in that solvent which has the smallest co-volume. It would therefore appear that variations in the refractivity of a dissolved substance are probably due to variations in its molecular volume in different solvents, and not to variations in its degree of ionisation. Two points, however, may be raised in this connection, (1) it still remains to be settled properly whether solute, solvent or both separately or in associated form change, in volume, and (2) if change in volume could counterbalance the change in refraction how do the other properties stand which undergo alterations simultaneously with the formation of solution. It may also be noted here that the determination of contractions in solution have shown that Walden's assumption that the molecular volume varies only slightly with the concentration in any given solvent is not general.

The effect on the refractive property of a substance by its association with a solvent could be studied by

determining the change in refractive properties taking place when a molecule of it is allowed to combine gradually with increasing number of molecules of solvent. Each addition of a molecule of a solvent may introduce changes in property of the resultant substance which may differ from any of the original components. This final property depends on the adjustment of all other properties e.g.,—thermal, electrical etc., a loss in one may introduce an equivalent gain in one or more of the other properties.

At present tabular statements are available in per cent by weight or by volume which are rather inconvenient in studying the effect of solvents on solute. Determination of properties of a substance by gradual addition of another substance in molecular proportions are considerably desirable.

2. *Polarisation.*

A light ray passing through a Nicol's prism prepared from Iceland spar gives emergent ray differing from the original. One of the planes is polarised and if this ray is examined by another Nicol's prism, it will be found that, on rotating the latter, the field of view appears alternately light and dark, the minimum of brightness following the maximum as the prism is rotated through an angle of 90°. Ordinarily the first prism is called the polarizer and the second the analyzer.

If a tube containing a solution of cane sugar is placed between the two prisms, after making the field of view dark by placing the axes of the two prisms at right

angles to each other, the field ligthts up. By rotating one of the prisms through an angle the field darkens again. Substance like turpentine having the property of rotating the plane of polarized light is called optically active. An optically active substance is called dextrorotatary when the analyzer has to be turned to the right i.e., clockwise to obtain darkness, and lævorotatory when the analyzer should be turned to the left for the purpose.

The refractivity of substances and their mixtures is general, but the polarisation of light is a property possessed by a few selected ones. This property is entirely dependent on the arrangement of the atoms in the molecule.

The magnitude of this property of a substance is measured in terms of angle of rotation mentioned above by means of instruments called polarimeter. This angle of rotation for pure substance depends on :—

(1) nature of the substance.

(2) length of the layer through which the light passes.

(3) wave length of the light used (the shorter wavelength generally gives greater angle of rotation).

(4) temperature.

When the substance is examined in solution the influencing factors, in addition to above, are :—

(1) nature of the solvent.

(2) concentration of the active substance.

The standard of measurement used in this connection is the angle of rotation produced by a liquid which in the bulk of 1 c. c. contains 1 gm. of substance, through a length of the column of 1 dcm. This angular deviation of light is called the specific rotation of the substance

and is represented by $[\alpha]_D^t = \dfrac{1}{l.d}$ for pure substance and

$[\alpha]_D^t = \dfrac{100\alpha}{l.c}$ for solutions.

Where [α]=specific rotation of the substance.

t = temperature of determination.

D = D line (sodium light).

α = observed angle of rotation.

l = length of the tube in decimetres containing the liquid through which the light passes.

d = density of the pure substance.

c = number of grams of active substance in 100 cc. of solution.

" Molecular rotation " or " molar rotation " is the product of the specific rotation and the molecular weight.

In considering the factors influencing the property of substance which can turn the plane of polarisation of light it may be noted that this property is derived from the position of an atom or atoms contained in a molecule. Carbon has been ascribed to give this property to the molecule of many commonly occurring organic compounds. And its magnitude depends considerably on the position of the rest of the atoms or groups of atoms in the molecule. Magnitude of specific rotation is considerably influenced by the nature of the radical which created such property. Several investigators have worked on this subject, but only a few typical instances will be quoted for the purpose of illustrating the nature of the influence that could be created by the introduction of different radicals

in a molecule on its optical activity. Guye[13] considered that the degree of the asymmetry of the molecule of an optically active compound with mass of each radical and the distance of its centre of gravity from the centre of the figure of the tetrahedron ultimately influence the sign and magnitude of the specific rotation. He, in support of his theory, gave numerous results amongst which the following are interesting :—

(1) Specific rotatary power increases with the molecular weight of radical introduced in the place of acidic hydrogen of tartaric acid.

				[α]
Methyl tartrate	...	...	...	+2·14
Ethyl tartrate	...	...	...	+7·66
Propyl „	...	...	...	+12·44
Isobutyl „	...	...	...	+19·87

(2) Substituted benzoyl group in dibenzoyl tartaric acid has been assumed to move the centre of gravity to the other side of the plane of symmetry which is situated between the COOH and OH groups ; this replacement reverses the sign of the rotary power. The centre of gravity of the molecule moves back towards the above mentioned plane of symmetry and thereby rotatary power is diminished by the subsitution of H in COOH group with an alkyl group : —

				[α]
Dibenzoyl tartaric acid			...	− 117·7
Methyl „	„	„	...	− 88·8
Ethyl „	„	..	...	− 60·0
Isobutyl „	„	„	...	− 42·0

If acetyl radical is introduced in the place of benzoyl radical in the above compounds the effect on the rotatery power is similar but the magnitude of the lævorotation is less on account of the molecular weight of the radical being less than that of the other :—

					$[\alpha]_D$
Diacetyl tartaric acid				...	− 23·1
Methyl	„	„	„	...	− 14·3
Ethyl	„	„	„	...	+ 1·0
Propyl	„	„	„	...	+ 6·5
Isobutyl		„	„	...	+10·3

Crum Brown [14] considered that the constitution of substituting radicals has an influence on rotatary power of the final molecule in addition to its mass as proposed by Guye. Examples have been shown contradicting[15] these hypotheses and modified ones proposed, but nothing seem to be completely decisive except that of the existence of a relationship between molecular structure and its optical activity.

Influence of change of temperature on the optical activity of substances has been noticed by Biot and subsequently more data published by several other investigators. Optical activity of a substance may increase, decrease or remain constant with variation of temperature. Formulae have been proposed by several investigators to establish the relationship between specific rotation and temperature but none of them unfortunately seem to attract any general importance.

Alkyl esters of tartaric acid afford considerably inter-

esting examples. Methyl tartrate gives $[\alpha]_D^{20} = +2.07$, no rotation at 6° C and negative rotation below 0° C. And others give maximum[16] at higher temperatures, some of them are given below :—

Ester.	Temperature.	Maximum molecular rotation.
Ethyl tartrate	175°	+30 9
n-propyl ,,	150	+41·65
Sec-propyl tartrate	144	+58·03
iso-Butyl ,,	120	+53 9
iso-Amyl ,,	151	+48·72
Allyl ,,	130	+43 24
Sec-Octyl ,,	160	+51·46

Di-trichloroacetyl derivatives of ethyl and iso-butyl tatrates give minimum[17] rotations at elevated temperatures.

It has already been mentioned that specific rotation of a substance can be determined by taking polarimetric readings of its solution of known strength by means of the formula given therein. But the figures obtainable by this method are materially influenced by the nature of the solvent and generally different from what it is in the pure condition. Waldon[18] has studied this problem with considerable thoroughness but the following typical[19] examples will serve the purpose of illustration of the phenomenon :—

Solvent.	$[\alpha]_D^{20}$ at infinite dilution.	
	Ethyltartrate.	Nicotine.
Formamide	$+30\cdot4°$	$-\ 70°$
Water	$+26\cdot85$	$-\ 77\cdot4$
Methyl alcohol	$+11\cdot5$	$-129\cdot4$
Ethyl alcohol	$+\ 9\cdot13$	$-140\ 1$
Benzene	$+\ 6\cdot1$	$-163\cdot5$
Ethene dibromide	$-19\cdot1$	$-183\cdot5$
Glycerol	$+10\cdot57$	—
n-propyl alcohol	$+\ 7\cdot4$	—
iso-Butyl alcohol	$+\ 6\cdot53$	—
Sec-Octyl alcohol	$+\ 5\cdot24$	—
Toluene	$+\ 4\cdot6$	—
O. Xylene	$+\ 2\cdot7$	—
m. Xylene	$+\ 1\cdot8$	—
p. Xylene	$+\ 0\cdot7$	—
Mesitylene	$-\ 3\ 0$	—
Chloroform	$-\ 3\cdot2$	—

Determination of effects of concentration on specific rotation of substances in solution is very useful in studying the relationship between solute and solvent. Influence of concentration on rotation of substances in solution has been appreciably found in many cases ; malic acid $C_4H_6O_5$, however, affords most interesting results. Schmeider[20] found that the rotation of an aqueous solution of malic acid was left handed in dilute solutions and right handed in concentrated solutions passing through a solution having no rotatary power at about 34% strength.

The following figures may be examined in this connection :—

(1) Specific rotation increases with concentration.

Malic acid. $C_4H_6O_5$ in water.[21]

%	$[\alpha]_D^{10}$	$[\alpha]_D^{20}$	$[\alpha]_D^{30}$
21 65	− 0·44	− 0 90	− 1·43
28·67	+ 0·33	− 0·35	− 0·83
40·44	+ 1·31	+ 0·54	− 0·12
53·75	+ 2·52	+ 1·73	+ 0·94
64·00	+ 4·10	+ 2·72	+ 1·99

d.Camphor $C_{10}H_{16}O$, in acetone.[22]

%	= 15·11	22·29	32·29	46·56
$[\alpha]_D^{13\cdot7}$	= 48·77	49·13	49·66	50 55

Quinine (anhydride) $C_{20}H_{24}N_2O_2$ in ethyl alcohol.[23]

%	$[\alpha]_D^{0}$	$[\alpha]_D^{10}$	$[\alpha]_D^{20}$
1	− 171·4	− 169 6	− 168·2
4	− 166·1	− 164 4	− 163·2
6	− 162·4	− 160·9	− 159·8

(2) Specific rotation decreases with concentration.

Barium d.Methoxyl succenic acid $C_5H_5O_6Ba$ in water.[24]

%	= 1·149	5 746	12·42	26·12
$[\alpha]_D^{18}$	= + 3·16	− 2·21	− 7·36	− 14·27

Cane sugar $C_{12}H_{22}O_{11}$, in pyridine.[25]

%	=	1	2	4	6 25
$[a]_D^{25}$	= +86·7		85·9	84·7	83·6

(3) Specific rotation increases, passes through maximum and then decreases with concentration.

