A NEW ERA IN CHEMISTRY

SOME OF THE MORE IMPORTANT DEVELOPMENTS IN GENERAL CHEMISTRY DURING THE LAST QUARTER OF A CENTURY

BY

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NEW YORK
D. VAN NOSTRAND COMPANY
25 PARK PLACE
1913

PREFACE

Although the development of chemistry has taken place more or less by leaps and bounds, it is difficult to fix an exact date as the beginning of the "New Era." The year 1887 marks the appearance of the first volume of the Zeitschrift für physikalische Chemie," and in this volume the epoch-making papers by Van't Hoff, on the "Relations between Solutions and Gases," and of Arrhenius on the "Theory of Electrolytic Dissociation" appeared. This date, 1887, is therefore taken as the beginning of the "New Era," which is, then, a quarter of a century old.

It is, however, clearly recognized, that there is a difference between the chemistry of twenty-five years ago and that of today. That this is really a difference in kind, is not always clearly understood either by those who have watched the development during that period, or by those who have not studied chemistry long enough to have the necessary perspective.

It has seemed desirable to point out as clearly as possible in what this difference consists; how these new developments were brought about and by whom. This is the object of this little work.

My apology for adding another book to the literature of chemistry, is that I have lived during the "New Era," have known well most of the men who have been instrumental in bringing it about, and have been a student of the three leaders in this movement — Van't Hoff, Arrhenius and Ostwald.

HARRY C. JONES

BALTIMORE, June, 1913

CONTENTS

CHAPTER I

PAGE
CONDITION OF CHEMISTRY IN 1887 1
Condition of Inorganic Chemistry before Mendeléeff . . . 1
Hypothesis of Prout 3
Periodic system of Mendeléeff and Lothar Meyer 4
Organic Chemistry in 1887 8
Type Theory of Dumas 9
Work of Kekulé 9
Celebration in honor of Kekulé's Benzene Hypothesis . . 12
Beginning of a Science of Chemistry 17

CHAPTER II

DEVELOPMENT OF THE LAW OF MASS ACTION 19
Importance of a generalization 19
Earlier views on mass action 20
Berthollet 21
Work of Rose 21
Dulong 22
Wilhelmy 23
Berthelot and Saint Gilles 23
Pebal and Than 24
Williamson 25
Discovery of the law of mass action by Guldberg and Waage 27

CHAPTER III

THE ENERGY CHANGES THAT TAKE PLACE IN CHEMICAL REACTIONS 31
Chemists first studied material changes 31
Work of Julius Thomsen on thermochemistry 32
Work of Hess 33

PAGE
Thermochemical work and deductions of Berthelot 34
Berthelot's chemical mechanics and statics 38
Criticism of the law of maximum work 40

CHAPTER IV

VAN'T HOFF, LE BEL AND GUYE AND THE ORIGIN OF STEREOCHEMISTRY 44
Work of Van't Hoff 44
Van't Hoff and the geometry of molecules 45
Observation of Pasteur 46
The relation pointed out by Le Bel 49
Van't Hoff and stereochemistry. 53
Symmetry of methane 54
Shape of a molecule of methane 55
Tetrahedral carbon atom 56
Asymmetrical tetrahedral carbon atom 56
Stereochemistry of carbon and other elements 57
The qualitative suggestion of Van't Hoff made quantitative by Guye 59
Testing Guye's hypothesis 61

CHAPTER V

THE PHASE RULE OF WILLARD GIBBS 66
The definition of phase and component 66
One component and two phases 67
One component and three phases 68
One component and four phases 70

CHAPTER VI

CHEMICAL DYNAMICS OF VAN'T HOFF AND CHEMICAL EQUILIBRIUM OF LE CHATELIER 74
Van't Hoff's conception of chemistry 75
Van't Hoff on reaction velocities 76
Le Chatelier on chemical equilibrium 80
Effect of temperature 81
Effect of pressure 81
Analogy between mechanical and chemical equilibria . . . 81

CHAPTER VII

PAGE
THE RÔLE OF OSMOTIC PRESSURE IN THE ANALOGY BETWEEN SOLUTIONS AND GASES 84
Generalizations discovered by Van't Hoff 84
Lecture by Van't Hoff 84
Pfeffer's measurements of osmotic pressure 89
Artificial semipermeable membranes 90
Law of Boyle for osmotic pressure 91
Law of Gay-Lussac for osmotic pressure 93
Principle of Soret 95
Avogadro's law applies to the osmotic pressure of solutions 98
Gas pressure and osmotic pressure 100
Van't Hoff saw the above relations from a few imperfect data 101
Measurements of osmotic pressure by H. N. Morse and coworkers 102
Results obtained by Morse 105
Exceptions to the above relations 108
Formulation of gas laws as applied to osmotic pressure 110

CHAPTER VIII

ARRHENIUS AND THE THEORY OF ELECTROLYTIC DISSOCIATION 112
Theories of electrolysis — theory of Grotthuss 113
Williamson's theory of solution 115
Clausius' theory of electrolysis 117
Arrhenius proposes the dissociation theory 118
Reception of the dissociation theory 121
Certain applications of the dissociation theory 123
Meaning of the term acid 124
No undissociated compound an acid. 126
Why are hydrogen ions acidic? 128
Meaning of the term base 130
Constant heat of neutralization of strong acids and strong bases 131
Explanation of constant heat of neutralization 132
Heat of neutralization of weak acids and weak bases . . . 133
Hydrogen and hydroxyl ions always combine when in the presence of one another 134

PAGE
Law of the thermoneutrality of salts 137
Properties of mixtures of electrolytes and non-electrolytes . 139
The meaning of substitution in chemistry 140
Ions are the active agents chemically 142

CHAPTER IX

THE SOLVATE THEORY OF SOLUTION AND THE IMPORTANCE OF SOLUTIONS FOR SCIENCE IN GENERAL 145
Generalizations of Van't Hoff and Arrhenius 145
Criticism of the generalizations of Van't Hoff and Arrhenius 147
Origin of the solvate theory of solution 148
Work of Jones and Ota 149
Work of Jones and Knight 150
Work of Jones, Chambers and Frazer 151
Explanation of results by Jones. 151
Work of Jones and Getman 152
Evidence for hydration in aqueous solution 152
Work of Jones and Bassett 153
The solvate theory 155
Spectroscopic evidence for the solvate theory. 155
What is meant by absorption of light? 156
What we mean by color in solution 157
Bearing of the absorption of solutions on the solvate theory 157
The grating spectroscope 158
Work of Jones and Uhler 159
Work of Jones and Anderson 159
Work of Jones and Strong 161
The radiomicrometer spectroscope 163
Work of Jones and Guy 164
The present solvate theory and the older hydrate theory of Mendeléeff 166
Bearing of the solvate theory of solutions 167
Importance of solution for chemistry in particular and for science in general 168

CHAPTER X

THE WORK OF WILHELM OSTWALD IN INAUGURATING THE NEW ERA IN CHEMISTRY 172
Ostwald the experimenter 173

PAGE
Dilution law 174
Ostwald's modification of Kohlrausch's law 176
Ways in which ions are formed 177
Absorption of light by solutions 180
Ostwald's theory of indicators 182
Allotropy 183
Oxygen and ozone 184
Sulphur 186
Chemical action without contact 188
Faraday's law and chemical valence 192
Catalyzers 196
True and pseudocatalyzers 196
Autocatalyzers 197
Catalysis and the chemical industries 197
Fixation of nitrogen 197
Characteristics of Ostwald the experimenter 198
Ostwald the founder and organizer of a school of chemistry 200
The founding of the Zeitschrift für physikalische Chemie 201
Text-books by Wilhelm Ostwald 204
Lehrbuch der allgemeinen Chemie 204
Grundriss der allgemeinen Chemie 205
Grundlinien der anorganischen Chemie 207
Wissenschaftlichen grundlagen der analytischen Chemie . . 209
Physiko-chemische Messungen 209
Thermodynamische Studien von Willard Gibbs 209
Klassiker der exakten Wissenschaften 210
Elektrochemie ihre Geschichte und Lehre 211
Overthrow of Scientific Materialism 211
Energetics 212

CHAPTER XI

INVESTIGATIONS BY THE STUDENTS AND COWORKERS OF WILHELM OSTWALD 215
Apparatus of Beckmann 215
Beckmann thermometer 217
Freezing-point apparatus 218
Boiling-point apparatus 218
Molecular weights of dissolved substances 220

PAGE
Dissociation of electrolytes 221
Investigations of Paul Walden 222
Liquid sulphur dioxide 223
Liquid hydrocyanic acid 223
Abnormal electrolytes 224
Organic solvents 224
WORK OF WALTER NERNST 225
The primary cell 225
Solution-tensions of the metals 227
Solubility investigations 229
Thermodynamics 230
ELECTROCHEMICAL INVESTIGATIONS OF M. LE Blanc . . . 230
Decomposition values of ions 231
Decomposition values and the theory of electrolysis . . . 232
Older theory of electrolysis. 232
Older theory of electrolysis erroneous 233
New theory of electrolysis 235
Decomposition values and the electrolysis of acids 236
Decomposition values and the electrolysis of bases 237
Decomposition values and the electrolysis of salts 238
Primary and secondary decomposition of water in electrolysis 240
WORK OF GEORG BREDIG ON COLLOIDAL SUSPENSIONS . . . 242
Method of making colloidal suspensions of the metals . . . 242
Colloidal suspensions of the metals are catalyzers 243
Preparation of colloidal suspensions 245
Why ions are necessary for precipitation 246
Precipitation not the natural condition in chemistry. . . . 247
Colloidal solution and colloidal suspension 248
Colloidal chemistry 249
MOLECULAR WEIGHTS OF PURE LIQUIDS 249
Method of Ramsay 250
Method of Longinescu 250
WORK OF HABER 251
SOLID SOLUTIONS 252
Diffusion in mixtures of solids 253
Lowering of vapor tension and freezing-point in solid solutions 253
Kinds of solids which can form solid solutions 253
WORK OF A. A. NOYES 255
Free ions in solution 255

PAGE
Conductivities at higher temperatures 256
Hydrolysis at high temperatures 256
WORK OF RICHARDS 257

CHAPTER XII

THE ELECTRON *and* RADIOCHEMISTRY 259
Earlier view of the atom 259
The electron 259
Constancy of the ratio $\frac{e}{m}$ 260
The cathode particle 262
What is the corpuscle? 262
Mass and inertia due to the electrical charge 263
The Electron 264
"The Overthrow of Scientific Materialism" 265
The electron theory of matter 265
The atom in terms of the electron theory 266
Rouland's conception of the atom 267
The electron theory and electrolytic dissociation 268
Meaning of intrinsic energy 269
The electron theory and the periodic system 270
RADIOCHEMISTRY 271
Discovery of the X-ray 271
X-rays and phosphorescence 271
Discovery of radium 272
Meaning of radioactivity 273
Alpha particles 273
The spinthariscope 274
The Beta particles 275
The Gamma rays 275
Properties of radium 275
Heat energy produced by radium 276
Whence comes the heat liberated by radium? 278
Origin of solar heat 280
Is there radium in the sun? 280
Radium the source of some terrestrial heat. 281
The emanation 282
Radium emanation produces helium. 282
Production of an element 284
Not transmutation 285

PAGE
Heat produced by the radium emanation 286
Induced radioactivity 287
Radioactive matter being unstable decays, and is also produced 287
Uranium X 288
Thorium X 289
EXPLANATION OF RADIOACTIVE PHENOMENA 290
The more important properties of radioactive substances 290
The older conception of the atom cannot explain radioactivity 290
The election theory and radioactivity 291
Heavier atoms more radioactive 291
Alpha particles tend to come off first 293
The chemical atom unstable 294
All atoms probably radioactive 294
Origin of radium 294
Radium produced indirectly from uranium 295
Ionium 295
Supposed transmutation of certain elements 296
Importance of physics and mathematics for chemistry . . . 297
APPENDIX 299
MENDELÉEFF 299
KEKULÉ 299
GIBBS 301
RAMSAY 302
VAN'T HOFF 303
ARRHENIUS 307
OSTWALD 309
INDEX 313

A NEW ERA IN CHEMISTRY

CHAPTER I

CONDITION OF CHEMISTRY IN 1887

THE science of chemistry has not developed continuously from the beginning. Some one discovered a generalization or made a fertile suggestion, and this guided the experimental work in chemistry for quite a period of time. The aim was to test the generalization or suggestion in question, to see how much truth was contained in it, or of how wide-reaching or far-reaching significance it was.

Then some one would announce another generalization, and the active chemists of the time would turn to the testing of it; and this would often change the entire trend of chemical work and chemical thought. Examples of this condition of things are the periodic system of Mendeléeff and Lothar Meyer, and the benzene hypothesis of Kekulé.

Condition of Inorganic Chemistry before Mendeléeff. — During the half century prior to 1869 a large number of chemical elements had been discovered. These had for the most part been isolated and their properties studied. They had been allowed to combine with one another, and the composition and properties of the various compounds formed had been the objects of investigation.

After Dalton proposed the atomic theory, these elementary substances were regarded as made up of ultimate units or atoms; and one of the leading problems of the chemist was to determine the relative weights or masses of these atoms. This was made possible especially by Avogadro, who proposed his hypothesis in 1811.

It was, however, soon found that one element often combines with another element in more than one proportion. This led to what appeared to be hopeless confusion in the determining of atomic weights, by simply analyzing the compounds containing the elements in question. If the compound contained one atom of one element united with one atom of another element, the determination of the relative amounts of the two elements in the compound would give at once their relative atomic weights.

When, however, one atom of one element combined with an unknown and indeterminable number of atoms of the other element, the problem of determining relative atomic weights by chemical analysis alone became hopeless.

It was the Italian chemist, Cannizzaro, who showed much later, how the hypothesis of Avogadro can be used to solve the problem of the relative atomic weights or masses of the chemical atoms.

The atomic weights of many of the best-known chemical elements were worked out with a high degree of accuracy, considering the crudity of the methods available for such work at that period, especially by Stas.

Chemists began to study these figures representing the relative atomic weights of the atoms. They soon came to feel that there is some close relation between the atomic weights of the different elements and their physical and chemical properties. A number of attempts were made to find such a relation.

Hypothesis of Prout. — The most serious and meritorious of these was the view advanced by Prout in 1815. If the most accurately determined atomic weights were expressed in terms of hydrogen as one, it was observed by Prout that they are all very nearly whole numbers. This he interpreted as due to the fact that all of the elements are made up of hydrogen. Their atoms are simply stable groups of hydrogen atoms, the number of such atoms in the atom of the element in question being expressed by the atomic weight of the element in terms of hydrogen as one. It was, however, soon found that there are elements whose atomic weights are not whole numbers in terms of hydrogen as unity, but are whole numbers and a half. It was then proposed by Marignac to halve the hydrogen atom, and consider all of the other atoms as built up of half hydrogen atoms.

Elements were then found whose atomic weights were unity and a quarter. It was then proposed to quarter the hydrogen atom, and to use this as the fundamental unit of which the atoms of all other substances were made.

Having once begun to divide the hydrogen atom the process could be continued indefinitely; and, consequently, the hypothesis of Prout soon fell into disrepute.

We shall see that the difficulty was that they did not subdivide the hydrogen atom often enough, or they would have been essentially where we are today with respect to the ultimate unit of matter.

The hypothesis of Prout is a generalization of great importance in the history of chemistry, whether it is rigidly true or not. It was the first comprehensive, rational attempt to correlate atomic weights and other physical and chemical properties of the elements.

P*eriodic System of Mendeléeff and Lothar Meyer.*—The English chemist, Newlands, in 1864[1] had attempted to arrange all of the elements in a table in the order of their increasing atomic weights, beginning with hydrogen. He observed that every eighth element is related, and arranged the elements in groups of eight, whence the so-called "octaves of Newlands." This arrangement, although very defective, was important in that it attempted to correlate the properties of all of the then known elements, and their atomic weights.

A generalization which fits the facts much better, was the periodic system of the Russian, Mendeléeff, and the German, Lothar Meyer. Mendeléeff in

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[1] Chem. News., **10**, 96 (1864); **12**, 83 (1865).

pounds which it would form with other chemical elements. These predictions went even into such details as the color and specific gravity of the element itself, and the color and specific gravity of its compounds. As is well known, a large number of these predictions made by Mendeléeff have since been verified with surprising accuracy and in incredible detail. A number of the predicted elements have been discovered, and have been found to have the calculated atomic weights. Their compounds have been made, and the properties of these compounds found to agree with those foreseen for them with surprising accuracy.

When a scientific generalization is announced, the least that can be expected of it is that it should be able to account for all, or nearly all of the facts which it is meant to correlate. A generalization is, however, of greater value in science when it can, in addition, predict the existence of facts then unknown and have these facts subsequently discovered. The generalization in question then becomes a working hypothesis, as it is rightly termed. It suggests new lines of work, and in this way leads to the development of the science in question.

The periodic system of Mendeléeff and Lothar Meyer was not only able to account for most of the facts of general chemistry, that were known at the time it was proposed; but was able to predict new and unknown facts, and to have these predictions subsequently verified.

This generalization exercised for a time a dominant influence in chemistry for each of the above reasons. Before it was proposed, general chemistry was a more or less disconnected mass of facts, which had been brought to light as the result of nearly a century of experimental work. Certain relations had been pointed out between certain of these facts. These relations were, for the most part, of limited scope, and were not of any very fundamental significance. When the periodic system was proposed, we had a comprehensive generalization which covered the facts of chemistry in general.

Furthermore, it was a working hypothesis; predicting undiscovered facts and suggesting new lines of work, which were taken up by both chemists and physicists.

The impression made by the periodic system upon chemists, imperfect and defective as this system was, was deep-seated. It dominated the thought and the work in general chemistry for quite a period after it was proposed. It may be said to have been the philosophy of general chemistry from the time it was announced until 1887; when another suggestion was made, as we shall see, which shared with the periodic system the attention of chemists and which is even more important.

The periodic system, then, converted general chemistry from pure empiricism into system; but it did not do more than make of chemistry a systematic branch of natural science. It never did, and it never could convert chemistry into a branch of exact science.

Organic Chemistry in 1887.—The condition of organic chemistry at the end of the period we are now considering was, in many respects, analogous to that of inorganic. It may be of interest to trace very briefly the more important steps in the development of the chemistry of carbon to the point where the new era in chemistry found it.

It is well known that the first organic compound was prepared artificially by Wöhler in 1828. Ammonium cyanate, when allowed to stand, passed over spontaneously into urea.

Four years later, 1832, Liebig and Wöhler published the results of their joint investigation on the radical contained in benzoic acid. They showed that benzoic acid, oil of bitter almonds and many of its derivations, contained a common group, C_7H_5O, which, unchanged, passed from one of these compounds to another. This group thus behaved like the elements of inorganic chemistry, and they called it a compound element, or an organic element. Since it occurred in benzoic acid and its derivatives they called this radical "Benzoyl." The discovery of an organic radical or element was of great importance, and this discovery dominated carbon chemistry for quite a period.

The next important advance in the chemistry of carbon was the discovery of the act of substitution. A number of isolated observations had been made of what we today know as substitution, but it was the French chemist, Dumas,[1] in 1834, who

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[1] Ann. Chim. Phys. [2], 56, 140 (1834).

first called attention to them. Laurent went much farther than Dumas,[1] and formulated the rule that when say chlorine replaces hydrogen in a compound the chlorine takes the place of the hydrogen, and the chlorine substitution product must have properties analogous to the original compound. This aroused the opposition of Berzelius, whose electrochemical theory was apparently threatened by the relations between acetic acid and trichloracetic acid.[2]

Type Theory of Dumas.—A little later, in 1839, Dumas transformed the substitution theory into the type theory, which referred carbon compounds to certain definite and well-known chemical types, such as water, ammonia, etc. The fact was pointed out by Dumas, that when substitution of one atom or group by another takes place, the chemical type remains unchanged. He reached this conclusion especially from his study of the relations between acetic acid and trichloracetic acid. The three positive hydrogens are replaced by what was supposed to be three negative chlorines, without changing the chemical type of the compound, but also without materially altering the properties of the compound.

Work of Kekulé.—We now come to the work of one who was destined to play a most prominent part in the development of the chemistry of carbon—

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[1] Lieb. Ann., **33**, 179, 159 (1840).

[2] See author's "Elements of Physical Chemistry," 4th edition, p. 350. (Macmillan Co., N. Y.)

August Kekulé. Organic chemists had dealt thus far chiefly with the radicals or groups which can be passed unchanged from one compound to another. It was Kekulé who first arrested attention to the now well-known fact that, to have a science of carbon chemistry, we must go beyond or within the radicals to the atoms[1] of which they are composed. An attempt had already been made by Frankland, in 1852, to do the same thing for inorganic chemistry. The importance of this step for organic chemistry, as we shall see, cannot easily be overestimated.

The atoms present in these organic radicals must be united, and Kekulé pointed out in 1859 that carbon must be regarded as a tetravalent element, having the power of combining with four hydrogen atoms, four chlorine atoms, or four univalent atoms in general; and further, that a carbon atom has the power of combining with another carbon atom. This led to the so-called "linking of carbon atoms." If two carbon atoms combine, one combining unit of one combines with one combining unit of the other. Two such carbon atoms would, therefore, have six remaining combining units—would be hexavalent. From this fundamental conception Kekulé was able to work out the constitution of the aliphatic carbon compounds, essentially as it is today. A much greater work, however, remained for Kekulé to do. There was a class of carbon compounds occurring in the natural oils which had a strong odor, and from this they were

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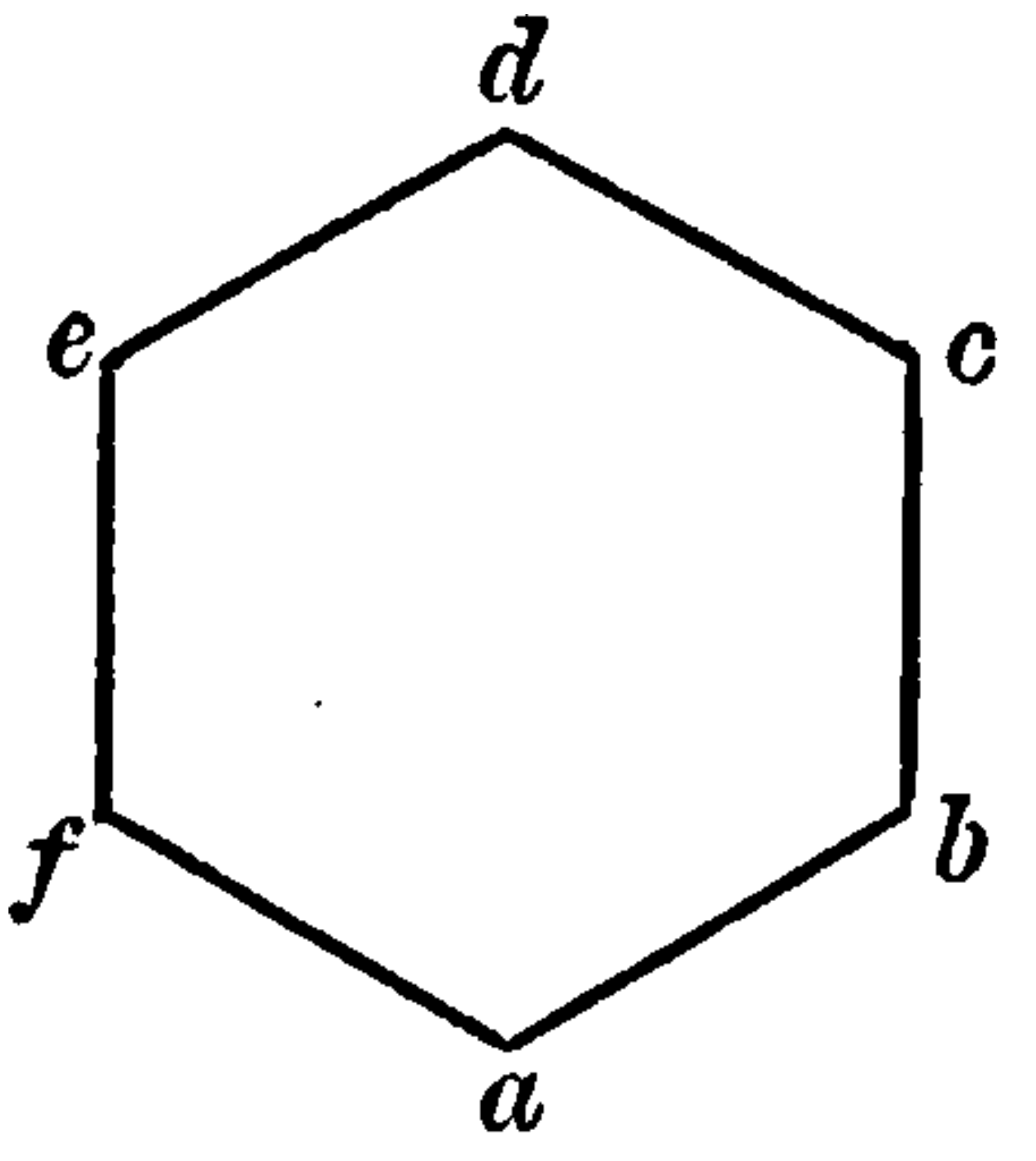
[1] Lieb. Ann., **104**, 129 (1857).

called aromatic compounds. These compounds contained more carbon than the corresponding aliphatic compounds, and Kekulé recognized that the simplest of them contain at least six atoms of carbon. He pointed out further, that the derivatives of the aromatic compounds have this in common; the chief product formed has at least six atoms of carbon.

Said Kekulé, "These facts justify the conclusion that in all aromatic substances there is one and the same atomic grouping, or, if you will, a common kernel, which consists of six carbon atoms."

A brief paper of fourteen pages, dealing with this subject, was first published by Kekulé in the Bulletin de la Société Chimique [3] 1, 98, (1865), dated January 27, 1865. A far more comprehensive paper of sixty-eight pages appeared shortly after in Liebig's Annalen,[1] on February 6, 1866. In the latter paper Kekulé proposed what has since come to be known as his "benzene hypothesis."

He suggested the two following formulas for benzene. Benzene is either a regular hexagon, with a carbon and a hydrogen at each solid angle, or it is a triangle.



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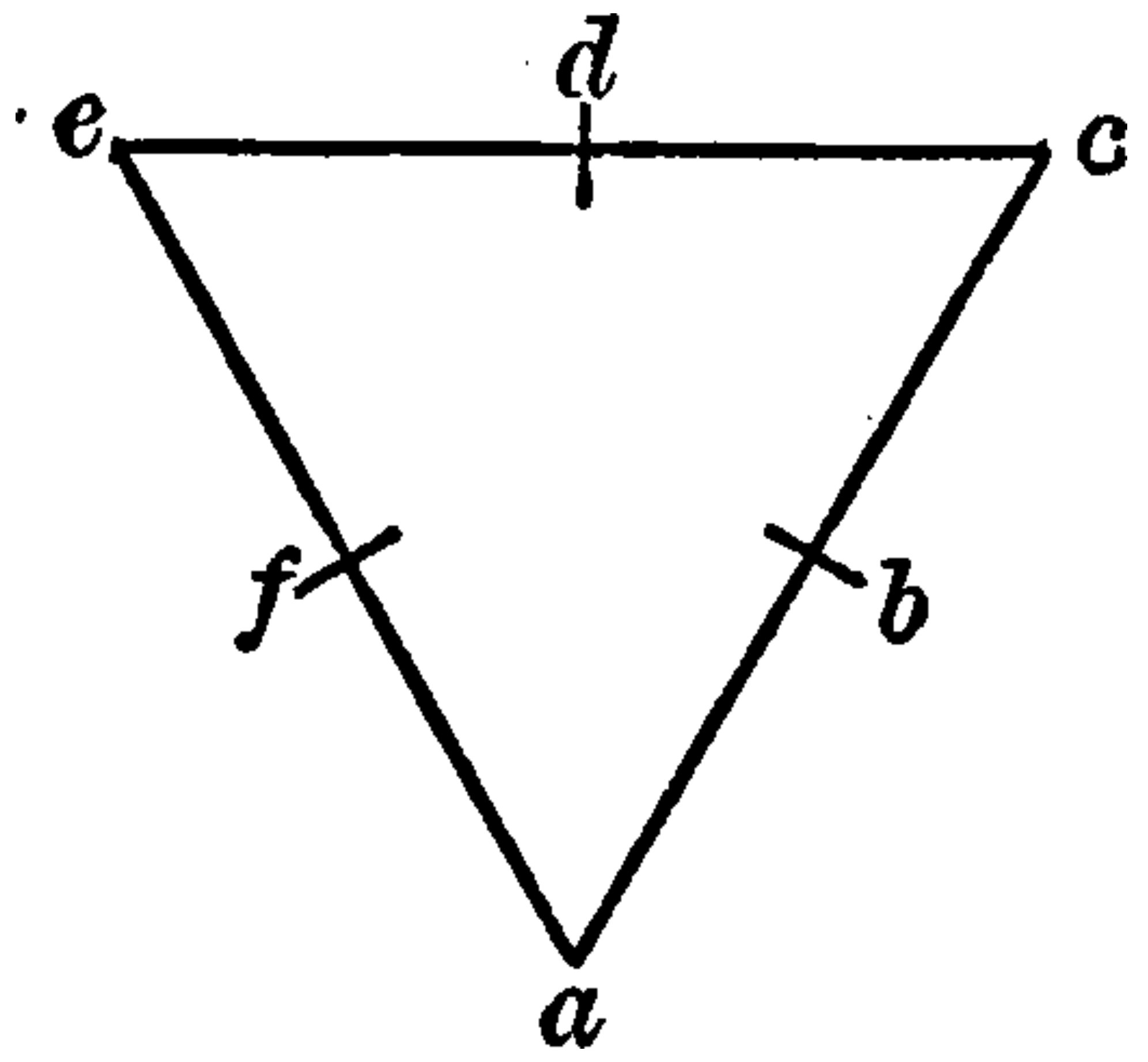
[1] Lieb. Ann., **137**, 129 (1865).

In the first figure[1] every carbon and hydrogen would bear the same relation to the molecule. In the latter case, the three carbons at *a*, *c* and *e* would bear a different relation to the molecule from the three carbons at *b*, *d* and *f*. The study of the substitution products led to the conclusion that three carbon atoms in benzene are different from the other three, and that, therefore, the second formula was the more nearly correct. This will be recognized to be nothing more nor less than the well-known hexagon formula, or the Kekulé formula for the constitution of benzene.



It is difficult to overestimate the importance of this suggestion on the subsequent development of carbon chemistry. This was not only an hypothesis which accounted for the facts then known concerning the chemistry of the aromatic compounds, but it was far more than this; it was a working hypothesis, suggesting new lines of work in every direction. The result was that it became the dominant thought in organic chemistry for quite a period. Indeed, as we shall see, until the significance of chemistry in three dimensional space was recognized.

Celebration in Honor of Kekulé's Benzene Hypothe-

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[1] Lieb. Ann., **137**, 158 (1865). *Ibid.*, 161.

Kekulé then gave a brief account of how he discovered the benzene theory.

"During my stay in London I lived for a long time in Clapham Road near the Commons. I frequently spent the evening with my friend, Hugo Müller, in Islington, on the other side of that enormous city. We talked about many things, but chiefly about our beloved chemistry. On one beautiful summer day, I traveled through the busy streets of that metropolis in the last omnibus, and as usual rode outside on the top of the omnibus. I began to dream. The atoms began to play antics before mine eyes. I had always seen each little particle in motion, but had never before succeeded in determining the nature of their motion. That day I saw how two smaller ones often united to form a pair, how the larger ones seized two of the smaller ones, and how the still larger held three and even four of the smaller, and how they all moved in vortices. I saw how the greater formed a row, and how the smaller were drawn along at the ends of the chain. I saw what the old master Kopp, my honored teacher and friend, pictured in such a charming manner in his 'molecular world,' but I saw it long before he did. The call of the conductor, 'Clapham Road,' awaked me from my dreams but I spent a part of the night transferring to paper at least sketches of each of these dream pictures. Thus arose the structure theory.

"The benzene theory had a similar origin. During my stay in Ghent, in Belgium, I lived in a fine room on the main street. My work room faced on a narrow side street, which, during the day, had no light. This was no disadvantage to a chemist who spends all of the days in the laboratory. I sat in this room and wrote on my text-book. It did not go well. My thought was on other things. I turned my chair to the fireplace and fell half asleep. The atoms again played antics before mine eyes. Small groups kept themselves modestly in the background. My mind's eye, trained by repeated sights of a similar kind, now distinguished larger forms of various shapes. Long rows united, becoming much thickened; all in movement snake-like twisting and turning. And see, what was that? One of the snakes seized his own tail, and thus confusedly appeared the picture before mine eyes. I awoke as by a flash of lightning. This time also I spent the remainder of the night working out the consequences of the hypothesis.

"Gentlemen, if we learn to dream we may find out the truth; but let us avoid publishing our dreams before they have been tested by the wide-awake intelligence."

And this Kekulé did. His hypothesis had been thoroughly tested by many, many wide-awake intelligences, in many directions before its origin was made public. Indeed, it is a question whether it would ever have been made public, had it not led to such important consequences in the development of carbon chemistry.

Kekulé's benzene formula may be said to have dominated chemical thought and work for at least two decades after it was announced. The number of compounds made and studied during this period, especially in Germany, was enormous; and both scientific and industrial chemistry would, consequently, profit by it. The Kekulé formula played a rôle in carbon chemistry that was somewhat analogous to, although not as comprehensive as that played by the Mendeléeff-Lothar Meyer periodic system in inorganic chemistry. They both accounted for most of the facts then known, and both of them suggested many new lines of work. They both, however, had their limitations. The hypothesis of Kekulé represented benzene as existing in *two dimensions* in space, and must, therefore, be regarded as only *symbolical.* It could not represent the actual condition of things in the benzene molecule.

The Kekulé formula was extremely useful in accounting for the facts then known, and in suggesting new lines of work; but like the periodic system probably did its very greatest service to chemistry as a systematizing agent. Before it was proposed organic chemistry was a more or less disconnected mass of empirically established facts, whose meaning was, for the most part, not understood. These generalizations enabled chemists to arrange their facts systematically, and to think of them intelligently. These two generalizations, discovered at very nearly the same time, converted, the one inorganic, and the other organic chemistry from almost pure empiricism into system, and this was of course a great achievement.

Beginning of a Science of Chemistry.—It will, however, be easily recognized by any thinking man of science that a *system* of chemistry is one thing and a *science* of chemistry is another; just as the making of brick is one thing and the building of the brick into a piece of architecture is another. The making of the brick is, however, a necessary forerunner to the construction of the building. It has been just so in chemistry. The period which ends about 1887 may be said to have been the "fact discovering" or "brick making" period. It was, of course, very important in itself, and absolutely essential to the subsequent development of a science of chemistry.

It was, however, not a science of chemistry, as it is frequently thought to have been by those who have not followed closely the later developments; and this is the point upon which it is wished to lay stress.

The "new era" referred to in the title of this little volume marks roughly the beginning of the transition from a system into a science of chemistry.

This transition was effected by means of certain generalizations, which were discovered for the most part between 1865 and 1888. What these generalizations were, by whom discovered, and so far as is known, how they were discovered, will now be pointed out. It may be said in advance, that, as far as is known, they were not revealed in dreams. The nature of most of them precludes this possibility.

The first of these in point of time was the discovery of the law of mass action; and the development of this conception, which required nearly a century, will now be discussed.

CHAPTER II

DEVELOPMENT OF THE LAW OF MASS ACTION

Importance of a Generalization.—I once heard Ostwald state in a lecture, that the highest aim of scientific research was the discovery of a generalization or law. This expression created opposition at first, but on careful reflection it became obvious what Ostwald really meant, and that he was right. I had always supposed that the aim of science was to discover truth, but it is often impossible to say at the time just how much truth there is in any given generalization or law. This remains for subsequent time to test. The best we can do is to discover a general relation to which the facts then known conform, and which will, perhaps, predict new facts; and then leave it to the future to determine whether this generalization is or is not an absolute truth.

If we glance over the history of almost any branch of natural science, we will see that what stands out prominently are not the individual facts pertaining to that science, but the generalizations or laws. Take the science of physics, which, from the comparatively simple and continuous nature of the phenomena dealt with, has advanced to a true science far more rapidly than chemistry; the landmarks in its history are the generalizations or laws. We think of the law of gravitation, of the conservation of energy, the first and second laws of thermodynamics, etc.

Most of the so-called laws of nature are not absolute truths, but are only approximations holding under limited conditions; those mentioned above being, however, so far as is known today, exceptions. Take the laws of gas pressure; the laws of Boyle, Gay-Lussac and possibly even the law of Avogadro. When these generalizations were proposed, they were supposed to be more generally true than subsequent work has shown them to be. In science, then, the best we can do is to discover generalizations, and leave it to the future to determine just how much truth they really contain.

We shall now trace the development of certain generalizations, which have transformed chemistry from system into science, and the first of these is the law of mass.

Earlier Views on Mass Action. — The first one to recognize clearly the rôle of mass in chemistry seems to have been the chemist Wenzel, as early as 1777. He showed that under certain conditions sulphuric acid will replace nitric from its salts, while under other conditions nitric acid will replace sulphuric acid from sulphates. Wenzel looked into the effect of the relative quantities of the substances reacting on the nature of the reaction, and concluded that the concentration of the reacting

resist ordinary strong acids and bases, at ordinary temperatures, to a remarkable degree.

Notwithstanding their stability and insolubility in water, they are continually undergoing decomposition in nature; due to the action of the very weak acid, carbon dioxide, in the presence of water. If we were to treat a stable silicate in the laboratory with moist carbon dioxide for a lifetime, we should hardly be able to detect the amount of decomposition effected and the amount of carbonate formed. Yet in nature we have the silicates being transformed into carbonates all over the surface of the globe by the carbon dioxide of the air. This is what is usually known as the "carbonation" of the rocks, and is effected by the mass action of the carbon dioxide in atmospheric air acting through geological epochs.

This example of the effect of mass was so general and so striking, that from the time of Rose until the present it has never been seriously questioned.

Dulong[1] studied the effect of potassium carbonate on barium sulphate, both when the two are fused together, and when they are boiled together in an aqueous solution of the carbonate. He found that the amount of barium carbonate formed was proportional to the amount of potassium carbonate present. This same reaction was studied quantitatively by Heinrich Rose,[2] and the facts interpreted essentially as we interpret them today.

[1] Pogg. Ann., [1], **82**, 273 (1812).

[2] *Ibid.*, **94**, 481 (1855); **95**, 96, 284, 426 (1855).

Wilhelmy. — The first to formulate the effect of mass on chemistry, for even a single reaction, was Wilhelmy.[1] He studied the inversion of cane sugar by acids, and showed that the velocity of inversion was proportional to the amount of sugar present.

Berthelot and Saint Gilles. — The first elaborate quantitative study of the effect of mass on chemical reactions was made by another distinguished French chemist of a much later date, Berthelot,[2] and working with him was Saint Gilles. It is very difficult to keep separate the names of Berthollet, who lived at the beginning of the nineteenth century, and Berthelot, who lived and worked from the middle of the century until a few years ago. This confusion is still further confounded by the fact that they are both Frenchmen, both are very prominent chemists, and both wrote books bearing such similar titles, as Berthollet's "Essai de Statique Chimique" and Berthelot's "Essai de Mécanique Chimique." Berthelot and Saint Gilles undertook an elaborate investigation on the formation of esters from organic acids and alcohols. This is one of the best reactions in all chemistry with which to study the effect of mass. When one equivalent of ethyl alcohol is treated with one equivalent of acetic acid, the reaction does not proceed to the end; indeed, does not approach completion. Equilibrium is reached when two-thirds of the theoretical

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[1] Pogg. Ann., **81**, 413 (1850).

[2] Ann. Chim. Phys. [3], **66**, 110 (1862).

amount of ester that could be formed if the reaction were complete, is formed. By increasing the acid relative to the alcohol, or the alcohol relative to the acid, the amount of ester formed is increased, and thus the effect of mass could be followed. This reaction is also well adapted to study the effect of mass, since the amount of ester formed under any given conditions can be so easily determined.

Berthelot and Saint Gilles took one equivalent of acetic acid and added from two-tenths of an equivalent to fifty equivalents of ethyl alcohol. The amount of ethyl acetate formed, varied from nineteen per cent, when two-tenths of an equivalent of alcohol was used, to one hundred per cent when fifty equivalents of alcohol were used to one of acetic acid.

This was the best possible experimental verification of the effect of mass on chemical reactions. All other conditions remaining the same, the amount of ester formed varied from nineteen to one hundred per cent, by simply changing the amount of the alcohol present.

One other piece of experimental work will be referred to, before taking up the investigation which led to the discovery of the law of mass action.

Pebal and Than. — It had been shown by Pebal and by Than that when ammonium chloride is volatilized, it undergoes partial decomposition; breaking down into ammonia and hydrochloric acid. It was further shown that when ammonium chloride is converted into vapor in the presence of either ammonia or hydrochloric acid, the chloride then volatilizes without undergoing decomposition.

Similar results were obtained with phosphorus pentachloride. When volatilized into atmospheric air, or into a vacuum, it undergoes partial decomposition. When converted into vapor in the presence of either of its decomposition products, phosphorus trichloride or chlorine, it volatilizes undecomposed.

The question arises, how does either of the decomposition products prevent the compound in question from decomposing? Since the decomposition of the ammonium chloride and phosphorus pentachloride is a function primarily of temperature, these substances at a given temperature will decompose, no matter what the nature of the atmosphere into which they are volatilized. Then, how can the presence of a decomposition product have any effect? To answer this question we must consider for a moment what is meant by chemical equilibrium.

Williamson. — Chemical equilibrium was for a long time regarded as a statical process. A chemical reaction proceeded so far and then stopped, and the point at which it stopped was the point of equilibrium of the reaction. This is all changed now, due to the English chemist, Williamson;[1] who from his work on the synthesis of ether from alcohol and sulphuric acid, showed that we must regard chemical equilibrium not as a statical, but as a dynamical process. A given reaction takes place and produces certain products. These products then react with

[1] Lieb. Ann., **77**, 37 (1851).

one another and reproduce the original substances. We have two reactions taking place simultaneously, the one being the exact opposite of the other. The initial reaction becomes slower and slower as the initial substances are used up, and the opposite reaction between the products of the first reaction becomes faster and faster as more and more of these products are formed. The result is that after a time these two counter reactions will acquire equal velocities, and this is the condition known as chemical equilibrium.

