

*The Tammann Memorial Lecture.*

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GUSTAV TAMMANN.

1861—1938.

GUSTAV TAMMANN was a contemporary of Ostwald, Nernst, van't Hoff, and Arrhenius, and with them laid the foundations of physical chemistry in the last years of the nineteenth century. He was born at Jamburg in 1861, just inside the borders of Russia. He was of German stock and on his father's side his forebears for some generations had resided in the Baltic States. His grandfather, Johann Tammann, was the steward of an estate near Walk, which belonged to the very influential von Berg family. His father, Heinrich Tammann, who was educated at Pernau and Dorpat, first practised as a physician at Jamburg and later at the Agricultural Institute of Gorki, under the protection of Count Frederich von Berg. His mother, Matilda Schünmann, was the daughter of a publisher who had moved to Dorpat from Lübeck. When Tammann's father died relatively young, his mother left Gorki to live with the Schünmann family at Dorpat, and it was there that Tammann was taught to read by his grandmother, Justine Schünmann.

He attended the preparatory school at Dorpat and later the Gymnasium, where usually he had the best marks in mathematics, history, and religion, though he was not so good in languages, especially Russian. A military career was open to him when General von Berg offered him a free place in the cadet school in Pleskau, but his mother declined to be separated from him. He went later to the Chemical Institute of the University of Dorpat and studied under Karl Schmidt, Lemberg, Bunge, and von Göttingen.

At that time the Dorpat-Yuriew University, which had been in existence since 1632, although essentially German in the spirit of its education, was under strong Russification. Despite a very onerous system of instruction and examination in Russian, and very large numbers of students, the University was remarkable for its academic freedom, and had a high reputation for medical, historical, and theological research. On the scientific side the emphasis was on subjects related to medicine. It is a remarkable tribute to the academic freedom of Dorpat that, in spite of this concentration in the medical field, two such important pioneers in physical chemistry as Ostwald and Tammann were able to lay the foundation of their life's work in Dorpat University.

Before Tammann had completed his final examination he was appointed second chemistry assistant under Karl Schmidt, in the place of Wilhelm Ostwald, who had obtained a professorship in Riga. In 1882 he completed his final examination and a year later submitted his "Kandidaten" thesis on the estimation of fluorine, which was published in the *Zeitschrift für analytische Chemie*. Then, on the advice of Lemberg, followed a period during which he studied plant physiology and microscopy, with a view ultimately to securing a post in an agricultural institute. He published several biochemical papers on the fluorine contents of plants and seeds, on osmotic pressures in living systems, and on fermentation processes. He finally decided, however, that agriculture was not to be his choice for a career, and that his real scientific interests lay in the borderland between physics and chemistry. His first research in this sphere was the determination of molecular weights by vapour-pressure measurements, and he published the results of his researches on this topic in Wiedemann's *Annalen (der Physik)* and in the *Mémoires* of the Academy of St. Petersburg. He could not afford to present his Doctor's thesis on this subject, since his financial means at that time were slender. Later, however, in 1887, his thesis on the Periodic Table of the elements gained him his doctorate.

After obtaining his Doctor's degree, Tammann thought that he should try to obtain a university post in Germany, since in view of his poor command of the Russian language he was unlikely to obtain promotion in a Russian university. In 1889, with this purpose in mind, he visited Germany and sought posts with Hermann von Helmholtz at the Berlin Physikalisch-Technische Reichsanstalt and with Ostwald in the flourishing school of physical chemistry at Leipzig, but was unsuccessful. His work on the vapour pressure and molecular weights in solution had been received favourably both in Germany and in Russia, but it was not along lines



GUSTAV TAMMANN, 1861-1938.

[To face p. 1961.]

then considered to be orthodox, since he was primarily interested in concentrated solutions. Ostwald, who was preoccupied with the investigations on dilute solutions which were yielding very profitable results at that time, withheld his full approval of Tammann's exploration of concentrated solutions. This was an indication quite early in his career that Tammann was beginning to strike out an independent path. Although his visit to Leipsig was unfruitful as regards securing a post, it had other important consequences since in Leipsig he became well acquainted with Nernst and Arrhenius, with whom "die Abende bei Bier verbracht werden."

Fortunately for him the promotion of Lemberg left vacant the position of first assistant at Dorpat, and the post was offered to him and he accepted it. His researches had brought him into contact with Mendeléeef, with whom he had excellent relations, and Mendeléeef strongly advised him to learn Russian. Opportunities for practising his Russian were limited in German-speaking Dorpat, so Tammann, during his vacations, made several visits to Russia. In 1890 he visited St. Petersburg and there met his future wife, Anna Mitcherling, whom he married in the same year, on his appointment as Dozent at a salary of 2000 roubles a year. A number of visits were made to Germany in this period, and in the Christmas vacation of 1889—1890 he worked with Nernst at Göttingen on the effects of pressure on the liberation of hydrogen by metals. After this visit he received an invitation to a professorship at Giessen, but declined the honour for financial reasons. He would have accepted had he been unmarried.

He was appointed by the Russian Government Ausserordentlicher Professor and Director of the Institute in 1892, and in 1894 he became Ordentlicher Professor. This very rapid promotion from first assistant to full professor in five years was due to his versatility and productivity in research, to his powerful personality, and to his capacity for work. His promotion at first was viewed with some misgivings by the Dorpat academic community because his research interests lay almost entirely outside the medical field, but as Tammann says laconically in his own unpublished autobiography, "after two to three years they became content." At Dorpat, he had very heavy teaching duties and he worked in the Institute alone and with students from 8 till 8, with a two-hour break at mid-day. In spite of his heavy teaching load, his period at Dorpat was most fruitful for research and he laid there the foundation of much that he did later in Göttingen.