Nicotine $C_{10}H_{14}N_2$ in water.[26]

% =	1·061	5·700	8·307	10 26	15 59	100
$[a]_D^{20}$ =	− 77·66	− 76·95	− 76·74	− 76·89	− 77 59	− 164 0

Unfortunately work has not been sufficiently extended to afford enough instances of variation as could be found and described in connection with other physical properties of solutions. But the variations shown above would be able to give conclusions needed for the present purpose.

Specific rotation of a substance in solution may be considerably interfered by the introduction of a third substance[27]. Boric acid, molybdates, tungstates, arsenates, antimoniates, and alkaline uranyl nitrates have been used by different investigators, in altering the rotation of solutions of tartaric, malic and lactic acids. Magnitude of interference, of course is dependent on the quantity of the added substance. Geruez found that about 10 per cent solution of malic acid having $[a]_D^{17} = -0.189$

indicates $+13\cdot26$ with an addition of $2\cdot017$ gms. of sodium molybdate $Na_2MoO_4, 2H_2O$ per 100 cc., whereas inactive solutions are produced with additions of 1 4, 2 85 and $4\cdot25$ gms of the substance, maximum and minimum rotations occurring at intermediate concentrations. According to Boeseken and Convert, the rise in specific rotation shown by certain sugars in the presence of boric acid is always accompanied by a marked increase in electrical conductivity. Probablity has been proposed that there is a particular configuration of the terminal hydrogen atoms and hydroxyl groups which favours the formation of compounds with boric acid. Most sugars, on dissolution in water, undergo a transformation which can be followed with the polarimeter, and is due to the transition from the α- to the β- form, or the reverse, until eqnilibrium is attained. Such a change may involve an increase or a decrease in the power to combine with boric acid, and hence a corresponding change in conductivity. The behaviour of α- and β- lactose in solution, in the presence and absence respectively of boric acid, has been examined. The effect of boric acid on the rate of change of rotation of both forms is practically negligible. The presence of a minute trace of impurity greatly affects the result and such experiments have been made at $12\cdot9^{\circ}$, $15\cdot5^{\bullet}$, $20\cdot0^{\circ}$ and 25°.

Muta-rotation :—Association theory of solntion considers that a reaction takes place between solvent and solute, and like chemical reactions this combination occurs with some velocity, Majority of the optically active substances have been found to combine with solvents very

quickly and attempts have not been made to measure them.
But many sugars, oxyacids, lactones of oxyacids, nicotine,
amines and nitro-camphor when freshly dissolved and
polarized give rotation values which gradually change
and become constant after a period depending on the
condition in which they are presented to react on each
other. Rotation may increase or decrease towards a
constant with a velocity of reaction which could be
influenced by catalysts. For sugars, dilute alkaline
solutions even 0.1% ammonia may cause immediate change
of rotatary power to the constant value Like chemical
reaction this is also enormously accelerated by increasing
the temperature. The following specific rotations[26] of
sugars in different conditions only indicate the effects of
association of solvent and solute.

	$[\alpha]$ Stable modification in solution.	$[\alpha]$ First labile modification in solution.	$[\alpha]$ Second labile modification in solution.
Dextrose	+ 52·7	+105·2	+22·5
Galactose	+ 81 6	+135·0	+52·3
Lactose	+ 52·5	+ 86·2	+ 34 4
Maltose	+138·0	+118·2	
Levulose	− 92·5	−104·0	
Arabinose	+104·4	+156·7	
Xylose	+ 19·2	+ 94·4	

Experiments on muta-rotation have been studied with
some thoroughness by only a limited number of investi-
gators[29] and resuts so far obtained can hardly be considered

to be exhaustive. Although investigation on this subject is very difficult on account of the uncertainty of purity of compounds to be dealt with yet there seem to be much known.

Lowry obtaining muta-rotation with camphor in non-aqueous solutions opposed the views of Fischer that the phenomenon is due to the hydration of solute (sugars) with the solvent (water) and considered the process to be due to some iso-dynamic changes. Association theory of solution, however, explains phenomena both in aqueous and non-aqueous solutions by the assumption that each pair of solvent and solute form compounds in molecular ratios same as the dilution which may differ in properties from any of the components or from what could be formed at any other dilution. This is true for all combinations so long as they can form solutions.

Phenomena of muta-rotation and other changes in physical properties of solutions with time have been explained by Riiber and others[30] by assuming that the molecules of the solute only undergo changes under the circumstances, but it would be interesting to know how the subject would stand if all such phenomena are explained in light of the association theory of solution and the change with time is due to velocity of the re-action between solute and solvent at those particular dilutions. It may be possible to explain all the facts without assuming the existence of any such new modifications of the solute which could not be isolated.

Magnetic rotation :—Faraday[31] discovered that any transparent body being placed in a magnetic field acquires the property of rotating the plane of polarisation of light

in the direction of lines of force. This magnetic rotation is proportional to the strength of the field, the thickness of the traversing medium, and the nature of the light used. Perkin[32] did lots of experiments on the subject some of which are very useful in considering the relation between solute and solvent in solution. His determinations of molecular rotation[33] in magnetic field of organic and inorganic bases and acids, and some ammonium salts in solution may be used in support of association theory of solution, namely the solvents and solutes form compounds in proportions same as their dilutions, all properties of which may differ from any of its components and from any other formed in other proportions.

The optical rotatary property of a molecule is acquired and altered by changing the constituents in the molecule, by action of solvent, by altering the dilution of the same solvent, by changing the temperature and by introducing it in a magnetic field. Now a question arises whether any change in optical rotatary property indicates simultaneous corresponding change in the structure of the molecule or indicate only a change in molecular vibration which would respond to the ray of light. The ultimate result is that the light ray passing through such medium receives a property imparted by the molecules of the medium. Thus whenever any rotation of light is observed it may be presumed that it must have come from the peculiar movements of the molecules of the medium through which the light has traversed. Consequently the molecules of the medium must prepossess a property of imparting such one to the light ray passing through it. Now it remains to

be considered how a molecule can acquire this property. If it is true that the molecules remain in a state of vibration and it is this property that could interfere with the ray of light which may come in contact while passing through it, one may not be irrational to think that the vibration of a molecule as a whole could be possibly interfered with without changing the intra-molecular relationship amongst the atoms or radicals composing the molecule. When a molecule is placed in a magnetic field it acquires such property of rotation which may not interfere with intra-molecular arrangement.

It is also rational to suppose that a molecule may acquire this property by undergoing some intra-molecular change, and effects of solvents may be considered amongst this class. Solvents combining with solute molecules interfere with or impart this property. When a third substance is introduced in a binary mixture a combination of three things takes place and the properties of the final product differ from the components and from any other that may form in a different ratio. The effect of combination of solute and solvent might change or not the internal condition of the associated molecule to affect all or any other properties, and the final resultant molecule reaches a state of equilibrium after neutralising all forms of energy,—thermal, electrical, etc.

Attempts have been made to correlate the optical properties of solutions with osmotic and other properties and although most of them have failed yet it may be some time interesting to know them[34], but it is not worthwhile to describe them here. Scheuer[35] determined several physical properties of solutions of diacetyl tartrate

and menthol each dissolving in a number of solvents. His investigations included determinations of viscosity, dilation, melting point, and rotation for light of different refrangibilities. From these results this investigator failed to notice, either in the liquid or in the solid phase, any sign of complex formation between solute and solvent molecules in solution. It would not be correct to draw conclusions from these results only that solute and solvent do not combine because formation of such compounds is attended with readjustment of all forms of energy and these few observations are too incomplete and inexhaustive to bring forward such generalisation.

Association theory of solution has succeeded in explaining above phenomena connected with optical properties of solutions. The electrolytic dissociation theory of solution seems to have totally failed to explain the magnetic rotatary properties of electrolytes. Very systematic attempts have been made by many eminent investigators[36] to establish relationship between this property and ionisation in electrolytes but the only rational conclusion that may be drawn from their results is that there can be no electrolytic dissociation in electrolytes. Smiles has summarised the results of experiments on the effect of solvent and dilution on the magnetic rotation of salts showing that this property increases, decreases, or remains constant with dilution depending entirely on individual nature of the substance. These results obviously do not harmonise with the conception that the solutes in an electrolyte partially break up into ions and number of the broken molecules increases

with dilution. There is no doubt that the electrical conductivity increases with dilution but the explanation put forward that that is due to the breaking up of the molecules in solution does not suit other properties.

Effects of dissolved state and dilution present strong evidences in favour of the association theory of solution. Perkin's work on the subject with amonium and sodium salts of formic and acetic acids when compared with that with ammonium nitrate affords interesting illustration. The rotatary power of ammonium nitrate is nearly equal to sum of the rotations of ammonia and nitric acid but the ammonium salts of halogen acids are quite abnormally high. In the cases of double salts[37] of $Na_2SO_4, MgSO_4$, $Na_2SO_4, CdSO_4$, and $Na_2SO_4, MnSO_4$ the rotations were found to be equal to the sum of the rotatary effects of the individual salts present there and in the cases of $NaCl, HgCl_2$, and $2KI, HgI_2$ larger increase in rotatary power has been noticed than that of the sum of the rotatary effects of each of the salts. These results have been interpreted to be the consequence of no rearrangement of atomic affinities in the former cases ; and in the latter cases atomic combination taking place, rotation gets so much changed. It is undeniable that the large increase in rotatary power produced by mixing of salts indicates some redistribution of the atomic relationship inside the molecules of the components, but in the cases where no such increase is noticed it need not necessarily be concluded that no reaction has taken place, on the contrary it may be concluded that the result of the reaction did not produce complex molecules of different rotatary activity.

Absorption.

When rays of light of different vibration are allowed to pass through gaseous, liquid or solid media of different substances, some of them pass through while others are absorbed. Presently absorption by liquid media will be needed in trying to disentangle the mechanism of the state of existence of solvent and solute in solution. Hartely[38], Julius[39], and Drude[40] did not quite agree in their opinions about the exact dynamic nature of this property. There are two kinds of absorption in solution, continuous and selective. The former decreases with dilution and ultimately disappears. A medium showing continuous spectra may show only selective one under the same conditions if the thickness of layer traversed is sufficiently decreased. Thus it will serve the purpose of the theory of solution to deal with the phenomenon of selective absorption which could be influenced by solvent and solute whereas the other is dependent only on the number of molecules present per unit area in the path of the ray of light. Hartley considers that the selective absorption of light is caused by sub molecular particles vibrating synchronously with the incident light waves. Julius gave a strong support to this view by showing that the absorption and emision spectra of simple substances are indentical. It seems reasonable from the results obtained by numerous investigators that the selective absorption is caused by intramolecular vibrations arising from atoms and groups of atoms.