With this conception in mind we can now return to the problem of the effect of either decomposition product on the dissociation of, say ammonium chloride by temperature. When the salt is volatilized at a definite temperature it undergoes decomposition, regardless of the nature of the atmosphere into which its vapor passes. The rate at which it decomposes is primarily a function of the temperature at which the volatilization takes place. As soon as some of the ammonium chloride decomposes into ammonia and hydrochloric acid, these begin to react with one another and reform ammonium chloride. The velocity with which this reaction takes place will depend on the amount of free ammonia and free hydrochloric acid present. If we have already in the atmosphere in which the salt is volatilized some free ammonia or some free hydrochloric acid, the reaction involving the reformation of ammonium chloride will proceed more rapidly, and there will, therefore, at any given instant be less of the ammonium chloride decomposed than if there was no excess of ammonia or of hydrochloric acid present. If the excess of either of the decomposition products is sufficiently great, the reaction involving the reformation of ammonium chloride may be made to have such a velocity, that at any given instant there is practically none of the ammonium chloride decomposed.

This illustrates, in a most admirable manner, the effect of mass or quantity on chemical reactions, and this is the reason why this subject was introduced in this place. By increasing the mass of either of the decomposition products, we increase the velocity of the reaction between the products of the initial reaction, until it becomes so great that the initial velocity becomes in comparison practically zero — the ammonium chloride is reformed practically as fast as it decomposes.

This is one of the most direct illustrations of the effect of mass in chemistry, of which it is possible to conceive.

Thus far the effect of mass in chemistry had been studied purely empirically. The method was to cut and try and see what result was obtained. This was, however, to give place at this time to a scientific study of the effect of mass on chemistry — to an exact mathematical formulation of its action.[1]

Discovery of the Law of Mass Action by Guldberg and Waage. — The Norwegian physicist, Guldberg,

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[1] See my "Elements of Physical Chemistry," 4th edition. Macmillan Company, N.Y.

and his son-in-law, Waage, the chemist, both in the University of Christiania, took up jointly the effect of mass action in chemistry. They studied a number of reactions experimentally, and found that the *velocity* of a chemical reaction is proportional to the masses of the substances reacting; or, what is the same thing, is equal to the product of the masses of the reacting substances times a constant. This, expressed algebraically, would be—representing the mass of one of the acting substances by p, and the mass of the other by q, and the velocity of the reaction by v—

$$v = p\,q\,k,$$

in which k is a constant whose numerical value depends upon the chemical nature of the substances entering into the reaction.

This is the law of mass action as applied to the velocity of chemical reactions. When applied to the equilibrium of reactions the law becomes as follows:

Equilibrium in chemical reactions is the point at which the two opposite reactions acquire the same velocity. If we represent the velocity of one reaction as—

$$v = p\,q\,k$$

the velocity of the counter reaction—

$$v_1 = p_1\,q_1\,k_1$$

in which p_1 and q_1 are the masses of the substances formed from the first reaction, now reacting with

tions upon which the newer developments in chemistry rest; the most remarkable feature of it being its extreme simplicity. Like the fundamental laws of nature in general, when we have discovered them we marvel at their simplicity.

CHAPTER III

THE ENERGY CHANGES THAT TAKE PLACE IN CHEMICAL REACTIONS

Chemists First Studied Material Changes. — When a chemical reaction takes place there are apparently two kinds of changes going on. The matter present rearranges itself in new combinations, new compounds are formed, and there are also changes in energy. Heat is always produced or absorbed, there is always a thermal change; and light or electricity may also be produced, depending on the conditions under which the reaction takes place. There are, then, in chemical reactions two kinds of changes, changes in matter and changes in energy. The first of these to be studied by chemists was the material changes, and this was perfectly natural. These were the most obvious. When certain substances were brought together they reacted and new compounds resulted. These could easily be obtained, analyzed, and their properties studied. These new substances were often very important, in that they served as the starting-point for the production of other substances for use in further chemical reactions. These compounds and those that resulted from them, thus often proved to be of value both for scientific and industrial chemistry.

The result of this earlier work was that chemists came to look upon the material transformations that take place in chemical reactions as the most important side of such transformations. Indeed, many of them seemed to have lost sight of any other side. This state of mind found expression in such terms as, chemical reactions are "accompanied" by thermal changes; showing that they regarded the material transformations as the important thing, and the energy changes as of subordinate importance.

We shall see that this is all wrong. To speak of chemical reactions being "accompanied" by thermal changes, is as much a confusion of cause and effect, as to speak of a cart being "accompanied" by the horse that draws it. The discovery of this fact, that in chemical reactions the energy changes are really the important things, and the material changes of subordinate importance from the standpoint of scientific chemistry, we owe to several men. The aim of this chapter is to trace the beginning of the development of this conception.

Work of Julius Thomsen on Thermochemistry.— Prior to 1850 the energy changes that take place whenever a chemical reaction goes on were, as already stated, practically ignored. It had been noted that there is in general a change in the temperature of substances when they react. The reacting substances usually become warm, and in some cases, very hot. In other cases heat is taken up when substances enter into chemical reaction. It had been observed by the great Frenchman, Laplace, working with Lavoisier, that the amount of heat required to decompose a chemical compound into its constituents, was exactly equal to that which is given out when these constituents unite and form that compound. This conclusion, we know today, is a necessary consequence of the law of the conservation of energy; but at the time of Laplace the law of the conservation of energy had not been discovered.

Work of Hess. — Ten years prior to the beginning of thermochemical work by Thomsen, Hess[1] had shown that the same amount of heat is set free in any given reaction, whether it takes place in one or in several stages. This was a matter of great importance, since it enabled chemists to study thermochemically, a large number of reactions which would otherwise have been excluded from such work.

Hess also made the important observation that when dilute solutions of neutral salts are mixed, heat is neither evolved nor absorbed, there is no thermal change. The meaning of this fact was not seen at the time it was discovered. Indeed, it seemed that this fact was directly at variance with the view that there is a thermal change whenever a chemical reaction takes place. We start with two salts, say potassium chloride and sodium nitrate. We mix dilute solutions of these two salts, evaporate the solution to dryness, and obtain the four salts; potassium chloride, potassium nitrate, sodium chloride and sodium nitrate. We start with two salts

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[1] Pogg. Ann., **50**, 385 (1840).

and thus obtain four. It seemed certain that a chemical reaction had gone on, and yet there was no thermal change.

This observation on the part of Hess gave rise to considerable difficulty. It was absolutely impossible to explain it in terms of anything known at that time. The explanation today is perfectly simple. When dilute solutions of neutral salts are mixed there is no chemical reaction. Everything is dissociated before the mixing takes place, and everything remains dissociated after the solutions are mixed. There is, therefore, no reason why there should be any thermal change. The chemical reaction takes place when the water is evaporated, and then there is a thermal change. The law of the thermoneutrality of salts is not only explicable in terms of what we know today, but is a necessary consequence of our present conceptions.

It was Julius Thomsen in Copenhagen who first took up a systematic study of the heat changes that manifest themselves when chemical reactions take place; and many of our best thermochemical measurements we owe to Thomsen.[1] His was, however, the type of mind that delights in accurate experimental work, and it remained for another to point out the most important consequences resulting from such works.

Thermochemical Work and Deductions of Berthelot. — The French chemist, Berthelot, with some of whose work we became familiar in the last chapter,

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[1] Thermochemische Untersuchungen, 4 volumes.

began his thermochemical investigations in 1865.[1] The results of his work, and the discussion of them were published in 1879, in his well-known "Essai de Mécanique Chimique, Fondée sur la Thermochemie."

Berthelot devised a number of forms of calorimeters for measuring the amounts of heat set free in chemical reactions. He also devised the explosion bomb for studying the thermochemistry of organic reactions. Most reactions between compounds containing carbon take place slowly, and organic reactions thus differ from inorganic. They start slowly, often have to be coerced in order that they will proceed at all, and then do not go to the end. In order that a reaction may be studied thermochemically it must proceed quickly to the end; otherwise, the heat that is given out over any considerable interval of time would be largely lost by radiation.

Most organic compounds combine with oxygen, but slowly when heated in atmospheric air. When heated, however, in the presence of concentrated oxygen they combine rapidly with it. Concentrated oxygen means oxygen under high pressure, and in order to have a gas under high pressure we must have a strong-walled containing vessel. Berthelot devised his well-known bomb, in which the combustion of organic compounds would proceed to the end at once; and the amount of heat set free could, then, be measured in the usual way.

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[1] Ann. Chim. Phys. [4], **6**, 290 (1865).

Berthelot was, however, not the type of mind to be limited even to fine experimental work. Indeed, it is a question whether his thermochemical measurements are as accurate as those of Thomsen. Berthelot made thermochemical measurements for a definite purpose, and that was to see to what far-reaching conclusions they would lead. He was looking for a relation between the heat liberated in chemical reactions and the direction which the reaction would take. He saw in the thermal change which, before his time, was supposed to "accompany" the reaction, the real cause of the reaction. He saw in chemistry, and probably for the first time, that the study of the energy changes which are the real cause of all chemical reactions, is the important thing, and the study of the material changes is of subordinate importance. He saw the true relation of cause and effect in chemistry, and let us now see what were some of the more important results of his investigations.

Berthelot, as the general result of his comprehensive studies, arrived at three principles, which he formulates thus.[1] The first he calls the *Principle of Molecular Work*, which he formulates as follows: "The quantity of heat given out in any reaction whatsoever, is a measure of the sum of the chemical and physical work done in this reaction." His second generalization, which he calls the

Principle of the Initial and Final State.—"If a system of simple or compound substances, under

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[1] Essai de Mécanique Chimique, Vol. I, pp. xxviii-xxix.

Berthelot's Chemical Mechanics and Statics. — At the beginning of the mechanics Berthelot[1] raises the question, "What are the general conditions that control chemical combination and decomposition; what systems are stable, what reactions are possible, and what are necessary under given conditions? These are the questions that continually present themselves to the chemist, and it is of the greatest importance that he should know how to solve them."

"Let it be clearly recognized at the outset that the formulas and the notation in use, express only the relative weights of the reacting substances and the nature of what produces them, without giving us the properties themselves of all of these substances, or the forces which are exerted between them."

This is a perfectly clean cut statement of what the chemical equations at that time expressed, and what they did not express; and shows that Berthelot was dissatisfied with them. They left out the most important thing, the cause of the reaction, and were, therefore, superficial. Berthelot then points out that because we ignore these fundamental facts, the science of chemistry was most imperfect; and the theories of chemical mechanics do not approach in their generality and their certainty the theories of celestial mechanics. He then calls attention to the importance of thermochemical measurements in founding an exact science of chemistry.

In his mechanics Berthelot then takes up the

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[1] Essai de Mécanique Chimique, Vol. II, p. 1.

specific problems of chemical combination and decomposition, and the conditions of equilibrium in homogeneous systems, in heterogeneous systems, and in solution. It would lead us beyond the scope of this work to discuss these matters any farther here. Details in reference to them can be obtained from the original work.

It is in the chemical statics that his law of maximum work is taken up. After defining his principle he says:[1] "We can conceive of the necessity of this principle by observing that the system which gives out the largest possible amount of heat, does not possess the energy necessary to accomplish a new transformation. Every new change requires the expenditure of work, and this cannot be done without the intervention of external energy. A system, on the contrary, which can give out more heat by further reacting, has in itself the energy necessary to effect this change, without the intervention of external energy."

We have already referred to Berthelot's corollary to his law of maximum work, which he calls

Theorem of the Necessity of Reactions. — A large number of typical and general cases, to which the law of maximum work applies, are then taken up and discussed. Also a number of apparent and real exceptions to this relation. Indeed, Berthelot has pointed out the exceptions to his law more clearly than his most ardent critics, and this fact seems often to have been forgotten.

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[1] Essai de Mécanique Chimique, Vol. II, p. 421.

In concluding this great work Berthelot says: "We have arrived at the end of our undertaking. This was to group the problems, and to work out the first principles of a new science, more general and more abstract than the description of individual properties, of the manufacture and transformations of chemical species. We have seen what are even the laws of these transformations, and we have investigated the causes, that is to say, the conditions which determine them"; and then in concluding; "This work, as limited as it is, is the first step in the new direction, which all are invited to assist in farthering until the entire science of chemistry has been transformed. The end in view is as high as this, that chemistry may pass from among the descriptive sciences, by connecting its principles and its problems with those of the purely physical and mechanical sciences. It is approaching more and more nearly to this ideal condition."

Criticism of the Law of Maximum Work. — The law of maximum work, or maximum heat evolution, thus discovered by Berthelot, has been subjected to much and severe adverse criticism. In my opinion it has often been unfairly treated. Of course it is not a rigid law of nature, it is not rigidly true; but no one has recognized this more fully than Berthelot himself, and no one has pointed out so clearly and comprehensively as he has done the apparent and real exceptions to his generalization.

Granting that it does not apply to all chemical reactions, its most violent opponent will admit that it does apply to a very large majority of all the reactions known to the chemist. Indeed, the exceptions as compared with the cases that conform to rule are of minor importance. We must, however, not fail to recognize them.

In judging of the value of this generalization, let us recall what was our knowledge of the cause of chemical reactions when Berthelot began his work. It was purely empirical and ungeneralized. We did not know of any general relation between chemical activity and any physical property of the reacting substances. We did not appreciate, even qualitatively, the meaning of energy changes for chemistry. We spoke of chemical reactions being "accompanied" by thermal changes, as has been said, and what did this mean? It meant that they entirely misunderstood cause and effect, taking the latter for the former. In a word, they had not the remotest conception of what really causes chemical combination; and they were content to label their lack of knowledge by the word chemical "affinity"; which says nothing more than that things react because they do.

This was about the state of mind when Berthelot appeared on the scene, and began the study of the energy changes that take place whenever we have chemical activity, and which cause all chemical action. He discovered the law of maximum heat evolution, which tells us that of several possible reactions between two or more substances, that one will take place which liberates the largest amount of heat; and when we examine all chemical reactions in terms of this conception we find that they nearly all conform to it.

A moment's thought will show that this generalization, even if not rigidly and universally true, was a great step in advance; was a great contribution towards converting empiricism and even system into science. It connected chemical action with thermal change, in a word with its cause; and showed us how, under any given conditions, the vast majority of chemical reactions will go. Berthelot was the first to recognize clearly the importance of the study of energy changes, for the foundation and development of a real science of chemistry. His own work, and generalizations, which I think have been underestimated, and in some quarters very much undervalued, contributed in no small measure to this end. He turned the attention of chemists from the study of material transformations alone to the study of their cause; from the relatively superficial side of chemical reactions to the scientific and much more profound problems of chemical science.

He connected chemical activity in general with thermal changes, and thus gave, in my opinion, an epoch-making contribution to chemistry. This is the reason why the work of this great Frenchman has been dwelt upon at some length, in discussing the influences and generalizations which have inaugurated the new era in chemistry.

An excellent, although brief account of the life and work of Berthelot has recently appeared from the pen of Prof. H. B. Dixon[1] of Manchester, England.

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[1] Journ. Chem. Soc. (London), **99**, 2353 (1911).

CHAPTER IV

VAN'T HOFF, LE BEL AND GUYE, AND THE ORIGIN OF STEREOCHEMISTRY

Work of Van't Hoff. — It required almost exactly a decade after Kekulé proposed his benzene hypothesis, for the next important step in the development of carbon chemistry to be taken. A Dutch child was born in Rotterdam in 1852, who was destined, at an early age, to exert an influence on chemistry as a whole which has never been surpassed, if it has ever been equalled. The son of a Dutch physician, Jacobus Henricus Van't Hoff was trained in the schools of Rotterdam and Delft, and completed his student work at the University of Leyden when twenty years old. He then went to Bonn to study with Kekulé. His experiences in Bonn were unsatisfactory. He could not see that the chemistry of Kekulé really led anywhere, as he expressed it, as far as the building up of a science of chemistry was concerned. It was his effort to get some clear conceptions of the chemistry of carbon that led him to write his book on carbon chemistry, "Ansichten über die organische Chemie." Van't Hoff, when working with Kekulé in Bonn and Würtz in Paris, was impressed with the purely qualitative nature of organic chemistry at that

it is said. When ordinary light is passed through a Nicol prism, all of the ether vibrations are reduced to one plane; the vibrations in all other planes being cut out by the prism. When light thus polarized is passed into a second Nicol prism, the plane of polarization is readily determined. The apparatus with a polarizing prism and an analyzing prism is known as a polariscope.

When the polarized light, after leaving the polarizing prism, is passed through certain liquid compounds of carbon, the plane of the polarized light is changed or rotated. Only certain compounds of carbon have this property.

This fact had been known for quite a time, but it was Pasteur who first discovered the real meaning of this phenomenon.

Observation of Pasteur. — Pasteur[1] observed that when the double sodium ammonium racemate was crystallized, two kinds of crystals separated from the solution. The faces of the tetrahedron which appeared on some of the crystals, differed from those that appeared on other crystals. On one set of crystals there were the right-handed tetrahedral faces, and on the other set of crystals the left-handed. By means of these faces or planes, it was a simple matter to separate the crystals of this salt into two groups; those that contained the right-handed, and those that contained the left-handed faces.

The remarkable fact, however, is this; that when

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[1] Ann. Chim. Phys. [3], **24,** 442 (1848); **28,** 56 (1850); **31,** 67 (1851).

the right-handed crystals were dissolved in water, their aqueous solution rotated the beam of polarized light to the right, and the aqueous solution of the left-handed crystals rotated the beam of polarized light to the left. The crystals thus contained a geometrical expression of their behavior towards polarized light.

Pasteur[1] obtained the free acids from the salts referred to above, and found that the one which came from the dextro-rotating salt was dextrorotatory; and the one that came from the laevo-rotating salt was laevo-rotatory. From racemic acid, which was optically neutral, there were thus obtained two optically active acids, one of which rotated the beam of polarized light to the right and the other rotated the polarized light to the left.

If racemic acid could be broken down into two optically active constituents, then racemic acid ought to be reformed if these constituents were mixed in the proper proportions. Pasteur mixed the two optically active acids, and obtained from the solution crystals of optically inactive racemic acid. Thus, an optically inactive compound was broken down into two optically active constituents, and from these constituents the optically inactive acid was synthesized. The relations between optically inactive racemic acid, and optically active dextro- and laevo-tartaric acids were thus plainly established.

From this work Pasteur saw clearly that optical

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[1] Ann. Chim. Phys. [3], **28**, 56 (1850).

activity is the expression of some kind of molecular asymmetry. He said,[1] "An asymmetric grouping of the atoms, corresponding to an object and its image in a mirror, must be present." He pointed out that the atoms in the laevo acid must have exactly the opposite arrangement to those in the dextro acid, and added, "We know, finally, that racemic acid is formed by the union of these two oppositely asymmetric groupings."

There is really nothing very remarkable about the conclusion that optical activity is caused by some kind of asymmetry. It is *à priori* inconceivable that a symmetrical molecule should rotate or change the plane of polarization of a beam of polarized light. If the molecule was symmetrical, whatever the action of one side of the molecule on polarized light, the other would be exactly equal and opposite; and the algebraic sum of the effects on the light would be zero. We must, obviously, have some kind of asymmetry in the molecule, actually to turn the plane of polarization out of the position which it had when the light left the polarizing Nicol.

That Pasteur had no idea how the molecules were asymmetric, or in what the asymmetry consisted, is shown from his statement,[2] "We know, on the one hand, that the molecular arrangements of the two tartaric acids are asymmetric; and, on the other

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[1] Recherches sur la Dissymétrie Moléculaire, p. 25, in Chemical Society Memorial Lectures. See also Pasteur Memorial Lecture by Frankland, p. 691.

[2] Frankland: Pasteur Memorial Lecture, p. 691.

that these arrangements are absolutely identical, excepting that they exhibit asymmetry in opposite directions. Are the atoms of the dextro-acid arranged in the form of a right-handed spiral, or are they placed at the apex of an irregular tetrahedron, or are they disposed according to this or that asymmetric arrangement? We do not know."

The discovery of the nature of this asymmetry remained for another.

The Relation Pointed out by Le Bel. — Two papers are usually referred to as being the foundation stones of stereochemistry or chemistry in space. One of these was published by the French chemist, Le Bel,[1] in November, 1874; and the other by the young, and at that time unknown Dutchman, Van't Hoff, on September 5, 1874.

The statement is not infrequently heard, that these two men made essentially the same contribution to the subject, and almost at the same time. Such is not the case. The attempt will be made to point out just what each contributed; and although Van't Hoff's paper appeared a little first in point of time, that of Le Bel will be first considered; because Van't Hoff went farther than Le Bel, and his work requires fuller and more detailed discussion.

The paper[2] by Le Bel bore the title "On the Relations which exist between the Atomic Formulas of Organic Compounds, and the Rotatory Power of their Solutions." Says Le Bel, "The work of

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[1] Bull. Soc. Chim. [2] **22,** 337 (1874).

[2] *Ibid.*, New Series, **22,** 337 (1874).

Pasteur and several other investigators has shown beyond question the correlation between the dissymmetry of the molecules and optical activity. If the dissymmetry exists only in the crystalline molecule, only the crystal would be active. If, on the contrary, it (the dissymmetry) belongs to the chemical molecule, it would manifest itself in the solution having rotatory power."

Le Bel then lays down the following fundamental principle,[1] the importance of which we today fully recognize. "Let us think of a molecule of a chemical compound having the formula MA_4. M is a simple radical or complex combined with four monatomic atoms, A, capable of being replaced by substitution. Let us replace three of these by simple or complex monatomic radicals; all of the three substituents being different from one another and, in turn, different from M. The substance obtained would be asymmetrical. The radicals R, R' R'' and A all corresponding to material points different from one another, would form an object which is not superposable upon its image in a mirror; and the remainder of the molecule, M, would not be able to reestablish the symmetry. It may be said, in general, that if a substance is derived from the type of compound represented by MA_4, by substituting the A's by three different atoms or radicals, its molecule will be asymmetric and it will have rotatory power."

We recognize at once that this is essentially the

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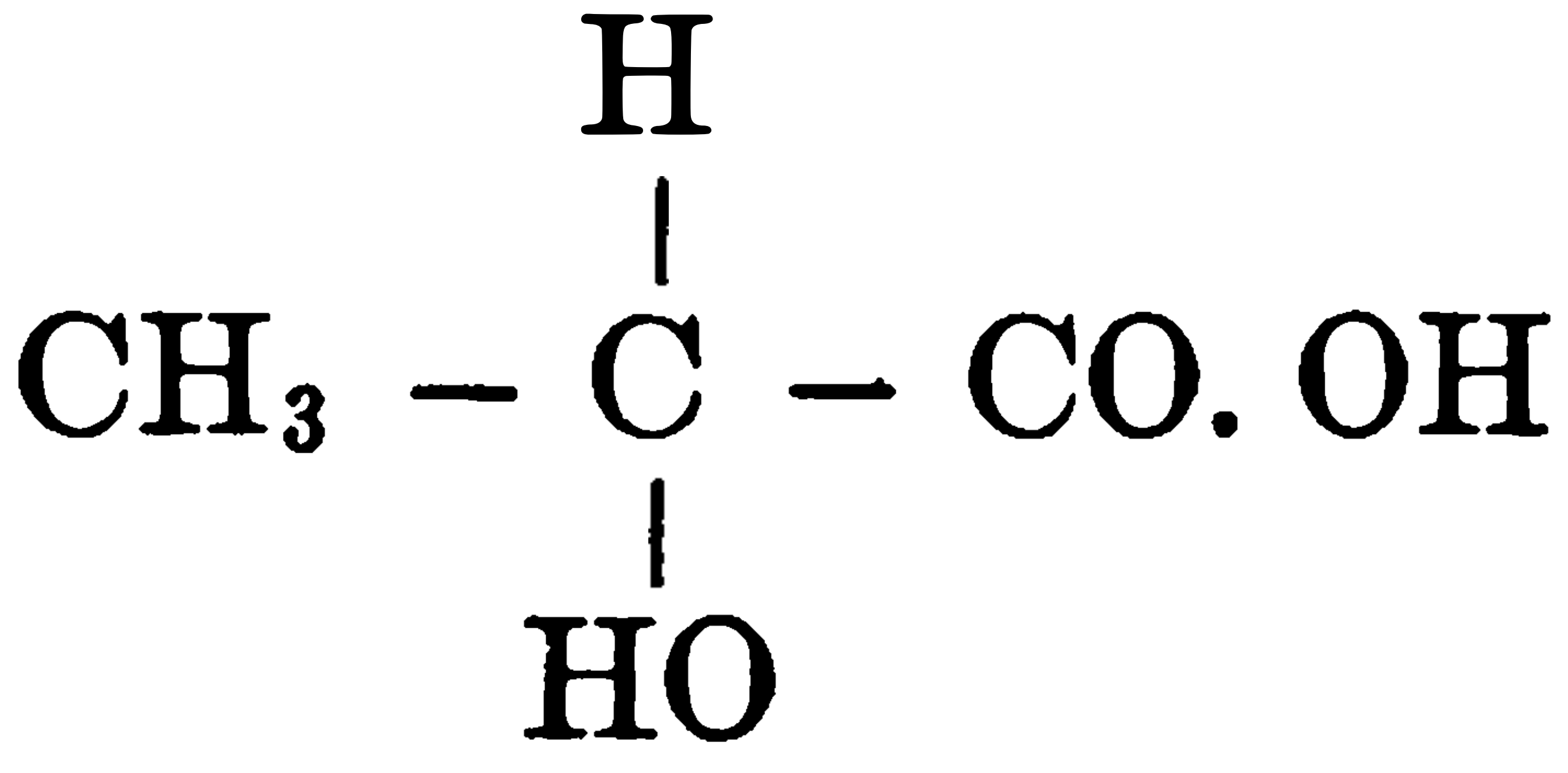
[1] Bull. Soc. Chim., New Series, **22**, 338 (1874).

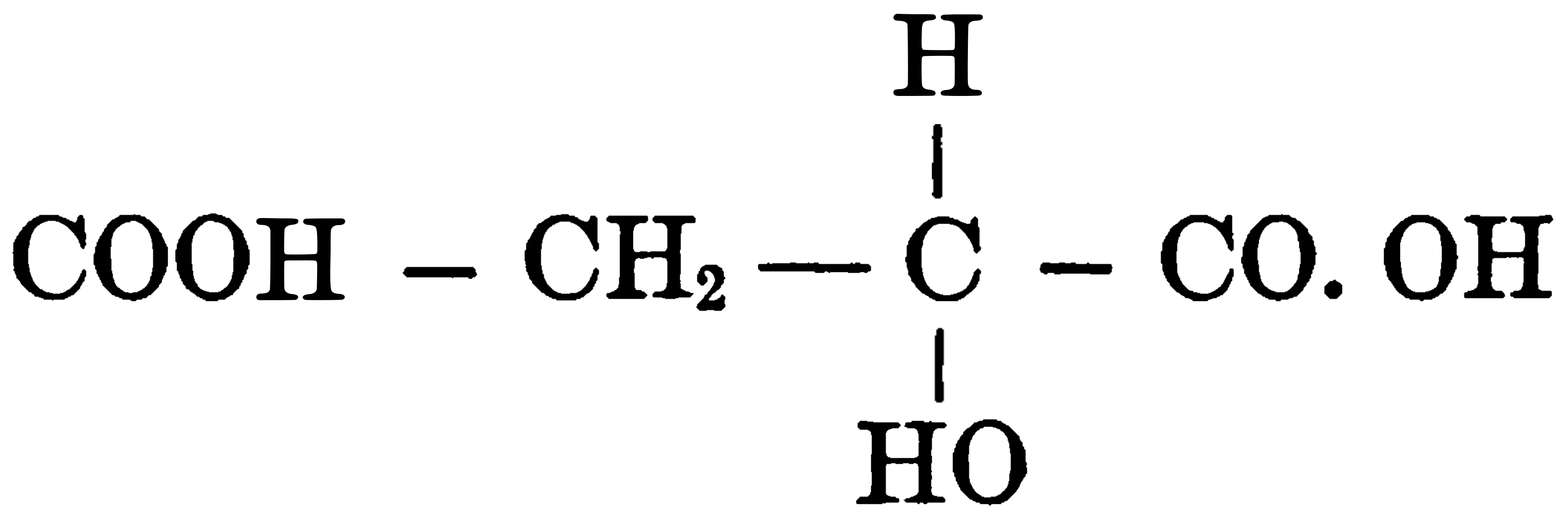
view of this subject which we hold today. Le Bel then points out certain exceptions to this general relation, and adds, "If it should occur that not only one substitution furnishes a single derivative, but that two and even three substitutions give one and the same chemical isomer; we should be obliged to admit that the four atoms, *A*, occupy the four corners of a regular tetrahedron, whose planes of symmetry would be identical with those of the molecule MA_4; in this case no bisubstituted substance would possess rotatory power."

Le Bel then gives a number of examples of optically active compounds, and shows that they all contain a carbon atom united with four different atoms or groups. Thus, lactic acid has the formula: —



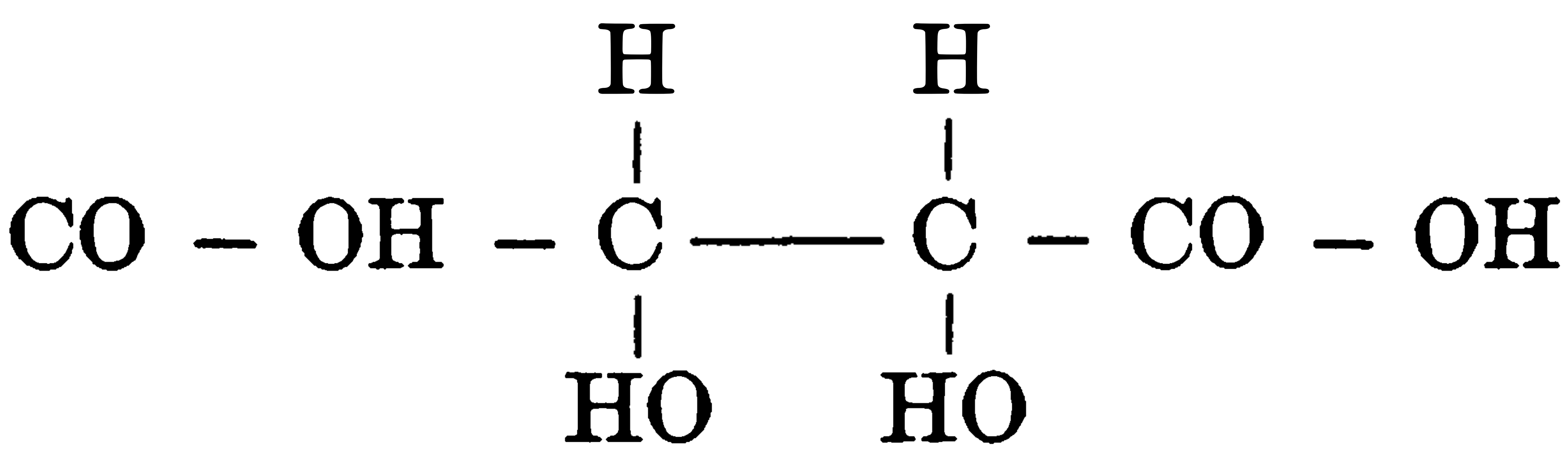
$$\mathrm{CH_3 - \underset{HO}{\overset{H}{C}} - CO.\,OH}$$

Malic, the formula —



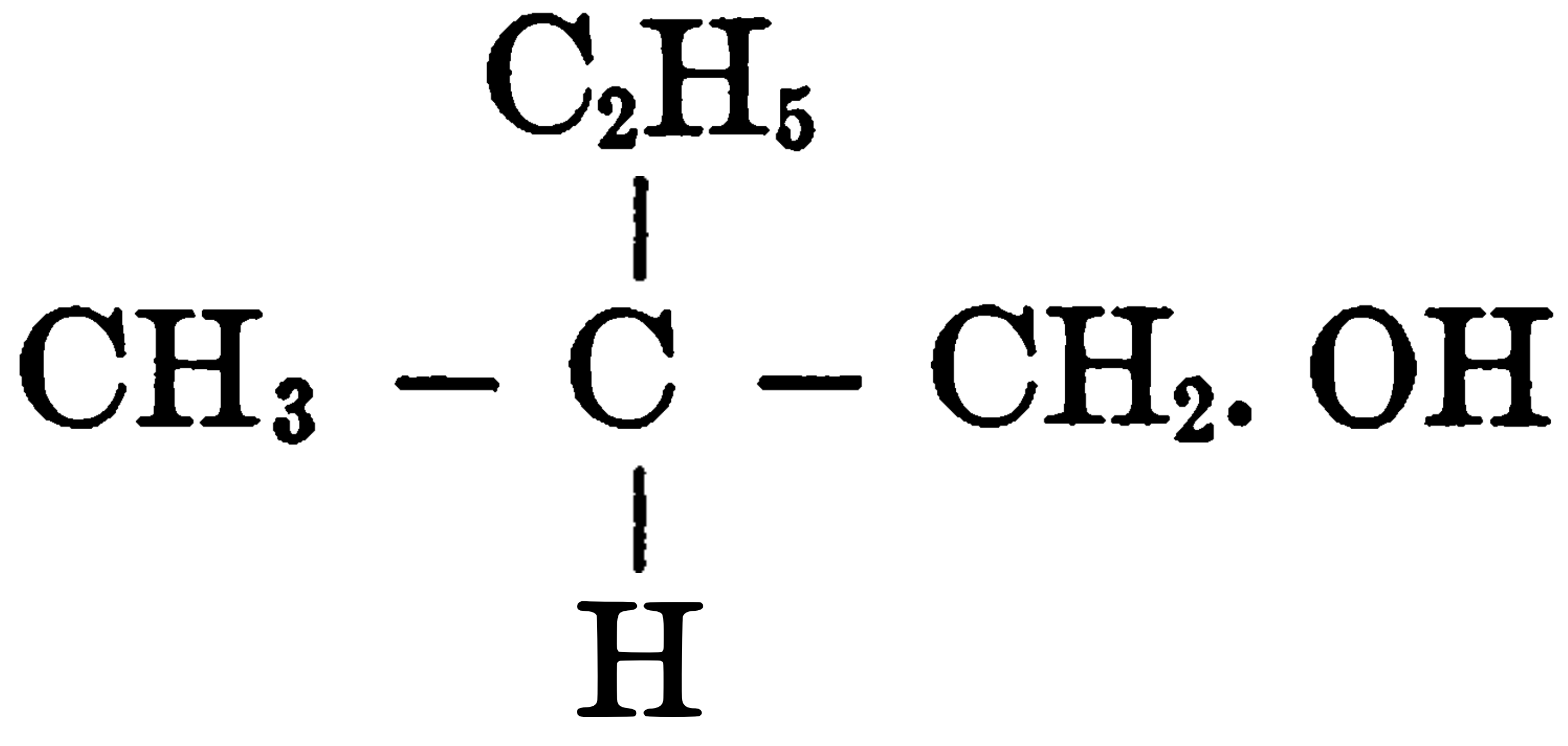
$$\mathrm{COOH - CH_2 — \underset{HO}{\overset{H}{C}} - CO.\,OH}$$

Tartaric acid is especially interesting, having the constitution —



$$\mathrm{CO - OH - \underset{HO}{\overset{H}{C}} —— \underset{HO}{\overset{H}{C}} - CO - OH}$$

We see that it contains not only one asymmetric carbon atom, but two. These would have the opposite effects upon a beam of polarized light; the one-half of the molecule turning it in one direction, and the other half turning it by an exactly equal amount in the opposite direction. The result would be that the substance would be racemic or optically inactive. A number of other examples of optical activity are taken up; amylic alcohol, the active variety, having the formula—



$$\begin{array}{c} C_2H_5 \\ | \\ CH_3 - C - CH_2.OH \\ | \\ H \end{array}$$

Le Bel points out as his last theorem that "When an asymmetric substance is formed in a reaction, . . . we have the formation of the two isomers of opposite symmetry, and in the same amounts."[1] This he shows is a necessary consequence of the mathematics of probabilities.

Le Bel thus goes much farther than Pasteur had gone. He not only shows that optical activity is the expression of asymmetry, but that this asymmetry is of the chemical molecule. He goes still farther, and points out the very important relation, that all carbon compounds which are optically active contain a carbon atom combined with four different atoms or groups, which we know today to be a practically general relation.

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[1] Bull. Soc. Chim., New Series, **22**, 346 (1874).

four different atoms or groups. Van't Hoff, however, did not stop here. He raised and answered the question, What is the actual geometrical configuration of the chemical molecules themselves — What is their shape?

To obtain data for solving this problem, Van't Hoff went back to the work of the chemist Henri and others, which showed that methane is a symmetrical compound. Let us look for a moment into this work.

Symmetry of Methane. — When one hydrogen of methane is replaced by say chlorine, monochlormethane is formed. This being a definite chemical compound, has certain well-defined properties which characterize it. This chlorine was then removed, its place being taken by say the nitro group. One of the hydrogen atoms of this mononitromethane was then displaced by chlorine. It is obvious that the second chlorine had replaced a different hydrogen atom from the first. The nitro group was then removed and hydrogen introduced in its stead. We thus had a second monochlormethane, in which the chlorine had displaced a hydrogen atom different from that replaced by the chlorine in the first monochlormethane. We thus had two monochlormethanes, obtained by replacing different hydrogen atoms in methane by chlorine. The important question then was, Do these two monochlormethanes have the same or different properties? A careful study of them showed that they had identical properties.

In a similar manner, the third and the fourth hydrogen atoms in methane could be replaced by chlorine, and a third and a fourth monochlormethane obtained. A study of all of these monochlormethanes showed that they all have the same properties; in a word, are all the same substance. This proves that the four hydrogen atoms in methane all bear the same relation to the molecule. Methane is, therefore, a symmetrical compound.

Shape of a Molecule of Methane. — Methane being a symmetrical compound the question arose, what geometrical configuration or configurations can it have? Given a central carbon atom, how can four atoms of the same kind—hydrogen, be arranged symmetrically about it? As Van't Hoff pointed out, there is but one geometrical configuration possible in three dimensional space. We are of mathematical necessity forced to conclude that methane must be represented by the regular tetrahedron. The carbon atom is at the centre of the tetrahedron, and the four hydrogen atoms at the four solid angles. This is the only possible figure in three dimensions, which would represent one central object and four objects of the same kind arranged symmetrically about it. We may think at first glance that the square fulfills all of the above-named conditions; the carbon atom being at the centre of the square and the four hydrogen atoms at the four corners. A moment's thought will show that such is not the case. The square is a geometrical figure in two dimensions only. Thus arose the conception of the *tetrahedral carbon atom.*

The facts which Pasteur had brought to light in connection with the optical activity of certain carbon compounds must now be accounted for. This Van't Hoff did in a most satisfactory manner. If the carbon atom at the centre of the tetrahedron was in combination with four different atoms or groups, then the molecule would be unsymmetrical. It is necessary that all four of the atoms or groups at the angles of the tetrahedron should be different, in order that two such tetrahedra should not be superposable. If two of the atoms or groups are the same, then two such tetrahedra could be superposed, and they would no longer bear the relation to one another of an object and its image in a mirror. We thus pass from the theory of the "tetrahedral carbon atom" to that of the *asymmetrical tetrahedral carbon atom.*

This theory of Van't Hoff explains the fact which, as has already been stated, was pointed out by Le Bel; that in the laboratory we never obtain the pure dextro, or the pure laevo form, but always a mixture of both in equal quantities. From the mathematics of probability, we would get just as many molecules having one of the two enentiamorphous configurations, as have the other; and by synthesis alone we should always obtain the racemic form, which is in accord with the facts.

The racemic form, which is a mixture of equal quantities of the dextro and the laevo forms, can be separated into its two constituents by a number of well-known methods. One of these, as we have already seen in discussing Pasteur's work, is the crystallization of certain salts of the acids in question. Another is the use of certain kinds of bacteria, which devour either the dextro or the laevo form and leave the other; and there are several other methods which it would lead us too far here to discuss. The point is that we obtain dextro and laevo forms — optically active forms — not as the direct result of synthesis, but by the application of certain methods to the inactive products of synthesis. These facts were all explained by the asymmetrical carbon atom theory of Van't Hoff.

Stereochemistry of Carbon and other Elements. — This suggestion of Van't Hoff almost at once made an impression. Chemists saw in it a great advance beyond anything that had been proposed up to that time. It made possible a chemistry in three dimensions in space. The constitutional formulas which had been used up to that period, represented compounds in only two dimensions, and, at best, could be regarded as only symbolical. Here was a conception which made possible the working out of the actual geometrical shapes of molecules, and the actual positions of the atoms in these molecules. Wislicenus, as has already been stated, was one of the very first to see the significance of this paper by Van't Hoff; and he was quickly followed by nearly all of the younger organic chemists of the time. The result was that the main current of organic chemistry was turned by this paper of eleven pages, written by the Dutch youth of twenty-two.

The influence of this work by Van't Hoff on the chemistry of carbon, has grown from the time it was published to the present. Indeed, the tetrahedron may be regarded as the philosophy of organic chemistry from 1874 to the present time. It has been the guiding thought in the study of the chemistry of carbon, and has suggested and largely controlled most of the best work in this field for the last thirty-five years. That its influence may be seen and appreciated, we need only mention the work of Fischer on the sugars, that of Wallach on the terpenes, that of Wislicenus, Baeyer, Hantzsch, Curtius, and many others. This conception of the tetrahedron was, then, of epoch-making importance.

Kekulé had converted empiricism in the study of carbon into system. Van't Hoff had made possible the beginning of a science of organic chemistry.

This suggestion of Van't Hoff was destined not to be limited to the chemistry of carbon. If we could work out the stereochemistry of carbon compounds, why not of the compounds of other elements? All chemical compounds must exist in three dimensions in space. Why not discover what this is for all of the elements, and express the constitutions of their compounds as they actually are? Constitutional formulae would then have a real meaning, and not be simply symbolical.

This was the natural state of mind in connection with the broad problem of stereochemistry; but the difficulties encountered in connection with elements other than carbon were so much greater than with carbon itself, that progress in this field has been comparatively slow. The greatest difficulty has been to get a definite and certain starting-point. What is the fundamental geometrical form for the compounds of each of the elements?

Some progress has, however, been made. Some light has probably been thrown on the stereochemistry of nitrogen, especially by the earlier work of Hantzsch and Werner; and the splendid experimental work of Werner[1] on the stereochemistry of cobalt, platinum, chromium, iron, etc., is to be placed among the most important investigations in the field of inorganic chemistry in recent times.

We can thus gain some idea of the influence of Van't Hoff on the future of his chosen science. We shall, however, see that much greater things were to come from this same brain a dozen years later, in laying the foundation for a science of chemistry in general.