During his tenure of the professorship at Dorpat, Tammann spent his vacations visiting various European universities and made the acquaintance of many famous physicists and physical chemists of his generation. In 1894 he paid a visit to Holland, where he met van't Hoff, Roozeboom, Kamerlingh Onnes, and Bemmelin, a visit which was to exert a very great influence in determining the direction of his researches into heterogeneous systems. He visited Nishni-Novgorod in 1896, and became interested in the oilfields of Baku. He had heard that paraffin oil was used in the canning of sardines, and carried out some investigations on the replacement of butter in part by paraffin oil in nutrition experiments with dogs, to their serious detriment. A consequence of this visit which was of more scientific significance was the isolation of some methyl derivatives of naphthalene from the crude oil. In 1897 he was in Stockholm to trace the preparations and apparatus left behind by Berzelius, and he was very largely instrumental, by his writings to the *Chemische Zeitung*, in securing the establishment of a museum in Stockholm to hold this material. In 1900 he visited Paris to study the metallurgical industries, and no doubt when there met Le Chatelier and became acquainted with his metallurgical techniques.

In the summer of 1902 Nernst enquired if he would consider an appointment as a special professor in charge of a research institute for inorganic chemistry in Göttingen. At that time there was, as a rule, only one professor of chemistry in German universities, who was an organic chemist, and branches other than organic chemistry were undeveloped. Under very considerable pressure from the German chemical industry, the German Government took steps to remedy the position. At Göttingen, Nernst was appointed as the director of an Institute of Physical Chemistry, and it was now proposed to extend this policy by the appointment of a professor of inorganic chemistry. This was the first chair of inorganic chemistry in a German university. Tammann visited Nernst to discuss the possibilities, and in the course of a walk around the walls of the ancient town, agreed to accept the invitation. He obtained permission of the Czar to give up his Russian citizenship and to accept this professorship.

He had found Göttingen to his liking when working with Nernst in 1890, and on his arrival he stated "extra Göttingen non est vivere." He remained true to this conviction, and the only move he made subsequently within his normal tenure of academic posts was to take over Nernst's own Institute of Physical Chemistry when the latter moved to Berlin. When he retired from full-time University appointment in 1930 he received an invitation to go to Riga, and this he accepted. There, very largely owing to the efforts of an old student, Dr. L. Nowack, he was generously supported by chemical industry and he vigorously continued his researches

on heterogeneous systems with the help of three to five assistants until 1937. In 1905 he became joint editor of the *Zeitschrift für anorganische Chemie*.

Gustav Tammann had three children, one son and two daughters.

#### RESEARCH

The tradition of Dorpat University lay in medical research, and Tammann's father and uncle were medical men, so that it was natural that his first researches were in the field of biochemistry. These in 1882 followed the analytical approach which was usual at that time, but, as his interests in the physical and physicochemical field broadened, he carried out investigations on the osmotic pressures of biological systems and on the mechanism of fermentation reactions. Although he was never to lose interest in these topics, in which he was active until 1896, his allegiance to them began to weaken when he commenced work on the vapour pressure of solutions in 1885; this was to give him a European reputation and to introduce him to men like Mendeleëf, Nernst, Ostwald, and Arrhenius. These contacts gave him an interest in a wide range of subjects, the Periodic Table, electromotive force, membranes, temperature coefficients of reaction velocity, etc., which contributed in some measure to the pattern of the mosaic which was to form his life's work. His main interest was to lie in the study of heterogeneous systems, and the stimulation for this seems to have arisen from his journey to Holland in 1894. He acknowledges this source of inspiration in his book on "Heterogene Gleichgewichte" in 1924. His fundamental approach to the heterogeneous equilibria between solids and liquids, the foundations of his technical approach to crystallisation processes, and the measurement of the influence of high pressures on heterogeneous systems were all carried out at Dorpat between 1897 and 1902. He also made contributions to homogeneous systems, making use of the conception of internal pressure. In this period he showed an omnivorous capacity for absorbing the thoughts of physicists and chemists of the time, and for appreciating the experimental methods then developing in Europe; from their ideas and techniques he was able to make a choice well suited to his own genius. The main outline of the Dorpat work would appear to be the marshalling of resources in wide variety for his investigations on heterogeneous systems, and his establishment of theoretical lines of approach which were to guide his enquiries into this relatively unknown field.

At Göttingen he continued the lines of work originated at Dorpat, but, influenced by the circumstances of his appointment as Professor of Inorganic Chemistry, his interests became more practical, and he was to devote a good deal of energy to the development of inorganic chemistry. He became interested in the application of his discoveries to industrial processes. His theoretical ideas and the experimental developments of the Dorpat period were consolidated in applications to metals, glasses, silicates, and mineral chemistry. These researches created new fields of pure and applied science which were to prove of very great importance to numerous chemical industries, and a source of inspiration to many workers in pure science.

The scientific communications of Tammann and his students are very numerous, and his work would prove very difficult to review had he not written several text-books and monographs, and numerous summarising papers which describe the very complex inter-relations of the separate investigations: as a consequence of these publications, Tammann's work is very accessible, and has had a great influence on the structure of physical chemistry. The main features of his researches will be described under appropriate fields of work.

#### *Internal Pressures and Properties of Solutions.*

Tammann's determinations of the vapour pressure of salt solutions led him to state in 1885 that the molecular depressions of the vapour pressure at the same temperature are the same for similar salts: van't Hoff's paper on osmotic pressure had not yet been published. In 1887, after van't Hoff's paper appeared, he made measurements on nearly 200 salts in water at 100° and discovered clear deviations from van't Hoff's theory. These deviations, which made a deep impression on him, he explained as due to the interaction between the solute and the solvent.

The analogy between the behaviour of gaseous and dissolved substances in the theories of van't Hoff and Arrhenius focused attention on the solute and almost entirely ignored the influence of the solvent. Although this was a very valid approach for dilute solutions, Tammann recognised its limitations and devoted particular attention to the interaction of the dissolved substances with the solvent. He summarised his investigations on this topic in a monograph entitled "Über die Beziehungen zwischen der inneren Kräften und Eigenschaften der Lösungen" (1907).