The molecules in the medium thus absorbing the

light energy may get it converted into (1) floursecent light (2) heat, and (3) chemical energy,

Solutions of substances, having strong absorption power, are often dealt with in these studies instead of pure samples. Solvents are selected in a way so that it has not got any absorption band in the region where the solute under investigation would show any. Ordinarily ethyl alcohol has been used by many investigators. While studying the absorption spectra in solution it has been noticed that although a solvent may not exert any absorption in the region of the spectra in question, yet it often influences on such absorption of the solute. Kundt[41] found that the absorption bands of the dissolved substances are pushed towards the red region of the spectrum by increasing the refractive index of the medium and therefore he recommended that when a comparative result of a series has needed they should be obtained with the same solvent and with the same molecular dilution ; unless study on the effect of dilution has needed. Variation of the thickness[42] of the layer of solution of uniform molecular concentration serve useful purpose for com parison of one substance with another. Photographic determination of absorption bands of camphor in alcoholic solutions in different concentrations and different thickness of layer traversed by light serve as important illustration for proving the action between solvent and solute. The effect of solvent on solute so far as absorption band is concerned is influenced by dilution, and in case of alcohol-camphor it is over 10 units on the logarithmic scale of reletive thickness of solution.

Miller[43], and Soret and Rilliet[44] tried to find out the relationship, if any between chemical constitution and absorption band. but the problem, however, had been exhaustively tackled by Hartley[45] and subsequently by a few others, who finally came to the conclusion that absorption spectra and chemical constitution of organic compounds were related. Position iso-mersim[46] in the benzene nucleus was found to influence absorption of light, the addition of methylene group caused the absorption bands to shift towards the red position of the spectrum in alkyl nitrates, alcohols[45] and amines[47]. Homologous alkaloids[48] like morphine and codeine, and quinine and cupreine have almost identical obsorption curves Although constitutive nature of the absorption is admitted yet Dobbie and Lander have shown that a given substitution has less influence on absorptions of complex bodies than on those of simpler compounds. Piperonylic acid and veratric acid are simple benzene derivatives.

COOH <====> O   COOH <====> OCH$_3$
             O⎤   OCH$_3$
            CH$_2$
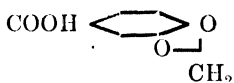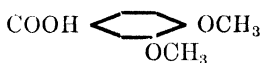
     Piperonylic acid.   Veratric acid.

have appreciably different curves whereas complex mole-cules of alkaloids of tetrahydrohereberine and corydaline,

C$_{12}$H$_{16}$NO$_2$ —< (O / O) > CH$_2$ CH$_3$C$_{12}$H$_{15}$NO$_2$ (OCH$_3$ / OCH$_3$)
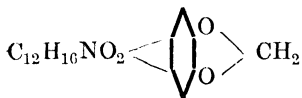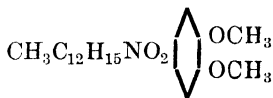
     Tetrahydrobererine   Corydaline

which possess the same relations to one another, have

practically the same absorption curve. Similar examples
have also been noticed in the cases with styrol (C_6H_5CH
$\leftrightharpoons CH_2$) and benzoic acid (C_6H_5COOH), and cinchonine
($C_{17}H_{19}N_2O.COOH$) and cinchotenine ($C_{17}H_{19}N_2O.COOH$)
very different spectra in the case with the first and almost
identical in the latter was found.

These results indicate how the absorption spectra
are due to the components constituting the molecule and
to what extent this property is influenced by the remaining
components of the same molecule. A valuable collection
of all results of this nature has been made by
Hartley[47] in discussing the relations between the type of
ultra-violet absorption and the structure of compounds.

Effect of dilution on the absorption power has
been noticed in the cases of dextroracemic-, and meso-
tartaric acids[50], in-active-, and dextro-, corydalines[51],
tetrahydrobere-berine and canadine, and dibenzoyl succinic
esters[52].

There are two bands shown by quinone, the one in the
ultraviolet region with its head at about 4000, and the
other in the visible region at about 2300 units The
former is benzenoid band and the latter, isorropic band, is
caused by dicarbonyl system. It will be found that in
alcoholic solution the benzenoid band is weak and the
isorropic band well marked. Hartley and Leonard[58] have
found that the two bands are nearly equally distinct in
etherial solutions. Kehrmann[54] has shown that, similarly
as the solvent, substitution of hydrogen atoms with
methyl group or halogen atom in p-benzoquinone would
influence the absorptive power of its carbonyl groups. In

determining absorption of derivatives of quinone in
alcoholic solutions the following steady increase in the
persistence of the benzenoid band had been noticed.
Change of dilution over which the band persists with

	%
Monochloro benzoquinone	42·0
2·6 Dichloro benzoquinone	55·0
Trichloro benzoquinone	77·0
Trichloro toluquinone	88·0

Intramolecular change undoubtedly influences the
absorption of light but the exact nature of the relationship
is not properly known. The absorption by nitrocamphor[54]
and its derivatives in solvents of varying composition
afford splendid examples of intramolecular change caused
by the solvent only. Lowry has also found that the
speed of change between normal and pseudo-nitro-camphor
can be easily controlled by the regulation of the solvent or
by the addition of a suitable third substance. A deep
band is developed, with its head at about 3100 units by
the addition of an alkali which it has been considered,
may not be due to isomeric change that takes place in
other non-alkaline solutions of nitrocamphor. These facts
serve useful purpose of illustrating the states of existence
of a substance in solution and in pure condition.

There are two factors by which a substitution may
influence the absorption of the parent compound, (i) the
mass of the substituent[55] and (ii) the residual affinity
of the substituent[56]. Hartley thinks that the increase in
the mass of the molecule caused by the insertion of a
substituent tends to retard the intra-molecular vibrations

and thus brings the absorption towards the red region of the spectrum. The influence of substitution with a particular group is greater on substances of low molecular weights than on compounds of complex molecular weights. Dobbie and Lander[57] have shown that insertion of methyl and other light groups has no effect on the absorption spectra of many alkaloids.

In studying the influence of the residual affirmity of the substituent it is necessary to eliminate or minimise the disturbing influence of the mass of the group. Thus it will be found that in mono-substituted benzene the absorption band due to benzene are not to any great extent disturbed if saturated atoms are attached to the nucleus, but with unsaturated atoms the disturbance is quite distinct[58]. In anisole $C_6H_5OCH_2$, the benzene spectrum persists but in a modified form; the benzene absorption, however, becomes quite indistinct in benzaldhyde C_6H_5COH, aniline $C_6H_5NH_2$, and nitrobenzene $C_6H_5NO_2$. In such cases a broad band appears near the visible spectrum and an additional interest is created to find that simultaneously with these effects refractive power and magnetic rotation are altered.

Effects of solvents on the absorption of light by substances are well illustrated and known in the cases with nitrophenols and cotarnine. Ortho-, para-, and meta-nitrophenols[59] present lots of differences in neutral solutions from those that could be found under similar circumstances in alkaline solutions. The solutes in neutral and in alkaline solutions differ in molecular structure. The nitro-group changes its consitution in different

iso-meric molecules and forms different compounds in alkaline solutions. Cotarnine is known to be capable of undergoing intra-molecular changes in different media of solvents. Their distinctions are manifested in their power of absorption of light. Cotarnine as an alkaloid when present as a salt possesses of (i) ammonium type[60], as a base liberated from these salts with alkali behaves like an (ii) aldehyde[61] and secondary base, and when obtained from isoquinoline it is said to possess (iii) carbinol[62] structure. Spectrographic[63] studies have proved very useful in establishing identities of these modifications. Dobbie[64] and his coworkers made extensive researches on this change of structure according to the state of existence in solution of phenyl acridine derivatives, cotarnine, hydrocotarnine, cyanhydrocotarnine and hydrastinine. These results furnish a great evidence as to how the relationship amongst the components of a molecule is dependent on the other molecules or groups of molecules with which they will come in contact during the state of existence.

The molecular structure of cotarnine also varies from the carbinol to the ammonium type according to the nature and composition of the solvent. Ether or chloroform keeps it as the carbinol form while alcohol converts it into the ammonium type. Conversion of one form into the other has been studied by taking a chloroformic or ethereal solution and then adding alcohol gradually. The following quantitative results were obtained by adding methyl alcohol to an ethereal solution of the base at odinary temperatures :—

% methyl alcohol	0	25	40	50	100
% Carbinol form of cotarnine	100	97·5	92·5	85·0	75 0
% Ammonium form of cotarnine	0	2·5	7 5	15·0	25·0

These reactions[65] causing changes of molecular structure have velocities like all other chemical reactions and this speed is influenced by light and heat. Colourless solutions of hydrazones do not change speedily when kept in the dark but very rapidly become deep yellow on exposure to sunlight.[66] This reaction, however, is not so pronounced in dilute solutions. The spectrum of the exposed solution gives the characteristic band of the hydrazone[67] group being thus changed into azo group :—

$$- NHN = CH.CH_3 - \rightarrow - N = N - CH_2CH_3.$$
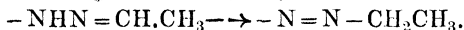
Bally found that in undergoing isomeric change produced by the action of light on the aldehyde hyrazones the phenomenon is accompanied by the appearance of well marked band in the visible region of the spectrum. The velocities of these reactions in solutions have been found to depend also on several other factors.

When substituted ammonium salts of halogen acids are converted into their corresponding hydroxides by the action of silver hydroxide in aqueous solutions strongly alkaline solutions having electrical conductivities same as those of the common alkali hydroxides are formed. In course of the determination of electrical conductivities of such substituted ammonium base, Hantsch[68] found that the value gradually decreased on keeping. Phenyl

acridine methiodide gives a good illustration of this phenomenon. Influence of time and temperature in the transformation of the carbinol form to the ammonium base type of contarnine in alcoholic or aqueous solution has been noticed by Dobbie[69].