The Qualitative Suggestion of Van't Hoff Made Quantitative by Guye. — Van't Hoff's suggestion, as important as it was with respect to the power of carbon compounds to rotate the beam of polarized light, is after all only qualitative. The presence of an asymmetric carbon atom is necessary in order that a carbon compound should be optically active. Carbon compounds, however, show very different optical activity. Some rotate the beam of polarized

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[1] Ber. d. chem. Gesell., **40**, 15 (1907).

light much more than others. Some rotate to the right, are dextro-rotatory; and others rotate to the left, are laevo-rotatory. It was very desirable that a quantitative relation between the asymmetry in the case of any given compound in question, and its optical activity, should be established. This has been done for a number of substances by P. A. Guye.[1] His hypothesis is stated in his own words. "If we admit with Le Bel and Van't Hoff, that the valences of carbon are directed towards the four corners of a regular tetrahedron, and if we call the *planes of symmetry of carbon* the six planes of symmetry which characterize the compound $C R_4$, it is evident that while the carbon remains symmetrical, the centre of gravity of the molecule will lie in at least one of the six planes of symmetry; and that, on the contrary, this centre of gravity will lie without the planes of symmetry when the carbon becomes asymmetric. Let us designate the distances from the centre of gravity of the molecule to each of the planes of symmetry of the carbon, by d_1, d_2, d_3, d_4, d_5, and d_6; the product of these distances —

$$d_1 \times d_2 \times d_3 \times d_4 \times d_5 \times d_6$$

which I call the *product of asymmetry*, remains zero so long as carbon is symmetrical (at least one of the six factors being zero), and has values different from zero when the carbon is unsymmetrical. Moreover, if we call these distances + or −, reckoned

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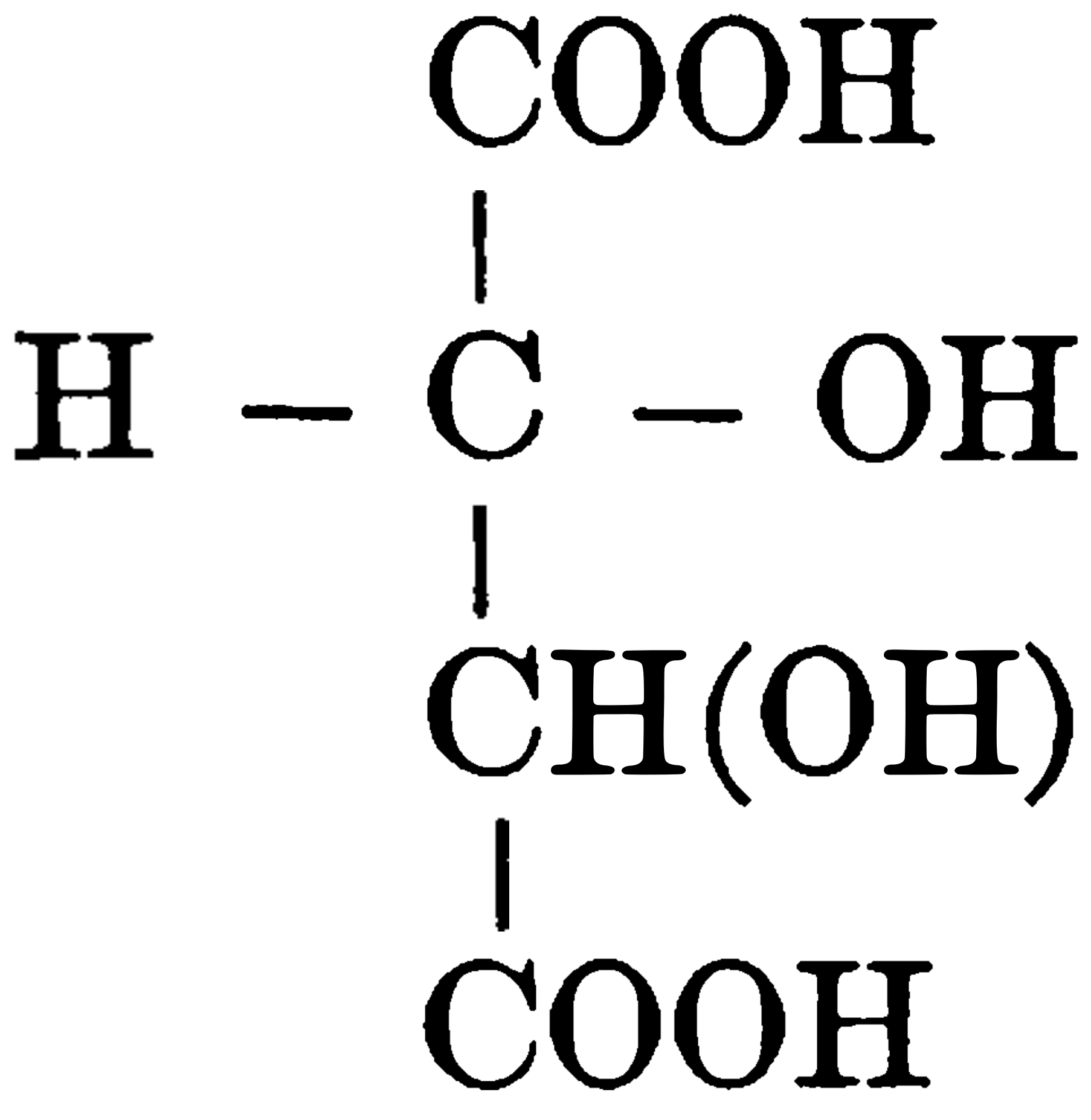
[1] Compt. Rend., **110**, 714 (1890).

symmetry to the other, the rotatory power of the substituent ought to have a sign opposite to that of the original substance."

The remainder of Guye's first paper is devoted to a discussion of results which test his conclusions.

A far more elaborate paper was published by Guye, in 1892,[1] dealing with the whole subject in a broad way; and giving the results of an elaborate series of investigations, which test the general correctness of his hypothesis. The first law is well tested by the esters of tartaric acid. Tartaric acid itself is represented thus —



$$\begin{array}{ccc} & COOH & \\ & | & \\ H - & C & - OH \\ & | & \\ & CH(OH) & \\ & | & \\ & COOH & \end{array}$$

"Let[2] us suppose the masses concentrated at the four corners of the tetrahedron, . . . we see that when the hydrogen of COOH is replaced by the groups CH_3, C_2H_5, C_3H_7, C_4H_9, the centre of gravity of the molecule is removed farther from the original planes of symmetry. According to the first and second principles the esters of dextro-tartaric acid should be dextro-rotatory, and the dextro-rotation should increase as the mass of the substituting group increases. This is in accord with the experimental facts."

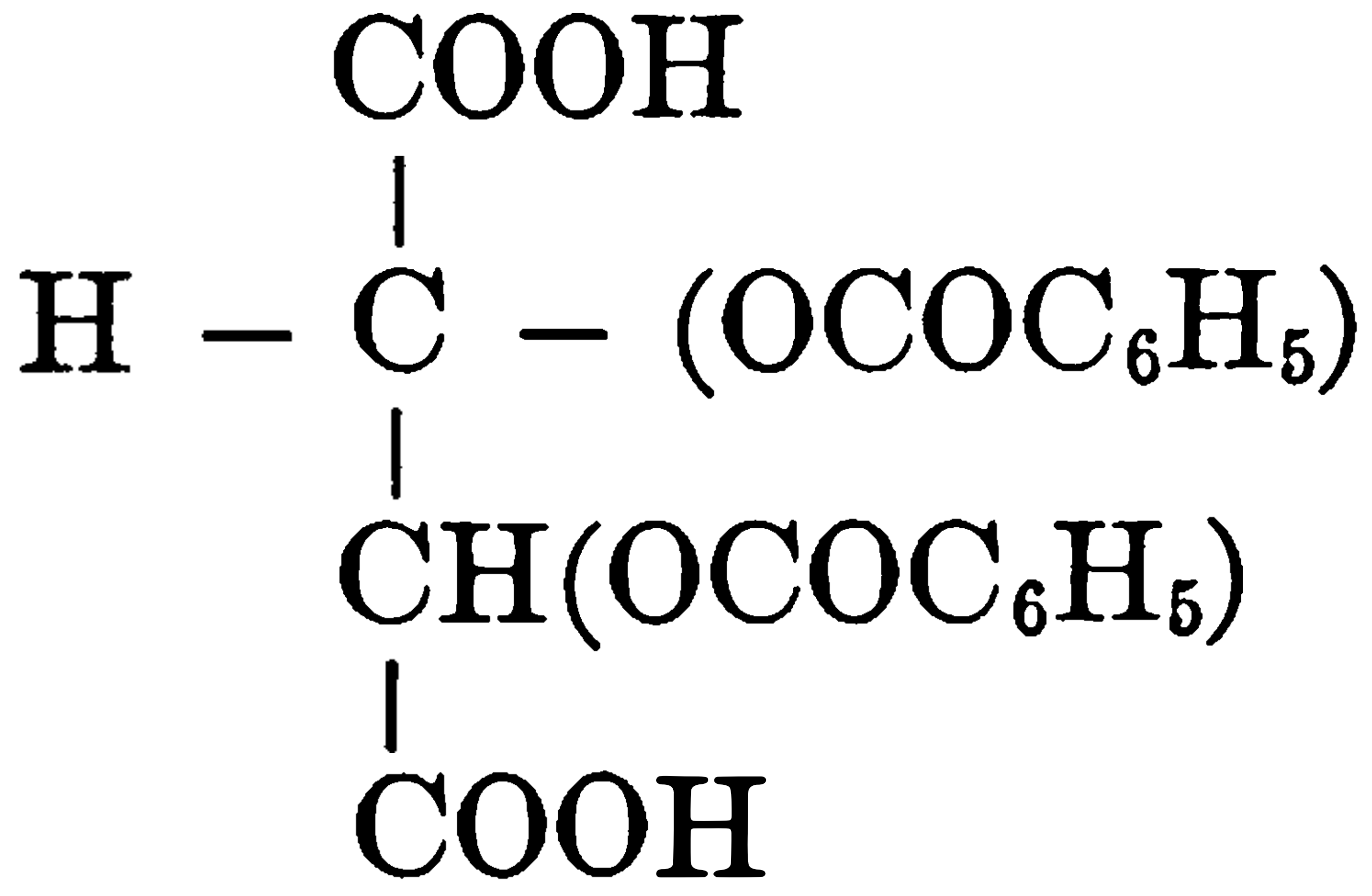
[1] Ann. Chim. Phys. [6], **25**, 146 (1892).

[2] Compt. Rend., **110**, 715 (1890).

	Rotation
Tartaric acid	+ ?
Methyl tartrate	+ 2.14
Ethyl tartrate	+ 7.66
Propyl tartrate	+ 12.44
Isopropyl tartrate	+ 14.89
Isobutyl tartrate	+ 19.87

"Let us now replace in dextro-tartaric acid the two alcoholic hydrogens by the benzoyl radical; we would then be substituting OH with a mass of 17, by the group $OCOC_6H_5$ having a mass of 121. The centre of gravity of the system would then pass from one side to the other of the plane of symmetry cutting $COOH - OCOC_6H_5$. From our third principle we would expect dibenzoyltartaric acid to be laevo-rotatory. This is the fact."

The rotation of dibenzoyltartaric acid is — 117.68. Dibenzoyltartaric acid is represented by the formula —



$$\begin{array}{c} COOH \\ | \\ H - C - (OCOC_6H_5) \\ | \\ CH(OCOC_6H_5) \\ | \\ COOH \end{array}$$

"We[1] can replace the H atoms of COOH by the radicals CH_3, C_2H_7, C_3H_7, C_4H_9. In this act of substitution the centre of gravity remains on the same side of the plane of symmetry cutting

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[1] Compt. Rend., **110,** 716 (1890).

$COOH-OCOC_6H_4$; but approaches more and more nearly to it (as the mass of the substituting group increases). From the first and second principles the esters of dibenzoyltartaric acid should remain laevo-rotatory like the acid itself, but they should be less and less rotatory" (as the mass of the substituent increases).

The experimental facts confirm this conclusion.

	Rotation
Methyl dibenzoyltartrate	− 88.78
Ethyl dibenzoyltartrate	− 60.02
Isobutyl dibenzoyltartrate	− 41.95

"We see that in replacing the groups COC_6H_5 by the acetyl groups $COCH_3$, the diacetyltartaric acid thus obtained ought to be laevo-rotatory, but less laevo-rotatory than dibenzoyltartaric acid; and that the methyl ether ought to be still less laevo-rotatory; and that when we pass to the ethyl ether, the centre of gravity of the molecule passes from one side of the plane of symmetry already referred to, to the other. The homologous ethers ought to be dextro-rotatory."

The facts are as follows:

	Rotation
Diacetyltartaric acid	− 23.14
Methyl diacetyltartrate	− 14.29
Ethyl diacetyltartrate	+ 1.02
Propyl diacetyltartrate	+ 6.52
Isobutyl diacetyltartrate	+ 10.29

Guye[1], in this work, showed that his first two laws applied to 105 active derivatives in 17 different series of active substances.

There are, however, exceptions to Guye's hypothesis in the simple form in which it was first proposed. This he points out himself. Other factors than the masses of the groups, such as their relative positions and mutual attractions for one another, must be taken into account before we have a complete theory of optical activity.

The hypothesis of Guye, while not a complete expression of the truth, is very important in that it is a successful first attempt to account quantitatively for the facts of optical activity, and even in its simple form has proved to be of great value.

[1] Ann. Chim. Phys., **6**, 25 (1892).

CHAPTER V

THE PHASE RULE OF WILLARD GIBBS

A GENERALIZATION was discovered by Willard Gibbs,[1] of Yale, which has played a rôle in the recent developments of chemistry. There are still wide differences of opinion as to the value of this generalization for chemistry, and as to its influence on the future developments of the science. This is the well-known Phase Rule. Gibbs showed how, by thermodynamic methods, the conditions of chemical equilibria can be systematically grouped.

The three independent variables are concentration, pressure, and temperature.

The Phase Rule expresses the conditions of equilibrium in terms of the relation between phases and components. Let us first see what is meant by a phase, and what by a component.

Definition of Phase and Component. — By phase is meant a homogeneous modification of a substance. In a heterogeneous system we always have more than one phase present. Take almost any chemical element or stable compound. It exists in three phases, solid, liquid, and vapor. Take sulphur, it exists in four phases, liquid, vapor, and two solid phases, and so on.

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[1] Trans. Conn. Acad., 1874–1878.

While the term component is frequently used to mean the constituents (chemical elements and compounds) present, it is not always so. Those constituents whose concentration can vary independently are components. With these definitions in mind, let us now see what the Phase Rule is.

One Component and Two Phases. — Take first the simplest case of heterogeneous equilibrium — a liquid in equilibrium with its own vapor. Let the liquid in question be water, and let us vary the temperature and measure the corresponding vapor-pressures for the different temperatures. We plot the temperature-pressure curve, and it has the form shown in Figure 1. In the region to the right and below the curve the vapor is the stable phase. In the region to the left and above the curve the liquid is the stable phase.

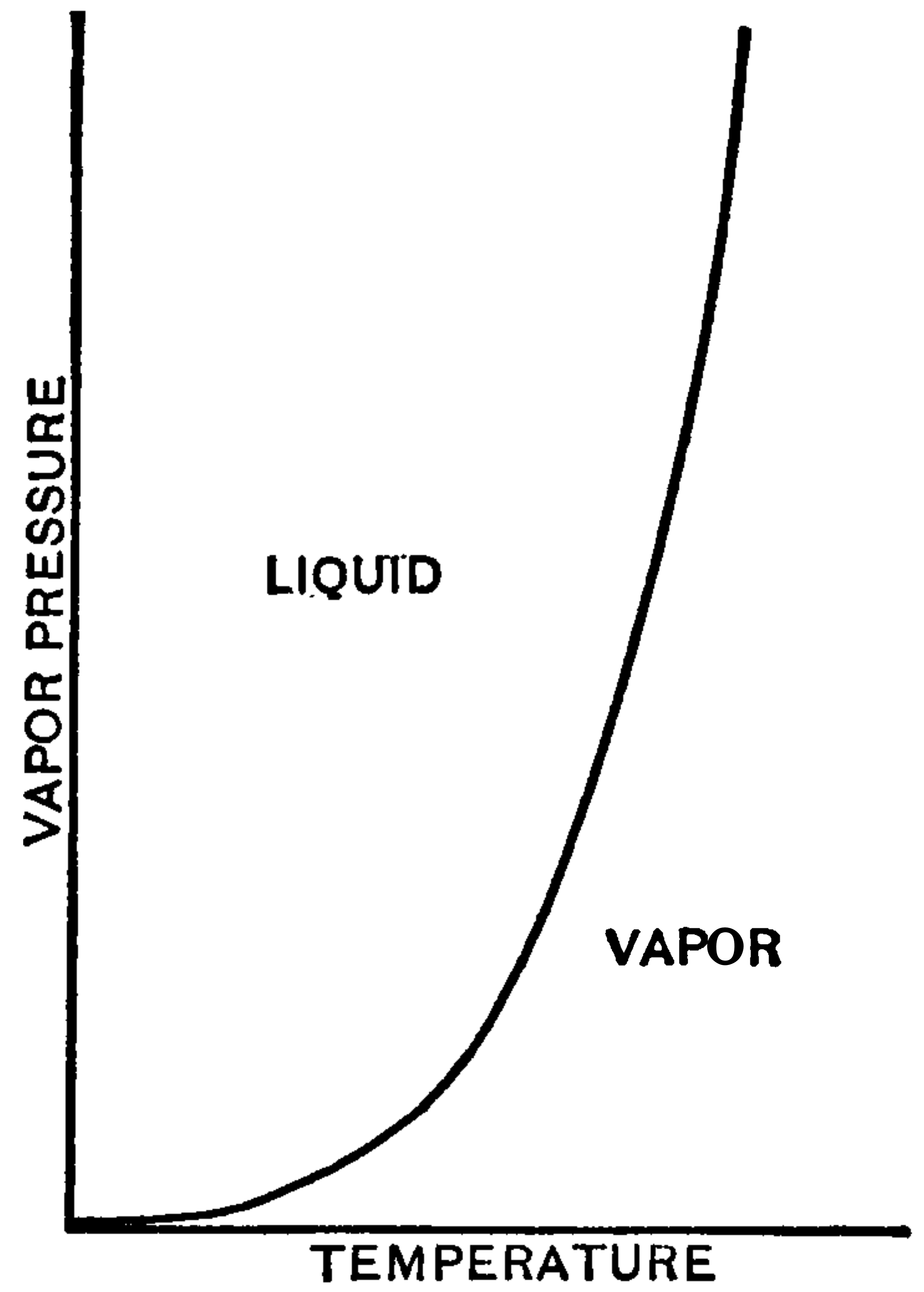

FIG. 1

Here we have one component, water, and two phases. As we move along the curve, for any given temperature the vapor-pressure is fixed. We can vary temperature or pressure as we like, but we cannot vary both without destroying the equilibrium. This system has, as we say, one degree of freedom. We can vary either the temperature or the pressure, but varying the one we fix the other.

One Component and Three Phases. — Let us take the next more complex system with one component and three phases. Let us take the three phases of water, solid, liquid, and vapor. If we plot the temperature-pressure diagram for the conditions of equilibria between the three phases of water, as we did above between the two, the diagram would have the form shown in Figure 2.

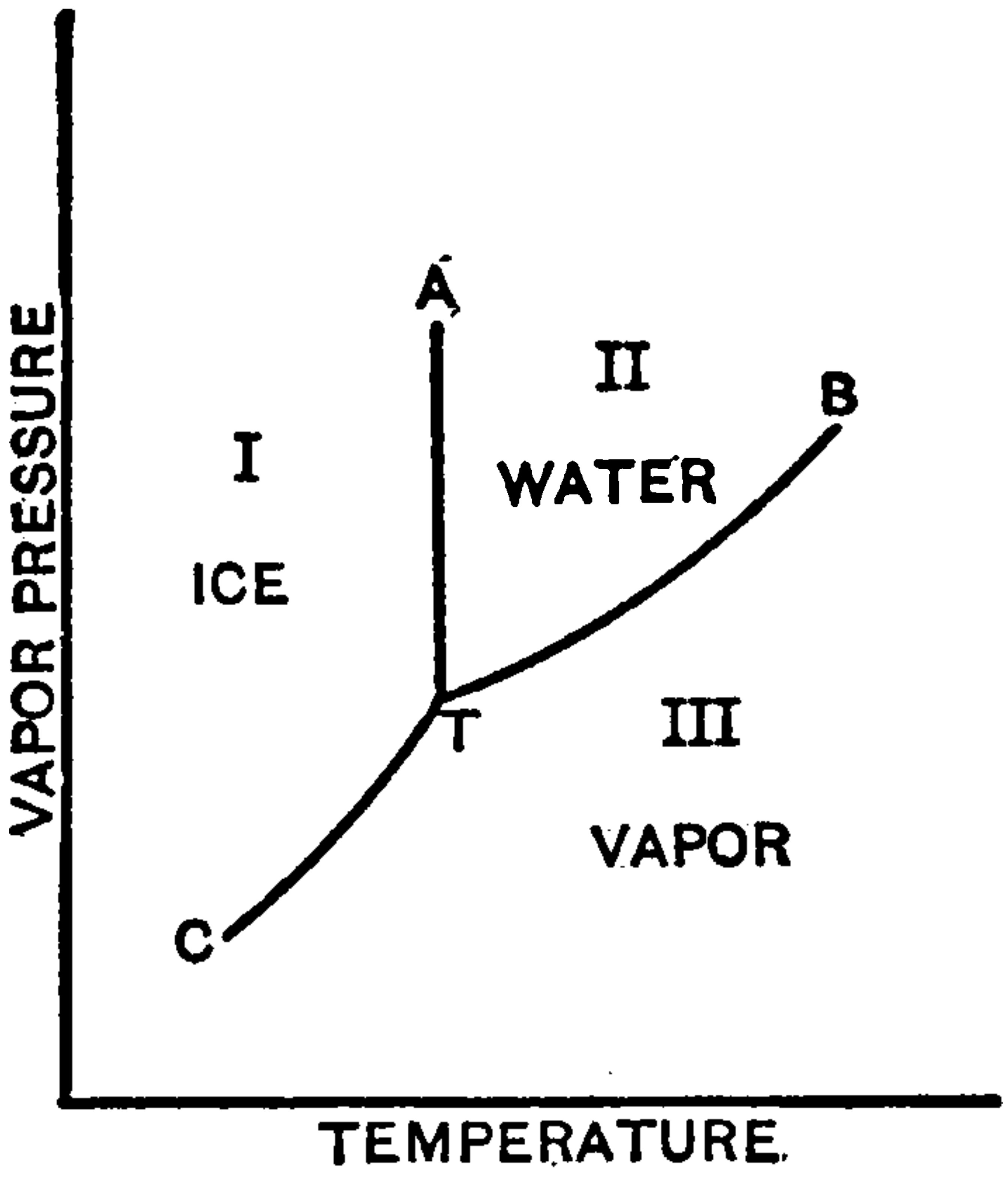

Fig. 2

Ice would be the stable phase in region I, liquid water in region II, and water-vapor in region III. The curves represent the conditions of equilibria between the three phases of water: *TA*, the equilib-

itself. We can now generalize this relation. Whenever the number of phases exceeds the number of components by one, we have one degree of freedom. Take, finally, the areas; *A T B*, *B T C*, and *A T C*. Within the first, liquid water is the stable phase; within the second, water-vapor is stable, and within the third, ice or solid water is the stable condition. How many degrees of freedom have we within any one of these areas? We can vary either the temperature or the pressure, provided we keep within the area in question, without destroying the equilibrium. We have, then, two degrees of freedom. Within any one of these three areas we have one phase and one component.

Whenever the number of phases equals the number of components, we have two degrees of freedom. Such is the phase rule applied to the three stable phases of water and as illustrated by them.

One Component and Four Phases. — Let us take up one more example — the stable phases of the element sulphur. Here we have two solid phases. This system, therefore, represents one component, sulphur, and four phases; vapor, liquid, and two solid phases.

The temperature-pressure diagram is represented in Figure 3. This diagram contains a number of points of interest. The points *O*, *B*, and *C* are all triple points; each representing equilibria between three phases. The curves each represent equilibria between two phases, and within each area only one phase is stable.

The Phase Rule admits of almost unlimited expansion. We can increase the number of components, which would increase the number of phases;

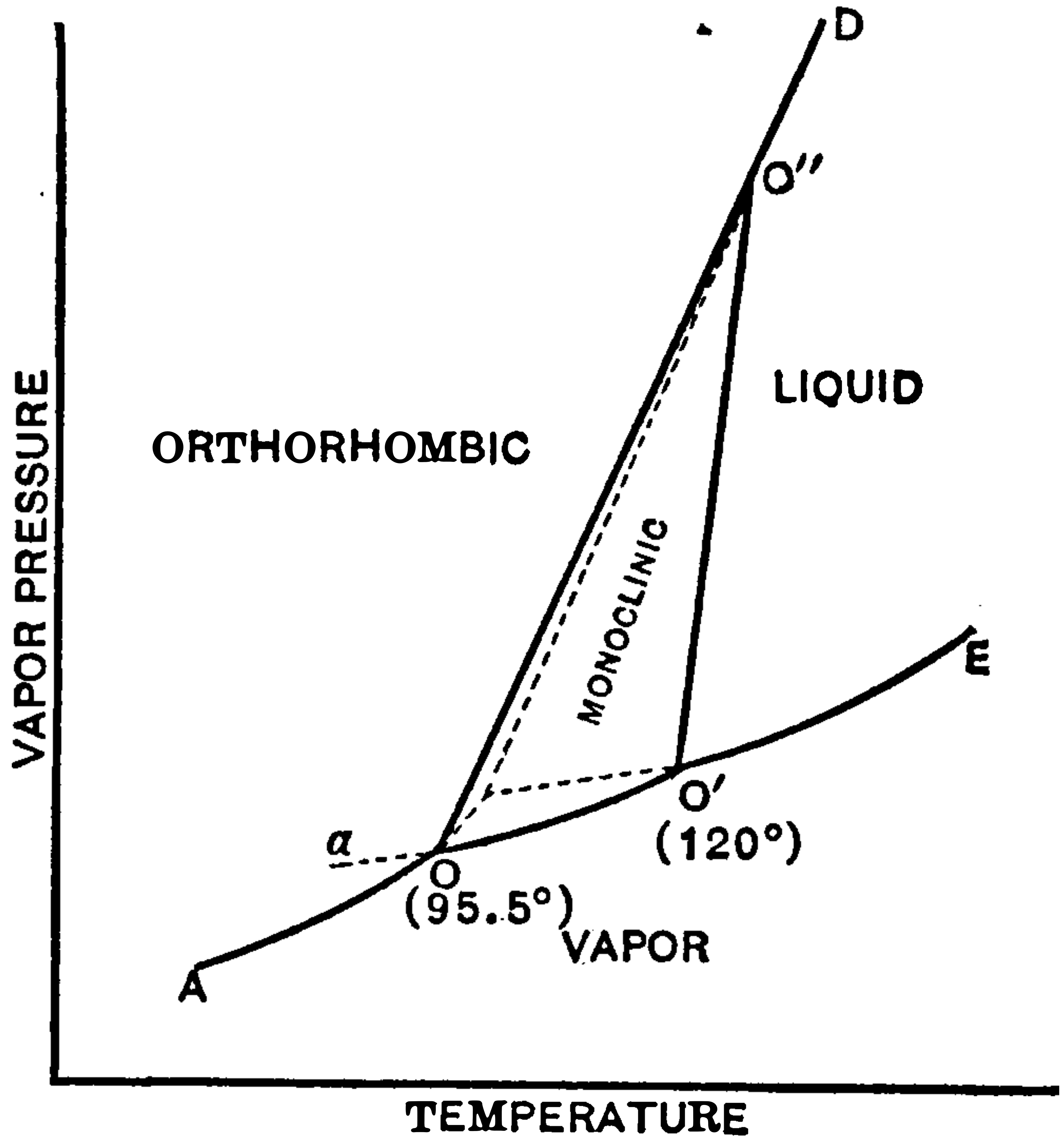

Fig. 3

and the complexity of the diagrams would thus be very greatly increased.

Again, in plotting the diagrams we are not limited to the two variables, temperature and pressure. We can vary the temperature, pressure and concentration; and then the diagrams occupy three dimensions in space—are solid figures.

An idea of the complexity and beauty of some of these diagrams can readily be gained by reference to the papers of Schreinemakers and others published in recent years in the "Zeitschrift für physikalische Chemie."

It was, as has already been stated, Willard Gibbs the American, who discovered the Phase Rule. It was published as part of an elaborate thermodynamical investigation on heterogeneous equilibria, in 1878, in a publication that is comparatively seldom seen.

The importance of this work was early recognized by Van der Waals, and it was Ostwald who translated these papers by Willard Gibbs into German, under the title "Thermodynamischen Studien" von Willard Gibbs. From that moment Gibbs' fame was world wide. He is one of the greatest and most original mathematical physicists that this country has ever produced, and one of the great mathematical physicists of the world.

The application of Gibbs' very general equations to the conditions of chemical equilibria, we owe largely to the Dutchman, Roozeboom; whose investigations, in terms of the Phase Rule, are to be regarded as among the best.

The solubility work of Van't Hoff, after he went from Amsterdam to Berlin, on the conditions under which the natural salt beds, such as those at Stassfurt, were laid down, was expressed in terms of the Phase Rule, and is to be regarded as one of the most elaborate experimental applications of this generalization.

From what has been said above, we can see what the Phase Rule, in its simplest expression, is. The question arises, Of what use is it in chemistry? There are very different opinions on this question. A few see in it the dawn of a new day, not only for chemistry, but for natural science in general.

If, however, we judge of its future by its past, it is fundamentally a convenient and suggestive shorthand method of expressing facts already established by experiment. The writer is, however, not unmindful of the fact, that from these diagrams new relations have been discovered, new compounds detected, and through them new work suggested.

Looking at the Phase Rule in as broad and impartial a manner as possible, I am unable to get away from the thought that by certain men it has been an overridden hobby.

CHAPTER VI

CHEMICAL DYNAMICS OF VAN'T HOFF AND CHEMICAL EQUILIBRIUM OF LE CHATELIER

WHEN we were discussing the work of Van't Hoff, which led to the foundation of stereochemistry, it was pointed out that when Van't Hoff was a student with Kekulé in Bonn, he became dissatisfied with the chemistry of that time. He was impressed especially by the fact that chemistry in general, and the chemistry of carbon in particular, was largely qualitative. Certain things were brought together; the reaction took place, and certain end products were formed. This to a mind of the type of Van't Hoff's was most unsatisfactory. He wanted to know not simply what is formed and how much of it, when certain substances were brought together and reacted; but he wanted to know the details of the reaction; how many and what kinds of intermediate products were produced, and especially the velocity with which the reaction took place, and the conditions of equilibrium when the reaction had apparently ceased. It was obvious that such questions as these must be solved before we could ever hope to have an exact science of chemistry.

It was this state of mind on the part of Van't Hoff, which led him so early in life to take up the elaborate series of investigations, the results of which were published from his laboratory at the University of Amsterdam in 1884, under the title "Études de Dynamique Chimique."

About seventeen years before this, the Norwegians Guldberg and Waage, as we have seen, discovered the law of mass action, and published their discovery in the announcements of the University of Christiania for that year. This generalization made comparatively little impression upon the chemical world for quite a time. This was probably due in part to the fact, as has already been stated, that the paper had been published in a place which would not be seen by many chemists; and partly to the fact that the chemists of that period did not look favorably upon the introduction of physical and mathematical methods into chemistry.

It was the work of Van't Hoff, just referred to, which arrested attention to the importance of the study of the velocities of reactions; not only from the standpoint of the law of mass action, but especially from that of thermodynamics, as Horstmann had already maintained.

Van't Hoff's Conception of Chemistry. — Van't Hoff's conception of chemistry at this time can readily be seen from a few paragraphs taken from the "Introduction" to his "Études de Dynamique Chimique."

"Progress in general in any science passes through two distinct phases. At the beginning all scientific research is of a descriptive or systematic kind.

Later it becomes rational or philosophical. It has not been otherwise with chemistry. . . .

"Scientific researches, in the first of these phases, are limited to collecting and coordinating the materials which form the foundation of a science. In chemistry they led to the discovery of new substances, to the knowledge of their chemical composition, and of their properties; with the object of enlarging the domain of the science, of assigning to each substance a suitable place in the general classification, and to be able to distinguish the substances from one another. If, in this phase, researches were extended to the study of relations between the properties of the different substances, or to their chemical composition, this was solely for the purpose of classification.

"In the second phase of the development, the researches are not limited to collecting and coordinating the materials, but these pass to the study of the causal relations. The initial interest which they had in a new substance has now disappeared; while the knowledge of its chemical composition and of its properties have a much greater value, becoming the starting-point in the discovery of causal relations. The history of every science consists in the evolution of the descriptive period into the rational period." It was Van't Hoff who has done more than any one else to effect this transformation in chemistry.

Van't Hoff on Reaction Velocities.—Van't Hoff, in this work, studied reaction velocities from the

that from the study of this third kind of chemical equilibrium, Van't Hoff would have discovered the Phase Rule, had it not already been discovered a few years earlier by Willard Gibbs.

Van't Hoff lays considerable stress upon the importance of Berthelot's law of maximum work, but thinks we should deal with chemical equilibrium from the more rigorous standpoint of thermodynamics introduced into chemistry by Horstmann.

"The work ends with the announcement of a thermodynamic conclusion, which, susceptible of a quantitative interpretation, and corroborated by experimental facts, appears to me to have the merits of the principle of maximum work, without its defects." Van't Hoff then enunciates his principle in the following words:

"Every equilibrium between two different states of matter (systems), by a lowering of the temperature is displaced from the side of the one of the two systems whose formation develops heat." (*Principle of mobile equilibrium.*)

Van't Hoff thus threw light on the entire field of chemical dynamics and statics, and it is not too much to say that all subsequent work in this field has been largely influenced by that of the Dutch master.

We cannot do better in closing the discussion of the "Études" than to quote Ostwald's words, taken from the brief sketch of the life of Van't Hoff written by him [1] for the "Jubelband" to Van't Hoff.

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[1] Zeit. phys. Chem., **31**, XIII and XIV (1899) Jubelband zu Van't Hoff.

"The principle of the fundamental equations for kinetics and equilibrium rests essentially on the molecular hypothesis, and mono- di- and trimolecular reactions were distinguished from one another. This took place in opposition to the older formulations of Guldberg and Waage, in which only the active masses in reaction equivalents were taken into account. Our investigator thus gave the correct bent to the development of the science. . . .

"The book contains, together with a large number of experimental investigations on the different problems of chemical dynamics, theoretical developments of great significance and fertility. These show a new side of the investigator, which has subsequently become more and more prominent as an original applier of thermodynamics, independent of all hypothesis, to chemical problems.

"In the application of thermodynamics to chemical problems he has always shown the hand of a master. As an indication of the breadth of his view, and his capacity to see what was essential in phenomena, we need mention only the formulation of the relation between chemical equilibrium and electromotive force; as well as his famous principle of mobile equilibrium, which points out the relations between the change of the conditions of a system and the nature of the processes which are brought about by these changes.

"The effect of the book was similar to that expressing his views on stereochemistry. It did not follow quickly, but was, therefore, so much the more profound. Investigation today returns again and again to the thoughts which were there developed; and the magnitude of the effect which it has exercised on the age and on research cannot yet be approximately estimated."

Le Chatelier on Chemical Equilibrium.—An investigation which attracted considerable attention, but which, in my opinion, is far less widely known than it deserves to be, is the "Recherches Expérimentales et Théoriques sur les Équilibres Chimiques" of Le Chatelier. This work was published four years after the "Études" of Van't Hoff.

Le Chatelier recognized clearly that equilibrium in chemistry is amenable to the same laws as in physics and in mechanics, which is an important step forward for chemistry. Chemical equilibrium is the condition where the opposite chemical reactions that are taking place have the same velocity. This is affected by certain external conditions, such as temperature, electromotive force, and pressure; and by certain internal factors such as the chemical nature of the reacting substances, their physical state and condensation, which determine the intrinsic energy of the substances.

These influences obey certain laws which he formulates as follows: The law of the opposition of action and reaction is "Every system in chemical equilibrium undergoes, in consequence of a variation of one of the factors of equilibrium, a transformation in such a sense as to produce a variation of sign opposite to that of the factor in question."

Effect of Temperature. — The effect of temperature Le Chatelier summarizes thus: "Every elevation in temperature produces on a chemical system in equilibrium a transformation corresponding to an absorption of heat; that is to say, if it takes place, produces a lowering of temperature. This law had already been announced by Van't Hoff for purely chemical phenomena. I have shown that this law is much more general than its author had supposed." The effect of electricity on chemical equilibrium is formulated as follows: "Every variation of electromotive force produced at one point of a system in equilibrium, produces a transformation of the system which causes at the point in question a variation in the electromotive force having the opposite sign.

Effect of Pressure. — The effect of changing the pressure is strictly analogous to that of changing the temperature. "The increase in the pressure on a chemical system in equilibrium brings about a transformation which tends to diminish the pressure." The effect of condensation, or concentration, or quantity Le Chatelier summarizes thus:

"The variation of the condensation of only one of the elements, effects a transformation in the sense that a certain quantity of this element disappears, which thus diminishes its condensation. This is the action of mass, whose applications are so numerous in all chemistry."

Analogy between Mechanical and Chemical Equilibria. — Le Chatelier shows very clearly the analogy between mechanical and chemical equilibria in what he calls the law of equivalence. "Given a mechanical system in equilibrium, it is possible to replace certain parts by other analogous parts, without changing the equilibrium. We can replace one spring by another spring, or by a weight. These different elements in a system are called equivalents. Experience has shown that two equivalent elements in a system in equilibrium can be substituted for one another without changing the equilibrium."

In mechanics this is summarized as follows: "Two forces which are equal to a third are equal to one another, and conversely."

In chemistry we have this same law. "Two elements in a chemical system, which are equivalent, that is, which can be substituted for one another without changing the state of equilibrium of the system, are indeed equivalent in any other chemical system; and, moreover, are mutually equivalent if they are opposed to one another, and reciprocally." Le Chatelier summarizes his study of chemical equilibrium in what he calls the law of the opposition of action and reaction,[1] which has already been referred to, and which, near the end of his work, he formulates in the following words:

"Every variation of a factor of equilibrium produces a transformation of the system which tends to make the factor in question undergo a variation of sign opposite to that which we have given it.

"That is to say, every elevation in temperature produces a reaction with absorption of heat, every

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[1] Les Équilibres Chimiques, p. 210.

increase in pressure a reaction with diminution in volume, and the same with electromotive force." Le Chatelier, in his "Les Équilibres Chimiques" has thus formulated the laws of chemical equilibrium. In this work he lays great stress upon the analogy between chemical processes and mechanical processes, between chemical equilibrium and mechanical equilibrium — analogies which are all important for chemistry. These analogies are so important for chemistry because they are true, and because, through their recognition, we are able to apply many of the laws of mechanics to chemistry. These laws of mechanics are amenable to mathematical treatment, and as Le Chatelier so clearly shows, through the heat changes that take place and which cause all chemical reaction, we can introduce thermodynamics into chemistry; and this he does in this admirable monograph.

"Les Équilibres Chimique" must then be regarded as one of the important factors which led us from the old chemistry to the new, from systematic to scientific chemistry.

CHAPTER VII

THE RÔLE OF OSMOTIC PRESSURE IN THE ANALOGY BETWEEN SOLUTIONS AND GASES

Generalizations Discovered by Van't Hoff. — We now come to the greatest work of that great Dutch chemist, Van't Hoff — his discovery of the relations between solutions and gases. This is not only the greatest contribution of Van't Hoff to the development of chemical science, but one of the very greatest contributions, as we shall see, to chemistry in all time.

It is of interest to see how Van't Hoff, from studying the problems of chemical reactions and equilibrium, should turn to a property which was then of interest chiefly to the botanist — osmotic pressure.

In 1894 Van't Hoff was invited by the German Chemical Society to deliver a lecture on his work on the nature of solution.

Lecture by Van't Hoff. — The writer, who was then studying with Ostwald, had the pleasure of hearing that lecture which has since become famous, and is now referred to simply as Van't Hoff's 1894 lecture, without any further qualification. There sat in the front row Helmholtz, Ostwald, Emil Fischer; and a number of other men of science were

with an extremely modest demeanor. This, as is well known to those who knew Van't Hoff at all closely, was one of his most striking characteristics. The speaker at first seemed a little nervous, due no doubt in part to the character of the audience he was facing, and in part to the fact that he probably suspected the motive in asking him to lecture in Berlin just at that time. Further, at this period in Van't Hoff's life he was of a somewhat nervous temperament, as I learned a few months later when I went to his laboratory to work with him. This was certainly due in part at least to the nervous tension under which he worked. I recall only one other man who worked with such concentration, and that is Rowland. Van't Hoff at this period not only worked under high tension, but he seemed to live under high tension. When one saw him on the street he moved as if on rubber, and this kind of living would, in time, of necessity react upon the nervous system. It may, on the other hand, have been due to his keen nervous sensibility, that he was able to work with such intensity.

Van't Hoff had not proceeded far with the lecture, when any initial nervousness entirely disappeared, and his manner of presentation made a deep and lasting impression upon his audience. Let us now see how Van't Hoff became acquainted with the work of the botanist, Wilhelm Pfeffer, on the osmotic pressure of solutions of cane sugar and a few other substances.

We can see this best from Van't Hoff's own statement taken from his 1894 lecture.[1]

"Young as I was, I desired to know the relations between constitution and chemical properties. The constitutional formula should be the expression of the entire chemical conduct.

"This was the origin of my 'Ansichten über die organische Chemie,' which is not known to you, and which is hardly worth knowing. It, however, had for me this value, it showed me very clearly an existing defect.

"Let us take an example. As is well known, oxygen in organic compounds exercises an accelerating action on almost all transformations. Oxidation of CH_4 is more difficult than oxidation of CH_3OH, etc.

"To obtain valuable relations in this field, an exact knowledge of reaction velocity is necessary; and I, therefore, went over to the study of reaction velocity and thus arose my "Études de Dynamique Chimique.'

"Reaction velocity was then the chief aim. Chemical equilibrium was, however, a close second. Equilibrium, on the one hand, based upon the equality of two opposite reactions, and, on the other, connected with thermodynamics, gave it a firm foundation.

"You see, to reach my object, I was getting farther and farther from it. This often happens.

"I must go further, for the question of equilibrium was very closely associated with the problem

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[1] Ber. d. chem. Gesell., **27,** 7 (1894).

of affinity, and so I took up first the simple phenomenon of affinity, which finds expression in the attraction of water.