His starting point was a correlation between the compressibility of water at various temperatures (Amagat) and the coefficients of expansion of aqueous solutions of electrolytes and non-

electrolytes. From the first he constructed volume-temperature relations at various constant pressures for a unit mass of pure water. From the second, he derived the volume-temperature curves, at atmospheric pressure only, of a constant mass of solvent in solutions of increasing concentrations. He showed that the effect of the solute on the expansion coefficient of the solvent was closely similar to the effect of external pressure on pure water.

Many of the properties of liquids had been explained by Laplace in terms of the conception of an internal pressure,  $h$ , the resultant of the attractive forces existing between the molecules. Tammann adopted this concept to explain the results mentioned above; he concluded that the attractive forces between the solute and solvent increased the internal pressure of the solvent, and that the increase in  $\Delta h$  was equal to that external pressure which was necessary to give for water the same volume-temperature curve as the solution. For both ions and neutral molecules, the increase in  $\Delta h$  was proportional to the concentration, and he inferred that the effects were not due solely to electrostatic forces.

A comparison of the behaviour of alcohol and water demonstrated the above inter-relations between internal and external pressure. Both the application of external pressure and the addition of solutes caused decreases in the coefficient of expansion of alcohol, whilst they caused an increase in that of water.

By pertinent use of thermodynamics, Tammann correlated the extensive data then available to him on the viscosities, heats of solution and neutralisation, optical properties, surface tensions, and vapour pressures of solutions and brought them into concordance with the changes in internal pressure of the solvent. Later he investigated the effects of pressure on the conductivity of solutions (1914), the Soret phenomenon (1914), and the influence of neutral salts on the potential of the hydrogen electrode (1925), and showed that the results were in conformity with the same idea.

Although many of Tammann's conceptions in this field have been tacitly accepted into the background of our knowledge of solutions, they have not had the same influence on the development of theory as his ideas on heterogeneous systems. The conclusions he reached were not expressible in terms of broad generalisations, simply understood, but required a knowledge of the structure of liquids and solids, which even now taxes the resources of modern statistical theory.

#### *Heterogeneous Systems.*

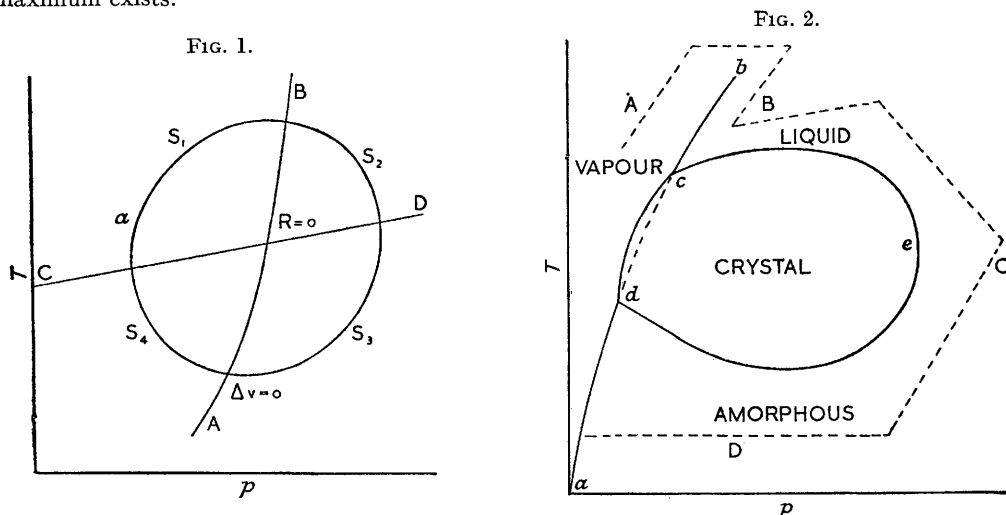
*Equilibrium Curves for One-component Systems.*—The experimental researches of Andrews and Cailletet on the equilibrium between a liquid and its vapour, and the theoretical interpretation by van der Waals of the critical point, had already been completed by the time Tammann commenced his researches on heterogeneous systems in 1895. The successful interpretation of the liquid-vapour curve encouraged Ostwald and others to apply similar ideas to the study of crystal-liquid systems. Tammann, however, pointed out that a continuous change from liquid to vapour above the critical point is possible because in both phases the molecules have random distribution. In crystals the molecules are oriented on a space lattice and accordingly the crystal and its melt will not become identical when their volumes are made equal. Therefore a terminus to the melting-point curves analogous to the critical point of the liquid-vapour curve was not to be expected. The same reasoning holds good for the equilibrium curve for two anisotropic phases.

Tammann has summarised his conclusions in this field in "Krystallisieren und Schmelzen" (1903), and in "Aggregatzustände" (1922). The first volume describes his researches at Dorpat, and the second incorporates his work at Göttingen as well. The theoretical standpoint was developed between 1895 and 1925 at a time when the methods of thermodynamics were being elaborated so that, whereas in the first volume he brings to bear on his problem the first two laws of thermodynamics in their simpler aspects, yet in the second he makes much use of the Gibbs thermodynamic potential,  $\zeta$ , and also of the Nernst heat theorem. His conclusions may be indicated briefly.