The brief account given above about the phenomenon of absorption of light by solutes in solution do not seem to contain any instance that would go against the association theory of solution as described elsewhere. Formation of compounds amongst solute and solvent may be assumed whenever this optical property presents any change in the solution. The disturbance of energy at particular conditions of solutions, where absorption of light is interfered with, assumes its equilibrium after acquiring such property. When the substances lose their such property after separation from the solvent it is reasonable to assume that they acquired the same by dint of their combination with the solvent.

4.   Fluorescence.

From very early days attemps have been made by several scientists[70] to discover the theory of the phenomenon of fluorescence but they do not seem to have come to an unanimous definite conclusion as yet. All that can be gathered from the discussions made on the subject is that the phenomenon may be due to or influenced by both intra-molecular reactions in pure state and in state of solution. The phenomenon of fluorescene has been associated with the existence of certain atomic groups in the molecule, e.g. isocyclic benzene, anthracence, acridine,

azine, oxazine, thioazine and pyrine rings, of course effects due to these groups of atoms are influenced by the presence of other groups in the same molecule.

A substance after absorbing light energy produces fluorescence, and in order that a substance could fluoresce it should be placed in a light of suitable wave length. A solution of quinine salt fluoresces in violet and ultra-violet light but does not do so when illuminated by a red light. A solution of eosin absorbs the green rays and fluoresces greenish-yellow. An acid solution of a quinine salt fluoresces pale blue, whilst it absorbs a portion of the ultra-violet light concluding obviously that the wave lengths of the absorbed light are shorter than those of the fluorescent light. Since it has been found that the fluorescent light does not enter into the substance it is concluded that the wave length is changed during its reflection from the surface, and this is known as Stokes's Law[71]. In studying fluorescence in solution Stokes noted that there is an optimum concentration for each fluorescent substance, the intensity of the fluorescent light increases, reaches maximum and then decreases again with concentration.

Attempts have been made by some investigators to make use of this property for analytical purposes and attention of the scientists is drawn to this branch of research since not only the results will be useful for industrial or technical purposes but also bring many conflicting theories into proper test.

Most of the investigations on fluorescence are done by taking the substance in solution. It has been noticed

that the effect of the solvent is often very pronounced. Thus a solute may give strong fluorescence in one solvent and much less or none in another ; and the colours of the fluorescence substances in different solvents very seldom agree. Solutes form compounds with solvents in ratio same as their dilution, and the property of fluorescence of such compounds composed of solute and solvent in different ratios need neither agree nor should be proportionate, since these compounds are likely to differ in properties from other similar ones formed at different dilutions and from the calculated average of those of the pure solute and solvent present there. The solvent alcohol forms fluorescent compounds with s-phenyl-di-p-nitropen-azothionium hydroxide and non-fluorescent with diphenyl-pyrone, on the other hand, sulphuric acid gives non-fluorescent solution with the former and bright fluorescent one with the latter. Some substances do not form fluorescent compounds with solvents in concentrated solutions but do so when the portion of the solvent becomes quite large 2 -methyl- 3 -amino 4- oxy-quinoline[72] is fluroscent only in dilute alkaline or acid solutions. Flourescence of eosin solutions in acid or alkali increases on dilution up to a certain limit. This behaviour lead some chemists[73] to think that it is the formation of ions that causes the increase of fluorescence on dilution and when it is too much diluted the weakening effect of decreasing concentration operates and fluorescenc diminishes with concentration at higher dilution. It does not seem necessary to think that ionisation does take place at all in such solutions as the pheonomenon is also

found in non-electrolytes The association theory explains the plenomenon in its own way, the compounds formed with solvent and solute in different proportions have their properties which need neither agree nor vary in the same ratio in which they are constituting the molecule. In view of the fact that majority of the fluorescent substances either contain a mobile atom or are capable of undergoing a change in constitution simply by a movement of the valencies of the component atoms it seems reasonable to think that there exists a connection between tautomeric change[74] and fluorescence. Hewitt thinks that a fluorescent substance must exist in more than one interchangeable forms ; one of them absorbing energy from the incident ray becomes converted into any other form, which performs the function of fluorescence and gets reconverted into its original state. This theory, however, is not inconsistent with the association theory of solution.

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CHAPTER IX

ELECTRICAL EFFECTS OF SOLUTION.

Studies on electrical properties of solution attracted considerable attention on account of its wide application for practical purposes in science, and in industry. Results connetcted with theory of solution may be mainly divided into two following classes :—

(1) Generation of electric current in solution.

(2) Conveyance of electric current through solution.

Generation of Electric Current in Solution.

Electrical equilibrium is disturbed by the production difference of potential when a substance passes into solution and when two different substances are placed in the same solution. If these are suitably connected by means of a metallic conductor electric current flows from the terminal of the higher potential to that of the lower and the reaction between solvent and solute proceeds with increased activity. Such system in which changes of energy are associated with changes of matter chemically in producing electro-motive force is called a galvanic element.

Galvanic elements can be prepared either by means of substances which conduct electrolytically or with the combination of these and carbon or metal electrodes. The former class has been investigated since a long time by Bois-Reymond (1867), Worm-Muller (1870), Paalzow

and a few others. If such an element is constructed with both metallic poles of the same metal and each immersed in solutions of a salt of metal of different concentrations, the two solutions being separated by suitable porous partition or by any other means so that they may not get mixed too soon, the ends of the metallic conductors on being connected by means of a wire a current will flow. Such a cell is called concentration cell. Here the electromotive force is generated by the osmosis of the solutions of different concentrations in mixing to form a homogeneous liquid. The molecules of solute in a concentrated solution is in combination with lesser number of solvent molecules than those in dilute solution and therefore there is a tendency to form compounds of solute and solvent in uniform ratio thus causing disturbance of electrical equilibrium. If C_1 and C_2 are the concentrations of the two solutions then the electromotive force or the difference of potential is expressed by the following equations at $15^\circ C$,—

$$E = 0 \cdot 057 \, \log \frac{C_1}{C_2} \text{ volts.}$$

and this equation, however, varies with temperature, which at $25^\circ C$ becomes ;—

$$E = 0 \cdot 059 \, \log \frac{C_1}{C_2} \text{ volts.}$$

It has already been noted in page 11 that the solubility of sparingly soluble substances could be measured by the measurement of electromotive force in a concentration cell system. The determination of solubility of silver chloride in decinormal potassium chloride

solution was done by setting up the following com-
bination :—

$$\text{Ag} \left| \begin{array}{c} 0\cdot1\text{n AgNO}_3 \end{array} \right| \left. 0\cdot1\text{n KNO}_3 \right| \left| \begin{array}{c} 0\cdot1\text{n KCl} \\ \text{saturated} \\ \text{with AgCl} \end{array} \right| \text{Ag}.$$
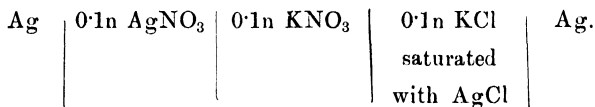
One pole was made up of a silver electrode in decinor-
mal silver nitrate and the other of a silver wire coated
with silver chloride, in a decinormal solution of a potas-
sium chloride which was saturated with silver chloride by
the addition of a few drops of silver nitrate. To prevent
the two solutions precipitating each other a decinormal
solution of potassium nitrate was interposed in an U
tube. The electromotive force observed was $0\cdot45$ volt at
$25°C$. This was of course composed of the electrode poten-
tials, and the diffusion potentials at the junctions of the
various electrolytes. In this case the latter may be neg-
lected as they fall within the limits of experimental error.
The observed difference of potential $0\cdot45$ volt was due to
the difference in concentrations of the silver ion in the
silver nitrate solution on the one hand and the silver
chloride solution on the other. Applying this E. M. F.
to the above mentioned formula,—

$$0\cdot45 = 0\cdot059 \log \frac{C_1}{C_2} .$$

The concentration C_1 of Ag in decinormal silver nitrate
is about $0\cdot084$ according to dissociation theory,

$$0\cdot45 = 0\cdot059(\log 0\cdot084 - \log C_2),$$
$$\therefore C_2 = 1\cdot95 \times 10^{-9} \text{ normal.}$$

The solubility in pure water may be obtained from

this solubility of silver chloride, in decinormal potassium chloride by the application of constant solubility product, $(Ag') \times (Cl') = $ constant.

On application of the above results to this the following value is obtained,

$$(1.95 \times 10^{-9}) \times (8.4 \times 10^{-2}) = 1.64 \times 10^{-10}.$$

The concentration of each of the two ions in pure water is the same and is equal to the square root of the above figure i.e. 1.28×10^{-5}. Thus the saturated solution of silver chloride in pure water at 25° C is 1.28×10^{-5} normal, which is equal to 1.82 mg. per litre. Kohlrausch obtained this solubility figure, 1.34 mg. per litre by conductivity measurements at 18° C.

Although the agreement of result obtained by this method with that of Kohlrausch from conductivity measurement is a great mutual support about the accuracy of the two methods yet at the present moment such conclusion need not be considered absolutely true because,

(1) this is rather a result of limited experiment and should be corroborated by results of many other substances at varying conditions,

(2) silver chloride is generated by the addition of a few drops of silver nitrate solution. In forming silver chloride a corresponding quantity of potassium nitrate is also formed, which remains in the field and it is not reasonable to think that this substance does not interfere with electric measurements, and

(3) validity of application of rule of constant solubility product inspite of the presence of a third substance, potassium nitrate, properties of which are not

identical with any of the other two solutes under the circumstances of the experiment, has not been properly established.

Generation of electricity in these cells has been explained by Nernst[2] on the assumption that all metals possess a property which he calls solution pressure or solution tension and that this property tends the metal to drive ions (positively charged) from itself into the surrounding solution. In these systems of concentration cells there occur two kinds of chemical reactions, (1) passing of the metal into solution and (2) formation of homogeneous solution by the mixture of different solutions used. Electrical property of substances concerned such as conductivity is changed as a result of the above mentioned reactions, therefore their electrical equilibrium within themselves must have been changed during the occurrence of the phenomena. It is quite rational to consider that when electrical equilibrium is disturbed with a change in concentration in solutions, such change is indicated by potentiometric measurements. Mostly the electrical properties of such resultant mixture are neither equal to those of any of the original substances nor equal to their arithmetical mean.