"Mitscherlich, in his 'Lehrbuch der Chemie' (4th edition, 1844, 565) had already discussed the question as to the magnitude of the attractive force which holds the water of crystallization in Glauber salt. He saw a means of measuring it in the reduced tension of the water of crystallization.

"If Glauber salt is introduced into a barometric vacum at 9°, the mercury is lowered about $2\frac{1}{2}$ lines (5.45 mm.) by the water-vapor that is given off. Water itself produces a lowering of 4 lines (8.72 mm.). The affinity of sodium sulphate for its water of crystallization corresponds, therefore, to the difference $1\frac{1}{2}$ lines (3.27 mm.), that is about $\frac{1}{16}$ of a pound ($\frac{1}{32}$ kg.) per square inch (2.615 cm.^{2}).

"This value, $\frac{1}{200}$ of an atmosphere, impressed me as unexpectedly small, for I had the impression that the weakest chemical forces are very great, as had appeared to me evident from, for example, Helmholtz' Faraday lecture.

"The question arose, whether in simple cases this attraction for water could not be more directly measured, and the aqueous solution is the simplest thinkable, much simpler than water of crystallization.

"Leaving the laboratory with these questions in mind I met my colleague De Vries and his wife. He was at that time engaged upon osmotic investiga-

then plunge the bladder into a vessel containing pure water. The water will pass into the bladder; the alcohol cannot pass out since the walls of the bladder are semipermeable, *i.e.*, will allow water to pass through but not alcohol, and the bladder will finally burst.

While it is such a simple matter to demonstrate qualitatively the existence of osmotic pressure, it is a very difficult matter to measure this force quantitatively. If we were limited to the use of natural semipermeable membranes, this would be absolutely impossible. The force for any appreciable concentration, is, as we shall see, so great that no natural semipermeable membrane could begin to withstand it.

Artificial Semipermeable Membranes. — An artificial semipermeable membrane was, however, discovered by Moritz Traube, which enabled Pfeffer to solve the problem of measuring the osmotic pressure of dilute solutions. When certain gelatinous substances are precipitated in the walls of unglazed porcelain cups, they have the property of semipermeability, *i.e.*, of allowing the water to pass through them and preventing the passage of the dissolved substance. This artificial membrane, being laid down upon a resistant support, the wall of the cup, can, if properly made, resist very considerable pressures, as the work of Pfeffer showed. Such a gelatinous substance is copper ferrocyanide.

If an unglazed porcelain cup is filled with a solution of potassium ferrocyanide, and then plunged into a vessel containing a solution of copper sulphate, the ferrocyanide will diffuse into the walls of the cup from within, and the copper sulphate into the walls of the cup from without, and where the two solutions meet in the walls, a gelatinous precipitate of copper ferrocyanide will be formed.

While this was the general method used by Pfeffer in making his cells, the above account gives absolutely no idea of the difficulties involved in carrying it out.

The porous cells must be very homogeneous, and years were spent by Pfeffer in learning, and then in teaching the potters how to make a sufficiently homogeneous porcelain to meet the requirements of the method. And after satisfactory cups were obtained, years more were spent in working out the necessary details in connection with the removal of air from the walls of the vessels, etc. To gain any adequate conception of the difficulties that were met and overcome by Pfeffer, his monograph[1] must be studied.

With this method Pfeffer succeeded in measuring the osmotic pressure of a few dilute solutions of a few non electrolytes like cane sugar, and a few electrolytes such as potassium nitrate and sulphate.

What did Van't Hoff do with these data, and what did he obtain from them?

Law of Boyle for Osmotic Pressure. — The first relation between Pfeffer's results, which seemed to have impressed Van't Hoff, was this. Pfeffer had

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[1] Osmotische Untersuchungen, Leipzig (1877).

measured the osmotic pressures of solutions of a substance like cane sugar, at different concentrations.

Van't Hoff noted that the osmotic pressure found is proportional to the concentration of the solution. This will be seen from the following data, taken from Van't Hoff's epoch-making paper[1] in the "Zeitschrift für physikalische Chemie."[2]

C	P	$\frac{P}{C}$
1%	535 mm.	535
2%	1016 "	508
2.74%	1518 "	554
4.0%	2082 "	521
6.0%	3075 "	513

C is the concentration of the solutions of cane sugar, P is the osmotic pressures exerted by them. The value of $\frac{P}{C}$ was noted by Van't Hoff to be nearly constant, which means that *osmotic pressure is proportional to concentration.*

The same conclusion was confirmed by certain measurements of the relative osmotic pressures of solutions, carried out by the botanist De Vries, who had first made Van't Hoff acquainted with the results of Pfeffer's work.

There does not seem, at first sight, to be anything very remarkable in the above relation. It simply says that if one molecule of cane sugar, in a given volume of solution, exerts a certain osmotic

[1] Zeit. phys. Chem., **1**, 481 (1887).

[2] Translated into English by myself as a part of Volume IV of "Science Memoirs," edited by Ames, and published by the American Book Company.

Lussac, or the law that deals with the temperature coefficient of gas pressure. Formulated, it is the pressure of a gas remaining constant, its volume increases $\frac{1}{273}$ for every rise in temperature of one degree centigrade; or, volume remaining constant, the pressure of a gas increases $\frac{1}{273}$ for every rise in temperature of one degree centigrade. It is this second formulation which concerns us most in the present connection. Does this law, or anything analogous to it, hold for the osmotic pressure of solutions?

Pfeffer not only measured the osmotic pressures of solutions of cane sugar of different concentrations, but the osmotic pressures of a given solution of cane sugar at different temperatures; and thus enabled Van't Hoff to calculate the temperature coefficient of osmotic pressure.

A solution of cane sugar at 32° gave an osmotic pressure of 544 mm. The osmotic pressure of this same solution at 14.15°, calculated on the assumption that Gay-Lussac's law held for the osmotic pressure of solutions, would be 512 mm. The osmotic pressure found was 510 mm.

A solution of sodium tartrate at 37.3° had an osmotic pressure of 983 mm. The osmotic pressure of this same solution at 13.3°, calculated from Gay-Lussac's law would be 907 mm. The osmotic pressure found was 908 mm. Other examples calculated from Pfeffer's measurements gave still worse agreement between the calculated and observed osmotic pressures; so that from Pfeffer's measurements alone it would still be impossible to say whether Gay-Lussac's law holds rigidly for the osmotic pressure of solutions.

This is not surprising when we consider the enormous difficulties involved in the simplest measurement of osmotic pressure. The results of Pfeffer are remarkably accurate when we consider the time when the work was done. Subsequent work, however, with improved cells and methods of measurement, as we shall see, has shown that Pfeffer's results contain very appreciable errors. It is, therefore, not surprising that from them alone we cannot decide whether Gay-Lussac's law does, or does not apply rigidly to the osmotic pressures of solutions.

Principle of Soret. — An indirect method of answering the above question has, however, been found. If a homogeneous solution is maintained throughout at the same temperature it will remain homogeneous. If, however, one part is kept warmer than the other the equality of concentration will soon disappear. The warmer part will become more dilute and the colder more concentrated, and the magnitude of this difference will depend on the difference between the two temperatures at which the different parts of the solution are kept. This principle, from its discoverer, is known as the *principle of Soret.*

How can this principle be utilized in connection with the problem in hand?

The reason why the warmer part of the solution becomes more dilute and the colder more concentrated than the original homogeneous solution, is because the osmotic pressure of a warm particle is greater than that of a colder one. Since osmotic pressure is the cause of all diffusion in solution, the greater osmotic pressure in the warmer part of the tube will drive the dissolved substance over into the colder part of the tube, until there is equality of osmotic pressure in all parts of the tube.

If the osmotic pressure of a dissolved particle increases with rise in temperature in terms of Gay-Lussac's law, then, for any given difference in the temperature of the two parts of the tube, we can calculate the difference in concentration which should exist when equilibrium has been established by diffusion. We can then carry out the experiment and see whether the difference in concentration found, agrees with that calculated on the assumption of Gay-Lussac's law.

If the calculated and observed values agree, then Gay-Lussac's law applies to the osmotic pressure of solutions. If they do not agree, then the law does not hold. Let us now compare the results of experiment with those of calculation.

The results are calculated as follows. From the concentration in the colder part, that in the warmer was calculated on the assumption that Gay-Lussac's law holds, and then the concentration found experimentally in the warmer part is given.

A solution of copper sulphate contained 17.332% in the part that was cooled to 20°. The part that

were allowed to stand, the different parts at the different temperatures, for a longer period of time; and then the colder and the warmer parts analyzed, gave results which agreed with those calculated on the assumption of Gay-Lussac's law, to within very narrow limits of experimental error. We are, therefore, justified in stating today, that Gay-Lussac's law applies to the temperature coefficients of osmotic pressure.

Avogadro's Law Applies to the Osmotic Pressure of Solutions. — The fact that the laws of Boyle and Gay-Lussac apply to the osmotic pressures of solutions, simply shows that the two sets of phenomena vary in the same way both with concentration and temperature. This proves that the one pressure is proportional to the other. It does not throw any light on the question as to the exact values of either pressure, or on the numerical relation between the two pressures in question.

This is after all the more important point. What is the actual osmotic pressure of a dissolved particle, compared with the gas pressure of a gaseous particle moving in the same space as that in which the dissolved particle moves?

This can be readily tested. Prepare a solution of the same concentration as a gas; measure the osmotic pressure of the solution, and the gas pressure of the gas, and then compare the two results. It should be obvious what is meant by the concentration of a gas. By concentration of a solution is meant the number of dissolved particles in a given volume; by concentration of a gas the number of gaseous particles in a given volume of space.

Van't Hoff[1] worked out the above relation, by comparing the osmotic pressure of a solution of cane sugar, taken from Pfeffer's measurements, with the gas pressure of hydrogen gas having the same concentration as the solution of cane sugar. The comparison is given in Van't Hoff's own words.

"We are dealing in the experiment in question with a one per cent solution of cane sugar, that is, one prepared by bringing together one part of sugar and one hundred parts of water. This solution contains one gram of cane sugar in 100.6 c.c. of the solution.

"If we compare the osmotic pressure exerted by this solution, with the gas pressure of a gas, say hydrogen, which contains just as many molecules in 100.6 c.c. as the cane sugar solution in question; therefore, $\frac{2}{342}$ grams of hydrogen ($C_{12}H_{22}O_{11} = 342$), a striking agreement manifests itself.

"Since hydrogen under one atmosphere of pressure and at 0° weighs per litre 0.8956 grams, and the above named concentration is 0.0581 grams per litre, we are dealing at 0° with 0.649 atmospheres of pressure; and, therefore, at t° with $0.649(1+0.00367t)$. If we give these results along with Pfeffer's we would have."

Van't Hoff then tabulates the gas pressures of hydrogen gas in one column, and the osmotic pres-

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[1] Zeit. phys. Chem., **1,** 493 (1897).

sures of the same concentrations of cane sugar in another column as follows:

Temperature (t)	Osmotic Pressure	$0.649(1 + 0.003667t)$
6.8	0.664	0.665
13.7	0.691	0.681
14.2	0.671	0.682
15.5	0.684	0.686
22.0	0.721	0.701
32.0	0.716	0.725
36.0	0.746	0.735

The comparison is thus made over quite a range of temperature. Van't Hoff then adds: "The osmotic pressure of a solution of cane sugar measured directly, is exactly equal to the gas pressure of a gas which contains in a given volume exactly the same number of gas molecules as there are molecules of cane sugar in the same volume.

"This relation holds not only for cane sugar but for other dissolved substances as invert sugar, malic acid, tartaric acid, citric acid, magnesium malate, and sulphate, which, from De Vries' physiological investigations, for equal molecular concentration of the solutions, show the same osmotic pressure."

Gas Pressure and Osmotic Pressure. — A moment's thought will show that this is a very remarkable relation. Think of a gas, on the one hand, and a solution, on the other. How apparently different are these two conditions of matter. In the gas the particles are comparatively free to move, and move even at ordinary temperatures, with very high velocities. A gas has no definite or fixed volume of

were remarkably accurate, considering the time when they were made and the difficulties involved. Subsequent work, as we shall see, with improved methods has, however, shown that these results contain very appreciable errors. Further, the data obtained by Pfeffer were very meagre. He had measured the osmotic pressures of only a very few substances and these over only a limited range of conditions.

From these few and imperfect data Van't Hoff, with that insight and foresight which are characteristic of the highest order of genius, saw the relations between the osmotic pressure of solutions and the gas pressure of gases, just discussed. The importance of the discovery of this general relation between solutions and gases will come out a little later. Suffice it to say here that this paper[1] by Van't Hoff of twenty-eight pages is one of the most important that has ever been contributed to chemistry.[2] It is a chemical classic, in the highest sense of that term.

It would not be desirable to close the discussion of the relations between osmotic pressure and gas pressure without referring briefly to the most recent and accurate measurements of osmotic pressure.

Measurements of Osmotic Pressure by H. N. Morse and Coworkers.[3] — Some fine experimental work has recently been done by H. N. Morse and his

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[1] Zeit. phys. Chem., **1**, 481 (1887).

[2] See Science Memoirs, vol. IV. Edited by Ames. (American Book Company.)

[3] We should mention especially Dr. Frazer and Dr. Holland.

collaborators on the osmotic pressure of solutions, especially of solutions of cane sugar. It will be recalled that Pfeffer prepared his semipermeable membranes by allowing the two solutions which are to form the membrane to diffuse into the walls of the unglazed porcelain cup; and where they meet on the inside of the innermost wall, the colloidal membrane was precipitated.

This is obviously an imperfect method, since diffusion is a slow process, and because the membrane thus formed would not be very compact, would not adhere firmly to the inner wall, and would not, therefore, withstand high pressure. Pfeffer himself had great difficulty in securing good membranes by this method, and was never able to prepare a membrane which would withstand more than a few atmospheres pressure. The result was that he was never able to measure the osmotic pressure of anything except very dilute solutions. In the case of cane sugar the most concentrated solution which he was able to use was only six per cent.

Morse discovered a method of making semipermeable membranes which proved to be very satisfactory. Instead of allowing the solutions which were to form the membrane when they came together, simply to diffuse into the porous walls from the two sides, he drove the ions into the walls electrically. He filled the porcelain cup with a solution of potassium ferrocyanide and plunged the cup into a solution of copper sulphate. He placed the cathode within the cup, and the anode around the cup in the solution of copper sulphate. The copper ions moved towards the cathode in the cup, *i.e.*, they entered the walls from without. The ferrocyanogen ions moved towards the anode, *i.e.*, they entered the walls of the cup from the inner side. These two ions met on the inner surface of the inner wall and formed the gelatinous, semipermeable membrane on the inner porcelain wall.

The advantage of the electrical method was, that by using suitable voltage and amperage, the ions could be *driven* into the wall and made to form a compact membrane, which would resist high pressure without a rupture. So much for the method of making the membranes.

The preparation of the cells themselves involved years of work. To find the proper clays was in itself a serious task, and to find the best mixtures of these clays involved a large amount of labor. Then, the making of the cell so that it would be sufficiently fine-grained and of homogeneous texture was the work of years. The cup must be just so fine-grained that the copper ion would move through a given pore in the wall, at the same time that the ferrocyanogen anion was just entering the pore from the inner side. The membrane would thus be formed in the inner wall, just filling the inner ends of the fine tubes in the porcelain wall.

Finally, the closing of the cell so as to withstand high pressures, and the proper manometer attachment, were all matters in which it was necessary to overcome many and serious difficulties.

	Weight-Normal Concentration									
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
	Ratio of Osmotic to Gas Pressure									
Temp.										
0°	(1.106)	1.061	1.061	1.060	1.069	1.077	1.083	1.093	1.104	1.115
5°	1.082	1.063	1.058	1.059	1.067	1.074	1.084	1.093	1.102	1.115
10°	1.082	1.060	1.059	1.060	1.066	1.073	1.083	1.092	1.102	1.113
15°	1.082	1.061	1.061	1.059	1.068	1.073	1.083	1.093	1.102	1.115
20°	1.084	1.062	1.060	1.060	1.067	1.073	1.084	1.093	1.103	1.115
25°	1.084	1.059	1.060	1.059	1.065	1.071	1.083	1.093	1.102	1.113
	(1.083)	(1.061)	(1.060)	(1.060)	(1.067)	(1.074)	(1.083)	(1.093)	(1.103)	(1.114)
30°	1.000	1.020	1.031	1.040	1.050	1.060	1.069	1.081	1.089	1.101
40°	1.003	1.011	1.024	1.038	1.046	1.054	1.059	1.067	1.076	1.085
50°	1.000	1.002	1.009	1.017	1.025	1.032	1.041	1.049	1.059	1.071
60°	1.000	1.001	0.999	1.000	1.006	1.015	1.020	1.027	1.033	1.044
70°	....	....	....	....	1.000	1.002	0.999	1.008	1.015	1.023
80°	....	....	....	....	....	....	....	1.001	1.000	1.000
90°	....	....	....	....	....	....	....	....	....	....
100°	....	....	....	....	....	....	....	....	....	....

however, a weight normal[1] basis was used the following relations manifested themselves.

The table contains the ratios of the osmotic pressures found, to the gas pressures of a gas occupying the same volume as that of the pure solvent present, and at the same temperature. The comparisons are made over a temperature range extending from zero to eighty degrees.

It will be seen that the ratio between osmotic and gas pressures remains practically constant from 0° to 25°; increasing slightly with increase in the concentration of the solution. At this temperature the ratio is not unity, and the increase with concentration is probably due to hydration. The constancy of the ratio over this range of temperature shows that Gay-Lussac's law applies to the osmotic pressure of these solutions over the temperature range in question. There is a range inclosed between the heavy lines where the ratio in question is not unity, and where it is not constant. It is impossible to say whether in this region the laws of gas pressure apply rigidly to the osmotic pressures of solutions.

Below the second heavy line the ratio in question becomes unity, and remains constant for all the concentrations and temperatures thus far studied; and it seems probable that it will be unity in all the blank spaces when they are filled in with the results of experiments which are now in progress.

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[1] Weight normal solution is a gram molecular weight of the substance in a litre of solvent.

Within this region we can, therefore, say that the laws of Boyle and Gay-Lussac apply rigidly to the osmotic pressures of solutions of cane sugar.

These most recent and accurate experimental results, then, confirm in general the conclusions reached long ago by Van't Hoff in connection with the relations between gas pressure and osmotic pressure. And Van't Hoff saw these relations from a few imperfect measurements of the osmotic pressure of a few solutions of a very few substances.

Exceptions to the Above Relations. — What has already been said is the truth, but it is not the whole truth. The laws of gas pressure apply to the osmotic pressure of solutions of a certain class of substances, the non electrolytes. By non electrolytes is meant those substances whose aqueous solutions do not conduct the current. These include especially the neutral organic compounds, *i.e.*, those substances which are not acids, bases, nor salts. The non electrolytes will be recognized at once to be the less interesting and the less important class of compounds. These are the substances that do not react readily. They have to be coerced into reacting. When they are made to react, the reaction proceeds slowly and does not go to the end. They appear to stop reacting while there are still some of the free substances present. Their reactivity generally manifests itself only when there is present some one of another class of substances, the electrolytes — and what is an electrolyte?

so-called normal molecular lowering of the freezing-point, and normal molecular lowering of vapor-tension was found only when Raoult turned to the organic compounds. Here the normal relation was nearly always found. It therefore appears bold to bring forward an Avogadro's law for solutions, as is here done; and I would not have allowed myself to do so, had not Arrhenius suggested to me by letter the probability that salts and the like are broken down into ions. As a matter of fact, so far as investigation has gone, it is solutions of non electrolytes which obey the law of Avogadro. These are not broken down into ions. Further experimental work must be done on the other solutions, since, from the assumption of Arrhenius, we can calculate the deviation from Avogadro's law from the conductivity."

Van't Hoff thus pointed out clearly the exceptions to the relations between osmotic pressure and gas pressure which he had discovered, that were presented by electrolytes. He was not able to explain these exceptions. This was left for Arrhenius.

Formulation of Gas Laws as Applied to Osmotic Pressure. — Van't Hoff, however, formulated the laws of Boyle and Gay-Lussac as applied to solutions, thus —

$$p v = R T$$

p is the osmotic pressure of the solution, v its volume, R is the gas constant, and T the absolute temperature.

For electrolytes he had to introduce a coefficient i, when the above becomes,

$$p v = i R T$$

He showed that the coefficient i has the value unity for non electrolytes, and was always greater than one for electrolytes.

Here Van't Hoff left the problem. Let us now see what Arrhenius did with it.

CHAPTER VIII

ARRHENIUS AND THE THEORY OF ELECTROLYTIC DISSOCIATION

JUST about the same time that Van't Hoff discovered the relations between the osmotic pressure of solutions and the gas pressure of gases, there came to his laboratory a young Swedish physicist, who was destined to exert an influence on chemistry which was little less than revolutionary. This young Swede was Svante Arrhenius, who was then about twenty-eight years old.

Arrhenius had already been working on the problem of the nature of solutions of electrolytes, and saw in his own views on this subject a possible explanation of the abnormally great value of the coefficient i, which manifested itself for electrolytes. Electrolytes are substances whose aqueous solutions conduct the current, and electrolytes are the substances which show the abnormally great values of the coefficient i, that is, show abnormally great osmotic pressures in terms of the laws of gas pressure. There must, therefore, be some connection between the abnormally great osmotic pressures and the properties which these solutions have of conducting electricity. An explanation of the abnor-

and the oxygen to separate at the other. What was the mechanism of this process?

Grotthuss pictured it as follows: Take a molecule of water next to the cathode. It was decomposed by the current and the hydrogen liberated on the cathode. The oxygen which was initially combined with this hydrogen to form a molecule of water now combines with the hydrogen of the next molecule of water, and sets another oxygen free from this molecule. This combines with the hydrogen of the next water molecule, and this continues until the anode is reached, when there is left a free atom of oxygen which separates at the anode.

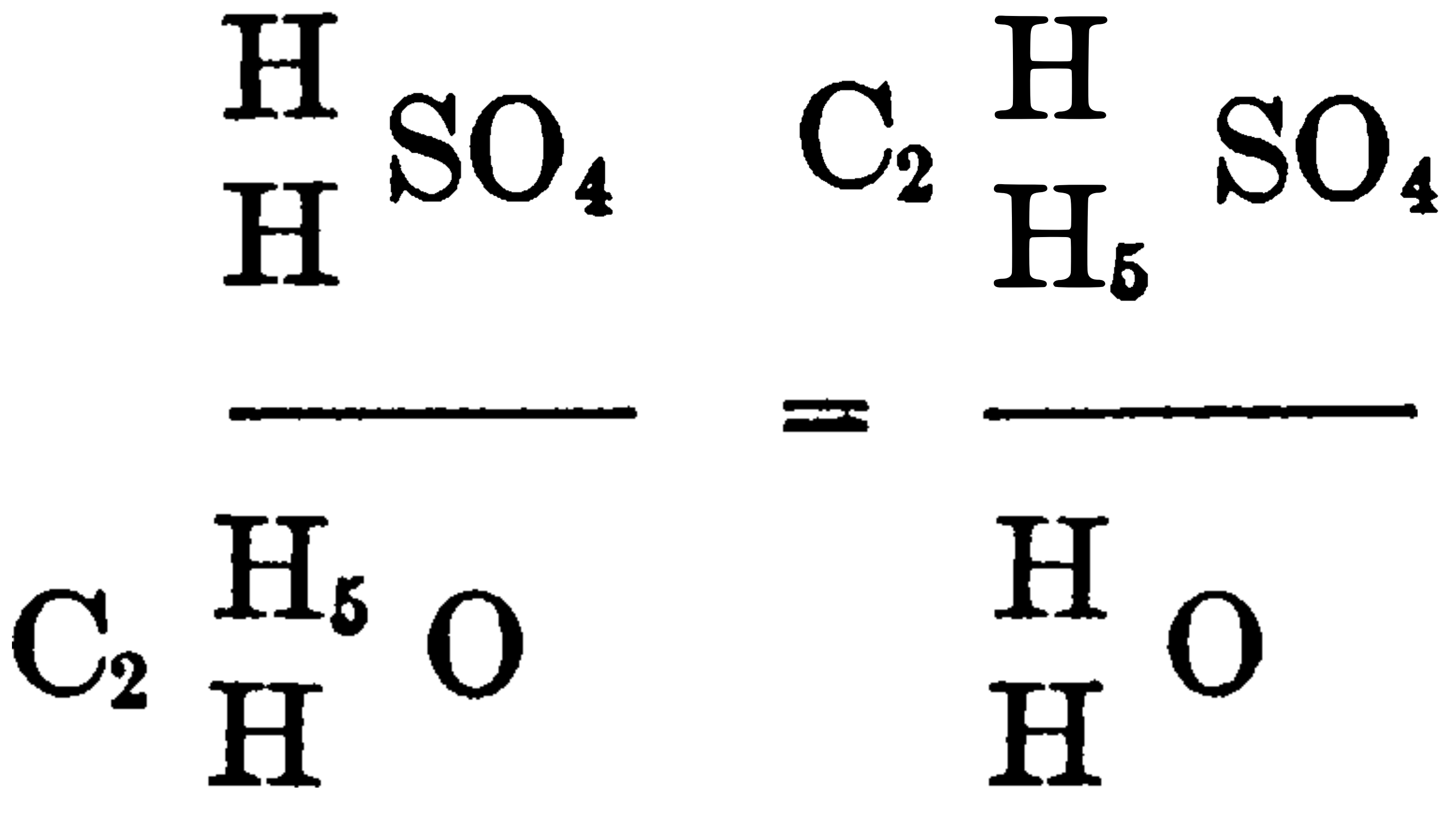
Thus was Grotthuss able to account for the phenomena that were then known in connection with electrolysis, and his theory held sway for about half a century.

Facts were finally discovered which could not be dealt with by the theory of Grotthuss. It was found that an electric current, which was so weak that if passed through water for one hundred and fifty years, would liberate only one cubic centimeter of electrolytic gas, would still pass through water and electrolyze it. Water is one of the most stable compounds known to man, shown by the large amount of heat that is liberated when it is formed from its elements hydrogen and oxygen, and also by the fact that such a high temperature (2000° C.) is required to begin decomposing it into its elements.

It is easy enough to show by calculation that such a current as that referred to above could never decompose one molecule of water. Still less could it decompose enough to liberate a cubic centimeter of electrolytic gas. The theory of Grotthuss, which requires the current first to decompose the water before it can cause its parts to separate at the poles, had, therefore, become untenable and insufficient. It must be supplemented by some suggestion which would account for these newly discovered facts.

Williamson's Theory of Solution. — The English chemist, Williamson,[1] proposed a theory of solution in 1851, which went so far beyond the facts that it bore only a remote relation to them. His paper is, however, of great importance in connection with the reversible nature of chemical reaction. His theory of solution will be very briefly referred to.

Williamson's paper bears the title "On the Theory of the Formation of Ether," and its title gives some idea of its contents. Williamson was working on the formation of ether by the action of sulphuric acid on ordinary ethyl alcohol. He recognized that the action proceeded in two stages, which are the reverse of one another. He formulates these two stages as follows:



$$\frac{\begin{matrix}H\\H\end{matrix}SO_4}{C_2\begin{matrix}H_5\\H\end{matrix}O} = \frac{C_2\begin{matrix}H\\H_5\end{matrix}SO_4}{\begin{matrix}H\\H\end{matrix}O}$$

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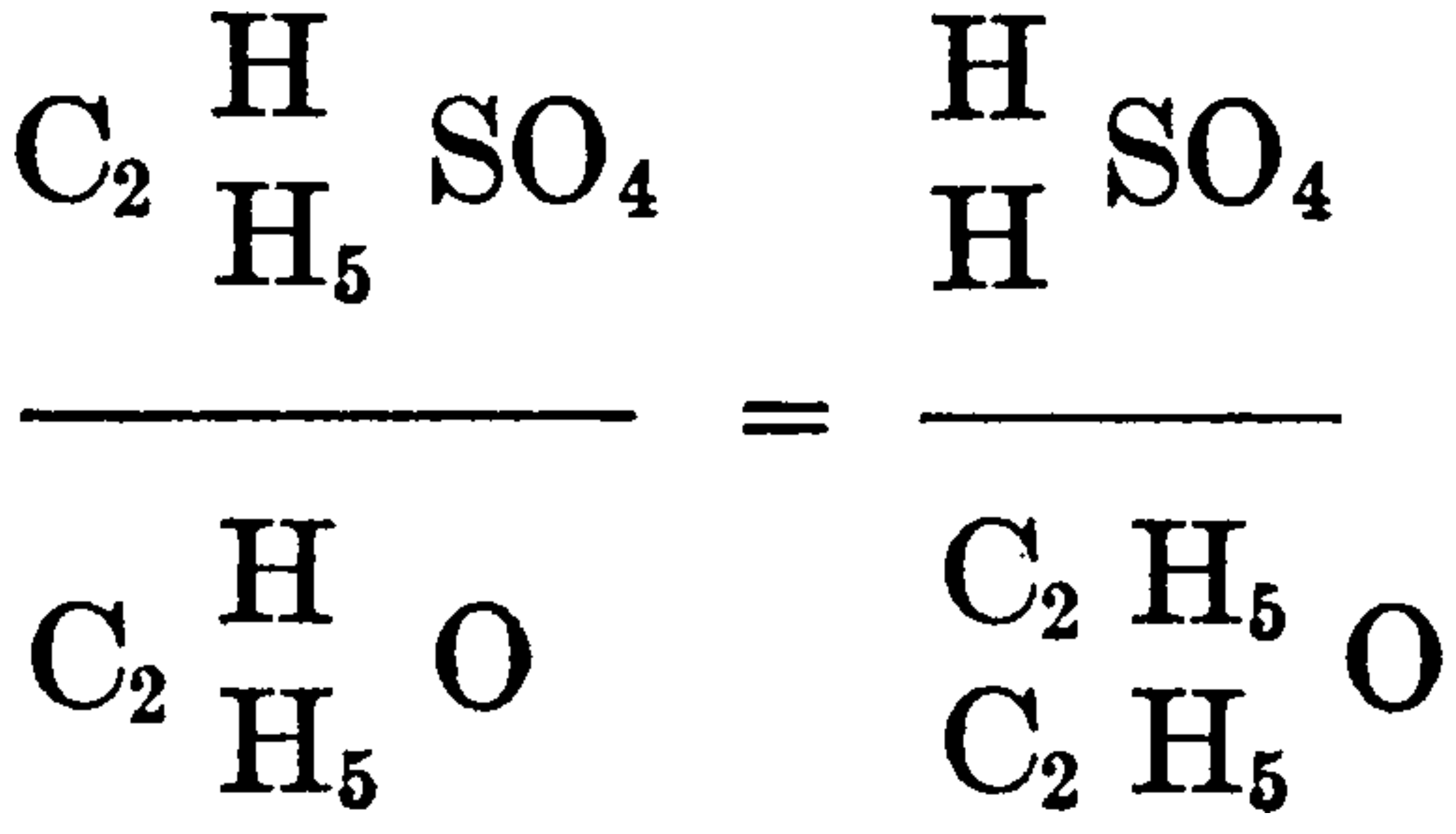
[1] Lieb. Ann., **77**, 37 (1851).

In this stage of the reaction we have one hydrogen atom of sulphuric acid replaced by the ethyl group.

The second stage of the reaction proceeds as follows:



$$\frac{C_2 \begin{matrix} H \\ H_5 \end{matrix} SO_4}{C_2 \begin{matrix} H \\ H_5 \end{matrix} O} = \frac{\begin{matrix} H \\ H \end{matrix} SO_4}{\begin{matrix} C_2 H_5 \\ C_2 H_5 \end{matrix} O}$$

Here we have the ethyl group of ethylsulphuric acid replaced by hydrogen, reforming sulphuric acid, and ordinary ether is produced.

The important point here is that in the first stage of the reaction we have a process going on, the replacement of hydrogen by ethyl, which in the second stage of the reaction is exactly reversed, the replacement of ethyl by hydrogen. The two reactions are thus exactly the reverse of one another.

Williamson could account for these facts only on the assumption that in solution everything is broken down into its parts or constituents. Thus, sulphuric acid is broken down into hydrogen and the group SO_4; ethyl alcohol into ethyl and hydroxyl. These parts are constantly recombining, and are being reformed as the result of decomposition. There is a constant exchange of parts going on, and from the mathematics of probability we would have every possible combination. In this way only could Williamson explain such facts as were brought

The action upon such a system of the infinitesimal current referred to above would be simply a directing one. The current would not have to break down any molecules of water. It would find "part molecules" already present, and would simply exert a *directing influence* upon these part molecules.

The essential feature of Clausius' theory then is, that in solution we have molecules and parts of molecules, and it is these latter which undergo electrolysis.

Arrhenius Proposes the Dissociation Theory. — This was the prevailing theory of electrolysis when Arrhenius took up the subject. Arrhenius had been interested in the electrolysis of solutions some time before coming to Van't Hoff's laboratory. Indeed, his inaugural dissertation in 1884 was on "Researches on the Galvanic Conductivity of Electrolytes." The first part was on "The Conductivity of Extremely Dilute Solutions," and the second part, published in the same year, had to do with the "Chemical Theory of Electrolytes."

In 1885 he published a paper on "The Action of Fluidity on the Galvanic Conductivity of Electrolytes."

Arrhenius[1] was therefore just the person to deal with such a problem as the one which had confronted Van't Hoff.

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[1] Zeit. phys. Chem., 1, 631 (1897). Translated into English by the author and published in the Science Memoirs, edited by Ames, vol. IV. American Book Company.

The paper by Arrhenius explaining the apparent discrepancy to the gas laws presented by electrolytes was published in the same volume of the "Zeitschrift für physikalische Chemie," in which Van't Hoff's epoch-making paper had appeared. The paper in question bears the title, "On the Dissociation of Substances Dissolved in Water."

Arrhenius, as he says himself, started with the view of Clausius, that in solution some of the molecules are broken down into parts. The statement on the part of Clausius is, of course, only qualitative, and Clausius gave us no means of making it quantitative.

The distinctive merit of this paper by Arrhenius was that he converted the qualitative suggestion of Clausius into a quantitative theory. His own words [1] in this connection are given. "In an earlier work, 'On the Galvanic Conductivity of Electrolytes,' I have designated the molecules whose ions move independently of one another as active, the remaining molecules whose ions are firmly combined, as inactive. I have also suggested the probability that, at extreme dilution, all of the inactive molecules of an electrolyte are converted into active. This assumption lies at the basis of the calculations given below. I have designated by the term activity coefficient the relation between the number of the active molecules, and the sum of the active and inactive molecules. The activity coefficient of an electrolyte at infinite dilution is, consequently,

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[1] Zeit. phys. Chem., **1**, 632 (1887).

assumed to be equal to unity. For greater concentrations it is less than one, and can be regarded as equal to the relation between the actual molecular conductivity of the solution, and the maximum molecular conductivity to which the conductivity of the solution in question approaches with increasing dilution. This, from principles already stated in my earlier work, holds for solutions which are not too concentrated, that is, solutions in which such disturbing influences as inner friction, etc., can be left out of account."

Arrhenius then goes on to calculate the value of the coefficient *i*, on the one hand, from conductivity, and on the other, from the lowering of the freezing-point of the solvent produced by the dissolved substance. He compares the two values of *i*, obtained by these two methods, for a number of non electrolytes; and shows that the values obtained by the two methods agree, and are always very nearly unity. He then compares the values of *i* as found by the above two methods for 15 bases, 23 acids, and 40 salts, and shows throughout a general agreement between the two values.

Arrhenius then takes up a number of other lines of experimental evidence bearing upon the problem in hand, and shows that they all point to the correctness of the conclusion, that when acids, bases, and salts are dissolved in water, more or less of the molecules are broken down into ions, the number depending upon the dilution of the solution.

during a long lifetime, should have hesitated to welcome the new conception with open arms. Yet the evidence for his theory presented in his first paper by Arrhenius was so varied and quantitative, that the new theory soon had many adherents. It quickly acquired the support of Ostwald and Van't Hoff, and this gave it the stamp of authority.

The objections that were at first offered to the theory were of two kinds; those based upon a lack of familiarity with the theory itself, and with the phenomena with which it was meant to deal, and these are of no interest to us, or to any one else.

Then came the objections which were based upon an intelligent desire to get at the truth. When chemists began to think of chemical phenomena in terms of the new theory, they encountered real difficulties, partly on account of the newness of the theory itself. The theory was thus called upon to prove itself, as it should be able to do. This kind of thoughtful, conservative criticism is always most useful in science. It is an antidote for extreme radicalism, which is hurtful in science as in everything else. The result has been that during the past quarter of a century about every rational objection has been offered to the theory of electrolytic dissociation that could be thought of. Facts have been cited, which, taken at their face value, seemed directly at variance with the theory. When these supposed facts have been tested by careful experimental work, they have in practically every case been found to be errors. The theory has met the unusually large number of objections unflinchingly; and it stands today as one of the corner-stones of the modern developments in chemistry. All things considered, it is one of the most important generalizations that has been reached in chemistry, certainly since the discovery of the law of the conservation of mass and the law of the conservation of energy.

This generalization was the outcome, in the hands of Arrhenius, of the discovery by Van't Hoff of the relations between solutions and gases, as a means of explaining the apparent deviations from these relations presented by electrolytes; and electrolytes, acids, bases, and salts, are the most important substances from the chemical standpoint. It is these substances which give us chemistry.

Certain Applications of the Dissociation Theory. — It is not intended to present here the various lines of evidence bearing upon the theory of electrolytic dissociation. To do so would require a volume much larger than this entire book, so many and varied are these confirmations of this great law. Further, it would today be as useless to furnish new evidence for the general correctness of the dissociation theory, as for the law of gravity, the law of the conservation of energy, or the second law of thermodynamics.

A very few applications of this theory will, however, be discussed to show how it correlates facts already known, how it predicts the existence of new facts which have subsequently been discovered, and how it makes possible the placing of the whole science of chemistry upon a good physical and mathematical basis.

Meaning of the Term Acid. — Acids have been known almost as long as chemical compounds have been studied. They had stable acids and unstable acids, weak acids and strong acids. Then the question arose, what is an acid? They soon found that acids have certain properties in common. They, in general, taste sour. This, however, would not do for a scientific definition of this class of substances, since in terms of it we could not say that hydrocyanic acid was an acid.

Chemists early began to study the composition of acids, to see whether they contained any common constituent. It was at first thought that they all contain oxygen; and oxygen was, for a long time, regarded as the element which is necessary for acidity. So firmly and deeply had this idea become ingrafted into the minds of chemists, that when hydrochloric acid was discovered they said it must contain oxygen because it was an acid. They could not find the oxygen, but that failed to convince the chemists of the time that it was not present. An acid without oxygen was to them unthinkable. Where was the oxygen in hydrochloric acid? It was not in the hydrogen. That was a well-recognized element. It must, therefore, be in the chlorine; and chlorine was, for a time, regarded as the oxide of an unknown element, which they called "murium," whence the name muriatic acid, which in commerce still persists.

definition will not do. Pass dry ammonia over metallic sodium and the compound NH_2Na — sodaamid — is formed at once by the direct displacement of one of the hydrogens of ammonia by metallic sodium. The above definition of an acid forces us to conclude that dry ammonia is an acid. Notwithstanding some work which led the investigator to the conclusion that ammonia is an acid, I think we should hesitate to accept this conclusion.

Then an acid was defined as a compound which would neutralize a base, and a base as a compound which would neutralize an acid; making the one class of substances depend upon the other, and then reversing the process and making the second depend upon the first. This kind of reasoning was, obviously, not scientific.

We know today what an acid is and can define it in a perfectly scientific manner. It is a compound which, in the presence of a dissociating solvent, yields hydrogen ions. Wherever we have acidity we have hydrogen ions, and wherever we have hydrogen ions we have acidity. The two terms, acidity and hydrogen ions, are coextensive.

It may, however, be objected to this definition that an acid is an acid only when in the presence of a dissociating solvent. Pure, dry, liquid hydrochloric or sulphuric acid would not be an acid at all, because there is no dissociating solvent present to produce ions.

No Undissociated Compound an Acid. — Such is the fact as abundant experiments have shown.

Pure, dry, hydrochloric acid gas, when liquefied, does not act on any metal, does not decompose carbonates, does not color blue litmus red. Pure, dry, hydrochloric acid gas when dissolved in a non-dissociating solvent such as dry benzene or chloroform does not have acid properties. It will not color blue litmus red. Exactly the same may be said about pure, dry sulphuric acid. It will not color blue litmus red.

I have seen the following experiment performed. Pure, dry sulphuric acid in a tube, and a piece of very carefully dried metallic sodium plunged into it. The sodium remained suspended in the acid just as quiescently as it would in ligroin. In performing this experiment the very greatest precautions must be taken to dry all of the materials used. All ordinary methods of drying are entirely insufficient.

All of these facts are, then, in perfect accord with the theory of electrolytic dissociation, and could have been predicted from it.

We now know why hydrogen in certain compounds is acidic when these compounds are dissolved in a dissociating solvent; and why hydrogen in other compounds is not acidic. From the former the hydrogen dissociates as an ion when they are dissolved in a dissociating solvent. From the latter it does not dissociate.

This, however, raises a further question, Why does hydrogen dissociate from some compounds as an ion, and not from others? This undoubtedly has to do with the nature of the atoms or groups with which it is in combination in the compound in question. The advance that the dissociation theory makes, even here, is obvious to any one who thinks. It is a very different thing to say that the one compound is an acid and the other is not, because the one yields hydrogen ions in solution and the other does not; and to say that hydrogen in the one compound is acidic because it is combined with a certain element, and in the other not acidic because it is combined with a certain other element; when the fact is that hydrogen while in combination with any other element is not acidic. The dissociation theory enables us here to take a great step forward, and to place the whole subject of acidity upon a rational basis.

Why are Hydrogen Ions "Acidic"? — This leads us to raise the question, what is meant by "acidic"? It is, in general, true that the hydrogen of acids can be replaced, as it is said, by metals. What does this mean? When we treat hydrochloric acid with zinc the zinc passes into solution and the hydrogen gas escapes. What does this really mean? What has actually taken place?

The zinc atoms in the metallic zinc have taken the positive charges from the hydrogen ions, and become charged, *i.e.*, zinc ions are soluble and pass into solution in the water present. The hydrogen ion having lost its charge becomes atomic, and two atoms of hydrogen combine and form a molecule of hydrogen gas. Molecular hydrogen is only slightly

is a typical and simple act of substitution. Further, that this act is purely an electrical one. We shall see a little later that all acts of substitution in chemistry are probably purely electrical acts; and just what are the relations between the substituted atom or group and the substituent was shown by Sir J. J. Thomson.