At the critical point of the liquid-vapour curve,  $\Delta v = 0$  and  $R_p = 0$  simultaneously, where  $\Delta v$  is the difference between the specific volumes and  $R_p$  is the heat of transformation. He emphasises that this condition does not arise on the melting-point curve. Tammann discussed the relation between the specific volumes and the heat of crystallisation of the two phases in terms of the so-called neutral curves. The neutral curve of the specific volume is the curve drawn on the  $p$ - $T$  plane for which  $dv = 0$ , and the neutral curve for the heat of crystallisation that for which  $dR_p = 0$ . In a discussion of the relation between these curves and the equilibrium curve for the melting point, he concludes that the diagram shown in Fig. 1 is compatible

with the Clausius–Clapeyron equation and with the customary molecular kinetic conception regarding the melting point. In this diagram the intersection of  $dv = 0$  and  $dR_p = 0$  lies within the closed equilibrium curve and not on the equilibrium curve itself. He points out that, although the closed curve is consistent with thermodynamics, it is not necessarily required that the closed curve should exist in actual substances. He believed, however, that the available experimental evidence was consistent with it, and he devoted considerable time and ingenuity in providing further evidence.

Fig. 2 shows one of the possible diagrams for the closed region of the crystalline phase in equilibrium along  $dce$  with the vapour, liquid, and amorphous phases. As will be seen in Fig. 2, the crystal–liquid curve  $ce$  is concave to the  $p$ -axis, giving a maximum. Tammann derived thermodynamic relations for its curvature, capable of experimental test, and he carried out measurements over a wide range of pressures in order to provide confirmation of the idea that a maximum exists.



Techniques for the study of phase changes at high pressures had been developed before by Amagat and Barus. Tammann, however, extended their scope up to 4000 kg./cm.<sup>2</sup>, and in rare cases up to 10,000 kg./cm.<sup>2</sup>. He elaborated methods for the study of volume and heat changes and equilibrium curves inside steel vessels up to high pressures. Bridgman extended this work to still higher pressures and achieved greater accuracy in many cases. Tammann makes considerable use of Bridgman's data in his later papers.

It was confirmed, in general, that the melting-point curves were concave to the pressure axis. For ethyldimethylcarbinol, triethylcarbinol, *o*-cresol, sodium, and potassium, this type of curvature was established, but the expected maximum on the curves was not reached at 3000 kg./cm.<sup>2</sup> and Tammann concludes that, in general, the maxima must lie at very high pressures. The author lists some 40 cases and quotes some 18 cases by Bridgman, and only for a few, of which Glauber's salt was one, was a maximum actually observed. Apart from these, the maxima, if they occurred, must be in the region 20,000–30,000 atm. Although Tammann found some further confirmation of his views in the study of polymorphic systems, it is clear that his original conception of a closed melting-point curve has been only very partially confirmed. The region of the curve, Fig. 2, where the amorphous state is represented in equilibrium with the crystal phase, would obviously take geological ages to observe, so that a complete confirmation or disproof is not to be expected except possibly from geological data. The Tammann curve is therefore, at the present time, mainly of interest as a scientific speculation, which formed a high-altitude platform from which Tammann dived to investigate so many problems of practical importance.

#### *Polymorphism.*

Mitscherlich discovered the dimorphism of sulphur and mercury iodide in the early part of the nineteenth century, and since that time many other cases of dimorphism and polymorphism have been described. Lehmann distinguished two kinds of polymorphism: (1) enantiotropy, where each form has its own region of stability, and the transformation of one form into the

other is reversible, and (2) monotropy, where only one form is stable and the transformations which occur are all irreversible. Tammann pointed out that Lehmann's description was incomplete since the parameters of state alone determine whether or not a transformation will be reversible or irreversible. Thus, the circumstances in a given case might be completely changed on increasing the pressure. He therefore made a very thorough study of the conditions controlling the relative stabilities of polymorphic forms and concluded that the best criterion for stability was the thermodynamic potential. Thus, one polymorphic form is totally unstable with respect to another over the whole field of state if its  $\zeta$  surface lies always above that of the other.

Tammann extended the interpretation of polymorphism by classifying polymorphs into different "thermal groups." There is one type of polymorphism for which the  $\zeta$  surface of the unstable form lies above that of the stable form without intersecting it. Such pairs he designates as "members of the same thermal group"; these are considered to be composed of similar molecules having the same molecular weight and molecular structure but disposed in different lattices. Their lattice energies will be different and this will be the major factor in deciding their difference in properties. Should the  $\zeta$  surfaces intersect, the polymorphs in question then belong to different groups in which not only the lattices but also the molecular units are different. The molecular units may be isomers or polymers with an appreciable heat of transformation. Associated liquids tend to give polymorphism of both types, and he suggested that the isomers or polymers occurring in the crystalline state may also exist in the liquid state as well. Liquids with a normal heat of evaporation usually give polymorphs which are members of one group only. He was interested in the meaning of molecular weight in the crystalline phase and concluded in 1914 that this could best be settled by X-ray methods.

Tammann opened up the field of study of the influence of pressure on polymorphism. He discovered that ice existed in three stable allotropic modifications, Ice I, Ice II, and Ice III, and determined their regions of stability on the  $p$ - $T$  diagram. Ten years later, Bridgman extended the pressure range up to 20,000 kg./cm.<sup>2</sup>, and completed the ice diagram as regards the stable forms, adding Ice V and Ice VI. Tammann returned to this field subsequently in order to test his ideas on different crystal thermal groups, and concluded that there were four, and possibly seven, monotropic forms in the group of Ice II and two monotropic forms in the group of Ice III, and he thought that there would probably be found other unstable polymorphs associated with the remaining stable ice forms. In the course of his work at high pressures he discovered polymorphic forms of phenol, silver iodide, methylene iodide, and urethane, and the number of cases was very greatly extended by Bridgman. Tammann pointed out that the transformation curves for Ice I-III and Benzene I-II give examples of transformations for which, at certain points on the  $p$ - $T$  curves, the value of  $\Delta v$  is still finite, although the heat of transformation is zero, thus confirming his views that  $\Delta v = 0$  and  $R_p = 0$  cannot hold simultaneously on the transformation curves.

Tammann's contribution to this field was that of a pioneer in the development of the experimental technique of following polymorphic changes in steel vessels at high pressures, in developing thermodynamical methods of study, in propounding some interesting and novel ideas concerning the atomic and molecular structures of the polymorphic forms and their melts, and in raising questions concerning metastability in heterogeneous systems.