The ionic theory while calculating P. D. explains the generation of electricity in concentration cells consisting of simple

<div align="center">Liquid/Liquid,</div>

by the assumption that the positive and negative ions generally tend to diffuse from the place of high concentration to that of low. If their velocities differ

across the boundary, the two other ends of the solutions being connected by electrodes of common metal and by means of metallic connection the current of electricity would flow till equilibrium is reached.

The same phenomenon of generation of electricity may be explained by the association theory of solution on the assumption that when two solutions of different concentrations are brought into contact,

$$\boxed{\frac{N}{1} \text{ Solution}} \ + \ \boxed{\frac{N}{10} \text{ Solution}} \ = \ \boxed{\frac{N}{5\cdot5} \text{ Solution,}}$$

osmosis or diffusion will commence at once to form solution of uniform concentration. Thus if $\frac{N}{1}$ and $\frac{N}{10}$ solutions are brought in contact the strength of the mixture after a lapse of time will be $\frac{N}{5\cdot5}$. Now the electrical properties of the resultant mixture are not arithmetical means of those of the original solutions; therefore a certain quantity of electrical energy is liberated or absorbed during the process. Thus a disturbance in the electrical equilibrium is created during the formation of association of solute and solvent in a different molecular ratio.

Conveyance of Electricity through Solution.

For the purpose of studying conveyance of electric current through solution the subject may be divided into two classes (1) non-electrolytes and (2) electrolytes. In disentangling theory of solution the former do not help

much as they do not allow electric current to pass through
them. In dealing with the latter, which convey electric
current the laws of Faraday and Ohm may form the chief
basis. These laws are expressed in the following
formulae—

$$(1) \quad C = \frac{E}{R}.$$

$$(2) \quad W = E \times C \times T = R \times C^2 \times T.$$

$$(3) \quad Wt = Z \times C \times T.$$

Where,   C = intensity of electric current,
         E = electromotive force,
         R = resistance,
         W = work done,
         T = time,
         Wt = weight of a substance deposited at any
              electrode as a result of conveyance of
              electric current through a solution,
         Z = electrochemical equivalent of the substance
              deposited.

When an electric current passes through a metallic
conductor there are manifestations of disturbances of
equilibrium of thermal, magnetic, energies, etc. and when
it passes through an electrolyte in addition to these some
chemical reaction takes place. This chemical reaction is
called electrolysis and it attracted more attention and
study than others. Whether any simultaneous generation
or absorption of other form of energy takes place when
electric current passes through a solution causing ultimate
decomposition of solvent need more systematic and
quantitative study.

It is presumed from the fact that electricity is generated or absorbed by chemical reaction that atoms in a molecule are in a state of combination by electric force, which practically means that chemical and electrical forces are either the same or nearly so. Definite proofs, however, are not available if these two forces are identical although it has definitely been established and could never be denied that the one could be often converted into the other. The chemical force, with which an atom or groups of atoms remain in a state of combination in a molecule of a compound, is the combination of all kinds of energies which are manifested during the formation or decomposition of such compounds.

Conductivity of electric current through solutions of a few salts like tetraethyl ammonium iodide in some non-aqueous solvents have been determined without properly establishing the exact nature of the chemical reaction that may have taken place (if any) as a result of passage of such current. But results have been considerably studied when an electric current is allowed to pass through aqueous solutions of substances like salts, acids and basses. Thus when aqueous solution of sodium chloride is used the products of decomposition may be shown as, —

$$NaCl = Na + Cl \dots\dots\dots\dots\dots\dots\dots (1)$$
$$2Na + 2H_2O = 2NaOH + H_2 \dots\dots\dots\dots\dots (2)$$
$$4Cl + 2H_2O = 4HCl + O_2 \dots\dots\dots\dots\dots\dots (3)$$
$$NaOH + HCl = NaCl + H_2O \dots\dots\dots\dots\dots\dots (4)$$
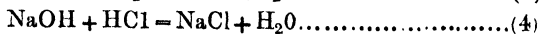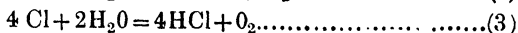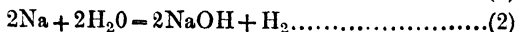
The sum of all these reactions is, however, the simple decomposition of water ;—

$$2H_2O = 2H_2 + O_2$$
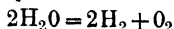
Such solutions are usually called electrolytes, and according to Faraday the components of electrolytes, that is, on the one hand hydrogen, metals etc., and on the other hand the halogens, the acid radicals etc., are called ions. The first named which travel down the current, are called cations, and those which travel up anions. Metallic conductors which touch the electrolytes are called electrodes, and the surface at which the anions appear is called the anode and that whereat the cations appear is called the cathode.

After performing a very large number of experiments Faraday formulated the general law to which all movement of electricity in electrolytes is subject :—

"In every electrolyte the quantity of ion separated out is proportional to the quantity of electricity which has passed through, and the same quantity of electricity passing through different electrolytes separates quantities of different ions that are in the same ratio with the chemical equivalents of those ions."

Faraday introduced into the same circuit dilute sulphuric acid and tin chloride, lead chloride, or lead borate and he led the same current through different beakers with sulphuric acid, using electrodes of different metals ; in all cases he found his law verified. It has also been proved by other investigators that in every case the electricity passed through has been strictly proportional to the quantity of ion separated out.

Fused inorganic salts and aqueous solutions of salts, bases and acids convey electric current producing chemical change which is called electrolysis. The conduction of

electricity through such media is dependent (1) on the nature of the substance and (2) on the condition in which it is presented for such reaction.

The nature of the ultimate products of decomposition followed by the passage of electric current through an electrolyte varies widely of which the simplest, NaCl $+ H_2O = NaCl + H_2 + O$, has already been noted. This is an instance of electrolysis of binary compounds where the acidic or basic radicals could not be further decomposed. Complications, however, easily arise when any or both these radicals are capable of further change. The following are a few instances of such complicated products :—

Sodium formate gives :—

$$2NaOOCH + 2H_2O = 2NaOH + 2CO_2 + 2H_2.$$

Sodium acetate gives :—

$$2NaOOCH_3 + 2H_2O = 2NaOH + 2CO_2 + C_2H_6.$$
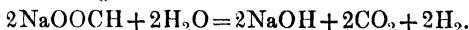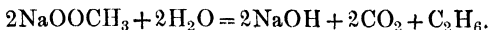
Salts of the higher fatty acids give the corresponding paraffins. Although in many cases the reactions are simple yet the few complicated instances are quite important. Nature of the chemical decomposition that would accompany depends on external circumstances, temperature, concentration, current density, etc.

When a solution containing a complicated molecule is electrolysed the products of electrolysis may change with the progress of the reaction as the current produces redistribution in concentration of the solution by the migration of solute molecules or their components. On electrolysing potassium silver cyanide, silver separates at the cathode, but by using small electrodes and strong currents the salt near the cathode is soon used up by

migration and hydrogen will evolve in the place of separation of silver.

Aqueous solutions of salts, acids and bases have attracted considerable notice of many investigators of electrochemistry in studying conduction of electric current through them. Pure water, however, does not appreciably conduct electricity and there are substances which are nearly non-conductors but whose solutions in water are quite good conductors. From this it follows that electrolytes have a special constitution with which their special property is connected. After the discovery of a number of organic compounds soluble in water producing non-conducting solution, Hittorf experimented over the subject very carefully. He drew attention to the fact that the power to conduct electricity and the power to exert chemical reactions were outcome of the same cause.

Hittorf accepted the ionic conceptions and nomenclature of Faraday and assuming a considerable mobility of ions in solutions stated that electric conduction is brought about by the positive and negative electricities moving through the conductor bound to their ponderable carriers, the ions. Clausius[3] pointed out that in every electrolyte there should be present number of ions capable of moving freely being split up to produce electrolytic conduction. He, however, did not apply any method for the determination of amount of such ions in the solutions.

Clausius having based on the kinetic hypothesis conceived that, "Owing to the collision of the molecules of the electrolyte with each other and with those of the

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solvent, one or other occasionally splits into its con-
stituents, and so gives the free ions " His contemporaries
brought further support from the comparative chemical
phenomena of the reactivity of gaseous substances at the
ordinary temperature and that of the aqueous solutions of
acids, bases and salts under the same conditions. A
mixture of hydrogen and oxygen does not form water
until it has been heated to between 400⁰ and 500⁰ ; a
mixture of hydrochloric acid and potash, however, when in
aqueous solution passes almost instantaneously into
potassium chloride although in the first case 68,000 Cal.
of heat are produced and only 13,700 Cal. in that of the
second. An instance of very slow action in solution has
also been quoted in this connection. The formation of
acetic ether from a mixture of alcohol and acetic acid—
that is, for a process much analogous with that of the
formation of salts—at least ten years are needed, at the
temperature of the room, to complete the reaction
parallel to which would be done almost instantaneously.
Thus an apparent case was made that it is necessary,
from chemical point of view, to suppose that compounds
which react instantaneously,—that is the electrolytes—
possess a special mobility of their parts or ions ; and that
those are the constituents of "salts". which are the ultimate
cause of electrolysis as well as of chemical reactions.

These[4] arguments of Clausius, Hittorf, and others are
not quite rational and the reactions of (1) combination of
hydrogen and oxygen, (2) neutralisation of caustic
potash with hydrochloric acid, and (3) esterification of
alcohol with acetic acid should hardly be brought in

the same field for the purpose of comparison. The heats of reaction need not indicate the quickness or the velocity of the reaction. If "owing to the collison of the molecules of the electrolyte with each other and with those of the solvent, one or other occasionally splits into its constituents, and so give the free ions" then such ions should also be present to help the esterification in the solution for the formation of ethyl acetate by the reaction of alcohol and acetic acid. It may be argued that the above spliting up takes place only in aqueous solution, but such reasoning should have hardly any value unless it is made clear why aqueous solution would have this special property. Besides if such assumption has to be made in the case of aqueous solutions it may be better assumed—or rather the assumption will be less complicated—that one of the chemical properties of some aqueous solutions is the acceleration of chemical reactions. Explanation of such behaviour through the assumption of formation of ions are not only superfluous but erroneous in the absence of any reasons why the same is developed in certain selected aqueous solutions only.