All of the above facts in connection with acids, and many more which space will not allow us to consider here, are explained, and for the first time by means of the theory of electrolytic dissociation. Without this theory, they would still be only so many empirically established, disconnected, and meaningless facts.

Meaning of the Term Base. — The term base was defined about as loosely as the term acid before we had the theory of electrolytic dissociation. We now know what a base is. It is a compound which, in the presence of a dissociating solvent, yields hydroxyl ions. Just as no pure, homogeneous substance is an acid, just so no pure, homogeneous substance is a base. A compound becomes a base only when it is dissociated and dissociated into the hydroxyl ion.

The term hydroxyl ion and base are coextensive. Wherever we have hydroxyl ions we have basic properties, and wherever we have basic properties we have hydroxyl ions.

The definition of the term base, like the definition and meaning of the term acid, we owe to the theory of electrolytic dissociation.

Constant Heat of Neutralization of Strong Acids and Strong Bases. — It has long been known that when a strong acid is brought in contact with a strong base, the amount of heat set free, if we work with comparable quantities of the different acids and bases, is a constant. It does not matter what the nature of the acid is or what base we use, provided they are all strong and the solutions dilute, we obtain the same amount of heat in the reaction.

The explanation of this fact, was, for a long time, a matter of difficulty. Indeed, it was impossible. When an acid was brought in contact with a base and the solution evaporated, a salt was obtained; and the nature of the salt was determined by the nature of the acid and by the nature of the base that were brought together. We had as many salts as acids and bases, and every process of neutralization gave its own distinctive salt. We apparently had as many different reactions in neutralization as we had acids and bases, and yet we always got the same amount of heat set free. Further, the amount of heat liberated in any given chemical reaction was a constant for the reaction in question. Here we apparently had a large number of chemical reactions all producing the same amount of heat energy. What was the explanation?

It was impossible to explain this phenomenon in terms of the older conceptions of chemistry. It is difficult to see how it would ever have been explained had not the theory of electrolytic dissociation been discovered.

Explanation of Constant Heat of Neutralization. — It has been stated that the heat of neutralization of strong acids by strong bases is a constant, if the solutions are dilute. Dilute solutions of strong acids and strong bases mean solutions in which the molecules are completely broken down into ions — all completely dissociated. This applies to dilute solutions of all strong acids and all strong bases.

We now know that what takes place whenever we bring together a solution of such an acid and such a base is represented in the following equation, in which $\overset{-}{A}$ is the anion of the acid and $\overset{+}{C}$ the cation of the base —

$$\overset{-}{A}\ \overset{+}{H} + \overset{-}{OH}\ \overset{+}{C} = H_2O + \overset{-}{A} + \overset{+}{C}$$

The process of neutralization consists simply in the union of the hydrogen ion of the acid with the hydroxyl ion of the base to form water; the anion of the acid and the cation of the base remaining after the process of neutralization in exactly the same condition as before. This is the same as to say that in the dilute solution the salt is completely dissociated. The molecules of the salt are formed only when the water is driven off; and the old error was in supposing that the salt was formed as the result of the process of neutralization. When the water, which holds the ions of the salt apart, is removed, they combine and form a molecule.

The process of neutralization is, then, the same thing, independent of the nature of the acid and

does the heat of neutralization approach the constant value for strong acids and strong bases, when both the acid and base are weak.

What is the explanation of this apparent abnormality? It was not explained, and apparently not explicable, before we had the theory of electrolytic dissociation. Now, the explanation is perfectly obvious.

When the acid or the base is weak it means that there is not complete dissociation, and dissociation has a thermal value, positive or negative. When incompletely dissociated acids and bases are brought together the dissociated portions react in the usual way; then the undissociated portions dissociate and, as has been said, this process either evolves or absorbs heat. The heat of neutralization of weak acids and bases, as measured, is really the heat of neutralization plus the heat of dissociation of the unionized portion, which may be a positive or a negative quantity. That the heat of neutralization of weak acids and bases would not be the same constant as the heat of neutralization of strong acids and bases, could have been predicted in advance from the dissociation theory; and it could further have been predicted that the heat of neutralization of weak acids and bases would not have been a constant at all, but would vary from acid to acid and from base to base; since the heat of ionization varies with every compound.

Hydrogen and Hydroxyl Ions Combine when in the Presence of one Another. — The above interpretation of what takes place in neutralization is based upon the assumption that the hydrogen and hydroxyl ions, when in the pressure of one another, do combine. There are a large number of independent lines of evidence all pointing to this conclusion. It would lead us too far here to discuss these in any detail. Take just one of them. Water is formed by the union of the hydrogen ion of acids and the hydroxyl ion of bases. If hydrogen and hydroxyl ions could remain in the presence of one another uncombined to any appreciable extent, then pure water would be a dissociated substance; the amount of the dissociation being determined by the degree to which these ions are uncombined.

The fact is that water is practically undissociated. Only one molecule of pure water in a million or ten millions is broken down into ions. This alone would show that whenever hydrogen and hydroxyl ions are brought together they combine; and there is abundant independent evidence for this same fact.

The importance for chemistry of the fact that hydrogen and hydroxyl ions cannot remain in the presence of one another uncombined is difficult to overestimate. Could these ions remain separate then an acid would not neutralize a base, and all salt formation from the process of neutralization of acids and bases would be excluded.

Further, could hydrogen and hydroxyl ions remain in the presence of one another uncombined to any appreciable extent, water would either be an unstable compound or would not exist at all.

The importance of water for chemistry is of the very greatest. Think in how many chemical reactions water is formed as one of the products. Indeed, it is the formation of water, *i.e.*, the union of hydrogen and hydroxyl ions which condition and cause most chemical reactions. It is not too much to say that if hydrogen and hydroxyl ions did not combine, at least three-fourths of all chemical reactions would be ruled out at once. This would mean the practical annihilation of chemistry.

The importance of water for chemistry and for science in general, simply illustrates what a remarkable compound it is. It is the best dissociant and the best solvent of all of the more common liquids. Its properties are, in general, *extreme* properties. It has the highest dielectric constant of all of the more common liquids. It is more associated than any other common solvent, *i.e.*, its molecules contain the largest number of the simplest chemical molecules; liquid water at ordinary temperatures being $(H_2O)_4$. It is made up of the two most important and the two swiftest ions, $\overset{+}{H}$ and $\overset{-}{OH}$; the former being the ion that gives us all acids and the latter the ion that gives us all bases.

Take its property of contracting to 4° and then expanding until it reaches the freezing-point. This property is possessed by comparatively few liquids. Did water not expand from 4° to zero the whole face of the globe would soon present a very different appearance. Fresh-water life would be exterminated in one cold winter in northern climates; and those

Evaporate the solution and we get the four salts; sodium chloride, sodium nitrate, potassium chloride, and potassium nitrate. We start with two salts and we end with four. This is certainly a chemical reaction, and it was well known that every chemical act involves a thermal change. Here was what seemed to be a chemical change, and the most sensitive thermometer then in use could not detect any appreciable thermal change. How could we reconcile these apparently irreconcilable facts?

There was no possible means of explaining these facts before we had the theory of electrolytic dissociation. Now, the explanation is obvious, is a necessary consequence of the theory; and the fact could have been predicted in advance from the theory.

When we mix dilute solutions of neutral salts there is no chemical act. Each of the salts is completely dissociated in its solution, and they both remain completely dissociated when their two solutions are mixed. The chemical act takes place when the water which holds the two ions apart is removed. There is then a chemical act and undoubtedly a thermal change. The chemical act, giving us four salts from two, takes place during the process of evaporation, and this is the point that was for a long time overlooked. It was supposed that the chemical act took place when the dilute solutions of the two salts were mixed.

We now know that in the above described mixing of the two solutions there is no chemical action. Everything remains after the process of mixing in the same condition as before. There is, therefore, no reason to expect any thermal change.

Properties of Mixtures of Electrolytes and Non-Electrolytes. — While we are dealing with mixtures and their properties the following systems are well worth considering. Take again the salts sodium chloride and potassium nitrate; mix their dilute solutions in equivalent quantities and study the properties of this mixture. Then mix solutions of potassium chloride and sodium nitrate of the same concentration as the original salts, and study the properties of this mixture. It will be found that the two solutions have the same properties.

Mix methyl chloride and ethyl bromide and study the properties of this mixture. Then mix methyl bromide and ethyl chloride in the same quantities as above, and study the properties of this mixture. It will be found that these two mixtures have very different properties.

Why this marked difference in the two cases? Without the dissociation theory it would be impossible to answer this question. With it the answer is obvious. In the first case we are dealing with electrolytes, which, in dilute solution, are completely broken down into their ions. The ions yielded by sodium chloride and potassium nitrate are, sodium, chlorine, potassium, and the ion $\bar{NO_3}$. The ions yielded by sodium nitrate and potassium chloride are sodium, $\bar{NO_3}$, potassium, and chlorine. We have the same kinds of ions in the two cases; and since we have used the same concentrations in both cases, we have the same numbers of the same kinds of ions in the two mixtures. These mixtures must, then, have identical properties.

In the case of methyl chloride and ethyl bromide, and ethyl chloride and methyl bromide we are dealing with non electrolytes, *i.e.*, with undissociated compounds. In the one mixture of these two substances we have methyl chloride and ethyl bromide molecules. In the other mixture we have methyl bromide and ethyl chloride molecules. In the two mixtures we have, then, different substances present, and we should expect to have different properties, and such is the fact.

These comparatively simple relations could not possibly be explained without the dissociation theory. With it their explanation is self-evident.

The Meaning of Substitution in Chemistry. — We have already referred to one simple act of substitution, the action of acids on metals. We saw that substitution, in this case, consisted in the transference of the electrical charge from the hydrogen which held it loosely, to the zinc which holds the charge more firmly and therefore takes it. Substitution in chemistry is one of the most common reactions. The question is, Is the above act of substitution typical of substitution in general, or is it a special kind which differs in nature from the more general act? We have seen that the action of an acid on a metal is purely and simply an electrical act. Is substitution, in general, electrical in nature?

therefore, takes it. It was the theory of electrolytic dissociation which first taught us the significance of electrical charges for chemical reactions and for chemistry.

The bearing of this work of Thomson was very broad. By means of it he was able to overthrow a long standing objection to the electrochemical theory of Berzelius; an objection which never had any real foundation in fact. It would lead us too far to discuss this relation here. It can only be referred to.[1]

Ions are the Active Agents Chemically. — Since electrical charges play such a prominent rôle in chemistry, the question arises, do uncharged parts ever enter into chemical reactions? This question has been long discussed and much experimental work has been done upon it. The evidence as I see it today is, that there is not the slightest reason to suppose that uncharged molecules can react chemically with uncharged molecules. A charged ion may react with a molecule, since there is a difference in potential between the two. Unless two bodies are at different electrical levels or potentials, I cannot see any physical possibility of them entering into a chemical reaction.

However this may be, there is abundant evidence that the ions are the most active agents chemically. Take a solution of an acid or a base that is completely ionized, it is more active in proportion to its concentration than any solution of the same acid

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[1] See "Elements of Physical Chemistry," by the author, 4th ed., p. 350 (Macmillan's, N.Y.).

or base that is not completely ionized. I mean that a thousandth normal solution of an acid or base is more than one one-thousandth as active as a normal solution, and this is because it is more dissociated.

The above fact is now so generally recognized, that we use the degree of dissociation as a measure of the strength of the acid or base; and the results obtained by this method are confirmed by those methods of measuring strength, in which the acid or base in question is allowed to effect a chemical reaction.

That molecules are comparatively inactive is shown by some facts already referred to, such as the inactivity of dry, liquid hydrochloric or sulphuric acid. Here we have the greatest possible number[1] of molecules of the acid in question in a given volume, and yet not a trace of chemical activity. Another fact illustrating the same point, is the lack of all chemical action between dry ammonia gas and dry hydrochloric acid gas.

Baker[2] showed this to be the case. He dried both of the gases with the very greatest care over phosphorus pentoxide, and brought them together in such a way that any change in volume, however slight, would be easily detected. There was not a trace of reaction.

The number of examples showing that molecules are chemical inactive are legion. It would lead us

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[1] There would be a few more molecules in a given volume in the solid, but these would be comparatively immobile.

[2] Journ. Chem. Soc. (London) **65**, 611 (1894), **73**, 422 (1889).

too far here to discuss any more such examples in detail, and it would be superfluous to do so. The explanation of such reactions and the lack of reactivity is the theory of electrolytic dissociation.

This theory thus accounts for the facts that are known, coordinating and correlating them; and it is most fertile in suggesting new and original lines of work. More could not be asked of it.

When we turn to liquids we know a good deal more. Here we have fairly reliable methods for determining molecular weights; but we know comparatively little about the fundamental laws of liquids.

With gases, however, it is quite different. Many of the fundamental problems in connection with gases have already been solved. We can deal with matter in the gaseous state by the only rigid and exact method—the mathematical.

Since Van't Hoff has shown the relation between solution and gases, we can apply what we know about gases to solutions; and the importance of this step will become apparent when we come to consider the meaning of solutions not only for chemistry, but for natural science in general.

The relations worked out by Van't Hoff, however, do not hold for solutions of substances in general; but only for solutions of non electrolytes, *i.e.*, those solutions which do not conduct the current. All of the electrolytes, as we have seen, show osmotic pressures that are too great in terms of the laws of gas pressure and their concentrations.

We have seen how Arrhenius explained these apparent discrepancies presented by the electrolytes. He showed that these substances in aqueous solutions are dissociated more or less into ions; the magnitude of the dissociation for any given substance being dependent upon the dilution.

Arrhenius thus supplemented the generalization reached by Van't Hoff, connecting solutions of non-electrolytes and gases, with the theory of electrolytic dissociation. These two generalizations taken together give us a satisfactory theory of very dilute, or "ideal" solutions as they were termed. These relations were soon recognized to hold only for very dilute solutions. They did not apply to a single concentrated solution of a single electrolyte or non electrolyte.

Criticism of the Generalizations of Van't Hoff and Arrhenius. — It was quickly pointed out that these generalizations of Van't Hoff and Arrhenius might be all very well for "ideal" or infinitely dilute solutions, but these are not the solutions in which we are most interested. These are not the solutions which give us chemistry. If we are to have a theory of solutions that is of the greatest value, it must certainly be a theory which takes into account the very solutions which we use in the laboratory.

This was a perfectly just criticism and one which could not be squarely met. The fact was that these relations, as important as they were for "ideal" solutions, did not apply to the real solutions which give us nature, and, therefore, give us the science of nature.

What did this mean? No one had the faintest idea. It was, to be sure, pointed out that the simple laws of gas pressure do not apply to the pressures of concentrated gases. It is necessary to modify the simple laws as was done by Van der Waals, and take into account, in concentrated gases, the spaces actually occupied by the gas molecules themselves, and the attractions of these molecules for one another.

No one succeeded in modifying the gas laws in a similar manner, or in any manner so as to make them apply to the osmotic pressures of even fairly concentrated solutions.

We think we know today the cause of the apparent anomalies presented by the real solutions with which we have to work.

Origin of the Solvate Theory of Solution. — A Japanese, Kenjira Ota, came to this country in 1899, by an unusual route, which touched at the bottom of the Pacific ocean. He came on a ship which foundered outside of the Golden Gate and sank. Ota just had time to adjust a life preserver, and fortunately had a room on the upper deck of the ship. When the boat sank he supposes that the weight of the water crushed in the roof of his stateroom, and having a life preserver properly adjusted he came to the surface like a cork. When he became conscious again he was being hauled into a small boat at the surface of the sea.

We would expect a man who had had such a fate, to do something unusual when he arrived, and he did.

I was interested at that time in the condition of double salts in solutions. We wanted to know whether a double salt, such as an alum or a double chloride, existed in solution as such; or whether it broke down first into the simple salts which apparently composed it, and then these dissociated in

chlorides by the freezing-point method, and soon found that from a certain concentration which was not great, the molecular lowering of the freezing-point increased with the dilution of the solution, just as we would expect it to do. From this concentration, as the concentration was still farther increased, the molecular lowering increased also with the concentration of the solution. The molecular lowering of the freezing-point thus passed through a well-defined minimum, increasing from a given concentration both with the dilution and with the concentration. This was a remarkable fact, and at first could not be satisfactorily explained. On examining the literature we found one or two cases on record, where the molecular lowering of the freezing-point seemed to pass through a minimum.

Work of Jones and Knight. — The work thus begun by Ota was very quickly taken up by Knight[1], who was working with me at that time. We extended the investigation to a much larger number of double chlorides and bromides, and found that the phenomenon first encountered by Ota manifested itself in every case. The molecular freezing-point lowering increased from a given concentration, with the concentration of the solution; and often attained a value much greater than would correspond to complete dissociation of the salt; although the salt at these concentrations was often dissociated not more than fifty per cent.

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[1] Amer. Chem. Journ., **22**, 110 (1899).

Work of Jones, Chambers, and Frazer. — The problem was then taken up more or less systematically at my suggestion and with my cooperation, by Chambers.[1] At this stage of the work the chlorides and bromides of the alkaline earths were studied, because they crystallized with large amounts of water, and I had already suspected a relation between water of crystallization and the apparently abnormal lowering of the freezing-point that we had observed. The minimum for the molecular lowering was found for every one of these substances. This work was a little later extended by Chambers and Frazer,[2] working in my laboratory.

Explanation of Results. — In 1900 I offered the first explanation[3] of these results. "How is it then possible to account for these abnormally great depressions of the freezing-point? There appears to us to be only one way. In concentrated solutions these chlorides and bromides must take up a part of the water, forming complex compounds with it, and thus removing it from the field of action as far as freezing-point lowering is concerned. The compound, which is probably very unstable, formed by the union of a molecule of the chloride or bromide with a large number of molecules of water, acts as a unit, or as one molecule in lowering the freezing-point of the remaining water. But the total amount of water present, which is now acting as solvent, is diminished

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[1] Amer. Chem. Journ., **23**, 89 (1900).

[2] *Ibid.*, **23**, 512 (1900).

[3] *Ibid.*, **23**, 103 (1900).

by the amount taken up by the chloride or bromide molecules. The lowering of the freezing-point is thus abnormally great, because a part of the water is no longer present as solvent, but is in combination with the chloride or bromide molecules. By assuming that a molecule of the halide is in combination with a large number of molecules of water, it is possible to explain all of the freezing-point results obtained."

Work of Jones and Getman. — The work at this stage was aided by a grant from the Carnegie Institution of Washington, and Getman was appointed assistant under this grant. He[1] took up the problem in a broad way, extending the work to a large number of typical substances. A method for calculating the approximate composition of the hydrates formed by the different substances at the different dilutions studied, was worked out, and a number of relations established; a few of these will be discussed here.

Evidence for Hydration in Aqueous Solution. — If substances in aqueous solution are combined with more or less of the water, then, those substances which combine with the largest amounts of water in solution, would be the ones that would bring the largest amounts of water with them out of the solution when they crystallize. If the explanation offered to account for the above described facts is correct, then, those substances which form, in the presence of water, the most complex hydrates, would be the ones which crystallize with the largest

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[1] Zeit. phys. Chem., **46**, 244 (1903); Phys. Rev., **18**, 146 (1904).

It is well known that molecular complexes in general break down with rise in temperature. The hydrates in solution would, therefore, be more complex the lower the temperature of the solution. The higher the temperature the simpler the hydrates.

Water of crystallization, which is water of hydration out of solution, should, therefore, depend upon the temperature at which the salt crystallizes. The higher the temperature at which the salt crystallizes, the smaller should be the number of molecules of water with which it crystallizes.

We knew that this fact was in general, true, before looking up the literature bearing upon it. We were, however, surprised to find in the literature such a large number of examples of this fact, and especially surprised to find the number of good examples of salts crystallizing with three, four, or even five different amounts of water of crystallization; depending solely upon the temperatures at which the crystals were formed. This was regarded as another line of evidence for the hydrate theory of solution.

One line of evidence after another for the view that there is combination between the dissolved substance and the solvent have come to light, until we have now more than a dozen such independent lines. It would lead us much too far here to discuss these in any detail. There is, however, one other line which must be touched upon before we leave this part of our subject.

The Solvate Theory. — Before taking up this evidence, we will add a word in reference to the power of substances to combine with solvents other than water, in which they are dissolved. Having found that combination with water is so general in aqueous solutions this question would naturally suggest itself.

The freezing-point method could not be used with many solvents other than water; since they do not freeze at temperatures which can be accurately measured. The rise in the boiling-point of a solvent produced by the presence of a dissolved substance, can be used to solve this question with such solvents as the alcohols, and this has been done.

The molecular rise in the boiling-point of alcohol produced by dissolved substances, has been found to pass through a minimum, just as the molecular lowering of the freezing-point passed through a minimum.

Further, the molecular rise in the boiling-point increased from this minimum with the concentration, to very considerable values; showing that a large amount of the solvent present was in combination with the dissolved substance. We shall see, especially from the spectroscopic evidence given below, that there is good reason to believe that dissolved substances in general combine with more or less of the solvent — in a word, solvation in solution is a general phenomenon.

Spectroscopic Evidence for the Solvate Theory. — The question arises, why study the action of light on solutions, in order to see whether there is combination between the dissolved substance and the solvent? Let us look briefly into this.

What is Meant by Absorption of Light? — Why are some solutions colored and others colorless? To answer this question we must first inquire into what is meant by the term "absorption of light." Why are some bodies opaque and others transparent to light rays?

Light, as is well known, is a series of waves sent out in the ether by the luminous object. These waves have very different wave lengths. White light is a mixture of a large number of these vibrations, having wave lengths that cover a very considerable range. The shorter wave lengths give us the sensation of purple, blue, and green; and the longer wave lengths of yellow, orange, and red.

An object is opaque to a beam of white light, when all of the wave lengths of the ether vibrations which constitute the white light, find something in the object in question which they can throw into vibration with wave lengths the same as their own. We usually call this phenomenon resonance, and say that an object is opaque to white light when all of the ether vibrations find something in the object which they can throw into resonance with themselves. It is very easy to see how resonance means opacity. If a vibration in the ether of a given wave length sets something in the object interposed in its path into vibration, the energy of the original ether vibration is expended in setting up the new vibrations, and the original ether vibration ceases.

hydrated it ought to have different resonance than it would have if only a little hydrated, or not hydrated at all. The solution should, therefore, have different "color," as we say, when we change the hydration of the dissolved particle.

We can easily change the solvation of a dissolved particle, and then we can see whether the color changes or not. We must not rely upon the eye alone to detect any slight change in the color of solutions, since the eye as a measure of color is a very rough instrument indeed. It only gives us the algebraic sum of the retinal stimuli, and as an analyzer of color is very defective.

The prism spectroscope, which has in the past been used so much in this connection, is now entirely out of date. It does not disperse the light sufficiently for the purposes in question. We now make use of a Rowland grating spectroscope which will be briefly described.

The Grating Spectroscope. — White light from a Nernst glower was allowed to pass through a fine slit and fall on the grating. From the grating it was received on the photographic plate. The solution whose absorption spectrum it was desired to study, was interposed between the source of light and the grating. The light absorbed by the solution manifested itself as dark lines and bands on the photographic plate. The advantage of the grating over the prism is the much greater dispersion of the light.

With the grating spectroscope, four assistants under grants to me from the Carnegie Institution of

Washington, have worked with me on the absorption spectra of solutions for the past seven years. These are Uhler, Anderson, Strong, and Guy.

Let us now see how the problem was attacked, and what were a few of the more important results obtained.

Work of Jones and Uhler. — Uhler[1] changed the composition of the hydrates in solution in various ways. He changed the *concentration* of the solution. The more concentrated the solution the simpler the hydrates. Increase in the concentration of the solution widened the absorption bands.

He then added a dehydrating agent to the aqueous solution of the salt in question. This simplified the hydrates present. The presence of a dehydrating agent, had the same effect on the absorption lines and bands as increasing the concentration. It widened them. A salt was then dissolved in alcohol, and more and more water added to the aqueous solution. As the amount of water present increased, the complexity of the hydrate increased. As the amount of water was increased the absorption bands became narrower and narrower.

The effect of the complexity of the hydrates present, on the absorption spectra of solutions, was thus unmistakable.

Work of Jones and Anderson. — Anderson[2] went much farther. He studied a very large number of substances, and showed that certain lines and

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[1] Carnegie Institution of Washington, Publication No. 60.

[2] *Ibid.*, No. 110.

bands are undoubtedly due to the presence of hydrates in the aqueous solutions; as, for example, the ultra-violet bands of solutions of cobalt salts.

The most important fact that was discovered by Anderson, as far as the solvate theory is concerned, is the following. In terms of this theory, when a salt is dissolved in water it combines with more or less of the water, forming hydrates. When dissolved in alcohol it combines with that solvent forming alcoholates.

It would seem that the hydrates ought to have different resonance from the alcoholates. The absorption spectrum of a salt in water should, therefore, be different from that in alcohol. This difference might be slight; but by selecting a salt with sharp absorption lines and bands, it ought to be detectable.

When we examined the literature bearing upon this point, we found nothing to indicate that our conclusion was borne out by the facts of experiment. The statement seemed to be generally accepted, that the absorption spectrum of any substance in solution was independent of the nature of the solvent in which it was dissolved, provided the solvent itself had no absorption.

Neodymium salts have many fine lines and bands. We worked out their absorption spectra in water as the solvent, and also in the alcohols. We found that the absorption spectrum in alcohol was *very different* from what it was in water. The alcohol spectrum was not the water spectrum

and bands manifested themselves which are characteristic of every solvent used, and which varied from solvent to solvent. Just how pronounced were these differences can be seen from a paper[1] that has recently been published. The number of "solvate" lines and bands that were found was very large, and the following interesting fact was discovered. Take two solvents as closely related as propyl and isopropyl alcohols, or butyl and isobutyl alcohols. By means of the absorption spectra of a salt dissolved in a given alcohol and in its isomer, we could distinguish between the two. There were absorption lines that were present in the alcohol, that were different from those which manifested themselves in the isomeric solvent.

This kind of evidence, which came to light in so many cases, leaves little to be desired. One other line has, however, come out in our most recent work on absorption spectra, which ought at least to be mentioned in the present connection.

The effect of *temperature* on the absorption spectra of solutions is very pronounced. As we raise the temperature the hydrates become simpler, and the absorption bands become wider and wider. This was shown by working in closed vessels up to about 200°, with both aqueous and non aqueous solutions. The effect of temperature on absorption spectra is, therefore, the same as increasing the concentration of the solution, and as adding a dehydrating agent to the solution. They all *widen*

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[1] Phil. Mag., **23**, 730 (1912).

the absorption bands. The effect of every one of these changes is to simplify the solvates existing in the solution. The effect upon absorption spectra is, thus, exactly the same as upon solvation, in every case; and indicates that solvation has much to do with the power of the dissolved substance to absorb light.

The point upon which it is desired to lay stress here is, however, the following.

The Radiomicrometer Spectroscope. — We have seen how far the grating spectroscope surpasses the old prism spectroscope. The grating spectroscope also has its limitations. It can be used to study absorption spectra only over the range to which the photographic plate is sensitive, since the spectra must be photographed. This is, after all, a comparatively limited range; extending from a little in the ultra-violet to a short way into the infra-red.

It is desirable to study the absorption spectra for shorter wave lengths than can be photographed, and especially for wave lengths longer than will affect the photographic plate. It is very desirable to work down as far as possible into the infra-red.

A great step has been taken in this direction by means of the radiomicrometer. What is a radiomicrometer? A radiomicrometer is a thermo-electric couple attached to a loop of copper wire, and the whole suspended between the two poles of a magnet. When a current passes through the wire loop, there is a deflection of the mirror attached to the system. Light from a Nernst glower is passed through a Hilger spectroscope with direct reading head, so that the wave lengths can be read off directly; and then light of one wave length or another thrown upon the junction of the radiomicrometer, and the deflection of the mirror noted. The solution whose absorption spectrum it is desired to study, is placed in the path of the beam of light between the source and the spectroscope, and any absorption detected by the deflections of the radiomicrometer.

By means of this instrument it was possible to detect and measure the intensity of the absorption spectra of solutions to wave lengths that were two, or two and a half, times too long to photograph. By this means the scope of study of absorption spectra was increased more than twice.

Work of Jones and Guy. — Guy,[1] who built the radiomicrometer now in use here, has recently found by means of it the following remarkable fact. The water in concentrated solutions of certain non-absorbing salts has less absorption of light than so much pure water. This was worked out by means of the radiomicrometer, which measures wave lengths as long and much longer than those which water absorbs almost completely. The fact that water in solution has less absorption than pure water, can be accounted for only on the assumption that in the solution a part of the water at least is in combination with the dissolved substance. The com-

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[1] Phys. Zeit., **14,** 278 (1913); Amer. Chem. Journ., **49,** 265 (1913).

The Present Solvate Theory and the Older Hydrate Theory of Mendeléeff. — The present theory of solvation in solution, or combination between solvent and dissolved substance, differs fundamentally and in many respects from the older hydrate theory proposed by Mendeléeff.[1] Mendeléeff supposed that when certain substances, such as calcium chloride and sulphuric acid, are dissolved in water, they form a few definite compounds with the solvent. Thus, sulphuric acid formed the hydrate $H_2SO_4.H_2O$; $H_2SO_4.2H_2O$; $H_2SO_4.25H_2O$; and $H_2SO_4.100H_2O$.

The existence of these hydrates was supposed to be shown by the fact that the specific gravity or density curve, when plotted against the concentration, seemed to show certain peculiarities or irregularities at points corresponding to the above compositions.

More accurate experimental work has shown that most, if not all of the irregularities are due to experimental error; and that there is not the slightest evidence for the theory of Mendeléeff. Further, the present theory supposes that these are not simply a few definite hydrates of any given substance in solution, but that there is a whole series of solvates in the solution; varying in composition from a few molecules of the solvent to one of the dissolved substance, to a very large number of molecules of the solvent to one of the substance. The present theory is not simply a theory of hydration in aqueous solution, but of *solvation in solvents in general.*

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[1] Ber. d. chem. Gesell., **19**, 379 (1886).

Bearing of the Solvate Theory of Solutions.—We recall that the theory of solutions as proposed by Van't Hoff and Arrhenius was a theory of "ideal," or "very dilute" solutions. The laws of gas pressure do not apply to the osmotic pressures of solutions even of medium concentration, and still less of very concentrated solutions. This was true even when we supplemented the generalizations of Van't Hoff by the theory of electrolytic dissociation.

This objection to the theory of solutions as left by Van't Hoff and Arrhenius, that it was not a theory of the real solutions with which we have to deal in the laboratory, was a perfectly valid one; and at that time there seemed nothing to do but to recognize its validity.

We now have the explanation of why it is that these laws which hold for very dilute solutions, do not apply at all to more concentrated. A part of the liquid present is combined with the dissolved substance, and is not present as solvent. Such solutions are much more concentrated than we would suppose them to be from the amount of dissolved substance which they contain. Thus, a solution of aluminium chloride which contains a gram molecular weight of the salt in a litre of solution, and which would, therefore, be supposed to be normal, is, in reality, about *five times normal.* Four-fifths of the water present is combined with the dissolved substance, and only about one-fifth is acting as solvent water. The solution is, then, in reality about five times as concentrated as we suppose it to be. It is not surprising that the laws of gas pressure would not apply to the osmotic pressure of a solution which was, in reality, *five times as strong* as we thought it to be. The conception of solvation in solution, and the working out of the complexity of the solvates in any given case, enable us to say just what is the real concentration of the solution. When we supplement the generalizations of Van't Hoff and Arrhenius by the solvate theory of solution, we have a theory of the real solutions with which we have to deal in the scientific laboratory. Taking solvation into account, the laws of gas pressure apply as well to more concentrated as to more dilute solutions. The solvate theory of solutions bears a relation to the theory of electrolytic dissociation, which is similar to the relation of the equation of Van der Waals to the simple expression of the laws of Boyle and Gay-Lussac. It extends the original theory from "ideal" to real solutions, making it a theory of solutions in the broad sense of that term.

Importance of Solution for Chemistry in Particular, and for Science in General. — We have laid considerable stress in the preceeding chapters, on the various theories that have been developed to account for the condition of matter when dissolved in a solvent. We have pointed out how fundamental was the step taken by Van't Hoff, when he showed that we can apply the laws of gases to solutions. The question now arises, Why is it so important to have

The science of geology is largely a branch of the science of solutions. The rocks and minerals crystallize out of molten magmas, which are simply solutions at more elevated temperatures; or are deposited from true aqueous solutions, colloidal suspensions or mechanical suspensions. The weathering of the rocks, which is going on all over the surface of the earth, is the act of certain substances, especially carbon dioxide, in solution.

Take the various branches of biology. How many of them are not fundamentally dependent for their existence upon solution? Take physiology, both vegetable and animal; or pharmacology; and they are fundamentally dependent upon the science of solution. We often say without carbon no life. It would be just as true to say without solution no life. An animal can live much longer without adding carbon—without food—than without water. The importance of solution for biology is thus obvious; and certain branches of physics, such as that which deals with the primary cell, depend for their existence upon solutions.

We can now see why a true theory of solution is of such fundamental importance. Solution is the condition of matter which underlies and determines chemical activity. If we are ever to have a real science of chemistry, we must first know the condition of matter in solution; since it is solutions which give us chemistry.

If we start with the Van't Hoff relations between gases and solutions, supplement these by the theory of electrolytic dissociation, and then supplement both of the above by the theory of solvation in solution, we have a very satisfactory theory of solutions in general.

The importance of a comprehensive and correct theory of solutions for the development of a real science of chemistry cannot easily be overestimated.

CHAPTER X

THE WORK OF WILHELM OSTWALD IN INAUGURATING THE NEW ERA IN CHEMISTRY

WE have seen the nature of the generalizations that were introduced into chemistry by Van't Hoff and Arrhenius, and we have gained some idea of the bearing of these upon the science.

The discovery of a generalization is one thing, and its wide reaching application is another.

The founding of a real science of chemistry from empiricism and system, using the generalizations of Guldberg and Waage, Berthelot, Willard Gibbs, Van't Hoff, Arrhenius, and his own, we owe almost single-handed to Wilhelm Ostwald.

The calling of Ostwald at the age of thirty-five from Riga to the University of Leipzig, in 1887, is an important event in the history of chemical science. He had already done experimental work in chemistry which was fundamentally different from the conventional chemistry of that time; and this work attracted the attention especially of Johannes Wislicenus, who was then professor of chemistry in Leipzig.

Here, in this larger and more scientific atmosphere, Ostwald developed as he could never have done in the Polish city. It may truly be said of Ostwald

broad way to the organic acids. Indeed, he studied the conductivities of about two hundred and forty of the more common organic acids, and calculated from their electrical conductivities their dissociations, by the well-known method of dividing the molecular conductivity at the dilution in question by the molecular conductivity at infinite dilution; or, as we say, at the dilution of complete dissociation. In this way Ostwald was able to determine the dissociations of acids at any dilution.

Dilution Law. — It was quickly recognized that the percentage dissociation of electrolytes in general increases as the dilution of their solution increases. This was a purely qualitative statement. What he wanted to know was, How rapidly does dissociation increase with dilution? Is there any simple expression connecting the change in the dissociation with the change in the dilution of the solution?

The only rational dilution law, even up to the present day, was discovered by Ostwald[1] in 1888. From the relations between gases and solutions, which had been pointed out a year before by Van't Hoff, and which are now so familiar to us, he deduced the well-known Ostwald dilution law; which is so simple that it can be discussed in some detail within the scope of this work.

If we represent the concentration of the solution, or the number of litres of it which contain a gram molecular weight of the dissolved electrolyte, by v, and the percentage dissociation of the solution by

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[1] Zeit. phys. Chem., **2**, 136, 276 (1888); **3**, 170 (1889).

λ, the following is the expression of the dilution law of Ostwald: —

$$\frac{\lambda^2}{(1-\lambda)v} = \text{constant}$$

The square of the dissociation, divided by one minus the dissociation, multiplied by the volume is equal to a constant.

This expression was found to hold satisfactorily for weak acids, but did not hold for strongly dissociated electrolytes; and we do not have at present any dilution law worthy of the name which does hold for all classes of electrolytes. Further, this law of Ostwald has not only a good experimental basis, but can be deduced from thermodynamics. It has, therefore, a good physical and scientific basis, and this is more than can be said of any one of the many so-called dilution laws that have been subsequently proposed. No one of them has any physical basis. They have been established purely empirically, *i.e.*, by cutting and trying; and like empirical relations in general, will probably disappear as soon as enough facts are brought to light which bear upon them.

In connection with this work on the dissociation of electrolytes, Ostwald overcame a difficulty which at first sight seemed to be really serious. If we wish to measure the dissociation of a strong electrolyte, that is, one which is greatly dissociated at any given dilution, we determine its molecular conductivity at the dilution in question, then increase the dilution of the solution until the molecular conductivity acquires a constant, maximum value, which is the value at complete dissociation. We then divide the former by the latter and we have the dissociation desired. This is all very simple.

If, however, the electrolyte is only weakly dissociated, the problem of measuring its dissociation is much more difficult. The dilution at which the dissociation would become complete would be so great that it would be impossible to apply the electrical conductivity method to it with any reasonable degree of accuracy. How was this difficulty to be overcome? We must know the value of the molecular conductivity at complete dissociation, before we can calculate the dissociation at any dilution.

It would lead us too far here to discuss in any detail the method that was worked out by Ostwald for solving this problem. It can only be referred to.[1] Suffice it to say that the method as Ostwald gave it to us works so satisfactorily, that we can now measure the dissociation of a weak electrolyte just as accurately and readily as we can that of a strongly dissociated substance.

Ostwald's Adaptation of Kohlrausch's Law.—The method still in use for measuring the conductivity of solutions we owe to the physicist Friedrich Kohlrausch. He showed that the power of ions in solution to carry the current was a function of their numbers and the velocities with which they

[1] Lehrbuch d. allg. Chemie, Vol. II, p. 693.

ardent and successful champion of the theory of electrolytic dissociation from the time it was first proposed by Arrhenius.

We are accustomed to think of ions being formed in one way, and in only one way. An electrolyte, *i.e.*, an acid, base, or salt, is thrown into a dissociating solvent such as water or the alcohols; and it is broken down by the solvent in question into an equivalent number of positively charged parts or cations, and negatively charged parts or anions.

It was Ostwald[1] who first showed that this is only one mode of ion formation, even if it is the most common method by which ions are formed. Another method is illustrated by the following reaction. Plunge a bar of zinc into a solution of a copper salt; the copper is deposited upon the zinc bar, and some of the zinc dissolves. This illustrates the case of an ion holding its charges loosely (copper), giving them up to an ion which holds them more firmly (zinc), and which, therefore, takes them. This is what takes place whenever one metal replaces another metal from its compounds; and is also strictly analogous to what occurs whenever an acid acts on a metal. An acid is nothing but a salt of hydrogen, and the hydrogen ion holds its charge very loosely; indeed, much less firmly than most of the metals. When a salt of hydrogen—an acid—is brought into the presence of a metal, the metal takes the charge from the hydrogen, becoming ionic; the hydrogen having lost its charge becomes atomic,

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[1] Lehrbuch d. allg. Chemie, Vol. II, p. 786.

then molecular, and escapes. This is but a method of ion formation.

Another way in which ions are formed is illustrated, as Ostwald points out, by such reactions as the following. Chlorine gas dissolved in water is almost completely unionized, shown by the fact that its aqueous solution conducts the current very little better than pure water. A bar of gold plunged into water remains almost completely unionized and consequently undissolved. When, however, a bar of gold is plunged into chlorine water the following takes place; the gold becomes a cation and the chlorine anions. In a word, the gold dissolves by passing from the metallic or atomic condition into the ionic, and the chlorine likewise passes from the atomic into the ionic condition. The one becomes cations and the other anions. This illustrates the condition where neither substance independently can form ions, but when both are present one becomes cations and the other anions.

The last mode of ion formation pointed out by Ostwald is, in some respects, the most interesting of the four. It illustrates one use of the term oxidation in chemistry. When chlorine gas is dissolved in water it is, as we have seen, for the most part unionized. If conducted, on the other hand, into a solution of ferrous chloride, the chlorine passes over into an anion and the bivalent ferrous ion becomes trivalent. This is made possible by the ionization of the chlorine. The bivalent ferrous cation can become a trivalent ferric cation.

There are, thus, at least four distinct ways in which ions can be formed, and this was first pointed out by Ostwald.[1]

Absorption of Light by Solutions. — The theory of electrolytic dissociation says that molecules of electrolytes in aqueous solution are broken down into charged parts or ions; the magnitude of the dissociation for any given substance being a function of the dilution of the solution. In very dilute solutions the dissociation of strong acids, bases, and salts is practically complete.

If a solution contains only ions, then all of the properties of such a solution are the properties of the ions and not of the molecules, since there are only ions present. Among the most obvious properties of solutions is their color. What relation exists between the color of solutions and their dissociation? This question was asked and answered by Ostwald in a paper[2] published in 1892; and in the following manner.

He took solutions of the various salts of permanganic acid with colorless cations. Thus, potassium, sodium, ammonium, lithium, barium, magnesium, aluminium, zinc, etc., permanganates, should have exactly the same color as hydrogen permanganate; since the color of all of these salts is due solely to the permanganate anion $\overline{MnO_4}$. This was a conclusion from the dissociation theory which could be

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[1] See also my Elements of Physical Chemistry, 4th edition, The Macmillan Company, N.Y.

[2] Zeit. phys. Chem., 9, 579 (1892).

results that were in keeping with the dissociation theory.

Ostwald's Theory of Indicators. — A natural outcome of this work was the theory of indicators proposed by Ostwald. Before this time indicators had been used largely mechanically. It was known that litmus in alkaline solution is blue and in acid solution is red; that phenolphthalein in acid is colorless and in alkaline is red, and so on.

Ostwald worked out all of these color changes in terms of the theory of electrolytic dissociation, and gave us the theory of indicators, which, in all essential points, is the theory we hold and use today.

Take the case of litmus. Why is it red in the presence of acids and blue in the presence of bases? In the presence of an acid the weak organic litmus acid is set free. Being a weak acid it is very little dissociated and its molecules are red. Thus, we have a red solution in the presence of acids. When a base is added, we have the salt of the base with the litmus acid formed; but a salt of even a weak acid is strongly dissociated. This salt dissociates at once, and sets free the anion of the litmus acid. This anion has a deep blue color. It is this anion which gives the characteristic blue color to alkaline solutions of litmus.