#### *Transformation of Unstable into Stable States.*

Tammann discovered new general principles which he published in the *Zeitschrift für physikalische Chemie* in 1898 and later summarised in "The States of Aggregation" (1925). He showed that there are two important factors involved in the transformation of unstable into stable states: (1) the genesis of crystallisation centres of the stable phase within the body of the unstable phase, and (2) the rates of growth of the centres of the crystallisation so formed.

*Spontaneous Crystallisation.*—He developed a very simple technique for the study of the crystallisation centres formed in supercooled liquids. This consisted in heating substances in closed narrow tubes to a temperature above the melting point and then suddenly cooling them in a bath at a known temperature for a fixed period. Crystallisation centres or nuclei were then formed which were not necessarily visible, owing to their slow rate of growth at the low temperature. They were, however, developable in a bath at a higher temperature in a range where centres of crystallisation did not readily form spontaneously.

Counts of the nuclei in the case of piperine (m. p. 129°) are given in Fig. 3 as typical of his results. The now well-known result that the optimum temperature for nucleation of a melt occurs many degrees below the m. p. is apparent. He studied 16 such systems, and found

that the optimum temperature for formation of crystallisation centres ranged from  $40^{\circ}$  to  $110^{\circ}$  below the melting point. There is a zone immediately below the melting point where nucleus formation occurs extremely slowly. This is the so-called metastable region, which Ostwald had discussed in considerable detail, particularly with reference to supersaturated solutions. Tammann demonstrated that the sharp demarkation between the metastable and labile states postulated by Ostwald was illusory, since crystallisation will occur in the metastable region even close to the melting point, if sufficient time be given for the observations. He found that the number of centres formed at a given temperature was not only dependent on that temperature, but also on the duration of heating above the melting point. Thus the "anisotropic molecules" in the liquid (or on the surface of the glass), necessary for the formation of centres, are decreased by extended heating at high temperatures.

The decrease in the rate of formation of centres below the optimum temperature he ascribed to the increase in the viscosity of the liquid as it approached the glassy state. This follows since the orientation of the anisotropic molecules about a centre of crystallisation will be hindered at high viscosities.

He demonstrated experimentally that the formation of centres obeys the laws of probability. He concluded, since the probability of centre formation in a supercooled liquid is low, that in order to form a centre a relatively large number of "anisotropic molecules" must meet simultaneously in one place. He found that Ostwald's law of stages for the order of appearance of centres of polymorphic forms is not generally true.

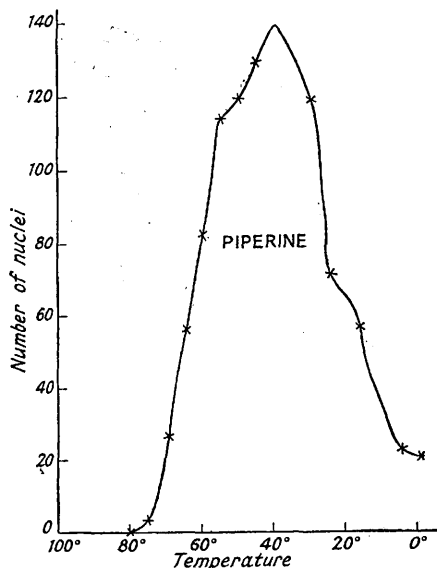
*The Linear Crystallisation Velocity.*—Tammann clarified the factors governing the rate of crystallisation from undercooled liquids. He measured the crystallisation velocity, *C.V.*, in glass tubing over a range of temperatures below the melting point, and the general character of the phenomena observed was as follows. The crystallisation is slow and erratic just below the melting point, owing to the irregular growth of large crystals. At about  $5^{\circ}$  below the melting point there is a steady prismatic growth parallel to the walls of the tube, the rate of which increases with decreasing temperature up to a maximum, and in some cases to a constant value. A constant *C.V.* is only obtained over a temperature interval if the rate of crystallisation is low. As the glassy state is approached the *C.V.* decreases, becoming negligible, owing to the retardation of molecular movement.

Tammann studied the devitrification of glasses and found that their stability is inversely proportional to the rate of formation of centres of crystallisation. If initially the melt is rapidly supercooled to give the glass, and subsequently the temperature is raised, then devitrification may take place with an evolution of heat and the temperature may sometimes rise as much as  $200^{\circ}$ . This occurs with  $\text{Na}_2\text{SiO}_3$  at  $500^{\circ}$ , when as a result of crystallisation the glass begins to glow. This phenomenon is also of significance when finely divided metals and oxides are heated.

#### Glasses.

As a consequence of his interest in the melting of solids and in crystallisation phenomena, Tammann investigated the properties of the amorphous state. His earlier work on the crystallisation of supercooled liquids is summarised in the previous section. In his later years, 1929 onwards, he was primarily interested in the physical changes occurring on the conversion of a glass into a liquid, particularly those occurring during the "softening interval." These researches are summarised in the monograph "Der Glaszustand" (1933). He defined the "softening interval" in terms of two temperatures which could be readily measured experimentally. This interval lies between  $t_g$ , the highest temperature at which brittleness vanishes, and  $t_l$ , the temperature at which the amorphous phase first shows the properties of a true liquid. For the latter, he chose the lowest temperature at which it was possible to obtain threads of the

FIG. 3.





amorphous material. He made use of organic molecules to establish the general principles before proceeding to borate and silicate glasses. The softening interval for simple organic and inorganic molecules was 23—29° independently of the chemical nature of the material, although the value of the mid-point  $t_m$  was a characteristic property of a chemical substance. There were, however, anomalous substances consisting of large molecules, such as high polymers, for which the softening interval was considerably greater.