Again the velocity of chemical reaction in non-electrolyte solutions are quite instantaneous in many cases. Alcoholic solutions of amines and acids are practically very feeble conductors but they react to form salts just as instantaneously as aqueous solutions of caustic potash and hydrochloric acid. Gaseous acids and gaseous ammonia, or any volatile bases when brought into contact would show quite a different type of activity in chemical combination than that of hydorgen and oxygen. It will be

explained later on that Bakers'[5] researches on the influence
of presence of even a trace of moisture in a chemical
reaction does not help the theory of ionisation in aqueous
solution in any way. If ions had anything to do with
the chemical reaction it might have been proportional to
its quantity available for the purpose. At any rate the
influence of the quantity of ions over the chemical
reactions on which the ionic hypothesis is based needs
proper establishment in order to prove the validity of
such assumption.

It is now necessary to describe the broad principles of
Van't Hoff's[6] theory of solution to consider the electrolytic
dissociation theory because much mutual support has
been brought to bear on each other. The fundamental
principles of Van't Hoff's theory are based on the
analogy that the molecules of solutes in a solution behave
in the same way as pure gas molecules in respect of the
relationship between pressure, volume and temperature.
These gas laws are true because the molecules of gases are
always at such a distance apart that they are not capable
of exerting an action on each other. In liquid or in solid
substances the molecules being in close proximity exert
specific reciprocal actions. In solutions the solute molecules
are sufficiently apart from each other and therefore they
behave like pure gas molecules. Like gases the characteri-
stic property of solutions is the power of extending
uniformly through any given space containing their
solvents. When a solvent is placed in contact with a pure
substance or its solution in another solvent a molecular
movement sets in at the partition, which continues till no

more distribution is possible. This subject is dealt with in Chapter VI on 'Osmotic Pressure'.

Van't Hoff considers the agreeable analogy of 'Osmotic Pressure' with 'Gas Pressure' very important, the pressures in respective cases being set up by the bombardment of solute molecules to the semi-permeable membrane and by the gas molecules to the sides of the vessel containing it. He also showed that some results of Osmotic Pressure compare very well with those of gases. Boyle's Law enunciates that pressure and volume are inversely proportional and Pfeffer's Law states that the Osmotic pressure and concentration are directly proportional. Gay-Lussac's law states that volume remaining constant pressure increases uniformly with the rise of temperature and a similar law has been proved by Van't Hoff from the results obtained by Pfeffer. The gas law of Avogadro being that the temperature and volume remaining the same equimolecular quantities of different gases exert the same pressure. A gram-molecule of a gas when occupying one litre volume at $0^{o}C$ exerts a pressure of 22.37 atmospheres. Pfeffer observed that the osmotic pressure of one per cent cane sugar solution is 0.649 atmosphere at $0^{o}C$. Therefore a gram-molecule of cane sugar ($C_{12}H_{22}O_{11}$ = 342) contained in a solution occupying litre volume exerts pressure $= \dfrac{342 \times 0.649}{10} = 22.2$ atmospheres. This agreement has been held to be of fundamental importance in proclaiming that Avogadro's law also holds good for solutions. This subject, however, has been subsequently verified in a representative manner without obtaining a

desirable satisfaction to justify such a great generalisation. It is rather unfortunate that this limited agreeable analogy has been used by earlier investigators as one of the main pillars of the dissociation theory of solution and thereby made a mutual support.

Van't Hoff's theory of solution could not explain the abnormal results obtained in the determination of osmotic pressure, lowering of vapour pressure, elevation of boiling point, and lowering of freezing point by the electrolytes. The difficulty, however, was afterwards overcome by Arrhenius. This powerful and celebrated investigator ascribed the deviations to dissociation of solutes present in the electrolytes into their ions. He also determined from the magnitude of the deviation the number of molecules which are dissociated, and thus claimed to have solved the problem left unfinished by Clausius. He conceived that ions are free by dissociation in an aqueous solution of potassium chloride, but the chlorine does not escape into air as a greanish yellow gas and the potassium does not act on the water because it is considered that the greenish yellow gas is the electrically neutral molecule Cl_2 and does not consist of separate atoms of Cl which are charged with a large amount of negative electricity, and similarly potassium is not present as compact metal, but in the form of strongly positively charged ions. These differences in properties of the same element in different forms have been considered to be similar to those exhibited by allotropic forms of the same element e.g., oxygen and ozone etc. Attempts have been made to explain considerable number of physico-chemical phenomena in light

of this dissociation theory which have already been treated in previous chapters.

Kohlrausch[8] discovered a method based on laws of Ohm and Faraday for the determination of electrical conductivity of solutions which has the speciality of using alternating currents, and up to this time this method stands better than any other. After this discovery numerous investigators started their investigations on this line using the following nomenclature—

Specific resistance is the resistance in ohm offered by a cube of one centimetre dimensions to a current of electricity.

Specific conductivity is the inverse of specific resistance.

Molecular conductivity is the conductivity of a solution containing one gram-molecule of solute when placed between electrodes of indefinite dimensions exactly one centimetre apart.

Equivalent conductivity is the conductivity of a solution which contains one gram-equivalent of solute, when placed between two electrodes one centimetre apart. In cases like potassium chloride KCl, a molecule of which contains two simple monovalent ions the equivalent conductivity becomes equal to molecular conductivity.

Kohlrausch and his followers established the following facts for dilute solutions in which one gram-equivalent of solute is dissolved in more than one litre of water.

(1) The equivalent conductivities of normal salts are of the same order of magnitude, but are not identical.

(2) The conductivities of all salts increase slowly with increase of dilution, which reach maximum

value at dilutions of 20,000 to 50,000 litres per gram-equivalent.

(3) The increase of conductivity is the least for salts which consist of two monovalent ions, nearly twice as great for salts containing one divalent and one monovalent ion, and nearly four times as great for salts containing both divalent ions.

(4) The equivalent canductivity of equally concentrated solutions of the most different salts can be represented as the sum of two constants, which are solely determined by their constituents, negative and positive ions.

Daniell[9] has been said to have observed differences in concentrations near the two electrodes in a solution which underwent electrolysis for sometime. Hittorf[10] made a thorough study of these changes in connection produced by electrolysis and tried to explain the phenomena on the assumption that the positive and negative radicals of the solute while remaining in dissociated states in solution are carried away in opposite directions by the electric current causing the electrolysis. When a current is passed through an electrolyte the numbers of positive and negative ions discharged at respective electrodes in a given time are equal but the velocities of the two are not equal. The speed of the anion and cation are often different, which causes the increase of concentration of the faster ion round the electrodes towards which it travels. The velocities of cation and anion are usually represented by u and v respectively ; and the total amount of electricity passed through the solution is proportional to the sum of the velocities of cation and anion, i.e. u and v.

If n be the fraction carried by the anion, then $1-n$ will be the fraction carried by the cation, from this it follows that,

$$n = \frac{v}{u+v} \text{ and } 1-n = \frac{u}{u+v}.$$

The values of n and $1-n$ are called transport numbers of anion and cation respectively. If the total amount of electricity which passes through the solution and the amount of one of the ions which have passed from the solution in the immediate neighbourhood of one of the electrodes, that is, the change of concentration of one of the ions round one electrodes be determined the transport numbers can be calculated. The total quantity of electricity is measured by the usual methods and change of concentration is easily determined by analysing a portion of the solution round one of the electrodes.

Determination of transport numbers has been a subject of considerable[11] study leading to the establishment of following facts :—

(1) Current strength has no influence on the ratio of the migration velocities.

(2) Variation of temperature has also very little influence.

(3) Concentration has a great changeable effect, — varying from too small to too high depending on the nature of the solute.

Potassium chloride solution does not give much change in concentration at the electrodes after electrolysis thus indicating the migration velocity of potassium and chlorine to be the same. Basing on this fact as also on the assump-

tion that chlorine in potassium chloride has the same migration velocity as on sodium chloride or in any other similar salt, many transport numbers were calculated which were sufficiently true for very dilute solutions, but several deviations were noticed with concentrated solutions, which also changed with concentration. Generalisations in this respect became further difficult on account of the fact that different salts behave differently,—salts consisting of two monovalent ions show the smallest deviations, salts with one monovalent and one divalent ion show greater deviations and salts with two divalent ions show the greatest deviations.

Association theory of solution does not admit any dissociation or ionisation of the solute in solution but assumes combination of solute with solvent. Any energy consumed during the process of solution is not due to the ionisation or dissociation but due to the combination of solvent and solute, which varies with dilution. Such change in energy may be expressed in the shape of change in, thermal, optical, electrical, properties etc. of solute, solvent and solution. Conduction of electricity through solution is not due to the dissociation or ionised molecules of salts and bases in solution because the fused salts and bases also conduct electricity without any dissociation or ionisation through the intervention of solvent. Fused silver chloride conducts electricity and is itself decomposed simultaneously. Davy discovered metals of the alkalies by electrolysing the fused bases of potassium hydroxide and sodium hydroxide. Lithium and magnesium may be easily obtained by passing electric current through their

fused anhydrous chlorides. Aluminium is manufactured on a very large scale by the electrolysis of fused aluminium oxide. Thus ionisation or dissociation in a medium is not necessary for conduction of electric current or electrolysis. It is not reasonable to say. when a substance conducts electricity, that it must have contained ions simply on account of this property.

Results obtained from the study of the reflection and refraction of X-rays by crystals[12] have been utilised in assuming the existence of ions in solid crystals. It has also been noted that these ions are responsible for the electrical conductivity of such substances. The subject however needs more experimental verification before considering the acceptance of the theory that ions present in a solid convey the electric current. Some of the non-conductors[13] mercuric cyanide, arsenic chloride, stannic chloride seem to need more examination in this connection.

It would be beyond the scope of this book to discuss the merits of the wave theory and the corpuscular or electron theory of electricity, but probably the latter is not quite suitable for the association theory of solution. Corpuscular theory is based mainly on the results of researches during the electrical discharge through a highly exhausted tube. Rays shot off from the cathode may be stopped by the interposition of some material placed in their path and when they strike the walls of the tube cause a vivid green fluorescence upon soda glass, blue on potash glass. These rays can be deflected in certain directions by a magnetic or electric field, or both simultaneously and therefore they have been assumed by the

corpuscular theory to consist of negatively charged particles. According to this theory, negative electricity consists of extremely small particles called corpuscles or electrons, which are all identical in size, and carry the same charge, and molecules and atoms are partly built up of them and of others containing an equal amount of positive electricity. This latter assumption is necessary to prevent spontaneous disintegration of the atoms due to the mutual repulsion of a number of similarly charged electrons. Thus corpuscular theory assumes that a neutral atom consists of numbers of corpuscles moving in various orbits, the number of such corpuscles and the kind of the motion they possess being the ultimate course of chemical and physical properties. The experimental evidence described above in favour of the real existence of corpuscles may not be enough for the assumption of such fundamental importance, but these, however, do not render it impossible to discuss the question of electrolysis without entering into the topics of constituents of atoms.