Take phenolphthalein. This is a very weak organic acid, which means one that is practically undissociated, and its molecules are colorless. This explains the lack of color in solutions of phenolphthalein to which an acid has been added. The molecules of the free phenolphthalein acid are set free and these are colorless. If a base is added to phenolphthalein, a salt of the base in question is formed, and this dissociates at once. When the salt dissociates, the anion of the phenolphthalein is set free, and this has the beautiful purplish-red color characteristic of phenolphthalein.

The color changes in the cases of other indicators were interpreted in an analogous manner. Although these views of Ostwald on indicators have been supplemented at some points by Stieglitz and others in an interesting way, they are in all essential features correct; and the publication of this theory placed the whole subject of volumetric analysis upon a far more exact and satisfactory basis.

Allotropy. — It has long been known that many of the chemical elements exist in more than one form. Take oxygen. We have ordinary oxygen and we have ozone. Sulphur exists in two solid crystalline forms; the orthorhombic or ordinary yellow sulphur, and the monoclinic variety. Selenium exists in a large number of allotropic modifications. Phosphorus exists in at least four forms; ordinary red phosphorus, ordinary white phosphorus, really white phosphorus, and black phosphorus. Carbon exists in a great many forms. We have the diamond, graphite, and Moissan has found a large variety of forms of amorphous carbon. Cohen has shown that many of the metals can exist in well-defined allotropic modifications.

Such are some of the allotropic modifications of the elements as known to us today, and in the future it is highly probable that a great many new examples of allotropy will be discovered. The facts of allotropy are interesting enough, but far more interesting and important is their explanation. This we owe to Ostwald.

Oxygen and Ozone. — Take the case of oxygen and ozone. These two modifications of oxygen, as they are termed, differ widely in properties from one another. Except for the fact that they can be converted the one into the other, they differ more widely in properties than chlorine and bromine. Each of these forms of oxygen can be prepared from the other, and, as just stated, each can be converted into the other. Let us see how these transformations from one form to the other can be effected.

If ordinary oxygen is sparked under certain conditions, ozone is formed. When an electric spark is passed through oxygen, electrical energy as such disappears, and the question arises, What becomes of it? Energy can be transformed only into energy. When energy disappears we must look for some other form of energy to appear in its place. Into what form of energy has the electrical energy which, in the above experiment disappeared, been transformed? We would suspect that it has been transformed into intrinsic energy. If this is true, then, ozone should contain more intrinsic energy than oxygen. Does it?

with all of the facts that are known in connection with this subject. How great an advance it is over the older attempt to explain the differences in the properties of these substances, can be seen by a glance at the older explanation, which said that the difference in the properties of oxygen and ozone is due to the fact that oxygen had only two atoms in the molecule and ozone three. This, we know today, explained nothing. They found these chemical and physical differences between oxygen and ozone, and they must be accounted for on the basis of some other difference between these two substances. Since both are gases their molecular weights could be determined. They found two atoms in the molecule of the one and three in the molecule of the other, and at once seized upon this physical difference to account for the other chemical and physical differences manifested by these two substances.

We know today, in the light of work which will be considered later, that the number of atoms in the molecule is rather a result than a cause of the difference between the properties of oxygen and ozone, and that this so-called explanation explains nothing. It was, however, the best that could be done at the time that it was proposed.

Sulphur. — Take one more case of allotropy; that manifested by sulphur. We know sulphur in two solid forms; one crystallizing in the orthorhombic and the other in the monoclinic system. Let us look at the facts in this case before attempting to explain them.

Orthorhombic sulphur is the more common form, stable at ordinary temperatures. When melted and allowed to cool slowly, it crystallizes in the monoclinic system, which is unstable at ordinary temperatures. If monoclinic sulphur is allowed to stand at ordinary temperatures, and especially if subjected to mechanical disturbance, it passes over into the orthorhombic form with evolution of heat. Heat energy is consumed in passing from orthorhombic to monoclinic sulphur, and, of course, given back again when monoclinic sulphur returns to orthorhombic. What is the explanation of these facts?

They all point to the conclusion that monoclinic sulphur contains more intrinsic energy than orthorhombic. We have a direct method of testing this conclusion. If a gram of orthorhombic sulphur is burned in oxygen we get a certain amount of heat liberated. When a gram of monoclinic sulphur is burned in oxygen we get a much larger amount of heat set free. Since we get the same amount of the same oxides of sulphur in the two cases, this thermal difference is the expression of the difference between the amounts of intrinsic energy in these two modifications of sulphur.

The monoclinic sulphur contains the larger amount of intrinsic energy, is the more active chemically, and is the more unstable. Monoclinic sulphur is, therefore, the analogue of ozone; while orthorhombic sulphur is the analogue of oxygen.

Just what is meant by intrinsic energy, and how all of the properties of a substance, both chemical and physical, are a function of the intrinsic energy present in the atoms and molecules of that substance, will appear when we come to consider somewhat later the work of Sir J. J. Thomson on this subject.

It should be noted that no attempt was made in the earlier days to explain the cause of the allotropy of sulphur. Not being gases they could not find out the number of atoms present in the molecules of either; and they had no explanation to offer in such cases as sulphur, phosphorus, carbon, and the like. We thus see what was meant by allotropy, and how it was dealt with by Ostwald. When we come to study the meaning of intrinsic energy we shall see the full significance of the allotropic modifications of the elements.

Chemical Action without Contact. — It was, before the time of Ostwald, an unalterable principle of chemistry, that in order to have chemical action we must have mechanical contact. Things must be brought together in order that they may react chemically. Ostwald showed that this was a misconception; that we can have chemical action without mechanical contact, and that the real significance of bringing things together in order that they may react chemically is not so much to secure mechanical contact as such, but electrical contact. He showed this by the following experiments.

He took a bar of pure zinc and attached to it a piece of platinum wire. At the end of the platinum wire he attached a piece of platinum foil to give a

a metal with high solution tension is meant one which has at its surface a high pressure or force which acts so as to drive metal atoms off of the bar of metal, into the solution in the form of ions. Zinc has a very high solution tension, and tends to throw zinc ions off of the bar into the solution. The hydrogen ions of the acid cannot get up to the bar and give up their charge to it. Zinc cannot dissolve until hydrogen escapes; in terms of the well-known principle that we cannot have appreciably more cations than anions in a solution. Hydrogen cannot escape until it gives up its charge. It cannot give up its charge to the zinc because of the high solution tension of the zinc driving zinc ions into solution. Hydrogen cannot escape and zinc, therefore, cannot pass into solution.

Platinum is a metal with a low solution tension. It, therefore, has very little tendency to throw ions into solution. Hydrogen ions can readily give up their charge to platinum. They do so and escape as ordinary hydrogen gas. The positive charge which they give up to the platinum is conducted over to the bar of zinc. The zinc atoms take up this charge, become ions, and pass into solution. This continues as long as there are any hydrogen ions present; as long, therefore, as there is any acid present. Zinc dissolves in an acid which does not touch it, and we, therefore, have chemical action at a distance.

The above explanation makes it clear why impure zinc dissolves in acids and why pure zinc does not.

The impurities in zinc, copper, arsenic, etc., are metals with low solution tension, and these play the same rôle as the platinum in the above described experiment. Being metals with low solution tension they allow the hydrogen of the acid to escape.

We can now understand also why we add platinic chloride to an acid which is to act on pure zinc. The platinic chloride is decomposed by the zinc, setting free metallic platinum. This allows the hydrogen ions of the acid to give up their charge and escape as described above.

The above experiment, then, illustrates a great many points of interest and importance. It is referred to here chiefly to illustrate chemical action at a distance. Another experiment was described by Ostwald in the same paper[1] in which the above was discussed, which also illustrates chemical action at a distance, but which also brings out a much more important principle, as we shall now see.

Pour into a beaker an aqueous solution of pure, ferrous chloride, containing no trace of ferric chloride. Pour into another beaker a solution of pure potassium chloride, and connect the two beakers with a siphon filled with some of the aqueous solution of the potassium chloride. Insert a platinum electrode into each beaker, and connect the two electrodes externally through a galvanometer. Conduct chlorine gas into the solution of potassium chloride which surrounds one of the electrodes and the following occurs:

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[1] Zeit. phys. Chem., **9**, 549 (1892).

The galvanometer shows a flow of electricity from the electrode surrounded by the potassium chloride into which chlorine gas has been conducted, over to the electrode surrounded by ferrous chloride. The ferrous chloride is rapidly transformed into ferric chloride, and this is the important point of the experiment. This transformation is effected by chlorine which does not come in contact with the ferrous chloride, and the experiment, therefore, illustrates chemical action at a distance; but this experiment bears directly upon a problem which is so much more fundamental for chemistry as a whole than the question of contact being necessary for chemical action, that we shall pass over at once to the consideration of this side of the experiment.

Faraday's Law and Chemical Valence. — What is meant by the term chemical valence? This depends largely upon the individual who uses the term. Frequently, it is not defined at all and discussed without definition, with the inevitable result that the discussion leads nowhere, and ends just about where it begins.

It was Wilhelm Ostwald who first showed the real significance of chemical valence; and the above experiment threw more light on this subject than any other experiment that has been carried out since Faraday discovered the law or laws which bear his name. Indeed, this experiment is, as we shall see, fundamental to all discussion of valence, and any discussion which ignores it is defective.

From his studies of electrolysis Michael Faraday,

physics during that long period preceding 1887, it is almost certain that some one would have seen the significance of Faraday's law for chemistry; in that it lies at the basis of all valence, before Ostwald pointed it out at the very end of the last century.

This condition is fortunately all changed now. No one today can study the science of chemistry without a good knowledge of elementary mathematics, and some knowledge of at least differential and integral calculus, any more than he can study the science of physics without a previous training in these subjects.

A univalent element, as Ostwald points out, is one that carries one unit charge of electricity, a bivalent element is one that carries two such charges, a trivalent element three such charges, an n valent element n such charges, and so on. Chemical valence is, then, nothing but the chemical expression of Faraday's law, or the number of unit electrical charges carried by an ion. Exactly what is meant by a unit electrical charge will appear when we come to consider the work of Sir J. J. Thomson.

If the above conception of chemical valence is correct, then we ought to be able to change the valence of an ion by adding electricity to it, or by removing electricity from it. It is right here that the last described experiment becomes so important. We raise the valence of the ferrous iron from two to the valence of ferric iron which is three, and how do we do it? By adding an electrical charge to it;

and we do it in such a way that we can say with certainty that nothing else takes place. The chlorine on one side of the above described system passes into ions, by taking negative electricity from the platinum electrode surrounded by the potassium chloride into which the chlorine gas is conducted. The chlorine taking negative electricity from the metal leaves the latter charged positively. This positive electricity flows around to the other electrode, as is shown by the deflection of the galvanometer through which it is made to pass in the circuit. The electrode surrounded by the ferrous ions now becomes charged positively. The ferrous ions, each with two positive charges upon them, take another charge and pass over into the ferric condition; where, as we know, each iron ion carries three positive charges of electricity.

We have thus synthesized chemical valence and out of what? Out of electricity; and we have done it in such a way as to leave no question of doubt. In this experiment it seems practically certain that nothing else has taken place in the iron except the addition of one electrical charge, and we have transformed the ferrous into ferric iron.

This is probably the most direct experiment bearing on the nature of chemical valence since the experiments carried out by Faraday, which led him to the discovery of his second law.

We can now deal with chemical valence in a rational way, since it has thus been placed upon a definite, physical basis; and since we can give a good physical definition of the term we are using. All of this we owe primarily to Ostwald.

Catalyzers. — The terms catalyzers and catalysis have been used ever since the time of Berzelius, who discovered the phenomenon which they are meant to describe. The term catalyzer means something which affects a chemical reaction by its presence alone, that is, without entering into the reaction. A fairly large number of catalyzers were discovered by Berzelius, and by those who came after him; but the whole subject had become more or less inexact and uncertain until it was taken up by Ostwald.

He pointed out that there are many reactions that are apparently catalytic, which are really not catalytic at all. The substance which accelerates or retards the reaction may, or may not enter into the reaction. If it does not enter into the reaction we have a truly catalytic process to deal with. The substance is a true catalyzer.

True and Pseudocatalyzers.—The accelerator or retarder of the reaction may, on the other hand, enter into the reaction, form compounds with the reacting substances, and then split off again and come out of the reaction in apparently the same condition as it was before it entered into the reaction. Such substances are not true catalyzers, but were called by Ostwald pseudocatalyzers, or false catalyzers. He went farther and pointed out methods based upon the order of the reaction in question, of determining in any given case whether a substance was a

Nitrogen and hydrogen under high pressure, that is, both gases very concentrated, are heated to about 500°, in the presence of some catalyzer, such as metallic uranium, iron carbide, etc. The nitrogen and the hydrogen combine and form ammonia, which is the essential step in the process. This method competes with those based upon the burning of the nitrogen of the air in the oxygen, by passing an electrical discharge through the mixture.

These are just a case or two in point. Many other applications of catalysis to the chemical industries have already been made, and it is safe to predict that we have thus far only touched the outskirts of this field.

Characteristics of Ostwald the Experimenter.— Such are a few, and a very few, of the many lines of experimental work which were carried out by Ostwald, while connected with the University of Leipzig. This one characteristic is most pronounced in all of his experimental work. He saw what was essential for the development of the science, and he devised experimental methods for attacking and solving these fundamental problems.

We shall see that the strongest side of Ostwald is that of the *organizer* and *founder* of a new school of chemistry. The organizer above all others must see what is important, essential, and fundamental. He must be able to cull these out from the scientific chaff. This was done by Ostwald as it has probably never been done by any one else in chemistry. The experiments and investigations that were planned and directed by him in what he calls "Die gute Zeit," that is, when in the old laboratory in Brüderstrasse in Leipzig, were fundamental. The question to be answered was almost always one that had vitally to do with one or another of the newer phases of chemistry.

The quantity of the experimental work that was done by Ostwald and his collaborators, between the time that he was called to Leipzig in 1887, and say, 1897, is simply appalling. A glance through his Journal, the Zeitschrift für physikalische Chemie, during this period, taking into account only the papers published under his own name, would give no idea of the investigations which he suggested and directed during this period. The work of his assistants and students, which was originated and guided by him, was practically all published under the names of the students alone, with the usual acknowledgement to Ostwald at the ends of the papers. This custom, which is even today so rare in scientific laboratories, shows the broad mindedness and unselfishness which are characteristic of this truly great man. To gain any adequate conception of the work done in the old Brüderstrasse laboratory during the ten years referred to, we must look not only at the names of the authors, but at the place from which the papers were written. This work has been collected and published in several large volumes. It is not too much to say that the experimental foundation for the new chemistry was laid during the ten years in question in Ostwald's old laboratory in Leipzig.

The amount of the work done was largely due to the influence of Ostwald's example. I have never seen his working power equalled. He could work, intensely, for more hours than any one I have ever known. This spirit of work extended from the leader to most of his coworkers.

Ostwald the Founder and Organizer of a School of Chemistry. — We have gained some idea of the variety and importance of the experimental work of Ostwald. His greatest achievement, however, is, as has already been stated, undoubtedly as an organizer and founder of a new school of chemistry.

The chemists, from Berthelot to Arrhenius and Van't Hoff, had been bringing to light generalization after generalization which were to be the corner-stones of the new chemistry. The discovery of these generalizations was one thing, but the applications of them to the facts of chemistry was another. Without Ostwald, with his uniquely comprehensive grasp of the facts of chemistry, and with his organizing mind, it is safe to predict that the full meaning of these generalizations for chemistry would not have been seen even at the present time. Without Ostwald, the development of the new school of chemistry would have been delayed for an indefinite period. As so often happens the right man comes at the right time; or perhaps the right time develops the right man. The result is, as we well know, that

Lehmann, Pettersson, Pfaundler, Ramsay, Schiff, and Thorpe. This serves to show how near we are in reality to the beginning of the new era in chemistry. The number of cooperators of the Zeitschrift is still twenty-two.

The first volume of the Zeitschrift für physikalische Chemie contains 678 pages. The third year, *i.e.*, in 1889, it grew to two volumes, with 616 and 680 pages respectively. This, however, soon proved to be insufficient to accommodate the rapidly-growing science, and in 1894 three volumes a year were published. This rate was continued until 1905, when it was found necessary to publish a fourth volume. The Zeitschrift appears now at the rate of from four to five large volumes of between six and seven hundred pages each, every year.

Such a growth of a purely scientific journal in twenty-five years has no parallel in the history of the physical sciences. It is now in its eighty-second volume.

A few words from the introduction to the first volume, explaining the aim and scope of the then new Journal, may not be uninteresting, especially considering the unparalleled growth and development of the new branch of science and of the Zeitschrift itself. It was taken by Ostwald from a speech by du Bois-Reymond in which he greeted Landolt as a new member of the Prussian Academy of Sciences; Landolt being the Professor of Physical Chemistry in the University of Berlin. Only a few excerpts will be given.

"In contrast with modern chemistry we can call physical chemistry the chemistry of the future." This was spoken by du Bois-Reymond in June, 1882. After praising the older structural chemistry, he calls attention to the importance of studying thermal changes, volume changes, changes in refractivity, etc., in order ever to have a really exact science of chemistry, and then adds, "When will this aim be reached? Who can say? Perhaps that Newton is now training his youthful powers in school; perhaps after several hundred years our successors may be as far as we are from transforming chemistry into mechanics. The way to begin this transformation is perfectly clear. Together with the further development of structural chemistry, *we must zealously till the field of physical chemistry in a somewhat broader sense. Mathematical, physical, and optical crystallography, refraction, and dispersion* (of light), *natural and magnetic circular polarization of light, spectrum analysis; thermochemistry with the mechanical theory of gases and dissociation* (of gases); *electrochemistry, especially since we have the electrochemical dualism; finally, the science of diffusion, to which belong absorption and solution; we must combine all of these and many others to form a complete picture of molecular processes.* This must all be accomplished before we can say that what the alchemists called 'The great work,' is done."

Did du Bois-Reymond live today, and could he see what has already been accomplished in so many directions, he would conclude that while "The great work" has not by any means been finished, yet it is well under way; and while we cannot say that we have one chemical Newton; we had, at the time he was speaking, three men in training for the "great work." These were Van't Hoff, Arrhenius, and Ostwald.

Text-Books by Wilhelm Ostwald. — Ostwald early recognized that an essential step in having the newer developments in chemistry recognized was to bring them together in systematic form.

Lehrbuch der Allgemeinen Chemie. — The first volume of his "Lehrbuch der Allgemeinen Chemie" (Text-book of General Chemistry) was published in 1885, while still in Riga. The second volume appeared in 1887, just when he came to Leipzig. This systematic summary of what was then known attracted immediate attention. The only comprehensive work then existing in the field of theoretical chemistry was Lothar Meyer's book, "Die Moderne Theorien der Chemie." (The Modern Theories of Chemistry.)

This work by Ostwald differed in many respects in kind from that of Meyer, and chemists saw in it the dawn of a new day.

The subject developed so rapidly that this first edition quickly became out of date, and Ostwald in 1891 published the first volume of the revised and greatly enlarged second edition. The second volume appeared in 1893, and the third in 1896.

This second edition has never been, and probably never will be completed. The subject grew

positively charged potassium ions, and repel the negatively charged chlorine ions. The result would be an excess of positive ions in the beaker next to the charged body, and an excess of negative ions in the beaker away from it. Remove the siphon and trap the excess of cations in the one beaker and the excess of anions in the other. Into the beaker containing the excess of potassium ions, introduce a platinum wire and connect this to earth. The excess of potassium ions will lose their charge and, being atomic, will act on water. The result would be a liberation of hydrogen gas around the platinum wire.

Ostwald says one chemist wrote him that he had tried this experiment and that it did not work. He was not able to see any hydrogen given off.

Everything that Ostwald said about this experiment undoubtedly takes place, as he afterwards showed.[1] The point is, that under the conditions under which the experiment would be normally carried out, there would not be enough hydrogen liberated to be seen; especially since hydrogen is soluble in water to a very appreciable extent.

Ostwald calculated the size of the hollow metallic condenser, which would be necessary, under the conditions of this experiment, to liberate enough hydrogen to be dealt with. He showed that it would have to be a hollow cube of metal whose edge was a kilometer in length. In a word, it would have to be a cubical metal box whose vertical edge would be three-fifths of a mile high.

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[1] Zeit. phys. Chem., 3, 120 (1889).

This experiment, however, served its purpose, to demonstrate the presence of free ions. It was thought by those who had not followed the newer developments that these were all very well as far as physical chemistry is concerned, but that they had no direct or important bearing on general chemistry. This was more or less natural.

Physical chemistry was looked upon as something distinct and apart from general chemistry.

Grundlinien der Anorganischen Chemie. — This wholly erroneous impression was corrected by the appearance of Ostwald's "Grundlinien der Anorganischen Chemie." In this work he applied the generalizations of physical chemistry to descriptive inorganic chemistry, and showed that through them, and through them alone, there was a possibility of a science of general chemistry.

Ostwald took the view that it is undesirable for the student to learn the older chemistry of atoms and molecules for a year or two, and then try to forget all this and think in terms of ionic chemistry. He thought it was better for the student to begin in the right way and learn what was true from the very outset.

This is all the more desirable, since the persistence of first impressions is well known. If the student starts out wrong, and learns at first what we today know is not true, he is crippled for life. He may struggle to get rid of these first impressions, but he will never entirely succeed.

The question then arises, why start a student in the wrong channels, with the intention of subsequently correcting him? The answer has been, for the sake of simplicity. Atomic chemistry is simpler than ionic. It is easier to think of an unchanged atom, than of an atom carrying a charge of electricity. This is true; but it raises the question, whether simplicity is the chief aim in teaching any branch of science. Especially is this the case when it is a question of simplicity versus truth. Ostwald points out the fact that, as any branch of science develops it makes greater and greater demands upon its students.

Physics has long since passed beyond the purely descriptive stage, and the teacher of elementary physics must face the science as it is and he does so. The same student is usually at the same time a beginner in chemistry and a beginner in physics. Why should the teacher of elementary chemistry not assume the same mental qualifications as the teacher of elementary physics, when they are both dealing with the same student?

Ostwald also shows that while modern chemistry makes greater demands upon the reasoning powers, it taxes the memory much less than the older, purely descriptive chemistry; and, further, scientific chemistry is much more interesting, and gives rise to a much higher order of intellectual pleasure and development.

The aim of this book by Ostwald was, then, no less than to raise general chemistry from the level of empiricism and a purely descriptive branch of

published his great work in the "Proceedings of the Connecticut Academy of Sciences," which is not frequently seen; and here it remained until Ostwald translated it into German. From the appearance of this translation Gibbs' fame was world wide. It became apparent that Gibbs had already in 1878 done, by means of thermodynamics, all that Helmholtz did independently in 1882, and very much more. This was really the introduction to Europe of Willard Gibbs, who has since come to be ranked by many as the first American man of science.

Klassiker der Exakten Wissenschaften. — Ostwald, in connection with founding the new school of chemistry, had read very extensively not only the literature of chemistry, but of science in general. Indeed, I have never met any one whose grasp of the literature of science is equal to his. In doing so, he had become impressed with the fact that the epoch-making papers of science, the great science classics, were widely scattered. Many of them were published in out of the way places, and some of them in languages not read by the general scientific world. It was, therefore, obviously desirable that these great key-stones in science should be made accessible to men and students of science in general.

This thought led to the publication of the "Klassiker der Exakten Wissenschaften," of which some 184 volumes have now appeared. In this series are the epoch-making papers not only of chemistry, but of physics, mathematics, etc. Ostwald continued the editorship of these "Klassiker," until pressure of work compelled him to hand it over to another.

Elektrochemie Ihre Geschichte und Lehre. — The above is by no means an enumeration of all of Ostwald's books. We have not even mentioned his enormous "Elektrochemie ihre Geschichte und Lehre," of 1150 large pages.

Overthrow of Scientific Materialism. — A paper appeared by Ostwald in 1895, bearing the above title,[1] which was destined to make a deep impression. He did not mean to discuss, under this heading, the subject usually treated under it; disclaiming at the very outset that he had any theological thought in mind.

What was the subject discussed, and why is the paper an important one?

We had been accustomed to look upon the objective universe as made up of two entities; matter and energy. These were the two things that we knew, and the only two. Ostwald pointed out that we look upon these two supposed entities in about the following manner: What we know is matter, and what we imagine is energy. This was natural in the historical development of things. We studied matter first and then energy; and it was only natural that we should come to lay the most stress upon what we thought we knew best.

The most important point brought out in the above-named paper by Ostwald was this: What we really know, and all that we can know through our

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[1] Zeit. phys. Chem., **18**, 305 (1895).

senses as we are at present constituted, are *energy and changes in energy.* The question arises, where did our conception of matter come from? *Purely from the imagination.* We cannot measure matter, we cannot deal with it even qualitatively. Then why was it created by the imagination? Simply to have something to which to attach the various manifestations of energy. We could not, at that time, think of energy in the abstract. We did not then know that energy alone, electrical energy, can have both mass and inertia. We must have something to which to attach the energy, and something which would have the well-known properties of mass and inertia; and this something we created out of our imagination and called it matter.

This paper by Ostwald, then, put so-called matter and energy in the proper perspective; and its significance is greatly increased by the fact that subsequent work by Sir J. J. Thomson and others has made it highly probably that matter, as we have ordinarily used that term, does not exist at all. More of this a little later.

Energetics. — This brings us to the most important single contribution of Ostwald to science in general, and to the science of chemistry in particular. Why do chemical reactions take place at all? Why do any two substances react? These are, of course, fundamental questions for the chemist to ask. They are often not asked at all. There are textbooks in chemistry in use today, in which they are not even raised, and these are among the most

out the relation of the changes in energy to the chemical reaction itself. It was Ostwald who first showed that the study of all of the energy changes in chemical reactions is absolutely essential to the foundation of a science of chemistry; in that these are the matters of fundamental significance; the material changes being as already stated of purely subordinate importance. The energy changes are the cause of all chemical reactions.

In concluding this chapter on Wilhelm Ostwald the chemist and man of science, a few words of a general character might be added. He carried out directly and through his cooperators an enormous amount of most valuable experimental work; but his greatest work is as an organizer and founder of a new school of chemistry. His influence in this direction has never been surpassed, if it has ever been equalled, in the whole history of chemistry. The kind of work which Ostwald did is the kind that requires time to value properly. It would be expecting too much to think that chemists in general would turn at once from empiricism and system to science.

The transition has, however, taken place with marvelous rapidity, and this we owe more than to all others to Wilhelm Ostwald. The next fifty years will properly evaluate the work of Ostwald the experimenter and organizer.

CHAPTER XI

INVESTIGATIONS BY STUDENTS AND COWORKERS OF WILHELM OSTWALD AND A FEW OTHERS

WE have now studied the great generalizations that have transformed chemistry from empiricism and system into science. We have seen what these generalizations are, and by whom they have been discovered. We have further seen how they have been applied to the facts of chemistry almost single handed by Wilhelm Ostwald.

The development of physical or general chemistry has consisted in further applications of these generalizations in many directions, which has brought to light many new and important relations. Some of these more recent developments will now be considered.

Apparatus of Beckmann. — The French chemist, Raoult,[1] had studied quantitatively the lowering of the freezing-points of solvents produced by dissolved substances. He had found, by working with a large number of solvents and a large number of dissolved substances, that the freezing-point lowering of any solvent by any dissolved substance is proportional to the ratio between the number of parts of the solvent and of the dissolved substance.

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[1] Ann. Chim. Phys. [5], **28**, 137 (1883); [6], **2**, 66 (1884).

He formulated his so-called law as follows: "If one molecule of any given substance is dissolved in say one hundred molecules of a solvent, the freezing-point of the solvent is lowered a constant amount, which is approximately 0.63°."

This was evidently an arithmetical property; a property which depended only on the ratio between the number of parts of the solvent and of the dissolved substance. These are the properties which are most worthy of careful study. When any given property changes with every change in composition, and changes with every change in the constitution of the compound, then, any relations which may come out as the result of its study are almost certain to be purely empirical; and being empirical will probably disappear as soon as enough facts are brought to light which bear upon them.

Whenever an arithmetical property is discovered, it should be studied with thoroughness and with the greatest care; since it is through the study of such properties that science is advanced.

Whenever we dissolve certain substances in a liquid solvent, the boiling-point of that solvent is raised. This is a general property of dissolved substances, provided the dissolved substance boils not less than 130° above the boiling-point of the solvent.

Raoult[1] showed that this is also an additive property. The rise in the boiling-point of a solvent by a dissolved substance depends only on the ratio between the number of parts of the solvent and of

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[1] Ann. Chim. Phys. [6], **15**, 375 (1888).

The writer owns one with an entire range of scale of only 0.6°, and which is graduated to $\frac{1}{1000}$ of a degree. With a lens it is quite simple to read the scale to $\frac{1}{10000}$ of a degree. This is the thermometer which I used in Ostwald's laboratory [1] for measuring the dissociation of electrolytes. This thermometer was of the Beckmann type, and was simply enlarged to make it more sensitive.

Freezing-point Apparatus. — The apparatus which was devised by Beckmann [2] for determining the freezing-points of solutions and solvents was so simple as to call for very little comment. It consisted essentially of two test-tubes, the one within the other, and an ample air-space between the two. This whole system was then inserted in a freezing mixture having the desired temperature.

Boiling-point Apparatus. — The determination of the boiling-point with a fair degree of accuracy, is a much more difficult matter than the measurement of the freezing-point of a solvent. This is due to the fact that the boiling-points of the solvents used in this work are more widely removed from ordinary temperatures than their freezing-points, and especially because the boiling-point of a liquid is so greatly affected by any changes in the barometric pressure. This will be seen at once from the definition of boiling-point, as the temperature at which the vapor tension of the liquid just overcomes the superincumbent pressure. The boiling-point,

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[1] Zeit. phys. Chem., **11,** 110, 529 (1893); **12,** 639 (1893).

[2] *Ibid.,* **2,** 638 (1888).

therefore, changes as this superincumbent pressure changes. A change of a millimeter in the barometer changes the boiling-point of methyl or ethyl alcohol about 0.04 of a degree. The changes in temperature which we have to measure by this method are always small, and are sometimes very small. The greatest accuracy must, therefore, be secured in measuring such changes.

Beckmann[1] devised a large number of forms of apparatus for measuring boiling-points. Some of these are fairly efficient. Others are too complex for general practical use.

Various means were devised by Beckmann for protecting the boiling liquids and solutions from the effect of radiation on to the colder object round about. Double jacketed apparatus containing more of the same boiling liquid was used.

It must, however, be said that in no one of the forms of apparatus devised by Beckmann does there seem to have been sufficient and effective protection against radiation. The long heat waves pass through glass and boiling liquids without any serious difficulty.

To protect the bulb of the thermometer from loss of heat by radiation, it must be surrounded by a metal heated to the same temperature as itself.

This is readily accomplished by a form of apparatus[2] which has been used in this laboratory for the

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[1] Zeit. phys. Chem., **4**, 544 (1889); **8**, 226 (1891); **18**, 473 (1895); **22**, 609 (1897); **39**, 129, 385 (1902); **57**, 129 (1907).

[2] Amer. Chem. Journ., **19**, 581 (1897).

past fifteen years. It consists simply in surrounding the bulb of the thermometer with a cylinder of platinum. This being immersed in the boiling liquid, is heated to exactly the same temperature as the bulb of the thermometer, which is the ideal condition. The metal radiates back on to the bulb of the thermometer just as much heat as it receives from the bulb, and thus the effect of radiation is practically eliminated.

This platinum cylinder also serves another very useful purpose. It cuts off from the bulb of the thermometer the recondensed solvent, until it has passed down through the boiling liquid and been reheated to the boiling-point. This is a very important point, and one that is not taken into account in any form of apparatus devised by Beckmann.

Molecular Weights of Dissolved Substances. — The freezing-point and boiling-point apparatus of Beckmann made these two methods generally useful in the laboratory for two purposes. Any arithmetical property can be used to determine numbers; or knowing numbers, can be used to determine relative molecular weights. The determination of molecular weights of substances in solution was the first general application of these methods. A number of solvents were used with the freezing-point method, and a much larger number with the boiling-point method. Substances in general in solvents in general were, then, studied by one or both of the above-named methods as to the weights of their molecules in solution.

ity method, in the early stages of the work, could not be used for measuring dissociation in even such a solvent as ordinary alcohol. The boiling-point method was, at that time, the only one available for this purpose. This method as left by Beckmann could not be used for this purpose, but has since been so improved[1] that it can now be employed to measure dissociation with a very fair degree of accuracy in non-aqueous solvents.

There has been an enormous amount of work done with both the freezing-point and the boiling-point methods. They have been used in solving a great variety of questions, and in throwing light on a large number of problems. The use of these methods we owe primarily to the thermometer devised by Beckmann, who has shown unusual skill in designing apparatus in general.

Investigations of Paul *Walden.* — No one of Ostwald's coworkers has attacked a greater variety of problems, or worked on them more successfully, than Paul Walden. The earlier work in the new field of chemistry had to do primarily with aqueous solutions. This was natural. Water is not only the most common solvent, but is the most general solvent known to man. It is easy to obtain water of a high degree of purity, and it is the solvent which gives us our chemistry of today. There, however, came a time when the more fundamental properties of aqueous solutions began to be pretty well under-

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[1] Amer. Chem. Journ., **19**, 753 (1897); Zeit. phys. Chem., **31**, 114 (1899).

stood. As soon as this was the case, the question arose, What about non-aqueous solutions? Do the relations that had already been discovered for aqueous solutions hold for solutions in solvents other than water? Such questions could be answered only by a systematic study of non-aqueous solutions.

Liquid Sulphur Dioxide. — One of the first to undertake this work was Paul Walden.[1] As early as 1900 he worked with liquid sulphur dioxide as a solvent. He measured the conductivities of a number of salts in sulphur dioxide, and showed that they were from one-fourth to one-half the corresponding values in water. Walden extended this investigation to a large number of other inorganic solvents,[2] and showed that sulphur dichloride, phosphorus oxychloride, arsenic trichloride, and antimony trichloride have marked dissociating power; while phosphorus trichloride, antimony pentachloride, silicon tetrachloride, sulphur trioxide, and bromine have very little dissociating power indeed.

Liquid Hydrocyanic Acid. — Centnerszwer, working with Walden, carried out an elaborate investigation in liquid cyanogen and in liquid hydrocyanic acid as solvents. It was found that liquid cyanogen has very little dissociating power. Liquid hydrocyanic acid has, on the contrary, very great dissociating power. Indeed, its dissociating power is greater than that of water itself. The case of hydrocyanic acid was a specially interesting one. It was

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[1] Zeit. anorg. Chem., **25,** 209 (1900); **29,** 371 (1902).

[2] Zeit. phys. Chem., **39,** 217 (1902).

pointed out first by Sir J. J. Thomson, that the dissociating power of liquids should stand in the same order as their dielectric constants, or specific inductive capacities. When it was shown that liquid hydrocyanic acid had greater dissociating power than water, the question arose, What about the value of its dielectric constant? This was determined and found to be about 95; the dielectric constant of water, under the same conditions, being about 78. The case of liquid hydrocyanic acid, instead of being an exception to the above deduction from the theory of electrolytic dissociation, fell right in line with that conclusion.

Abnormal Electrolytes. — Walden[1] found some very remarkable results in certain inorganic solvents such as sulphur dioxide and arsenic trichloride. When certain substances which are neither acids, bases, nor salts are dissolved in these solvents they show marked conductivity. The substances in question are; tin, sulphur, phosphorus, arsenic, antimony, chlorine, bromine, and iodine. These Walden called "abnormal electrolytes."

They are certainly "abnormal," for it is very difficult to see how they could break down into cations and anions in the presence of a liquid solvent, being themselves elementary. About the way in which such elements dissociate in solution, we know at present practically nothing.

Organic Solvents. — Walden, after having studied more inorganic solvents than all other investigators,

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[1] Zeit. phys. Chem., **43**, 385 (1903).

discovered by the Italians Galvani, and Volta, about one hundred years before that time. It was discovered quite one hundred years before its action was fully understood. Much that had been written about the primary cell was little more than words. When Nernst took up the problem, there was still a difference in opinion among physicists as to what is the chief source of the electromotive force in primary cells. There are three possibilities. It might be at the contact of the two metal electrodes with one another. It might be at the contact of the two electrolytes with one another, or it might be at the surfaces of contact of the two electrodes with the two electrolytes.

Some held that the chief source of the electromotive force was at the surface of contact of the two metals; others, that it was at the contact of the two electrolytes; and others still, that the seat of the energy was the contact of the electrodes with the electrolytes.

Some light on the action of the primary cell as a whole was thrown by Willard Gibbs in this country, and later by Helmholtz in Germany, from their thermodynamic investigations, as has already been mentioned. Neither of them, however, was able to take the primary cell to pieces, as it were, and determine just how much of the electromotive force came from one place, and just how much from another. This was left for Nernst, and was made possible by the generalizations which had already been discovered by Van't Hoff and Arrhenius.

This work of Nernst is so technical and mathematical, that it is impossible to go into it in any detail in this little book.[1] The best that can be done here is to give some idea of how he attacked the problem, and the fundamental principles of which he made use.

A primary cell may be regarded as two metals, each surrounded by an aqueous solution of one of its own salts; the two metals being connected, and the two solutions connected by a siphon filled with one of the solutions.

Solution-tensions of the Metals. — Given a bar of metal, say zinc, surrounded by an aqueous solution of some zinc salt. There are, according to Nernst, two forces operative at the surface of the zinc. The osmotic pressure of the zinc ions in the solution, tending to drive the zinc out of solution on to the bar, and a force which Nernst calls the solution-tension of the metal, which tends to drive the metal ions off of the bar into the solution. These two forces oppose one another.

When the metal throws ions into the solution it becomes charged negatively, since the metal ions always carry a positive charge of electricity. When metal ions separate from the solution on to the bar of metal, they give up their positive charges to the bar, and the metal electrode thus becomes charged positively.

Whether a bar of metal loses or receives ions

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[1] For a discussion of this work see my "Elements of Physical Chemistry," 4th ed., pp. 446–475 (Macmillan's, N.Y.).

depends upon whether the solution-tension is, or is not, great enough to overcome the counter force—the osmotic pressure of the metal ions in the solution. In constructing a primary cell we must, therefore, choose one metal with a very high solution-tension, like zinc; and another metal with a very low solution-tension, like copper. The zinc in such a cell is, then, always negative; because it loses cations to the solution of zinc salt. The copper is always positive because it receives cations from the solution of the copper salt. The result is, that in such a cell, which is nothing but a Daniell cell, if we use zinc sulphate around the zinc bar and copper sulphate around the copper bar, the current always flows on the outside from the copper to the zinc.

It is not possible, within the scope of this work, to discuss in any detail this investigation by Nernst, as already stated. It may be said that the problem of the simpler forms of primary cells was solved by Nernst. The chief source of the electromotive force is at the surfaces of contact of the electrodes with the electrolytes. There is a small source of electromotive force at the contact of the two electrolytes with one another; and when two different metals are used as the electrodes, where these come in contact there is another small source of electromotive force. The magnitude of each of these, for any given cell, was carefully worked out.

This method of attacking the problem of the primary cell is limited to those cells whose electrodes

precipitated. The salt that is precipitated is pure, and this is the very best method of purifying a salt like sodium chloride. Nernst showed what the meaning of this process is, and then went much farther. He[1] used the method of the change in the solubility of a salt produced by adding another salt with a common ion, to measure the dissociation of the second salt. Extensive experimental application of this method has been made by A. A. Noyes[2], who has subsequently cast some doubt on the rigidity of the so-called solubility principle.

Thermodynamics. — It is impossible to say at present how extensive and serviceable applications can be made to chemistry of the recent thermodynamic relations pointed out by Nernst. They seem to have theoretical justification, but do not appear to hold when applied to the facts of experiment. His work, dealing with the specific heats of substances at low temperatures, is certainly interesting.

Electrochemical Investigations of Le Blanc. — The whole subject of electrochemistry has come very much to the front in the last decade or two. Indeed, twenty-five years ago we hardly knew what was meant by the subject of electrochemistry. A few electrolytic separations of the metals were made in an empirical way, without knowing why the various steps were taken, or what were the underlying principles involved. Electrometallurgy was then almost unheard of, and the electrosynthesis of

[1] Zeit. phys. Chem., **4**, 372 (1889); **26**, 152 (1898).

[2] *Ibid.*, **6**, 241 (1890); **9**, 603 (1892); **16**, 125 (1895).

compounds not even dreamed of. Quantitative analysis is now largely changed, as far as the determinations of the metals are concerned. Electrometallurgy is a new industry, and electrosynthesis very much to the front in the chemical industries.

What has brought about such a revolution in the condition of things in the short period of a quarter of a century? No one piece of work has contributed more in this direction than the investigation of Le Blanc now about to be discussed.

Decomposition Values of Ions. — All cations carry a positive charge, and all anions a negative charge. While all of the cations carry a positive charge, they do not all carry the same amount of positive electricity. Faraday's law, as we have seen, tells us that univalent ions carry one positive charge, bivalent ions two positive charges, etc.

Further, and this is the important point in the present connection, ions of the same valence do not hold their charge or charges with the same firmness. Indeed, every ion holds its charge with a degree of firmness which is characteristic of the ion in question. Thus, potassium holds its charge with a different degree of firmness, as we say, from calcium, which, in turn, is different from zinc, and so on.

The problem which Le Blanc solved, while working in Ostwald's laboratory, was what voltage is required to discharge the charge from the various ions. He[1] solved this problem by seeing what was the smallest voltage that would just cause a con-

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[1] Zeit. phys. Chem., **8**, 299 (1891).

tinuous current to flow through the solution of the electrolyte. He worked out the *decomposition values* of the ions, as he termed the values found; and these values had significance in more directions than could possibly have been foreseen.

Decomposition Values and the Theory of Electrolysis. — One of the first results of Le Blanc's work on decomposition values, was to overthrow the erroneous theory of electrolysis which had held sway for more than a half-century. This old theory of electrolysis was the outcome of the Clausius theory, to which reference has already been made. Take the electrolysis of an acid. What took place? Hydrogen was liberated at one pole and oxygen at the other. Where did these gases come from?

Older Theory of Electrolysis. — The hydrogen ions from the acid moved over to the cathode, gave up their charges, and escaped as hydrogen gas. The anion of the acid moved over to the anode, gave up its charge and not being volatile could not escape. Take nitric acid; the $\overline{NO_3}$ anion moved over to the anode, gave up its charge, and then "acted on" water, reforming nitric acid and liberating the oxygen from the water.