He showed that many physical properties changed rapidly on passage through the softening interval, and that the changes resembled in some measure, although they were not so abrupt as, those occurring on melting. He emphasised, however, the continuous nature of the changes on passing from a glass through a liquid to a gas, and pointed out that this process could not involve a phase change. From a study of the changes in volume, specific heats, dielectric constant, optical and elastic properties, etc., he concluded that a glass could be regarded as a supercooled liquid for which the rotational movements of the molecules had been frozen. He discussed the further implications of this conclusion in later papers, in terms of his theories of polymerisation and internal pressure.

In this field, also, Tammann was a pioneer who laid the foundation of the experimental and theoretical approach which others have since followed and elaborated. Although Tammann was mainly interested in the fundamentals, he gave considerable thought to the practical applications of his researches to the glass industry, and contributed numerous papers on technological aspects to the *Glas Technische Berichte*.

#### *Silicates.*

An account of Tammann's scientific environment would be incomplete without a reference to the influence of Lemberg, who was his teacher at Dorpat. From him he acquired a geochemical outlook and he saw that much of his work on heterogeneous systems and high pressures would have practical applications in the statics and dynamics of geochemistry. Nevertheless, he entered this field only at a few points, and one of the most important of these was his work on silicates, which he began at the same time as his work on alloys. In 1904, with Wittorf he studied the action of alkali carbonates on silica, and then followed investigations on the preparation of silicates, on phase diagrams of double silicates, silicate thermochemistry, and on the interaction of nontronite and kaolin. He interested himself in the question of the constitutional formula of silicates. He found there was no appreciable lattice diffusion of silica in the crystalline lattice, and from this concluded that the term "molecule" was not applicable to any of the components of the structure of crystalline silicates. This is in accord with the modern description of the structure of silicates.

Among his researches of direct geochemical interest was that on Wiecherts's earth structure, in which he showed experimentally in 1924 that a three-layer system was possible with silicates, sulphides, and iron-nickel, with sulphides forming the middle layer. Also, with Jander in 1925, he studied the relationships of gold and platinum to silicate melts. Although he took a great interest in it throughout his life, he was content in the main to leave the development of geochemistry to others.

#### *Thermal Analysis.*

Within the first year of Tammann's occupation of the professorship at Göttingen, he published a paper "Über die Ermittlung der Zusammensetzung chemischer Verbindungen ohne Hilfe der Analyse." In this he described his methods of thermal analysis, which are based on the measurement of cooling curves and their interpretation. The interpretation of these thermal effects in terms of Roozeboom's classical methods of representation of heterogeneous systems made it possible to construct accurate phase diagrams. As a consequence of Tammann's work, the introduction of the precise terms now in common use clarified the terminology for describing heterogeneous systems.

Thermal analysis was an important technical advance since it very largely superseded the laborious and inaccurate methods of hand-picking crystals out of a solidified mass and the subsequent gravimetric analysis. It also removed much of the vagueness which had hitherto entered into the construction of phase diagrams. It established the criteria for determining the existence of chemical compounds and solid solutions and for studying quantitatively the relations between them and the liquid phase. The changes occurring after a melt had solidified could also be followed, and compound formation detected even in the solid state. This was the beginning of the study of solid reactions.

Microscopic examination, already developed by Osmund, Sorby, and Le Chatelier, was largely used by Tammann to supplement the information gained from thermal analysis. Whereas thermal analysis gave the details of the chain of events leading to the production of an alloy, microscopic analysis gave the final composition and structure of an alloy when it was cold. To aid in this analysis, Tammann enriched our knowledge of the etching procedures to bring out the details of the microstructure of polished surfaces.

He demonstrated the existence of a "Zwischensubstanz" between the polycrystalline grains of an alloy (1922), and studied its bearing on recrystallisation. The impurities, mostly non-metallic, were concentrated at the surface of the grains, and he developed methods for the removal of the metal without gas evolution, which left behind the network of film previously covering the grains. This was done very elegantly in the case of metallic cadmium by exposure of the metal to a solution of ammonium nitrate.

In his first paper developing the methods of thermal analysis, he determined the phase diagram for sodium amalgam, which system he had previously studied in 1889 at Dorpat by freezing-point methods, and demonstrated that the metal was dissolved in mercury as atoms. With Wittorf in 1904 he examined the NO-NO<sub>2</sub> system. The dark blue substance which was formed from a mixture of these two gases on cooling was shown unequivocally to be N<sub>2</sub>O<sub>3</sub>. The borates which had proved particularly intractable by the normal methods yielded the composition of their compounds without any difficulty: the ratio of Na<sub>2</sub>O to B<sub>2</sub>O<sub>3</sub> was shown to be 1:2, 1:3, and 1:4, without any possibility of error. The method was successfully applied to double salts of all kinds, and in the hands of Tammann's colleagues and students, who came to him from all over the world, elucidated the structures of a very large number of metal and inorganic salt systems.

#### *Metals.*

Tammann, in his introduction to "Metallographie" (1914), mentions Roozeboom and Le Chatelier as pioneers in the application of the laws of heterogeneous equilibria, and Le Chatelier, Osmund, Roberts-Austin, Heycock, Neville, Heyn, and Weyt as the first to carry out useful experiments on mixtures of metals. However, these investigations were limited in general to the study of the beginnings of the crystallisation process, and not until the methods of thermal analysis were available was it possible to study the formation of intermetallic compounds and solid solutions with any precision. Tammann planned his investigations on a broad basis. He was a theoretician as well as an experimentalist and was able to impose a unity on the whole field which was lacking before.

One of Tammann's collaborators, G. Masing, in a paper to the memory of Tammann, explains that he saw that the field of enquiry into metals was so vast that it was not possible to make an impression on it in a reasonable time, working single-handed. He also saw that simple new techniques were needed to enable rapid progress to be made. He found these techniques in taking cooling curves and in microscopical analysis, and there soon gathered round him a large number of collaborators, which made it possible to make a very thorough survey of the metallographic field in his own lifetime.