When two electrodes possessing a suitable difference of electrical potential are introduced in an electrolyte electrolysis takes place. Variation of products of electrolysis, however, with the variation of conditions under which electrolysis is carried out does not encourage acceptance of the simple view of the phenomenon proposed by the electrolytic dissociation theory.

Association theory of solution does not consider that the solutes undergo dissociation in an electrolyte in the absence of any electric current. All phenemena of electrolysis could be explained by the assumption that the

associated molecules, between two eloctrodes provided with constant supply of difference of potentials, arrange themselves along the lines of force present in the field in the same way as the particles in a magnet. The transmission of electric current from one pole to another takes place by vibration received and delivered by actual contact of the associated molecules with the electrodes. The series of consecutive associated molecules of solute and solvant between the two poles along the lines of force behave like an elastic rod, which receives vibration from one end and delivers through the other in the same direction as the current. Both the ends of such rods and those of the electrodes meet while vibrating in the same way as the ends of the electrodes of an electric arc. Disintegration of associated molecules takes place on account of vigorous vibrations at the junctions. After disintegration some of the components of the associated molecules are set free and the rest combines with a portion of the molecule, next towards the other electrode forming the conducting rod, to rebuild a complete molecule ; and the fraction liberated from this second molecule repeats the process with the third and the propagation of the operation is continued till the terminal one is affected, when a corresponding fraction is set free. All these reactions take place with considerable speed and facility on account of the existence of the state of vibration during the conduction of electric current. The portion of the rod consumed by decomposition is replaced from the rest of the solution by the natural tendency of fluidity to fill up internal gaps.

The decomposition of solute or solvent molecules

occurs according to the conditions present for the purpose. A part of an associated molecule is liberated at one electrode and the balance at the other. While this decomposition takes place the total amount of undecomposed solvent molecules, that formerly remained associated with the decomposed molecule, will be set free; and their distribution between the two portions of the original molecule liberated at the electrodes, will take place a cording as their comparative affinities for the solute molecules. If the solution is $KCl,100H_2O$ and the products of decomposition are K and Cl, the distribution of $100H_2O$ between K and Cl will be as $50H_2O$, K and $50H_2O,Cl$, if there are no changes of concentration at the two electrodes. But in other cases where there will be changes of concentrations at the two electrodes, the phenomena will be due to carrying of unequal number of solvent molecules by the two portions of the decomposed molecules liberated at two poles.

Electrical conductivity in solution is due to the conduction of electricity in the same way as the solid conductors[14], and investigation on electrolysis by Vollie and Chassagny[17] needs extension and amplification in this connection.

Ordinarily when weak current is passed through dilute solutions the reaction is very mild and products are often uniform and if these two conditions are varied with varying solutes considerable variation in products of electrolysis are obtained. In the electrolysis of aqueous solutions of platinic chloride[15], it has been shown that only hydrogen is liberated at the cathode when weak

current is used and a deposit of platinum is obtained with strong current. Such difference of prdoducts of decomposition is chiefly due to the variation of vibration available for the purpose. Development of heat in electrolytes[16] during electrolysis has not been well studied and needs considerable experimental results in this connection. John experimented with copper sulphate and zinc sulphate, and stated that the quantities of electricity used up, or rather converted into heat, in overcoming the resistance to conduction and other secondary influences[17], are inversely preportional to forces of affinity of the ions of the electrolyte. Influence of concentration on the products of electrolysis has been well illustrated in the case of hydrochloric acid[18], a subject, deserves consideration in this connecion.

Ostwald and Nernst[19] described experiments in favour of their statements that the ions are present in the solution in a free state and that no part of the charge is used up in their liberation. The fact that no charge is used up in the formation of ions suit very well with the association theory of solution in respect of the assumption that no ions are formed and if there be any formation of ions in solution there would be some disturbance of energy in some form or other. Consumption of no energy in the formation of ions in electrolytes would be a fact against the dissociation theory' of solution. Their experiments using mercury electrode contained in a tube for observing small quantities of hydrogen seem very useful and need good deal of amplification. It seems probable that the associated solute molecules in solution form a flexible

chain, as stated already between two electrodes along the line of forces arranging themselves in a way so that the basic radical of one faces the acidic radical of the other. This chain behaves like an elastic rod, and when receives an impact from one or more molecules on account of kinetic motions drifts away from the line of force causing passage of sparks at its both ends. As soon as a chain is displaced another is formed as long as difference of potential is maintained.

Complicated products of electrolysis of salts of organic acids were obtained by numerous authors[20] and attempts hove been made by several of them to explain the phenomena of such complications. All these experimental observations are quite highly ineresting but the conclusions drawn by various investigators are not quite illuminating and perhaps could be better explained by the association theory of solution. It is possible that ordinary text book writers were not quite sure of the conclusions drawn by the investigators, and therefore, it may be, that they could not pay proper importance to such subject in their books. It is always necessary to draw possible generalisations and conclusions from experimental facts but the sagacity shown by some of the investigators on this subject does not bring so much credit. Many of them have been done without reasonable experimental verification. Conclusions drawn by several were proved to be wrong by subsequent investigators by means of fresh facts.

Tho association theory of solution, finds no difficulty in explaining such phenomena; the passage of sparks

or vigorous vibrations at both ends of the hypothetical rod cause violent decomposition, nature of which depends on the factors which could influence an electric spark, and on the properties of the associated molecules of solute with solvent. Unstable nature of the organic acid radicals leads to the production of considerable variation in the products of electrolysis depending on the (1) concentration, (2) temperature, (3) current density, (4) anode potential, (5) nature of solvent, (6) presence of another substance in solution, and (7) material of anode. Although some experiments have been done by Gordon, Murray, Gibson, Robertson and Fairweather and Walker to show the variation of products with the variation of above conditions of electrolysis yet it appears that exaggerated generalisation has been done in the absence of reasonably representative data.

Mycroscopic examination of polished metallic electrodes after electrolysis showed a peculiar crater-like formation on the surface, suggesting that the surface of the metal had been blown open by an internal explosion[21]. This observation gives a leglitimate support to the hypothesis that electrolysis is the result of passage of spark during the conveyance of current. It is rather too early to lay considerable importance on the results of Wien, though his researches showing deviations from Ohm's law for electrolytes add strong arguments against the dissocation theory of solution in respect of the fact that it does not provide any assumption for the purpose. On the contrary the association theory accommodates quite easily such results since it assumes that conduction of

electricity in solution is dependent on the nature of the associated molecules and on the energy available from the vibrations that pass through the solution. This investigator found that for certain electrolytes the conductivity increases with increasing voltage at a rate greater than that may be expected on the basis of the increased temperature when the temperature-coefficient is normal. The increase in conductivity is made up cf two separate effects, the Joule heat effect and an increment which is proportional to the voltage. The latter increases rapidly with increasing valency of ions and corresponds with departure from Ohm's law, also ap· proaches a limiting value when the voltage is very high or the concentration is very low. The valency of the ions exerts a marked effect on the attainment of this limit, since both increasing concentration and higher valencies shift the limit in the direction of higher values.

It is now necessary to consider what other similar properties are acquired by substances in coming in contact with water and its allied substances. Salts, bases and acids acquire variable electrical properties in aqueous solutions and this subject has been representatively described. Manifestations of considerable new properties are shown by some matters by the presence of water even in small quantities. Development of such properties according to the association theory of solution is due to the formation of new compounds with two brought in contact. Such associated molecules set up a change in the kinetic movements of the whole body including them-

selves and those that are not so associated, if any such be present there, causing aquisition of corresponding new properties. Behaviour of matters in the presence of very small quantities of water have been studied by Baker and Dixon[22]. Combustion of carbon monoxide, dissociation of ammonium cloride vapour and action of sulphuretted hydrogen on salts of heavy metals are not successful in the absence of water. Explosion of a mixture of carbon monoxide and oxygen by electric spark did not take place ordinarily in the absence of water vapour. The explosion in the absence of moisture was effected when a third gas containing hydrogen, e.g. H_2S, C_2H_6, H_2CO_3, NH_3, C_5H_{12} or HCl, were present instead. And traces of other gases like CS_2, SO_2, CO_2 N_2O, C_2N_2 or CCl_4 did not help the same explosion like water vapour. Baker's studies in the change of properties of substances on drying seem very useful and investigators should follow them very carefully. Boiling points of trioxide and tetraoxide of nitrogen were raised by $44°$ and $47°$ respectively when they were allowed to stand for a long time in contact with phosphoric oxide. He prepared a number of liquids in a high state of purity and sealed them up in vessels containing purified phosphoric oxide. In many cases, direct contact of the liquids with the drying agent was avoided on account of possible chemical reaction, the drying being then dependent on the removal of water from the continually changing vapour. The substances were thus dried for eight or nine years. He obtained the following results of different types.

	Period of drying in years.	Original boiling point.	New Boiling point.	Rise
Bromine	8	63°	118°	55°
Mercury	9	358	420-425	62
Haxane	8½	68·4	82	14
Benzene	8½	80	106	26
Carbon disulphide	—	49·5	80	30
Carbon tetrachloride	9	78	above 112	34
Ethyl ether	9	35	83	48
Methyl alcohol	9	66	above 120	54
Ethyl ether	9	73·5	138	60
Propyl alcohol	9	95	134	39

He[23] also found afterwards that melting points and vapour densities of substances when extraordinarily dried considerably differed from those obtainable from the same substances when not dried by means of any lengthy process. A definite fractional distillation of dried benzene was done, the highest temperature observed being 87°. The melting points of sulphur trioxide (dried for 20 years), bromine (dried for 10 years), and benzene (dried for 10 years) have been found to be 61°, 4·5°, and 6°, respectively. The vapour density of ether (dried for 10 years) has been found to be 81·7, more than double the normal, and of methyl alcohol, dried for the same length of time, to be 45, compared with the normal value 15. These changes of properties of substances on drying have been ascribed by the author to be a confirmation of the

theory of allotropy of Dr. Smits of Amsterdam with whom he discussed the results.