Take the case of a base. What took place in the electrolysis of say potassium hydroxide? The hydroxyl ions moved over to the anode, gave up their charge, and then the two hydroxyl groups reacted with one another forming a molecule of water and liberating oxygen gas which escaped. The potassium cation moved over to the cathode, gave up its

ion from the dissociated water; and then makes the metallic potassium go over and "act on" water; which means take the charge from the hydrogen ion that came from the water, and which must hold its charge more firmly than the potassium, otherwise the hydrogen and not the potassium would have given up its charge originally. The old theory thus leads to an absurdity at the cathode.

Take the condition around the anode. What happens? The $\bar{NO}_3$ goes over to the anode, and finds there hydroxyl ions from the dissociated water. Which will give up its charge? Obviously the one that holds its charge less firmly. The old theory says the $\bar{NO}_3$ gives up its charge. The $\bar{NO}_3$ must, therefore, hold its charge less firmly than hydroxyl. After the $\bar{NO}_3$ has discharged, then the old theory has it "acting on" water. What does this mean? It means that it takes the charge from the hydroxyl ions from the dissociated water. But the hydroxyl ions must hold their charge more firmly than $\bar{NO}_3$; otherwise hydroxyl and not $\bar{NO}_3$ would have given up its charge originally. This old theory thus leads to an absurdity also around the anode.

The old theory of electrolysis, which is still retained in certain places as a satisfactory explanation of the facts, thus leads to an absurdity as to what takes place around the cathode; and to an equal absurdity as to what takes place around the anode, and, therefore, must be rejected as entirely untenable.

It is one thing to show that the old theory of electrolysis is untenable, and another to show what is the correct theory of electrolysis. The work of Le Blanc does this in a most convincing manner, and this is why this work and electrolysis are taken up together in this place.

New Theory of Electrolysis. — The present theory of electrolysis will be stated first, and then the results obtained by Le Blanc given, in so far as they bear on the theory.

Take the electrolysis of an acid. What takes place? The hydrogen ions from the acid go over to the cathode and find there hydrogen ions from the dissociated water. Both give up their charge; it being impossible to say whether it is the hydrogen from the water or from the acid which loses its charge first, since all ions of a given kind, say hydrogen, are supposed to hold their charge with equal firmness. At the anode, the anions, say $N\overline{O}_3$, find the hydroxyl anions from the dissociated water. The hydroxyl, and not the $N\overline{O}_3$, gives up its charge. The $N\overline{O}_3$ simply remains around the anode, paired off against the hydrogen cations which came from the same molecules of water as the hydroxyl which discharged their charge to this pole and then reacted with one another, forming water and liberating oxygen.

In terms of this theory, the electrolysis of an aqueous solution of an acid is nothing but the electrolysis of the ions of water, *i.e.*, hydrogen and hydroxyl; the concentration of the hydrogen ions being essentially those of the acid in question, and the concentration of the hydroxyl ions being that which exists in water due to its dissociation. If we use solutions of different acids having the same concentrations of hydrogen ions, then, in terms of this theory, their decomposition values ought to be the same; since it is simply the decomposition of hydrogen ions around the cathode and hydroxyl ions around the anode, of certain definite concentrations.

Decomposition Values and the Electrolysis of an Acid. — We shall now see how the decomposition values found by Le Blanc confirm the above deduction from theory. Using normal solutions of strong acids, which contain in a given volume hydrogen ion concentration of the same order of magnitude, he found the following decomposition values.[1]

Acid	*Decomposition Value*
Sulphuric	1.67 volts
Nitric	1.69 "
Phosphoric	1.70 "
Monochloracetic	1.72 '
Dichloracetic	1.66 '

The constant decomposition values for acids is thus in keeping with the present theory of the electrolysis of acids.

Take the electrolysis of bases. What takes place? The hydroxyl ions from the dissociated base move over to the anode. They find there hydroxyl ions from the dissociated water; and it is impossible to say which hydroxyl ions lose their charge. Probably all of them do; but since there are so many

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[1] Zeit. phys. Chem., 8, 315 (1891).

Another relation comes out when we compare the decomposition values of acids and bases. For the same concentrations each is, as we have seen, a constant. More remarkable, however, is the fact that they are the *same constant.* How do we explain this? Very easily. A normal solution of a strong acid contains just as many hydrogen ions as a normal solution of a strong base contains hydroxyl ions. The decomposition value is proportional to the product of the number of hydroxyl ions present times the number of hydrogen ions. In the case of the normal solutions of the strong acids and bases named above, this product is a constant for every acid and every base, and, therefore, the acids and bases have the same decomposition values.

Take the electrolysis of a salt such as potassium nitrate. The potassium cation moves over to the cathode, and finds there hydrogen ions from the dissociated water. The hydrogen ion, holding its charge less firmly than the potassium, gives it up. The potassium remains paired off against the hydroxyl that came from the same molecule of water as the hydrogen which escaped. At the anode the $\overline{NO}_3$ ions find the hydroxyl ions from the dissociated water. The hydroxyls, holding their charges less firmly, give them up, form water and oxygen which escapes. The $\overline{NO}_3$ remains paired off against the hydrogen that came from the same molecules of water as the hydroxyls which have discharged.

Decomposition Values and the Electrolysis of Salts. — If this conception of what takes place in the electrolysis of a salt is correct, then the decomposition value of a salt is the voltage required to discharge hydrogen ions at the concentration at which they exist in an aqueous solution of a salt of given concentration; and of the hydroxyl ions at the concentration at which they exist in the aqueous solution of the salt. In the electrolysis of a salt the hydroxyl ions are continually increasing in numbers around the cathode, and this drives back the dissociation of the water around this pole; it being a general principle that the presence of a common ion drives back the dissociation which yields this ion. When water dissociates it yields hydroxyl ions. The presence of hydroxyl ions around the cathode, therefore, diminishes the dissociation of water which yields the hydroxyl ions.

In a similar manner the hydrogen ions collect around the anode, and this drives back around this pole the dissociation of the water which yields also hydrogen ions. The result is a diminution in the number of hydrogen ions around the cathode, and of hydroxyl ions around the anode, and a consequent increase in the decomposition value of the salt.

The experimental results obtained by Le Blanc showed larger decomposition values for salts[1] than for acids or bases.

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[1] Zeit. phys. Chem., 8, 311 (1891).

Salt	*Decomposition Value*
Ammonium nitrate	2.08 volts
Sodium nitrate	2.15 “
Sodium sulphate	2.21 “
Potassium nitrate	2.17 ‘
Potassium sulphate	2.20 ‘
Calcium chloride	1.89 ‘
Calcium nitrate	2.11 ‘
Strontium chloride	2.01 ‘
Strontium nitrate	2.28 ‘
Barium chloride	1.99 ‘
Barium nitrate	2.25 “

The experimental results thus confirm the conclusion from the theory of electrolysis that we hold today.

The essential difference between the old theory of electrolysis which we must now discard, and the new theory is, that the former represents the decomposition of water as a secondary act. The water is not decomposed directly by the current, but indirectly by the products of the electrolysis. Thus, potassium ions give up their charge and then “act on” water.

Primary and Secondary Decomposition of Water in Electrolysis.—The new theory of electrolysis represents the decomposition of the water as a primary act of the current. It is the hydrogen and hydroxyl ions of the water that are themselves discharged directly by the current.

If it is the water which is decomposed directly by the current, then the question arises, Why add an acid, base, or salt to it in electrolysis? We add

Blanc bore on more questions than simply the nature of electrolysis. He showed that every given ion requires to discharge it a definite voltage, which is characteristic of the ion in question. Suppose we have mixtures of several kinds of cations — mixtures of several salts; by suitably choosing the voltage we can effect quantitative separations of these substances from one another. The result has been a fundamental change in the methods of quantitative analysis of the metals within the last twenty years. We now effect electrolytic separations of nearly any metal from any other metal by means of the current, by suitably choosing the voltage and amperage. We owe this application of the differences in the decomposition values to Classen in Europe and especially to Edgar F. Smith in this country. We can gain a fair conception of the number of separations that can thus be effected by consulting the works of Classen [1] and of Smith,[2] that deal with this subject.

Work of Georg Bredig on Colloidal Suspensions. — The question of colloids and colloidal chemistry has come very much to the front in the last few years. While the scope of this book will not allow any detailed discussion of this subject, yet a few of the leading investigations in this field will be considered.

Method of Making Colloidal Suspensions of the Metals. — Bredig devised a method for preparing

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[1] Quantitative Chemical Analysis by Electrolysis.

[2] Electrochemical Analysis.

colloidal solutions or suspensions of the metals, which has proved to be a general one as far as the most insoluble metals are concerned.[1] This method consisted in taking two bars of the metal in question, bringing them near together under water, and passing an electric discharge between the bars under the water. The metal in question is torn off under these conditions in a finely divided state, and remains suspended in the water as a colloidal suspension. The liquid is wine-colored, and when seen under a strong microscope looks perfectly homogeneous. By this method colloidal suspensions of platinum, iridium, gold, silver cadmium, and nearly all of the metals that do not act on water, have been prepared.

Colloidal Suspensions of the Metals are Catalyzers. — The colloidal suspensions of the metals were found to have very remarkable properties. They were found to be excellent catalyzers, and to effect many of the same reactions that are brought about by the organic enzymes. Thus, finely divided platinum will oxidize alcohol to acetic acid in the presence of the oxygen of the air, just as the ferment *mycoderma aceti* will do. Oxalic acid is broken down by finely divided metals, just as it is by yeast. These finely divided metals invert cane sugar just like the organic ferments. The reaction which was studied most thoroughly from the standpoint of the analogy between the action of colloidal suspensions of the metals and organic enzymes, was the decomposition

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[1] Zeit. phys. Chem., **31**, 258 (1899).

of hydrogen dioxide. This substance is decomposed by all of the finely divided metals, and also by all of the organic ferments. It is an especially good reaction to study from this standpoint, because the velocity of the decomposition can be so readily measured.

That the metals decompose this substance catalytically is shown by the fact that the reaction is, as we say, of the first order; that is, the metal does not enter into the reaction at all, only the mass of the hydrogen dioxide present undergoing change.

The analogy between the action of the finely divided metals and the organic enzymes is strikingly illustrated by the behavior of poisons on the two. The same substances which poison the ferments and which retard the rate at which they decompose hydrogen dioxide, also "poison" the platinum and retard the rate at which it effects the same decomposition. Thus, mercuric chloride and hydrocyanic acid, in the merest traces, poison the organic enzymes. The same quantities produce almost exactly the same effect on the finely divided metals, with respect to their power to decompose hydrogen dioxide. A few examples will be given.[1]

Poison	Effect on the Decomposition of H_2O_2 by Blood	Effect on the Decomposition of H_2O_2 by Platinum
Hydrogen sulphide	No catalysis at all	Action much retarded
Mercuric chloride	Practically no catalysis	" " "
Hydrocyanic acid	Action much retarded	" " "
Hydroxylamine	No catalysis	" " "
Amylnitrite	Much weakened	" " "

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[1] Zeit. phys. Chem. **37**, 66 (1901).

addition of non-electrolytes will fail to precipitate the arsenic sulphide.

These facts are of nothing less than fundamental importance for the whole science of chemistry. In order to have precipitates formed we must, then, have ions present. This fact has a certain kind of interest of its own, but becomes incomparably more interesting when we know why this is the case. The explanation of this fact we owe to Burton[1] working in the laboratory of Sir J. J. Thomson.

Why Ions are Necessary for Precipitation.— Before we can understand the answer to the above question we must recognize the following fact. If two electrodes are placed in any colloidal suspension and a current passed, the colloidally suspended particles will all move either to the one pole or to the other. This shows that the colloidally suspended particles are charged electrically; and since all of the particles of any given colloid move to the same pole, it shows that all of the particles of any given colloid carry the same kind of a charge. The colloidal particles are, then, all charged positively, or are all charged negatively. How does this prevent them from precipitating?

What is the electrostatic action of like charges of electricity? They repel one another. These like charges upon the colloidal particles repel one another, and prevent the colloidal particles from being drawn together and from forming a precipitate.

What is the effect of adding ions? Take a col-

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[1] Phil. Mag., **12,** 472, (1906).

loidal particle all of whose parts are charged, we will say, positively. This means that the water around them is charged negatively. Add an electrolyte to such a system. This means that we add both cations and anions. The anions, or negatively charged bodies, equalize the positive charges upon the colloidal particles; and the cations, or positively charged ions, are paired off against the negative charges on the water. The result is that the charges upon the colloidally suspended particles are equalized, and these particles are as if they were not charged.

Surface-tension between the particles and the water round about now gets in its full force. The action of surface-tension is always to cause the object to have the largest volume for the smallest surface. It thus draws the colloidal particles together into larger masses, which diminishes their surface and a precipitate is formed.

P*recipitation not the Natural Condition in Chemistry.* — Precipitation is one of the most important phenomena in all chemistry, and we are so familiar with precipitation from our analytical days, that we are accustomed to look upon it as the natural condition when a solid is formed as the result of a reaction between two solutions. We see from the above that such is not at all the case. A moment's thought will show why this is true. When substances react, they react, we believe, molecule for molecule. The solid when first formed either has molecular dimensions, or there are only a few molecules of the solid aggregated. The colloidal solution, or at most the colloidal suspension, is the natural condition of solid matter when first formed as the result of a reaction.

The question then arises, how does this solid matter come together and form solid chunks which can be filtered off as in qualitative and quantitative analysis? The work above referred to answers this question and answers it for the first time satisfactorily.

Colloidal Solution and Colloidal Suspension.—We have used the term colloidal solution and also the term colloidal suspension. What is the difference between the two? It is apparently a difference in the coarse-grainedness of the substances in question. If the substance is very finely divided in the presence of the solvent we have a colloidal solution. If it is in a coarser state of aggregation we have a colloidal suspension, and a still coarser condition is a simple mechanical suspension.

A few years ago we knew only solutions and mechanical suspensions. Now we have every stage represented, from true solutions which lower the freezing-point and lower the vapor-tension of the solvent in terms of Raoult's laws; and which exert osmotic pressures that obey the gas laws. We have colloidal solutions in which the particles are apparently much more coarse-grained, which show some of these properties to a slight extent; then the colloidal suspensions, some of which are sufficiently coarse-grained to be seen under a powerful micro-

Method of Ramsay. — Ramsay's method was based on the surface-tensions of liquids and the change in the surface-tension with temperature. He was able to show what liquids are associated and what are not associated; and for the associated liquids to calculate the degree of their association at the different temperatures. Water was found to be one of the most associated of liquids, having at ordinary temperatures the formula $(H_2O)_4$. Water, it will be remembered, is the best dissociating of all of the more common liquids. This raises the question as to whether there is any connection between the dissociating power of liquids and their own association. That there is such a general relation was shown by Dutoit.[1] Other things being equal, the more associated a liquid the greater its power to dissociate the molecules of electrolytes dissolved in it. One of these properties is not proportional to the other, yet there is the general relation between the two. This is one of the reasons why it is so important to determine the molecular weights of pure, homogeneous liquids.

Method of Longinescu. — The method of Longinescu[2] is delightfully simple. He found the following relation to hold:

$$\frac{T}{T'} = \frac{d}{d'}\sqrt{\frac{n}{n'}}$$

in which T is the absolute temperature at which one

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[1] Compt. Rend., **125,** 240 (1897).

[2] Journ. Chim. Phys., **1,** 289 (1903).

of the liquids boils, T' the absolute temperature at which the other liquid boils; d and d' are the densities of the two liquids in question at zero, and n and n' the numbers of atoms in the molecules of the two liquids. If we take some simple, unassociated liquid, for which T, d, and n are known, we determine T' and d' and from these data calculate n', which is the quantity desired; since, knowing the number of atoms in the molecule, and the simplest chemical formula, we know at once the degree of association.

Guye[1] shows that the "molecular refraction" is proportional to the true molecular volume of a supposedly spherical molecule.

A constant times the molecular refraction he calls the "critical coefficient." "The critical coefficient of a substance is equal to the sum of the critical coefficients of the atoms which form its molecule, increased in certain cases by a coefficient which depends on the nature of the unions between the atoms."

This enabled Guye to determine the molecular weights of liquids at their critical point. Knowing the critical coefficients of the various atoms within the molecule in question, and determining the critical coefficient of the compound, he could calculate at once the association of the molecule.

Work of Haber. — One of the most original workers today in the field of physical or general chemistry is F. Haber, formerly of Karlsruhe, now at the Kaiser

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[1] Ann. Chim. Phys. [6] **21,** 206, 211 (1890).

Wilhelm Institute in Dahlen near Berlin. Haber's work has had to do largely with the reactions of gases both from the experimental and thermodynamical standpoints. We have already referred to Haber's method for the fixation of nitrogen, which, it will be remembered, consists in the union of hydrogen and nitrogen under pressure, at an elevated temperature, in the presence of a catalyzer. This investigation by Haber, the results of which can be so easily summarized in one concise statement, is one of the most scientific and interesting in the last few years. An account of it has recently been published by Haber and Rossignol.[1] The thoroughly up-to-date and scientific method which was employed throughout this work, makes it in a sense a model of what a research should be. Thoroughness, both in the theoretical treatment and experimental verification of deductions from thermodynamics, is its most striking characteristic. The Kaiser Wilhelm Institute with Haber, Beckmann, and Willstätter, will, in the future, probably be one of the most active and productive chemical institutions in the world.

Solid Solutions. — The work that has been done on the subject of *solid solutions* must be mentioned. We heard very little about solid solutions until Van't Hoff published his now well-known paper on this subject in 1890.[2] Van't Hoff showed in this paper that certain mixtures of solids have all the

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[1] Zeit. f. Elektrochem., **19**, 53 (1913).

[2] Zeit. phys. Chem., **5**, 322 (1890).

Ciamician[1] and his coworkers. They have shown that single ring compounds can form solid solutions only with other single ring compounds. Thus, benzene can form solid solutions only with such compounds as; thiophene, pyrrol, pyridine, etc.; napthalene only with indol, quinoline, etc.; phenanthrene with anthracene, carbazol, etc. This work is most highly significant in connection with the real meaning of constitutional formulae as chemists have used them. It here finds expression in the power of substances to form solid solutions with one another.

Excellent work has been done in many directions by a large number of investigators in Holland. We should refer especially to the work of Cohen, on the allotropic modifications of the elements. The work of the Russians has been as varied as it is valuable in the recent developments of general chemistry. The investigations of the French, Scotch, and English, especially Ramsay, Walker, and Donnan, have contributed greatly to the building up of a science of general chemistry. We should not be unmindful of the investigations that are being carried out in Norway, Sweden, Austria, and Italy, many of which have played a prominent rôle in connection with the recent developments.

Our own countrymen have turned to physical or general chemistry from the very beginning of the modern developments. Their influence has been felt in nearly every direction, and their investigations should be discussed at length individually, did

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[1] Zeit. phys. Chem., **13**, 1 (1894); **18**, 51 (1895); **44**, 505 (1903).

the scope of this little book permit, but unfortunately it does not.

We must, however, mention especially the work of A. A. Noyes and of T. W. Richards.

The Work of A. A. Noyes has been continued almost from the beginning of the period we have referred to as the "New era" up to the present.

His first important investigation was in cooperation with Nernst in Ostwald's laboratory, on the solubility of salts with reference to the measurement of their dissociation. This has already been referred to under the work of Nernst. Some of his most recent investigations have been along solubility lines, but from a somewhat different standpoint.

Free Ions in Solution. — One of the most interesting investigations that has come from the laboratory of Noyes, had to do with the demonstration of the existence of free ions in solution. Lobry de Bruyn[1] had shown that when a saturated solution of a salt is centrifugalized, the salt, being heavier than the solvent, is thrown to the outside of the centrifuge and a part of it is precipitated.

Noyes reasoned that if a dissociated salt is subjected to rapid whirling in a centrifuge, the heavier ion should be thrown to the outside, and a partial separation of the ions in the solution thus effected. This separation should manifest itself in an electromotive force, or potential difference between the outside and inside of the centrifuge, the outside having the sign of the heavier ion.

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[1] Rec. Trav. Chim. Pays-Bas., **23**, 218 (1904).

He had constructed a very powerful centrifuge, consisting of a tube some two feet in length, which he could whirl very rapidly. He was able to produce differences in potential of a good number of millivolts, and the outside always had the sign of the heavier ion, just as was predicted.

Conductivities at Higher Temperatures.—One of the most important investigations that Noyes has carried out, is on the conductivities of aqueous solutions of electrolytes up to the critical temperature of water. This was done in closed steel bombs, lined on the inside with platinum, into which insulated electrodes were inserted.

He found that the conductivities increased rapidly with rise in temperature, acquiring very great values at high temperatures. Thus, a solution of potassium sulphate, which at 18° had a molecular conductivity of 133, at 218° had a molecular conductivity of 1065, and at 306°, a conductivity of 1725; and similar increases were observed with all of the electrolytes studied.

One other result was obtained at elevated temperatures with the conductivity bomb, which must be mentioned.

Hydrolysis at High Temperatures. — Salts of weak acids or bases, are, as we say, hydrolyzed by water at ordinary temperatures. This means that they are broken down by the water into the free acid and the free base. This hydrolysis, Noyes showed, increased very rapidly with rise in temperature. So rapid was the increase in the hydrolysis with

provided. The skill that he has displayed in the direction of the so-called third decimal is not exceeded, if it is equalled, by any one living today.

The work of Richards on amalgams, from both the theoretical and experimental standpoints, is of great value and importance.

Richards has, however, not limited his activities to the most refined experimental work. He has shown great ability and skill in dealing with scientific problems from the theoretical side. His work, both theoretical and experimental, in connection with the effect of pressure on the atoms is widely known, and well deserves to be. He has made it highly probable that the atom is compressible, and the significance of this is far reaching. Much of the work of Noyes and Richards has been done with the aid of grants from the Carnegie Institution of Washington.

CHAPTER XII

THE ELECTRON AND RADIOCHEMISTRY

Earlier View of the Atom. — The atom was regarded as the ultimate chemical unit, prior to the beginning of the time that we have designated the "New Era." Indeed, it was made so by definition. An atom of any given element was the smallest part of that element that ever entered into chemical combination. An elementary atom was something that could not be transformed into anything else, and from which nothing else could be obtained.

This state of mind was perfectly natural, since at that time there was not the slightest reason for supposing that anything simpler than the atom could be obtained from the atom. This is now all changed, as we shall see.

The Electron. — The English physicist, Sir J. J. Thomson, showed that an isolated electrical charge, moving with high velocity through a perfectly elastic medium, such as the ether, could have both mass and inertia; *i.e.*, could have those very properties that we are accustomed to ascribe to matter.

The isolation of this electron, and the study of its properties, we owe also to Sir J. J. Thomson. Let us now study this work of Thomson in some detail.

The simplest condition of matter, and the one about which we really know something, is the gaseous. A gas represents matter in the most dilute state, and, further, matter in the gaseous state conforms to the rigid laws of mathematics, as is shown by thermodynamics.

Thomson turned his study to gases, and dilute gases at that. He investigated the transmission of electricity through very dilute gases. It is well known that electricity can readily be passed through a so-called vacuum tube, *i.e.*, through a tube filled with a very dilute gas. Under these conditions there were given off from the cathode very small particles, known as cathode particles, which fly over to the anode. The question is, What are these particles? Are they molecules or atoms? According to the view then prevailing they could not be smaller than atoms, since nothing smaller than atoms could exist.

Thomson worked out a method[1] for determining the ratio of the charge e, carried by these particles to their mass m. That is, he experimentally determined the value of $\frac{e}{m}$.

Constancy of the Ratio $\frac{e}{m}$. — The first point of interest and importance brought out by Thomson, was that the ratio $\frac{e}{m}$ is constant for the cathode particle, no matter from what gas it was split off. This was obviously a very remarkable fact. It

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[1] See the Author's "Electrical Nature of Matter and Radioactivity," 2d ed. (D. Van Nostrand Co.).

as being incapable of yielding anything else. It was obvious that the definition would have to be revised.

The Cathode Particle. — The question still remains, what is this cathode particle — this common constituent obtained from all gases? What is its mass as compared with the mass of the atoms?

The experiments referred to above not only led Thomson to conclude that the mass of the cathode particle is constant, regardless of the source of that particle; but led him also to the actual mass of this particle relative to the mass of the lightest atom, which is the atom of hydrogen.

What is the Corpuscle? — He showed that the mass of the cathode particle is only about $\frac{1}{1800}$ of the mass of the hydrogen atom. In a word, by means of the electrical discharge there had been split off from the hydrogen atom, and from the atoms of other elementary and compound gases, something which had a mass that was only $\frac{1}{1800}$ of that of the lightest atom. The question still remained, What is this subatomic particle? It carried an electrical charge. It must, therefore, contain energy — electrical energy. What else did it contain? It had mass and inertia, and the conclusions of Thomson and Lorentz, that an electrical charge alone can, under certain conditions, have mass and inertia, were not then fully understood and appreciated. It was generally supposed at that time that only matter can have mass and inertia. This cathode particle must then be a small piece of matter, only a small fraction of an atom, which had the mass and inertia, and attached to this was a charge of negative electricity.

This cathode particle, or *corpuscle* as it was termed, was, then, both matter and energy.

Thomson had shown, as has been stated, that isolated electrical charges moving with high velocities can themselves have mass and inertia. The cathode particles or corpuscles moved with very high velocities. Thomson had measured these velocities, and had shown that the corpuscle moves about one-tenth as fast as light. The electrical charge on the corpuscle, moving with this velocity, would have some mass and some inertia. The question now is, How much? How much of the total mass and inertia of the corpuscle is due to the electrical charge present, and how much to the matter? This was the question which Thomson now took up and solved.

Mass and Inertia due to the Electrical Charge.— If *all* of the mass of the corpuscle were due to the moving electrical charge, then, it is a simple matter to calculate how much the mass of the corpuscle would increase for a given increase in the velocity of the corpuscle. The actual increase in the mass of a corpuscle for a given increase in its velocity was then measured by Thomson in the following way. The B rays shot off by radium are really nothing but corpuscles, as we shall see. These are shot off from the radium with very different velocities. Kaufmann determined the masses of these B particles moving with different velocities, and Thomson found that the more rapidly moving particles had the greater masses. The increase in the mass with increase in velocity was exactly what would be calculated on the assumption that *all* of the mass of the corpuscle was of electrical origin. The agreement between the calculated values and those found experimentally, then, argued in favor of the assumption on which the calculation was based. In a word, *all* of the mass of the corpuscle was of electrical origin.

If all of the mass of the corpuscle is due to the electrical charge that is present, then, why assume that there is anything else in the corpuscle except the electrical charge? We know things by their properties, and only by their properties. If *all* of the properties of the corpuscle are accounted for by the electrical charge which we know is present, why assume that there is anything else present? There is, of course, no reason for doing so.

Electron. — The corpuscle is then nothing but an isolated, negative charge of electricity. This we now call the electron. The consequences of this conclusion are most fundamental and wide-reaching. The electron was obtained from all gases, elementary and compound. It is, therefore, the common constituent of all things and the only common constituent known. But the electron is an isolated negative charge of electricity. The isolated, negative electrical charge is, then, the fundamental unit of which all so-called matter is made. The ulti-

A number of attempts have already been made to isolate the positive electrons, corresponding to the negative electrons. It is doubtful whether any of these attempts can thus far be regarded as successful. The "granular" nature of negative electricity has been demonstrated in the discovery of the negative electron, or electron as it is termed. It seems highly probable that positive electricity is also granular or atomic, as we say, but it has not yet been proved. We, therefore, say that the electrons are distributed in a field of uniform positive electrification, which simply means that we have not thus far discovered the heterogeneous nature of positive electricity.

The Atom in Terms of the Electron Theory. — The atom, in terms of the electron theory of matter is, then, made up of a large number of electrons distributed in a field of uniform positive electrification. These electrons are arranged in a definite system within any given atom, and are moving in definite orbits and with very high velocities within the atom. The chemical atom has been likened to the solar system, within which the electrons play about the same rôle as the planets. The interelectronic spaces are very large compared with the spaces occupied by the electrons themselves; just as the interplanetary spaces are very large as compared with the spaces occupied by the planets.

It should be pointed out, that Thomson does not at present seem to think it proved that the number of electrons in the atom is equal to the atomic weight of the atom in terms of hydrogen as unity, multiplied by 1800. Indeed, he seems inclined to the view that there is only a comparatively small number of electrons in the atom.

Others have, however, suggested that the methods used are capable of demonstrating the existence of only those electrons which are in the more unstable positions. They think that most of the electrons within the atom cannot be detected by the present methods.

Rowland's Conception of the Atom. — The chemical atom, which was hitherto regarded as simple, as an ultimate unit, is now known to be very complex, and this suggests a statement which I heard Rowland make a good many years ago. Long before we had any suspicion that the ultimate unit of which all matter is made was electricity, I heard Rowland reason as follows. He said the chemists say that the molecule of mercury in mercury vapor is monatomic, *i.e.*, there is but one atom in the molecule. If this is true, then the atom of mercury itself must be at least as complex as a piano. The atom of mercury gives out a large number of spectral lines, *i.e.*, sets the ether vibrating in a large number of wave lengths at the same time. This to Rowland was inconceivable in an ultimate unit. The vibrator or resonator must be complex to set up simultaneously so many vibrations in the ether.

This was at a time when practically every chemist regarded the atom as a simple unit, which could not be decomposed into anything else, and could not be made from anything else. Now we find Rowland's conclusion verified both theoretically and experimentally. This illustrates the definition of genius as the type of mind which has an insight into phenomena, and a foresight of phenomena, not possessed by ordinary minds, for Rowland was a genius.

The Electron Theory and Electrolytic Dissociation. — A few applications of the electron theory to the facts of chemistry will be made just to show how it explains phenomena hitherto entirely not understood. Take the simple reaction that is involved when molecules of electrolytes are dissolved in a dissociating solvent such as water. We have known for a long while that the molecules are broken down into charged parts or ions, but we had absolutely no idea of how this took place — of the *modus operandi* of the process.

In terms of the electron theory it is perfectly simple. Take a salt like potassium chloride. When it is thrown into water an electron passes from the potassium over to the chlorine. The chlorine having received an additional electron thus becomes charged negatively, while the potassium having lost an electron becomes charged positively. If we are dealing with bivalent ions we have simply a transfer of two electrons. Take barium chloride. The barium loses two electrons, one to each of the chlorines; the latter becoming charged negatively, while the barium has, consequently, two positive charges upon it. Take, again, a salt like potassium sulphate.

probably affects the velocities of the electrons within the others. There is probably a slowing down of the electrons, which means a diminution in the intrinsic energy of the system. This loss in intrinsic energy is expressed by the heat, light, etc., which manifest themselves when the reaction takes place.

In endothermic reactions, where heat is converted into intrinsic energy, each atom must accelerate the velocities of the electrons within the others.

We can now deal with intrinsic energy in a rational and scientific manner.

The Electron Conception and the Periodic System.—Thomson showed how the electron theory can be used to account for such facts as are expressed by the periodic system of the elements. He calculated the number of electrons in the plane through the centre of atoms of the first and second groups of this system, and showed how the electron theory could account for the valences of these various atoms. It would lead us too far to discuss this in any detail.[1]

The most important application of the electron theory, all things considered, is to the facts of radiochemistry. The theory was proposed and worked out just before the facts of radiochemistry were discovered; and these facts could not possibly have been explained without this theory. More of this after some of the most important facts of radiochemistry have been considered.

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[1] Phil. Mag., **7**, 257 (1904).

RADIOCHEMISTRY

Discovery of the X-Ray. — In 1895 the announcement was made by Röntgen then at Würzburg, now in Munich, that he had discovered a new kind of radiation. This radiation had properties which differentiated it sharply from any other radiation known. In some respects it resembled light, and in others differed markedly from light. Its most distinctive property was its great power to penetrate objects that were opaque to light. It would penetrate sheets of the metals of considerable thickness, and other solid objects of very great thickness. It could not, according to its discoverer, be reflected, refracted, nor polarized. It was produced in a cathode discharge tube, where the cathode particles fall upon the walls of the tube, on the anode, or in general, upon solid matter. This was of course the discovery of the X-ray.

X-Rays and Phosphorescence. — These rays were shown to come from the spot on the glass on which the cathode rays impinged. This spot was always phosphorescent, and this is the important point in the present connection.

The X-rays were shown to be a set of irregular pulses sent out in the ether, and not a series of regular vibrations. This explains their great penetrating power.

The point where the X-rays strike the walls of the vacuum tube is always phosphorescent. This led at first to the assumption that there is some connection between the fluorescence and the origin of the X-rays. Indeed, Henri Becquerel[1] took up the study of naturally phosphorescent substances, to see whether any of them gave out a radiation analogous to the X-ray. The result, as is well known, was the discovery of the natural radioactivity of uranium, which was found to give off a radiation in some respects analogous to the X-rays; in other respects different from it.

Discovery of Radium.—This led Becquerel[2] to start Mme. Curie on an investigation of uranium ores, from the standpoint of their radioactivity. She soon found that certain ores of uranium were more radioactive than uranium itself; and these ores did not contain more than 60 per cent of uranium. There was only one conclusion to draw from this fact, and that was that these uranium ores contained something that was more radioactive than metallic uranium.

Mme. Curie then set about to isolate this radioactive constituent of pitchblende. The separation of radium from pitchblende by Mme. Curie is one of the most complex separations that has ever been effected. While it cannot be discussed here in any detail, it should be read in the original[3] paper by all chemists. The separation was, however, not quite as difficult as would at first sight appear. The way the radium went in any given

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[1] Compt. Rend., **122**, 501, 689, 762 (1896).

[2] A brief sketch of the life and work of Becquerel by Lodge has recently appeared. Journ. Chem. Soc., **102**, 2005 (1912).

[3] Ann. Chim. Phys. [7], **30**, 99 (1903).

is, therefore, the most rapidly moving particle of matter known to man. Moving with such enormous velocity, and having a mass which is four times that of the hydrogen atom, it has an enormous amount of kinetic energy.

The Spinthariscope. — This fact is utilized in an instrument called the *spinthariscope.* This consists of a screen covered with some phosphorescent substance like zinc sulphide, placed at a distance of a few millimeters from some radium chloride or bromide. The screen is seen through a lens. Where the alpha particles strike the phosphorescent screen, bright patches of light appear and quickly disappear; hence, the name of the instrument from "spintharis" a spark.

We thus see the result of the action of the individual alpha particles as they fall on the phosphorescent screen; each particle where it strikes producing a patch of light. Since these alpha particles are helium atoms, we probably see the action of individual helium atoms on the phosphorescent screen.

It is well known that when the radiations from radium pass through a gas, the gas is partly ionized. It is the alpha particles, having such a large amount of kinetic energy, which do most of the ionization of a gas. It is the alpha particles which affect a photographic plate, and, as we have seen, excite phosphorescence.

The alpha particles, on account of their large masses and sizes, have very little power to penetrate matter.

The Beta Particles. — The beta particles given off from radium carry a negative electrical charge, as shown by the way they are deflected in a magnetic field. Furthermore, they have been discharged and their charge shown to be negative. The mass of the beta particle is almost exactly the same as that of the cathode particle, = $\frac{1}{1800}$ that of the hydrogen atom. The average velocity of the beta particle is about one-half the velocity of light, varying, however, over a considerable range.

A comparison of all of the properties of the beta particle, with the corresponding properties of the cathode particle, shows that the two are practically identical. The beta particles are simply more rapidly moving cathode particles, and, consequently, have greater power to penetrate matter. The beta particles are, then, essentially electrons.

The Gamma Rays. — The gamma rays have great power to penetrate matter. They exist wherever the beta rays exist. They are not deflected in a magnetic field. A comparison of the properties of the gamma rays with those of the X-rays, shows that the gamma rays are essentially identical with the X-rays. The gamma rays have greater power to penetrate matter than the X-rays. They can penetrate, to some extent, a foot of solid steel.

Properties of Radium. — So much for the radiations that are given out by radium. A few of its other properties will now be considered. Radium salts are self-luminous. A pure radium salt can readily be seen in a dark room, giving out large quantities of light. A radium salt can also charge itself electrically, by the loss of the electrically charged radiations of one kind which it sends out.

The radiations from radium have the power of ionizing media through which they pass. This is true even of good dielectrics or non-conductors of electricity, such as pure liquids, and also such solids as paraffin. The radiation from radium can effect certain chemical reactions, and decompose the most stable of chemical compounds. When a pure radium salt is kept in a tube of sodium glass the glass soon becomes brown, due to the decomposition of the sodium silicate and the liberation of metallic sodium. When a radium salt is kept in a potassium glass tube, the glass becomes deep purple due to the liberation of metallic potassium.

The physiological action of the radiations from radium is well known. These disintegrate the tissues, and cause bad burns as was experienced by Becquerel and others. The disintegrating action on skin cancer and other skin affections has made it probable that radium has value as a curative agent.

Heat Energy Produced by Radium. — One of the most remarkable properties of the element radium is that of producing heat energy. This was first observed by Mme. Curie and Laborde.[1] They noted that salts of radium keep themselves at a temperature which is constantly higher than the surrounding medium. This led to an accurate

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[1] Compt. Rend., **136**, 673 (1903).

the power of producing energy, or at least, of transforming some other form of energy into heat in almost unlimited quantity.

The more conservative, however, began to look around for the source of the heat energy, and found it.

Whence Comes the Heat Liberated by Radium?—The alpha particles are shot off from radium with very high velocities, about one-tenth that of light. They have large masses, about four times that of the hydrogen atom. They, therefore, have large kinetic energy which is expressed by $\frac{1}{2}mv^2$; m being the mass and v the velocity of the particle. These alpha particles are, then, little cannon balls shot off all of the time from the radium. They, as we have seen, have very little power to penetrate matter.

Take the alpha particles shot off from the radium that is not on the surface of the pile of radium salt, but beneath the surface. These alpha particles will strike some of the solid radium bromide above them and be stopped. Their kinetic energy is converted into heat, and this has been regarded as the source of the heat that is liberated by radium.

A moment's thought will show that the above explanation really explains nothing. Given the alpha particles, moving with their high velocities, and it is a perfectly simple matter to account for the heat that is produced when they are stopped. But before we can really account for the heat energy set free by radium, we must account for the high velocities which the alpha particles have. We must know something about the source of the energy which imparted these high velocities to the alpha particles. Given rapidly moving cannon balls, it is perfectly simple to account for the heat energy that is liberated when they are stopped. But if we wish to know the real source of the heat energy that is liberated when the cannon balls are stopped, we must know the source of the energy which set the cannon balls in motion.

What is the source of the energy which shoots the alpha particles off from the radium atom with such enormous velocities? This is the fundamental question. It must be the intrinsic energy in the radium atom itself, and we now know what is meant by intrinsic energy. It is the kinetic energy of the moving electrons. This kinetic energy must be greater, many times greater, in the radium atom than in the atoms of any other well-known substance. This is most easily explained by assuming that the electrons within the radium atom move with much higher velocities than the electrons within the atoms of other elements. Their greater kinetic energy explains, as we shall see, the greater instability of the radium atom. These more rapidly moving electrons fly off more readily than slower moving electrons, and hence the greater radioactivity of radium. The great heat production by radium is to be referred to the great amount of intrinsic energy in the radium atom, and comes from a part of it. Radium is, therefore, a storehouse of energy, representing the most concentrated energy known to man.

Origin of Solar Heat. — One or two applications of the amount of heat set free by radium is of more than usual interest. The origin of solar heat has long been a problem. It was at one time supposed to be due to the raining down of meteoric matter from space into the sun. This was stopped when it struck the sun, and its kinetic energy converted into heat. This theory was, however, found to be insufficient.

Then we had the theory of Helmholtz, which said that solar heat is produced by the sun shrinking up. It is a hot body cooling, and as it cools it shrinks; the outer surface falling in on the inside. This produces an enormous amount of heat, and the theory was supposed to be sufficient to account for all of the heat radiated by the sun.

Physicists and other men of science have always been suspicious that there is some other source of solar heat than would be indicated by either of the above theories. A possible source of a part of solar heat is radium, if radium is present in the sun. The first question is, Does the sun contain radium?

Is there Radium in the Sun? — There is no *direct* evidence of the existence of radium in the sun. Notwithstanding the supposed fact that certain lines of radium have been described as occurring in the solar spectrum, these "coincidences" with known lines of radium are so poor that we cannot accept the evidence. There is, however, very good indirect evidence of the existence of radium in the sun. As we shall see, all of the terrestrial helium

on the basis of it being a hot body cooling from a certain temperature to the present temperature. Rutherford called attention to this factor.

Emanation. — Rutherford[1] discovered that there is a gas in radium salts, which can be separated from them by fusing the salt, or by dissolving it in water and passing some neutral gas through the aqueous solution. This gas, which, as we shall see, has very remarkable properties, Rutherford termed the *emanation.* This gas can be condensed to a liquid at − 152°.

The amount of radium salt that has thus far been isolated with a high degree of purity is only a few grams. Salts of radium contain only a very small fraction of a per cent of the emanation. The total amount of the radium emanation that has thus far been obtained at any one time is, therefore, only a fraction of a cubic millimeter. Notwithstanding its small quantity the properties of the emanation have already been studied pretty thoroughly. Let us now see what are some of its many remarkable properties.

One of the most striking characteristics of the radium emanation is its instability. It breaks down quickly into other things, and what these are will be considered a little later. Its molecular weight was determined by the diffusion method and was found to be about 200.

Radium Emanation produces Helium. — If after the emanation has been removed from radium the

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[1] Phil. Mag., **49**, 1 (1900).

radium is set aside for a time, it regains its emanation. This shows that the emanation is being produced by the radium. Radium can be very often deemanated, and just as often produces a new crop of the emanation. This shows that the production of the emanation is a continuous process, going on all of the time, and this probably continues during the whole life-history of the radium.

The emanation, after it has been removed from the radium, itself undergoes decomposition. It was found that it half-decomposed in 3.7 days. The emanation from thorium had a much shorter life-history, undergoing half-decomposition in about one minute.

It will be recalled that the rate at which radium gives off heat was independent of the conditions to which the radium was subjected. It liberated heat just as rapidly at a very low, as at ordinary, or very high temperatures. It is just so with the decay of the radium emanation. It goes on at a perfectly definite rate, independent of external conditions. It takes place just as rapidly at ordinary as at elevated temperatures. This lack of a temperature coefficient differentiates this decomposition from an ordinary chemical reaction. The very remarkable fact was discovered by Ramsay[1] and Soddy, that when the radium emanation breaks down it yields among other things the element helium, and this leads to a word in reference to the discovery of the element helium upon the earth Helium had long

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[1] Phil. Mag., **4**, 581 (1902).

been known in the sun. It was discovered there, spectroscopically, by Sir Norman Lockyer.