The experimental equipment of the Göttingen school for the investigation of metals was extremely simple—a Bunsen burner, a container of cast iron, in which there was a metal crucible in the form of a tube surrounded by sand, and where necessary protected by the passage of hydrogen from a Kipp, a thermoelement, and a millivoltmeter. This was all that was needed, apart from the normal polishing equipment and a few microscopes.

Tammann's researches were summarised in his "Lehrbuch der Metallographie," which was published in 1914, 1921, 1923, and under a change of title to "Lehrbuch der Metallkunde" in 1932. These accounts enable us to trace the growth of the subject until the impacts of Tammann's work had become world wide. In the publications of the metallographic researches at Göttingen, Tammann allowed his collaborators considerable independence. They covered a very wide range of binary and, later, ternary alloy systems, including many papers on iron and steel of considerable industrial importance. An important feature of his work on metals was his interest in their physical properties. His collaborators made many investigations of the electrical conductivity, magnetism, hardness, heat capacity, heats of formation, and thermoelectromotive force of alloys and intermetallic compounds.

*Formation of Compounds and Solid Solutions.*—Tammann's first paper on this subject in 1906 was entitled "The Capacity of the Elements to Form Compounds," and he points out the large gaps in knowledge on this question, especially of intermetallic compounds. By 1925 he

had very considerably reduced this gap by means of 121 papers on metals from his laboratory. This interest in the Periodic Table probably originated in his contacts with Mendeléeff in the Dorpat period, and the paper in 1906 illustrates the very wide breadth of the foundation on which he organised his researches.

He has summarised the results in a number of tables which give details of the capacities of the elements to form compounds and solid solutions. He attempted to deduce the rules which govern these processes, but he finds that there is a tendency for metals to behave individually, conforming to very few rules. Elements in natural groups, that is, vertical groups of the Periodic Table, form very few compounds with one another and, when a given element forms compounds with one member of a natural group, it tends to form compounds with all members of the same group. There were, however, some exceptions to these rules.

The simplicity of the valency relations which occur in metallic salts breaks down almost entirely in the intermetallic compounds, and there is very little correspondence between the valencies for the two classes. This is illustrated by the formation of compounds of the type  $\text{NaZn}_{12}$ ,  $\text{FeZn}_7$ ,  $\text{NiZn}_3$ , etc. There was a tendency for compounds of the same valency types to be formed among members composing a natural group, but the exceptions to any rule he was able to formulate were very numerous.

According to Mitscherlich's rule concerning isomorphism, it would be expected that elements in the same vertical column of the Periodic Table would form solid solutions (mixed crystals), whilst elements far removed from one another would not do so. This is, in general, true, but it required a specially constructed Periodic Table to bring out the regularities. For example, Mn, Fe, Co, and Ni form solid solutions with Cu, Ag, and Au, which elements are brought together into close relation in Staegmüller's Periodic Table.

*Cold Working and Recrystallisation of Metals.*—Tammann began research with O. Faust in 1910 on the hardening of metals by cold working, and continued to publish papers on this subject until he retired in 1938. He gave a comprehensive interpretation of the processes involved in the deformation of metals and the recrystallisation processes which occur on heating, which, however, owed much to the earlier work of Ewing and Rosenheim. The unco-ordinated polycrystalline structure of a metal freshly crystallised from its melt is converted on cold working into a lamellar structure in which thin metal sheets have been produced and sheared over one another along glide planes. If a metal, such as copper, with polished surfaces be deformed above the elastic limit and examined microscopically, fine, dark, parallel lines are seen on the polished surfaces. These represent the intersection of glide planes with the surface. These planes first appear at the elastic limit of the metal and are not all produced at the same pressure, since the force which will cause gliding depends on the orientation of the individual crystallites with respect to the applied force. Tammann deduces that in the permanent deformation of crystals, parts of the crystals slide over one another along glide planes which are of two types—(1) those due to translation of one part of the crystal over another, and (2) those due to a combination of sliding, translation, and rotation of the parts of the displaced layer to form twin lamellæ.

On recrystallisation, new crystallisation centres are formed in the disorganised layers between the lamellæ which, at sufficiently high temperatures, grow and reform a polycrystalline structure. The number of new centres formed, and hence the size of the resulting crystals, depend on the amount of cold work.

Tammann investigated these phenomena from the chemical, crystallographic, and thermodynamic points of view. He studied the structure, hardness, elasticity, recrystallisation velocity, flow properties of metals, volume changes, heat evolution, conductivity, solubility, resistance to chemical attack, thermoelectric power, electromotive force, ferromagnetism, and crystallite orientation of worked metals. His textbook on Metallography contains an account of his theory, which he extended subsequently in summarising papers. In 1929 in the *Zeitschrift für anorganische und allgemeine Chemie* he summarised the results of twenty years' work on recrystallisation of metals, organic and other substances, and demonstrated the important part played in recrystallisation by thin films of impurities lying between the crystal grains.

These films, which consisted of oxides and silicates in the case of metals, or salts in the case of glacier ice, stabilise the polycrystalline structure. In the absence of such a film the usual polycrystalline structure should disappear at sufficiently high temperatures to give rise to crystals with their axes orientated in only a few preferred directions. On cold working, the continuity of the film is broken down, and therefore recrystallisation can pass the old grain boundaries. Repeated cold working, followed by recrystallisation, thus leads to the production of large crystal grains. It is of interest that the cold working of metals is used as a preliminary in one of the present-day methods of making single crystals.