Thus instances are available regarding the influence of water in changing various properties of matter. Smits[24] assumes that every phase contains two different kinds of molecules, an active and an inactive varieties, and that these are in equilibrium. In intensive drying the equilibrium is shifted to the inactive side, so that the molecules which remain after drying are only inactive It is rather difficult to say if such results of Baker and others should help the "theory of allotropy" of Smits, since such extremely dry substances are not very stable as the case with other instances. It may be difficult to change a substance allotropically yet if it is once changed it often does not go back to its original condition easily. In one of Smits's experiments (Jour. Chem. Soc., 1924, 125, 1074) a sample of nine month's dried benzene, which (liquid) boiled at 87^0 had a chance of coming in contact with a small quantity of moist air, gave (liquid) boiling point 80.9^0. Consequently the effect attained after 9 months' intensive drying had almost completely disappeared by the introduction of a minute quantity of water. At any rate it is not yet proved so conclusively how the change of properties acquired by prolonged intensive drying could disappear by the introduction of moisture and whether such properties are stable against original conditions containing moisture. The reason why moisture should take part in the allotropic formation is neither properly suggested nor understood as yet, nor it has been proposed how these minute traces of moisture are present with

such substances, in a state of solution, in a state of combi-
nation or in a state of mechanical mixture. It is
true that the properties are changed, but it is not quite
definitely established that the change of properties is due
to the substance passing into another modification.

Some scientists[25] have argued that chemical reactions
take place in aqueous solution on account of ionisation
but there is no need to do so as there are sufficient number
of cases where chemical reaction would take place in non-
aqueous media with practically the same vigour. Pre-
cipitation of silver iodide from alcoholic solution of silver
nitrate and methyl iodide is just as quick and quantitative
as that would be the case in aqueous solutions of potas-
sium iodide and silver nitrate.

Various ways in which water affects the various pro-
perties of matters are now mentioned in a representative
manner, in large quantities it causes electrical properties
strikingly changed, and in small quantities it makes them
chemically active, and boiling point, melting point, etc.,
altered. The electrolytic dissociation theory took advan-
tage of representing water as H.OH and put forward
many explanations combining "H" or "OH" with some
part of the substances. But any such explanation is not
useful in explaining the part played by gases containing
"H" causing the explosion to take place in dry mixture
of CO and O.

A matter may exist in three states,—solid, liquid and
gaseous, and the difference is often attributed to the
different motions of its molecules. As the matter
changes from solid to liquid and from liquid to gas, its

molecules get more and more motion. In this connection it would not be irrational to presume that different substances move with different kinds of motion, varying in frequency, and amplitude. If two such substances are mixed to produce solution the resultant product will have a resultant kinetic motion which may differ from any of that of its components and that of the mean of them. It is reasonable that the change of property exhibited by solutions or by substances in the presence of small quantity of water is partly or wholly due to the change in kinetic motions. It may be true that electrical and other properties of matter depend on the internal movements of electrons contained in its atoms or molecules yet it is not unreasonable to presume that the same electrical and other properties are changed owing to the change in movement created by the introduction of water or any similar molecules in small or large quantities. This hypothesis may lead to a reasonable assumption that the phenomena of solution and solubility are functions of nature of the kinetic motions possessed by the solvent and solute.

The influence of the mass of the substance reacting per unit weight of another substance had been a subject of study by Wenzel, by Berthollet, by Pe'n de St. Gillers, and by Guldberg and Waage. The last two investigators found that the chemical activity of a substance is not proportional to the quantity present, but to the amount present in unit volume of the reacting mixture, or to its concentration. Thus they enunciated the law of mass action that,—the amount of chemical reaction is proportional to the active mass of each of the substances reacting,

active mass being defined as the molecular concentration of the reacting substance. In attempting to apply this law of mass action to the properties of various electrolytes considerable discordant results were obtained and much more divergent opinions were expressed. It does not seem useful to enter into such discussion as no satisfactory conclusion could be arrived at till more experimental data are available.

Bodenstein's[26] researches on the equilibrium in gaseous system between hydrogen, iodine, and hydroiodic acid increased considerable importance of the law of mass action. A similar instance of the decomposition of phosphorous pentachloride into phosphorous trichloride and chlorine,

$$PCl_5 \rightleftarrows PCl_3 + Cl_2$$

being reversible in a gaseous system afforded an useful study of this matter. Investigators are requested to work on the suitability of the association theory of solution regarding the similar reversible re-action between solvent and solute with reference to the law of mass action.

Aqueous solutions of different salts react differently on the indicators. A solution of an aluminium salt is distinctly acid and a solution of carbonates of alkali metals is distinctly alkaline. The dissociation theory explains such phenomena stating that the salts dissociate in solution and the indication of acidity is due to the presence of hydrion and that of alkalinity due to the presence of hydroxion. Aqueous solutions of some salts when sufficiently diluted deposit oxides or hydrated oxides leaving behind acidic radical as free acid in solution. According

to association theory these are due to the fact that when large quantity of water is added the compounds formed with solvent and solute become unstable on account of overbalance of the chemical affinities amongst the final compounds formed over those of the decomposed compounds. The reaction of acidity or alkalinity in aqueous solutions of salts on indicators may be explained without assuming the pre-existence of decomposed components of solute. When an indicator substance is introduced in such solutions it subjects itself to action by all the acidic and basic radicals present in the field. The final selection of radicals for the reaction between the indicator and the components of the solute takes place according to the comprative affinities they offer. Thus the pre-existence of the components of the solute in decomposed state in solution need not be assumed. The real decomposition takes place after the introduction of the indicator when selective chemical reaction takes place ; and this pheno-menon, however, is quite different from what takes place when oxide or hydroxide is separated as result of dilution of solutions of salts like aluminium sulphate, lead acetate, etc.

Ostwald believed in the dissociation theory of Arrhenius and thought that the reaction is universal for solutes in electrolytes, and obeys the law of mass action. He worked out the following formula :—

$$K = \frac{a^2}{(1-a)v}.$$

Where,

$K =$ equilibrium constant,

v = volume of solution containing unit mass of the solute,

a = fraction of the solute molecules contained in v volume of solution dissociated into ions.

This relationship has also been expressed in terms of electrical conductivity measurements. If,

μ_v = conductivity at a molecular dilution v,

μ_∞ = conductivity at an infinite dilution,

then, $a = \dfrac{\mu_v}{\mu_\infty}$.

Substituting this equivalent of a in Ostwald's original formula,

$$K = \frac{\mu_v{}^2}{\mu_\infty(\mu_\infty - \mu_v)v}.$$

Considerable number of experiments were done to verify the accuracy of this law which is commonly known as the Ostwald's dilution law; both agreeable and disagreeable results were obtained. This variation is due to the difference in properties of compounds formed at different dilutions. The results would have agreed well had the properties of associated molecules of solute and solvent formed at different dilutions borne any ratio with the quantities of their components. Any agreement observed is due to the approximate variation of their properties with dilution. An interesting disagreement was shown by Tansley[27]; his results of acetoxime hydrochloride are given below, v = volume in litres containing one gram equivalent of the substance and K = Ostwald's hydrolytic constant,—

v =	8	16	24	32	40	48	80	100	120
$K \times 10^3 =$	18·0	12·6	9·52	7·58	6·32	5·67	3·81	3·29	2·78

This author tried his results with several other formula and found one of them suitable for the purpose. It remains to be seen how other results suit with this formula.

Among the numerous investigators who worked on the validity of dilution law of Ostwald, Van Laar's[28] researches need mention. This author, in considering the causes of the divergences from Ostwald's dilution law which are exhibited by many aqueous and alcoholic solutions, is led to the important conclusion that although the ratio yields a degree of dissociation, yet this value is not that which one obtains in the absence of the current ; the dissociation thus determined is, therefore, incorrect. The cause of the alteration of the dissociation during the passage of the current is, in the author's opinion, the great difference which exists between the temperature of the actual conducting ions and the salt molecules, and that of the liquid as a whole Armstrong and Worleby[29] published an elaborate paper where the view is put forward that hydrolysis is essentially an associative process which involves the association and direct interaction of two complexes, one of which consists of the hydrated hydrolyte and the other hydrated catalyst Such associated systems are being constantly produced, broken down and reformed in such a manner that while some give rise to the original components, others are resolved into the products of change. They ventured to claim that the explanation given by them of the process of hydrolytic change as simple, consistent, in harmony with the facts, in accordance with chemical experience, and

generally applicable. In their opinion, the ionic dissocia-
tion hypothesis does not afford an explanation of the facts.
They go so far as to assert that there is now sufficient
evidence that the hypothesis is a false one.

Attempts have been made by some investigators to
explain contractions in solution by a theory of electrostric-
tion[30]. But it does not seem suitable to take up the study
of the validity of this theory till a definite conclusion is
arrived at regarding the relationship of the volume of the
solution with the volumes of its components. It has
already been said (see page 37) that the volume of the
solution is related with the kinetic movements of the
associated molecules.

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INDEX OF AUTHORS

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ERRATA.

Page	Line		
3	1	*Omit*	"before."
4	11	*For*	"change" *read* "changes."
4	10*	*For*	"Experiment" *read* "Experiments."
5	8	*For*	"class" *read* "clash."
12	13*	*After*	"have been" *insert* "done."
25	3*	*After*	"solutions" *insert* "of."
41	5*	*For*	"—17" *read* "—1·7."
41	2*	*For*	"103070" *read* "1·03070."
82	3*	*For*	"(T'—TK" *read* "(T'—T)K"
89	8*	*After*	"accurate" *insert* "results".
92	14*	*For*	"1478" *read* "14·78."
92	10*	*For*	"1026" *read* "1·026."
106	1*	*After*	"investigator" *insert on top* "8."
111	10	*For*	"are" *read* "were."
113	2*	*After*	"Pressure" *insert* "and."
136	6*	*For*	"similarly" *read* "similarity."
160	1*	*For*	"Elagden" *read* "Blagden."
163	1	*For*	"NH$_4$ C" *read* "NH$_4$ NO$_3$."
164	15	*For*	"Beckmen" *read* "Beckmann."
165	11	*For*	"177" *read* "17·7"
176	4*	*For*	"same that are" *read* "same as that were."
183	5*	*After*	"case" *insert* "with."
205	10	*For*	"R'" *read* "R"."
212	1	*Omit*	"a" *after* "is."
226	11	*After*	"as" *insert* "to."
247	11	*After*	"production" *insert* "of."
264	15	*For*	"connection" *read* "concentration."

* From bottom.