Lord Rayleigh had shown that atmospheric nitrogen was heavier than pure nitrogen prepared by heating ammonium nitrite. Sir William Ramsay had studied the cause of this difference, and the result was the discovery of argon in atmospheric air. Ramsay extended his investigations of the atmosphere, and soon discovered the presence in it of very small quantities of the element helium. He had shown that the element helium is present in certain water, and in certain minerals, especially those that contain uranium.

The element helium is readily detected by the presence of the yellow D_3 spectrum line, which is very close to the D_2 line of sodium.

When the emanation from radium was introduced into a sparking tube, which is simply an empty glass tube with two electrodes sealed into its ends, and the spark passed, there was no trace of the helium spectrum present; the spectrum of the emanation itself being the only one seen. When the tube was set aside for a time, indeed, for only a few days, the original spectrum of the emanation disappeared, and the *spectrum of helium* made its appearance.

P*roduction of an Element.* — Thus was produced from another substance the element helium. Such an announcement of course attracted very wide attention, and this experiment was repeated. The first suspicion was that the helium was occluded in the radium salt, and was given off when the emana-

for such statements. The spontaneous production of helium from the radium emanation is one thing, and the production of one chemical element from another by artificial means is another.

The radium emanation is unstable and breaks down spontaneously into a number of things; among them being the element helium. This decomposition goes on at a rate that is absolutely beyond our control. We cannot retard it. We cannot accelerate it even by raising the temperature at which it takes place. This is obviously an entirely different matter from taking a stable chemical element, bringing some artificial means to bear upon it, and thus transforming it into another elementary substance.

The production of helium by the radium emanation is not a transmutation of one element into another, as that term was understood by the alchemists, or as it is understood today.

Heat Produced by the Radium Emanation. — We have seen that radium is capable of producing enormous quantities of heat. Indeed, quantities that are several million times as great as that evolved in the most exothermic chemical reaction. Further, the amount of heat liberated is independent of the temperature to which the radium is subjected. These are all unique facts. They are not analogous to anything that was known prior to their discovery.

A much more remarkable fact, however, remains to be discussed. About *three-fourths* of all the heat that was supposed to be given off by radium is given out by the radium emanation. When we consider the amount of the emanation in radium this fact is scarcely believable. The largest amount of radium emanation thus far obtained is only a fraction of a cubic millimeter; and, yet, this gives off three-fourths of all of the heat liberated by radium. The radium emanation, then, represents a concentration or condensation of energy, so great that it is literally inconceivable.

Induced Radioactivity.—When the radium emanation is deposited upon other objects it renders them radioactive by induction, as it is called. The radium emanation induces radioactivity on all objects on which it is deposited. This induced radioactivity decays or disappears, as the emanation which causes it decays.

When the radium emanation decays it yields, as we have seen, the element helium. It also yields a number of other things. These are radium A, B, C, D, E, and F, each of which is transformed into the following, losing α, or α, β, and γ particles and rays; the final product of decomposition being probably lead. There are good reasons for supposing that all of these substances are chemical elements.

Radioactive Matter being Unstable Decays, and is also Produced.—We have seen that the radium emanation, which has most of the radioactivity of radium, and gives off three-fourths of the total heat evolved, undergoes rapid decay. We have also seen that deemanated radium, when set aside and allowed to stand, produces another crop of the emanation. This second crop can be removed and a third is produced, and so on. The production of the radium emanation from radium goes on during the whole life-history of the radium, which is between 2000 and 3000 years.

We have learned from the work of Henri Becquerel that the element uranium is radioactive. Indeed, it was the first naturally radioactive substance to be discovered. The element thorium is also radioactive and has an emanation of its own. Indeed, the thorium emanation was the first emanation discovered by Rutherford. The question arises, Do these mildly radioactive elements, uranium and thorium, produce from themselves any radioactive forms of matter?

Uranium X. — Sir William Crookes[1] found that when a solution of a uranium salt is treated with a solution of ammonium carbonate, the precipitated uranium dissolves in an excess of the carbonate.

There is, however, a small residue which does not dissolve in the excess of ammonium carbonate. This residue is highly radioactive, and, indeed, contains most of the radioactivity of the uranium. When this substance is thus removed from uranium the latter is scarcely radioactive at all. This substance was called by Crookes uranium X.

When uranium, from which uranium X has been separated, is allowed to stand for a time, it produces another crop of uranium X, and this apparently

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[1] Proc. Roy. Soc., **66**, 409 (1900).

science until a few years ago. We must now see what is the explanation of such phenomena.

EXPLANATION OF RADIOACTIVE PHENOMENA

The More Important Properties of Radioactive Substances. — The more important facts brought out as the result of studying the radioactive elements are:

The property possessed by certain elements of giving off radiations — alpha, beta, and gamma radiations; the alpha radiation being atoms of the element helium. Thus, certain chemical elements are giving off something continuously from themselves.

Certain elements are capable of producing from themselves radioactive forms of matter; uranium produces uranium X, which decomposes yielding a number of new elements; thorium yields thorium X, which decomposes producing a number of new elements; radium produces the radium emanation, which decomposes yielding a number of new elements.

The radium emanation breaks down yielding among other things the well-known element helium.

All things considered, the most remarkable property of the radioactive elements is the production of enormous amounts of heat energy. This is especially true of the radium emanation.

The Older Conception of the Atom Cannot Explain Radioactivity. — The older chemical conception of the atom makes it impossible to explain a single one of these phenomena. If we regard the chemical element as a dead, inert, ultimate unit, we would have the mere facts of radioactivity staring us in the face without being able to account for a single one of them. Radioactivity would, therefore, either be pure empiricism, or at best somewhat systematized. We would have today no science of radioactivity.

This, as we know, is not the case. We have a science of radioactivity, due to the discovery of the nature of the atom by Sir J. J. Thomson, and the application of the results of Thomson's work to the facts of radiochemistry by Rutherford.

The Electron Theory and Radioactivity. — In terms of Thomson's work we know that the simplest atom is tremendously complex, and we know in the main in what its complexity consists. The atom is made up of a large number of isolated negative charges of electricity, or electrons as they are termed, moving with high velocities, each in a definite orbit, in a field of uniform, positive electrification. It is very easy to see how an atom is unstable. Some of the electrons in their flight get into a position relative to the other electrons, where they are carried out of the atom, and are thus thrown off into space. These electrons may escape in groups giving us the alpha particles, or they may escape singly, giving us the beta particles.

Heavier Atoms more Radioactive. — The heavier atoms contain the larger number of electrons, and these, other things being equal, would be the most unstable. It is worthy of note that the heavier atoms are the most radioactive. The heaviest atom of them all is uranium. Its atomic weight is 238.5. Uranium is one of the more radioactive elements. Next to uranium, in the order of atomic masses, is the element thorium, with a mass of 232.5. Thorium is one of the more radioactive elements.

The most radioactive element of them all, as far as the widely distributed substances are concerned, is radium. Its atomic mass is 227. The radium atom is, therefore, smaller than the atom of uranium or the atom of thorium, and yet radium is at least a million and a half times more radioactive than uranium. This is, however, not at variance with the general relation between atomic masses and radioactivity. We have seen that radium possesses an enormous amount of intrinsic energy. This is shown in part by the fact that the radium emanation produced by radium gives off such an enormous amount of heat energy. This heat must come ultimately from the intrinsic energy in the radium atom. We have also seen that intrinsic energy is the kinetic energy of the moving electrons. The enormous amount of intrinsic energy in radium can be best explained by its electrons having very high velocities. Since the radium atom apparently has so much more intrinsic energy than any other well-known atom, we can conclude tentatively that its electrons probably move with much higher velocities than the electrons in atoms of other elementary substances. If the radium electrons move with such relatively high velocities, they would be more likely to fly off from the atom than the more slowly

the successive decomposition products of thorium, uranium, and actinium.

The Chemical Atom Unstable. — The key to the explanation of radioactive phenomena is, then, the unstable chemical atom. The electron theory of Thomson and Lorentz shows how an atom can be unstable, and thus gives us the basis for explaining radioactivity.

All Atoms Probably Radioactive. — The question arises, Are only the larger atoms radioactive? Are these the only atoms that are unstable and are breaking down into simpler things? We know that these are the most unstable. What about the others? There is today a reasonable suspicion that all of the elements are more or less radioactive, are more or less unstable. Indeed, some of them, such as potassium and radium, have been shown to be slightly radioactive. If all of the elements should be shown to be breaking down into something simpler, then we would have in the inorganic or dead world a process going on which is exactly the reverse of that which characterizes living matter. Here we have a building up of the complex from the simpler — an *evolution.* If the chemical elements are continually breaking down into simpler things we have in the inorganic world a *devolution;* the exact opposite of evolution in living matter.

The Origin of Radium. — A word before concluding this part of our subject as to the origin of radium itself. We have said that the life-history of radium is between two and three thousand years. This means that none of the radium now present existed more than twenty-five hundred years ago. The question that arises is this: Will radium twenty-five hundred years hence be all decomposed, or is it being produced, and if so from what?

Radium occurs in general in uranium minerals. From this fact, it was for a time supposed that uranium produces radium directly. Indeed, salts of uranium were freed from radium and set aside to see whether radium would be produced by them. Negative results were obtained. More recent work by Soddy, McCoy, and Boltwood has shown that the amount of radium in uranium minerals is proportional to the amount of uranium in these minerals. This makes it highly probable that there is a genetic relation between the uranium and the radium.

Radium Produced Indirectly from Uranium. — If the radium is not produced *directly* by the uranium, perhaps it is produced *indirectly*. There may be one or more products intermediate between the uranium and the radium.

Ionium. — Boltwood has isolated one such intermediate product, which, from its ionizing power, he terms *ionium*. The existence of this intermediate product has been confirmed by the subsequent work of Marckwald and Keetman.[1] The sequence of products from uranium, through ionium and radium to lead, is then as follows:

Uranium — Uranium X — Ionium — Radium Emanation — Radium A — Radium B — Radium C —

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[1] Ber. d. chem. Gesell., **41,** 49 (1908).

Radium D — Radium E — Radium F — Polonium — Lead.

This brief sketch of some of the phenomena presented by radioactive substances is all that the scope of this work will allow. Any one who is interested in the subject of radiochemistry must consult some larger work[1] dealing only with this subject.

Supposed Transmutation of Certain Elements. — From what has been said above, it will be seen that the spontaneous production of helium from the radium emanation is not a transmutation of an element in the sense in which that term has been used. Certain experimental results have, however, been described which would be true transmutations. Sir William Ramsay stated several years ago that he obtained a trace of lithium from copper by allowing the radium emanation to act on an aqueous solution of a copper salt. The weakest point in his experiment seems to have been that it was carried out in glass vessels, and nearly all glass contains more or less lithium. These experiments were repeated by Mme. Curie in platinum vessels and no lithium was obtained.

Ramsay subsequently stated that when certain salts of zirconium, thorium, silicon, and bismuth were treated in solution with the radium emanation, they continued to give off carbon dioxide. He interpreted these facts as due to the transmutation of

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[1] See the author's "Electrical Nature of Matter and Radioactivity," 2d ed., (D. Van Nostrand Co.).

introduction of physical and mathematical methods into chemistry. Whenever we have succeeded in solving any fundamental problem in general chemistry, it has been through the application of physical methods. There is scarcely an exception to this statement.

The question then arises, What is the future of chemistry? The answer is reasonably obvious. The old, purely descriptive chemistry will drop more and more into the background. Chemistry will become every year more physical and more mathematical; and students of chemistry will learn what they are already beginning to realize, that they can do little or nothing with the science of chemistry, without having first acquired a good knowledge of the fundamental principles of physics, and an elementary knowledge of the higher mathematics.

For my own part I have no doubt that the development of chemistry in the next fifty years, along physical and mathematical lines, will far exceed its development in these directions during what we have called the "New Era."

Let all who have the interest of chemical science at heart work to this end; since in this way, and in this way only, can chemistry ever become a real branch of exact science.

APPENDIX

In concluding this work it has seemed desirable to add a few pages of a personal character. It has been my good fortune to have known, in one capacity or another, nearly all of those whose work has made possible the "New Era" in chemistry. These men have been the leaders in chemistry, and it is always of interest to learn something of the personalities of really great men.

Mendeléeff. — The two men who contributed most towards converting empiricism into system in chemistry were Mendeléeff and Kekulé. I met Mendeléeff in London in the spring of 1894. His was a most impressive personality; of medium height and stocky build, his long, shaggy gray hair and enormous cranium gave him an unusual appearance. His intense interest in science in general, and in the nature of solution in particular, his disregard of the ordinary social forms, his unkempt appearance, all pointed to a man of genius, whatever that may mean.

Kekulé. — Kekulé was the exact opposite of Mendeléeff. He was as handsome as a picture, and evidently solicitous about his personal appearance. I heard him lecture in the summer of 1892. His

German lacked the gutteral so often heard, and was really musical. This was probably due in part to the fact that he had been so long in Belgium, and had spoken so much French, and in part also to his inheritance.

His lecture was on hydrogen dioxide and ozone. It was unusually clear, and delivered with an elegance of manner that made a deep impression. The most memorable feature of the lecture was that he interpreted all of the facts in terms of the constant valency of the atoms present, and then spoke at some length upon this subject. This was almost a necessary outcome of his views on chemical constitution. Personally, he was one of the most genial of men, and at that time was especially interested in pyridine, upon which he had just finished an elaborate investigation.

The influence of Kekulé on carbon chemistry was greater than that of any one man of his time, and could be compared with that of Liebig; and it probably surpassed even that of his teacher, Liebig himself. As he himself said in his celebrated lecture before the German Chemical Society in 1890, he belonged to no school. He was a pupil of Liebig, also of Dumas, Gerhard, and Williamson.

He was rather a founder of a school. His oldest pupil was Baeyer; and Emil Fischer and Victor Meyer, not to mention a number of brilliant younger men, can be regarded as belonging to this same general school. The influence of Kekulé on carbon chemistry from 1865 to 1885 can almost be com-

Ramsay. — When returning from my studies of two years on the continent of Europe, I spent three weeks in London in the spring of 1894. During this time I saw much of Ramsay both in the laboratory and in his home. The genial, attractive, and hospitable characteristics of the man were just such as to draw to him a young man. He impressed me then as having the most skillful pair of hands that I had ever seen at work in the laboratory. His glass-blowing, quartz-blowing, his manipulation in general, were unique.

The possession of these characteristics has manifested itself in his subsequent work, which represents the finest skill of which the experimenter is thus far capable.

One incident is really of historical interest in connection with the discovery of argon. The evening before I sailed for home I was invited to dine with Ramsay at his home. It being in May his family had already gone to Scotland. After dinner, over the cigar, he told the story of Rayleigh's discovery that atmospheric nitrogen was heavier than chemically pure nitrogen. He said Rayleigh has asked me to cooperate with him in isolating this heavier constituent in the nitrogen of the atmosphere. He then outlined the program which he had marked out for solving this problem. He was going to remove the oxygen from the air with hot copper. The nitrogen was to be taken out with hot magnesium; the ordinary constituents, carbon dioxide and ammonia, having been removed by the usual methods. In this way, said Ramsay, the heavier constituent in atmospheric nitrogen will be left behind, and we can then study it.

Any one who has followed the discovery of argon, recognizes at once that the above program was subsequently carried out to the letter. Indeed, Ramsay could have written, that evening, his paper on the discovery of argon, and simply waited for the predicted facts before publishing it. This incident shows the way in which Ramsay's mind worked. He had an insight into phenomena, and a foresight that has proved of incalculable value to him. The importance of the discovery of argon is augmented by the fact that it led to the subsequent discovery of helium, neon, xenon, and krypton; and the transformation of the radium emanation yielding helium, the most important of all. This insight and foresight have been defined by some as genius.

Van't Hoff. — The three epoch-making contributions of Van't Hoff to chemistry have already been studied at some length. These are: His theory of the asymmetric, tetrahedral carbon atom; his work on chemical dynamics and equilibrium; and by far the most important of all, from the standpoint of a science of chemistry, the relations between gas pressure and osmotic pressure. His study of solid solutions would be regarded as very important, and by itself considered, it is. This is, however, so overshadowed by his greater generalizations, that it is often forgotten in dealing with the work of this brilliant man.

As has already been stated, Van't Hoff was called to Berlin, and accepted the professorship in the University and membership in the Prussian Academy of Sciences, in 1896. From this time to his death in 1911 Van't Hoff held these positions. His work while in Berlin had to do primarily with the study of the conditions under which the inland salt deposits, such as those at Stassfurt, were formed. It consisted essentially in the study of the effect of one salt on the solubility of another salt, and the plotting of the results in terms of the Phase Rule.

I have heard Van't Hoff himself state that he did not regard this work as being in the same class with his earlier generalizations, which is obviously true to any one who has followed all of his investigations.

Van't Hoff, as is well known, contracted tuberculosis, probably while studying an eruption of Vesuvius. He thought that the dust lacerated his throat and lungs, and that the *tubercle bacillus* then began its work — a theory which is very plausible, as all who have visited Naples will recognize. His untimely death at the age of fifty-nine removed from chemistry the one who has probably contributed more epoch-making generalizations to that science than any one who has ever lived.

I worked in the laboratory of Van't Hoff in Amsterdam for a short while in the early spring of 1894. My object was to study his method of investigating and his habits of thought. I found him a man of small stature and of a decidedly nervous temperament. The latter came no doubt in part

which he had tabulated all of the results obtained by all of those who up to that time had worked on this problem. He said: "I have been studying these data for some time, but I cannot make much out of them." Today we know why. Certain conditions which affect such results had not then been discovered, and all of those results contained appreciable and varying errors.

Another incident which occurred in Van't Hoff's laboratory will illustrate his mental habit. Just before that time Baeyer had described a terpene derivative which was optically active, and which he thought did not contain any asymmetrical carbon atom. I asked Van't Hoff what he thought of it. He replied, "We must have patience, it will come out all right," and it did. When the constitution of the compound in question was finally worked out, it was found to contain an asymmetric carbon atom.

Van't Hoff's mind, as has been stated, was of the generalizing type. He told others what their experimental results really meant, and this is one of the rarest and one of the most valuable types of mind. Personally, he was characterized by modesty, simplicity, and naturalness. These might be termed the three graces of true greatness. Whenever we meet their opposites, we are liable to suspect that they are invoked to conceal natural incapacity and weakness. He was a true and sincere friend, and most hospitable to his friends.

Van't Hoff enjoyed what is not given to many men who are greatly in advance of their day. He lived to see the value of his work generally recognized and appreciated. He was elected an honorary member of most of the learned academies and societies of the world. He was awarded the first Nobel Prize in chemistry, which alone illustrates the opinion of him held by his fellow chemists. Van't Hoff was not only a great man of science, but a great man.

Arrhenius has contributed one of the greatest generalizations to science, the theory of electrolytic dissociation, and this is of such wide-reaching and fundamental significance that one such generalization is enough for any man. Before this generalization was proposed, there seems to have been no clear conception of just how chemical reactions take place or between what. Things were simply brought together in the most empirical manner, certain reactions took place, and practically the entire attention was fixed upon the end products. The result was the accumulation of many facts, the meaning of which could not possibly be understood. A very few of these have already been referred to under the discussion of the dissociation theory.

Arrhenius came upon the chemical scene just at the right time. He showed that chemical action takes place only between bodies which are charged to different electrical potentials, and thus placed chemical action upon a physical and rational basis. His generalization did more than this. It correlated great masses of apparently more or less disconnected facts, and brought out relations between such facts which had a real significance and meaning. This was not one of the least important functions of the theory of electrolytic dissociation for chemistry. The bearing of this theory on the nature of solutions of electrolytes has already been considered in sufficient detail for the present purpose.

I worked in the laboratory of Arrhenius in Stockholm in the summer of 1893, and thus began a friendship which has grown with time. Arrhenius was at that period interested in the old Mendeléeff theory of hydrates, and we worked on a problem bearing upon that theory. The results of the work were to show that this theory was fundamentally wrong.

Arrhenius was professor in what was then called the Stockholm High School, but which has since become the University of Stockholm. He was later called to the University of Berlin, but when the Nobel Research Institute was built for him in Stockholm, he decided to decline the call.

Personally, Svante Arrhenius is one of the most genial and jovial of men. His friends are almost as numerous as his acquaintances. When a few years ago it was proposed to publish a "Jubelband" to him in the series of the "Zeitschrift für physikalische Chemie," to celebrate the twenty-fifth anniversary of the announcement of the theory of electrolytic dissociation, it was found necessary to publish two volumes, so many were those who desired to contribute. Arrhenius was awarded one of the earlier Nobel Prizes, and he, like Van't Hoff, has lived to see his great generalization become one of the

spent in writing some book, they were devoted to painting, and he has made quite a reputation for himself as an artist. His interest in art took graphic form, and we have his little book, "Letters on Art." The aim of this work is to introduce the scientific method and scientific principles into the preparation of the canvas and into painting itself.

Ostwald, as has already been pointed out, called attention to the fundamental importance of energy changes for chemistry. Indeed, he showed on philosophical grounds, that we really know nothing but energy and changes in energy. When he purchased his country estate it was then only natural that he should name it "Energie." Here he now lives and follows his own bent. He has become a "Monist" in philosophy, and since the accident to Haeckel, has become the recognized leader of Monism. One of his most recent works, which is still appearing, is "Sunday Sermons on Monism." He was president of the recent Congress of Monists which met at Hamburg.

The spirit of the organizer still manifests itself in his efforts to secure a German, and also an American centre for all of the literature of chemistry. His organizing power has gone even beyond the range of chemistry or of natural science. He has been impressed by the fact that books are published in all sizes, and irregularity is the key to the appearance of any library. This is easily seen to be both inconvenient and homely. He has started a move in Germany, which it is to be hoped will become world-wide in its scope, to publish all books in a few standard sizes. This, like most of the organizing suggestions that come from Ostwald, is based upon good, hard common sense.

A visit of a day to Ostwald at Gross-Bothen is worth a transatlantic trip. You cannot be in his presence for ten minutes, without realizing that you are facing a really great man. His breadth of knowledge, his depth of interest, his unbiased judgment of men and ideas, his originality and many-sidedness, all taken together make him one of the most interesting personalities of the age.

In him again the perfect naturalness and simplicity of manner which characterize the truly great are most pronounced. Ostwald has lived to see the influence of his work. He has been awarded the Nobel Prize in chemistry, and has been elected a member of nearly all of the learned scientific and philosophical societies. He has lived to see chemistry largely transformed from empiricism and system into science, due in no small measure to his own organizing power.

An original and systematic mind, a kindly and generous heart, a many-sided genius is Wilhelm Ostwald.

Atoms are all probably radioactive, 294
Atom unstable, 294
Autocatalyzers, 197
Avogadro's hypothesis, 2
Avogadro's law applies to the osmotic pressure of solutions, 98

Baeyer on stereochemistry, 58
Baeyer's address in honor of Kekulé, 13
Baker, on the inactivity of dry ammonia and dry hydrochloric acid gas, 143
Base, meaning of the term, 130
Bases, constant heat of neutralization of strong acids and strong, 131
Bases, decomposition values and the electrolysis of, 237
Bases, heat of neutralization of weak acids and weak, 135
Bassett, work of, 153
Beckmann boiling-point apparatus, 218
Beckmann freezing-point apparatus, 218
Beckmann's apparatus, 215
Beckmann thermometer, 217
Becquerel discovers natural radioactivity, 272
Becquerel shows that uranium is radioactive, 288
Benzene hypothesis of Kekulé, 9, 11, 16
Benzene hypothesis of Kekulé, celebration in honor of, 12
"Benzoyl" discovered by Liebig and Wöhler, 8
Berthelot and Saint Gilles, on mass action, 23
Berthelot, generalization of, 172
Berthelot's chemical mechanics and statics, 38
Berthelot, thermochemical work and deductions of, 34
Berthollet, on mass action, 21
Berzelius discovers catalysis, 196
Berzelius' electrochemical theory, 9, 142
Beta particles, 275
Biology and solution, 170
Boiling-point apparatus of Beckmann, 218
Boltwood on radium in uranium minerals, 295
Boyle's law of osmotic pressure, 91
Bredig, work of on colloidal suspensions, 242
Bunsen, portrait of in the Zeitschrift, 201

Cannizzaro showed the meaning of Avogadro's hypothesis, 2
Carnegie Institution of Washington aided work on the absorption spectra of solutions, 158
Carnegie Institution of Washington aided work on the solvate theory of solution, 152, 153
Carnegie Institution of Washington aided work of Noyes and Richards, 255, 257
Catalysis and the chemical industries, 197
Catalysis, discovered by Berzelius, 196
Catalyzers, colloidal suspensions of the metals are, 243
Catalyzers, true and pseudo, 196
Cathode particle, 262
Celebration in honor of Kekulé's benzene hypothesis, 12
Cell, primary, 225
Chambers and Frazer, work on the solvate theory of solution, 151

Characteristics of Ostwald the experimenter, 198
Charge electrical, mass and inertia due to, 263
Chemical action at a distance, 188
Chemical and mechanical equilibria, analogy between, 81
Chemical dynamics of Van't Hoff, 74
Chemical equilibrium, Le Chatelier on, 80
Chemical equilibrium of Le Chatelier, 74
Chemical valence electrical in nature, 194
Chemistry, beginning of a science of, 17
Chemistry colloidal, 249
Chemistry, condition of in 1887, 1
Chemistry, importance of solution for, 168
Chemistry, precipitation not the natural condition in, 247
Clausius' theory of electrolysis, 117
Collie and Patterson on the supposed transmutation of the elements, 297
Colloidal chemistry, 249
Colloidal solution and colloidal suspension, 248
Colloidal suspensions of the metals are catalyzers, 243
Colloidal suspensions of the metals, method of making, 242
Colloidal suspensions, properties of, 245
Colloidal suspensions, work of Bredig on, 242
Color in solution, what we mean by, 157
Component and phase, definition of, 66
Component one, and four phases, 70
Component one, and three phases, 68
Component one, and two phases, 67
Concentration, osmotic pressure proportional to, 92
Condensed systems, equilibrium of, 77
Condition of chemistry in 1887, 1
Conductivities at high temperatures, 256
Constancy of the ratio $\frac{e}{m}$, 260
Constant heat of neutralization, explanation of, 132
Constant heat of neutralization of strong acids and strong bases, 131
Corpuscle, 262
Crookes discovers uranium X, 288
Curie, Mme., discovers radium, 272, 273
Curie, Mme., on the transmutation of the elements, 296
Curie, Mme., production of helium from the radium emanation, 285
Curtius, on stereochemistry, 58

Dalton proposed the atomic theory, 2
Daniell cell, 228
Decay of radioactive matter, 287
Decomposition of water in electrolysis, primary and secondary, 240
Decomposition values and the electrolysis of an acid, 236
Decomposition values and the electrolysis of bases, 237

Decomposition values and the electrolysis of salts, 238
Decomposition values and the theory of electrolysis, 232
Decomposition values of ions, 231
Deslandres, production of helium from the radium emanation, 285
De Vries acquaints Van't Hoff with the measurements of osmotic pressure by Pfeffer, 88
Diffusion in mixtures of solids, 253
Dilution law, 174, 175
Dissociation electrolytic and the electron theory, 268
Dissociation electrolytic, Arrhenius and the theory of, 112
Dissociation of electrolytes, 221
Dissociation of weakly dissociated compounds measured by Ostwald, 176
Dissociation theory, Arrhenius proposes the, 118–120
Dissociation theory, certain applications of the, 123
Dissociation theory, reception of the, 121
Distance, chemical action at a, 188
Dixon's lecture on Berthelot, 43
Du Bois-Raymond, address by, 202, 203
Dulong, on mass action, 22
Dumas, on substitution, 8
Dumas' type theory, 9
Dynamics chemical, of Van't Hoff, 74

Editors of the Zeitschrift, original associate, 201
Electrical charge, mass and inertia due to, 263
Electrochemical investigations of Le Blanc, 230
Electrolysis, Clausius' theory of, 117
Electrolysis, new theory of, 235
Electrolysis of an acid, decomposition values and the, 236
Electrolysis of bases, decomposition values and the, 237
Electrolysis of salts, decomposition values and the, 238
Electrolysis, older theory of, 232
Electrolysis, older theory of, erroneous, 233
Electrolysis, primary and secondary decomposition of water in, 240
Electrolysis, theories of, 113
Electrolysis, theory of and decomposition values, 232
Electrolytes, abnormal, 224
Electrolytes and nonelectrolytes, properties of mixtures of, 139
Electrolytes, dissociation of, 221
Electrolytic dissociation and the electron theory, 268
Electrolytic dissociation, Arrhenius and the theory of, 112
Electron, 259, 264
Electron and radiochemistry, 259
Electron theory and electrolytic dissociation, 268
Electron theory and radioactivity, 291
Electron theory and the periodic system, 270
Electron theory, atom in terms of the, 266
Electron theory of matter, 265
Elektrochemie, ihre Geschichte und Lehre, 211
Element, production of an, 284
Emanation, 282

Gibbs, Thermodynamische Studien von Willard, 209
Gibbs, Willard, phase rule of, 66, 69
Grating spectroscope, 158
Grotthuss, on electrolysis, 114
Grotthuss, theory of, 113
Grundlinien der Anorganischen Chemie, 207
Grundriss der Allgemeinen Chemie, 205
Guldberg and Waage discover the law of mass action, 27
Guldberg and Waage, generalizations of, 172
Guye, on a quantitative study of stereochemistry, 59, 60
Guye's hypothesis, testing, 61–64
Guye, work of on stereochemistry, 44
Guye's method of determining the molecular weights of pure liquids, 251
Guy, work of on the absorption spectra of solutions, 164

Haber, on the fixation of nitrogen, 197
Haber, work of on the fixation of nitrogen, 252
Handbuch der Allgemeinen Chemie, 205
Hantzsch and Werner, on the stereochemistry of nitrogen, 59
Hantzsch, on stereochemistry, 58
Heat energy produced by radium 276
Heat liberated by radium, whence comes the? 278
Heat of neutralization, explanation of constant, 132
Heat of neutralization of strong acids and strong bases, constant, 131
Heat of neutralization of weak acids and weak bases, 135
Heat produced by the radium emanation, 286
Heat terrestrial, radium the source of a part, 281
Heavier atoms more radioactive, 291
Helium on the earth, discovered by Ramsay, 284
Helium produced from the radium emanation, 282
Helmholtz at Van't Hoff's lecture, 84, 85
Helmholtz on the primary cell, 226
Hess, thermochemical work of, 33
Heterogeneous equilibria, 77
Homogeneous equilibria, 77
Horstmann, 78
Hydrate theory of Mendeléeff, the present solvate theory and the older, 166
Hydration in aqueous solution, evidence for, 152
Hydrocyanic acid, liquid, 223
Hydrogen and hydroxyl ions always combine when in the presence of one another, 136
Hydrogen ions, why acidic, 128
Hydrolysis at high temperatures, 256
Hydroxyl and hydrogen ions always combine when in the presence of one another, 136

Indicators, Ostwald's theory of, 182
Induced radioactivity, 287
Industries chemical and catalysis, 197
Inertia and mass due to the electrical charge, 263
Initial and final state, principle of, 36

Inorganic chemistry, condition of before Mendeléeff, 1
Intrinsic energy, meaning of 259
Investigations by coworkers of Ostwald, 215
Investigations of Paul Walden, 222
Ionium, 295
Ions are formed, ways in which, 177
Ions are necessary for precipitation, 246
Ions are the active agents chemically, 142
Ions, decomposition values of, 231
Ions formed by direct dissociation of molecules, 178
Ions formed by interchange of charge, 178
Ions formed in oxidation and reduction, 179
Ions free, in solution, 255

Jahn at Van't Hoff's lecture, 85

Kekulé, 299
Kekulé, benzene hypothesis of, 9, 11, 16
Kekulé's benzene hypothesis, 1
Kekulé's benzene hypothesis, celebration in honor of, 12
Kekulé's lecture before the German Chemical Society, 13
Klassiker der Exakten Wissenschaften, 210
Knight, work on the solvate theory of solution, 150
Kohlrausch's law, Ostwald's modification of, 176
Kossel at Van't Hoff's lecture, 85

Landolt, at Van't Hoff's lecture, 85
Laurent on substitution, 9
Law, dilution, 174, 175
Law of the thermoneutrality of salts, 139
Le Bel and stereochemistry, 49
Le Bel showed that carbon must be united with four different things to be asymmetric, 51
Le Bel, work of on stereochemistry, 44
Le Blanc's electrochemical investigations, 230
Le Chatelier, chemical equilibrium of, 74
Le Chatelier, on chemical equilibrium, 80
Le Chatelier's law of chemical equilibrium, 83
Lecture by Van't Hoff, 84, 88
Lecture by Van't Hoff, quotation from, 87, 88
Lehrbuch der Allgemeinen Chemie, 204
Leipzig, University of, Ostwald called to in 1887, 172
Liebig and Wöhler discovered "Benzoyl," 8
Light, what is meant by absorption of, 156
Liquids, molecular weights of pure, 249
Litmus, 182
Lobry de Bruyn's centrifugal experiment, 255
Lockyer discovered helium in the sun, 284
Longinescu, on the molecular weights of pure liquids, 249
Longinescu's method of determining the molecular weights of pure liquids, 250
Lowering of vapor tension and freezing-point in solid solutions, 253

Marckwald on ionium, 295

Marignac modifies Prout's hypothesis, 3

Mass action, development of the law of, 19

Mass action, discovery of the law of, by Guldberg and Waage, 27

Mass action, earlier views on, 20

Mass and inertia due to the electrical charge, 263

Material changes, first studied by chemists, 31

Materialism, overthrow of scientific, 211, 265

Mathematics and physics for chemistry, importance of, 297

Matter, electron theory of, 265

Maximum work, criticism of the law of, 40

Maximum work, principle of, 37

McCoy on radium in uranium minerals, 295

Meaning of the term acid, 124

Meaning of the term base, 130

Measurements of osmotic pressure by Morse and coworkers, 102

Measurements of osmotic pressure by Pfeffer, 89

Mechanical and chemical equilibria, analogy between, 81

Mechanics and statics, Berthelot's chemical, 38

Membranes semipermeable, artificial, 90

Mendeléeff, 299

Mendeléeff's periodic system, 1, 4

Mendeléeff, the older hydrate theory of, and the present solvate theory, 166

Messungen, Physiko-Chemische, 209

Metals, colloidal suspensions of the, are catalyzers, 243

Metals, colloidal suspensions of the, method of making, 242

Metals, solution-tensions of the, 227

Methane, shape of a molecule of, 55

Methane symmetrical, 54

Meyer, Lothar, periodic system, 1, 4

Mixtures of electrolytes and nonelectrolytes, properties of, 139

Mobile equilibrium, 78

Molecular weights of dissolved substances, 220

Molecular weights of pure liquids, 249

Molecular work, principle of, 36

Morse and coworkers measure osmotic pressure, 102

Morse's method of making semipermeable membranes, 103, 104

Morse's results, 105, 106

Morse's results show relations between gas pressure and osmotic pressure, 107

Necessity of reactions, theorem of the, 39

Nernst's solubility investigations, 229

Nernst's thermodynamics, 230

Nernst, Walter, work of, 225

Neutralization, explanation of constant heat of, 132

Neutralization of strong acids and strong bases, constant heat of, 131

Neutralization of weak acids and weak bases, heat of, 135

Newland's arrangement of the elements, 4

Pebal and Than, on the dissociation of the vapor of ammonium chloride, 24
Periodic system and the electron theory, 270
Periodic system of Mendeléeff and Lothar Meyer, 4
Pfeffer, on osmotic pressure, 86
Pfeffer's measurements of osmotic pressure, 89, 92
Phase and component, definition of, 66
Phase Rule of Willard Gibbs, 66, 69
Phases four, and one component, 70
Phases three, and one component, 68
Phases two, and one component, 67
Phenolphthalein, 182
Phosphorescence and X-rays, 271
Physics and mathematics for chemistry, importance of, 297
Physiko-Chemische Messungen, 209
Precipitation not the natural condition in chemistry, 247
Precipitation, why ions are necessary for, 246
Pressure, effect of on equilibrium, 81
Primary and secondary decomposition of water in electrolysis, 240
Primary cell, 225
Principle of maximum work, 37
Principle of molecular work, 36
Principle of the initial and final state, 36
Principle of Soret, 95
Production of an element, 284
Prout's hypothesis, 3
Pseudocatalyzers and true catalyzers, 196
Radioactive, all atoms probably, 294
Radioactive, heavier atoms more, 291
Radioactive matter decays and is produced, 287
Radioactive phenomena, explanation of, 290
Radioactive substances, more important properties of, 290
Radioactivity and the electron theory, 291
Radioactivity cannot be explained in terms of the older conception of the atom, 290
Radioactivity induced, 287
Radioactivity, meaning of, 273
Radiochemistry, 271
Radiochemistry and the electron, 259
Radiomicrometer spectroscope, 163
Radium, discovery of, 272
Radium emanation produces heat, 286
Radium emanation produces helium, 282
Radium, heat liberated by, whence comes the, 278
Radium in the sun, 280
Radium, origin of, 294
Radium produced indirectly from uranium, 295
Radium produces heat energy, 276
Radium, properties of, 275
Radium, the source of some terrestrial heat, 281
Ramsay, 302
Ramsay and Shields on the molecular weights of pure liquids, 249
Ramsay discovered argon and helium, 284

Ramsay on the transmutation of the elements, 296

Ramsay showed that the radium emanation produces helium, 283

Ramsay's method of determining the molecular weights of pure liquids, 250

Raoult, on freezing-point lowering, 215, 216

Raoult's law, 217

Ratio $\frac{e}{m}$, constancy of the, 260

Rayleigh, on the density of atmospheric nitrogen, 284

Rays, gamma, 275

Reaction velocities, Van't Hoff on, 76

Reception of the dissociation theory, 121

Results obtained by Morse, 105, 106

Richards, work of, 257

Roberts-Austen on diffusion in mixtures of solids, 253

Röntgen discovers the X-ray, 271

Roozeboom, work on the phase rule, 72

Rose, on mass action, 21

Rowland's conception of the atom, 267

Rutherford discovered the emanation, 282

Rutherford discovers thorium X, 289

Saint Gilles and Berthelot, on mass action, 23

Salts, decomposition values and the electrolysis of, 238

Salts, law of the thermoneutrality of, 139

School of chemistry, Ostwald the founder and organizer, of a,200

Science, importance of solution for, 168

Science of chemistry, beginning of a, 174

Secondary and primary decomposition of water in electrolysis, 240

Semipermeable membranes, artificial, 90

Shape of a molecule of methane, 55

Soddy, on radium in uranium minerals, 295

Solar heat, origin of, 280

Solids, diffusion in mixtures of, 253

Solids, kinds which can form solid solutions, 253

Solid solutions, 252

Solid solutions, kinds of solids which can form, 253

Solubility investigations of Nernst, 229

Solution and biology, 170

Solution and geology, 170

Solution colloidal and colloidal supsension, 248

Solution, evidence for hydration in aqueous, 152

Solution, free ions in, 255

Solution, importance of for chemistry in particular and for science in general, 168

Solution in nonaqueous solvents, "solvent" absorption bands in, 161

Solution, origin of the solvate theory of, 148

Solution-tensions of the metals, 227

Solution, the solvate theory of, and the importance of solutions for science in general, 145

Solution, what we mean by color in, 157

Solution, Williamson's theory of, 115
Solutions, absorption of light by; work of Ostwald, 180
Solutions and gases, rôle of osmotic pressure in the analogy between, 84
Solutions, bearing of the absorption of on the solvate theory, 157
Solutions, bearing of the solvate theory of, 167
Solutions, solid, 252
Solutions solid, lowering of vapor-tension and freezing-point in, 253
Solvate absorption bands in solution, 160
"Solvate" bands in different solvents, 162
Solvate theory, 155
Solvate theory, bearing of the absorption of solutions on the, 157
Solvate theory of solution, and the importance of solutions for science in general, 145
Solvate theory of solution, bearing of the, 167
Solvate theory of solution, origin of the, 148
Solvate theory, spectroscopic evidence for the, 155
Solvate theory the present, and the older hydrate theory of Mendeléeff, 166
Solvents, organic, 224
Soret principle as applied by Arrhenius, 97
Soret, principle of, 95
Spectroscope, grating, 158
Spectroscope, radiomicrometer, 163
Spectroscopic evidence for the solvate theory, 155
Spinthariscope, 274
Stas determined atomic weights, 3
Statics and mechanics, Berthelot's chemical, 38
Stereochemistry and Van't Hoff, 53
Stereochemistry of carbon and other elements, 57
Stereochemistry, work of Van't Hoff, Le Bel, and Guye on, 44
Stieglitz, on indicators, 183
Strong, work of on the absorption spectra of solutions, 161
Substitution in chemistry, meaning of, 140
Sulphur, 186
Sulphur diagram, 71
Sulphur dioxide, liquid, 223
Sun, is there radium in the, 280
Suspension colloidal, and colloidal solution, 248
Suspensions colloidal, of the metals are catalyzers, 243
Suspensions colloidal of the metals, method of making, 242
Suspensions, colloidal, properties of, 245
Suspensions, work of Bredig on colloidal, 242
Symmetry of methane, 54

Temperature, effect of on equilibrium, 81
Temperature, effect of, on the absorption spectra of solutions, 162
Temperatures, high, conductivities at, 256
Temperatures, high, hydrolysis at, 256
Tetrahedral carbon atom, 56
Tetrahedral carbon atom, asymmetrical, 56
Text-books by Ostwald, 204

Van't Hoff shows that Avogadro's law applies to the osmotic pressure of solutions, 98
Van't Hoff, work of on stereochemistry, 44
Vapor-tension and freezing-point lowering in solid solutions, 253
Velocities, reaction, Van't Hoff on, 76
Volta discovers primary cell, 226

Waage and Guldberg discover the law of mass action, 27
Waage and Guldberg, generalizations of, 172
Walden, Paul, investigations of, 222
Wallach, stereochemistry of the terpenes, 58
Water diagram, 68
Wenzel, on mass action, 20
Werner and Hantzsch, on the stereochemistry of nitrogen, 59
Werner, on the stereochemistry of a number of elements, 59
Wilhelmy, on mass action, 23
Willard Gibbs, phase rule of, 66, 69
Williamson, on chemical equilibrium, 25
Williamson, on the synthesis of ether, 115, 116
Williamson's theory of solution, 115
Wislicenus, on stereochemistry, 58
Wissenschaften, Klassiker der Exakten, 210
Wissenschaftlichen Grundlagen der Analytischen Chemie, 209
Wöhler prepared urea artificially, 8

X-ray, discovery of, 271
X-rays and phosphorescence, 271

Zeitschrift für Physikalische Chemie, 201
Zeitschrift, growth of, 202
Zsigmondy on colloidal chemistry, 249

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