*Order and Disorder in the Arrangement of Atoms in Crystals of Solid Solutions of Metals.  
Resistance Limits.*

During the First World War, Tammann studied personally the behaviour of solid solutions towards different forms of chemical attack, and found that the nature and extent of the attack depended on the method of preparation and on the pre-treatment of the alloy. This work he summarised in 1919 in the *Zeitschrift für anorganische und allgemeine Chemie*, which he dedicated to Mitscherlich, the discoverer of isomorphism. Alloys consisting of mixtures of a less noble metal with a noble metal, for example, Cu-Au or Ag-Au, when formed directly from the melt, were resistant to chemical attack by acids, oxidising agents, sulphides, etc., when the percentage of the nobler metal exceeded a resistance or parting limit. He found that alloys prepared by electrolysis did not possess this resistance. He showed that when a solid solution is prepared by slow cooling from the liquid state, the temperature is sufficiently high for the establishment of an equilibrium state among the atoms by inter-lattice diffusion, whereas in alloys prepared at room temperature by electrolysis a haphazard distribution of the atoms is obtained.

The resistance or parting limits for alloys annealed at high temperatures occur at simple ratios of the mole-fractions of the components. The value of the ratios, however, depends on the alloy and on the chemical reagent. For attack by nitric acid, the resistance limits are at ratios 1/8, 2/8, 4/8, 6/8, or 7/8 in different alloys, and Tammann was able to give a reasonable interpretation of the significance of these ratios in terms of an ordered distribution of the atoms of the solid solutions on "partial" or "super-lattices." On the other hand, a statistical examination of the distribution of atoms in a disordered state showed that no protection of a less noble by a noble metal was to be expected in such a state.

He made a thorough survey of the electromotive force and other physical properties of a number of solid solutions and found extensive support for his view that in annealed solid solutions there was an orderly distribution of atoms. He also studied the resistance limits of a number of solid solutions of inorganic salts.

In 1920 and 1922 Tammann made an important contribution to the study of the attack of metals by oxygen, the halogens, and hydrogen sulphide, where he originated the method of using the interference colours produced in the surface film to give a measure of thickness. He showed that in the attack by iodine the parabolic law held,  $dy/dt = p/y$  or  $y^2 = 2pt$ , but that in the oxidation of metals an exponential law,  $dy/dt = (1/ab)e^{-by}$ , represents the increase in thickness with time.

*Reactions in the Solid State.*—Tammann used the method of thermal analysis to investigate with his students numerous systems involving the breakdown of solid solutions, and the formation and decomposition of chemical compounds. The importance of diffusion in the solid state in facilitating these changes was realised by him. He considered diffusion as occurring by "Platzwechsel" of the atoms, and he determined the minimum temperatures at which this exchange was possible. For metals it occurred at  $0.3T_s$ , for oxides, salts, and some silicates at  $\sim 0.5T_s$ , and for organic molecules sometimes as high as  $0.9T_s$ , where  $T_s$  is the melting point.

He studied the phenomena which arise when pressure is applied to metal powders, and showed that alloys similar to those obtained from the melt could be manufactured by this method. This process, however, required a minimum temperature; at low temperatures even the application of very high pressures was unable to produce appreciable consolidation. These methods and ideas have been taken up fruitfully since, and one of his students, Hedvall, has paid particular attention to the interaction of solid powders and to reaction between solids.

*Glacier Ice.*

The flow of ice in glaciers under pressure attracted much attention towards the end of the nineteenth century, and the first theoretical explanations were based on the idea that under pressure partial melting occurred. The movement in glaciers was supposed to be due to the movement of ice grains over one another, as a result of liquefaction at points of contact. The view was put forward that a substance will melt beneath a loosely fitting piston at pressures much lower than those required with compression under a tightly fitting piston. Poynting, Ostwald, and Niggli developed this point of view by investigating various types of thermodynamic cycles to represent the process, but these led to results demonstrably mistaken, as Tammann showed. He developed methods for the study of the flow of solids under high pressures and demonstrated that ice could, in fact, flow appreciably at  $-28^\circ$  under pressures at which there can be no partial melting. His explanation is based on that which he gave for the deformation of metals, and the occurrence of very large grain size of ice crystals in arctic glacier ice he interpreted as due to recrystallisation facilitated by the destruction of the film around the grains by plastic flow.

*Biochemical and Other Researches.*

Investigations on the fermentation reactions involving the use of emulsin, salicin, and invertin were carried out at Dorpat between 1888 and 1896. Tammann found that the reactions did not proceed to completion or to an equilibrium state, as was the case with normal catalytic reactions. They were brought to a standstill by reaction by-products, and after removal of these products the reactions commenced again. He showed that the Arrhenius relation applied to the temperature coefficient of the natural decrease in activity of the ferments, but not to the fermentation reactions themselves. In 1904 he showed that there was a decrease in the virulence of bacteria after subjection to high pressures, and later he studied the poisoning of bacteria with metal ions.

He also worked on the permeability of membranes and concluded that the permeability could not be entirely explained in terms of their behaviour as molecular sieves, but that the solubility of substances in the membrane also played a part. Tammann used freezing-point and conductivity methods to distinguish between the isomers and polymers of metaphosphates. In 1902 this work formed almost his sole claim to the title of inorganic chemist. As examples of isomers were  $\text{Na}_2(\text{PO}_3)_2$  and  $\text{Na}_3(\text{PO}_3)_3$ , and of polymers  $\text{Na}_2[\text{Na}_4(\text{PO}_3)_6]$  and  $\text{Na}_4[\text{Na}_2(\text{PO}_3)_6]$ . In the cases of the last two substances he showed that alkali metal appeared in the negative ion. In his method of formulation of these complex compounds he anticipated Werner.

## APPRECIATION

Tammann's active period of research extended from 1883 to 1938. He was a contemporary of Ostwald, Nernst, van't Hoff, and Arrhenius, and was associated with them in laying the foundations of physical chemistry. The work of his contemporaries was, however, so closely inter-related and interwoven that it is often not easy to decide to whom belongs the credit for a particular discovery. Tammann's theoretical work was much more isolated than that of his contemporaries, for he surged ahead of the advancing wave of science into regions where his contemporaries and their successors had difficulty in following him. His researches on the internal pressures of solutions and on the equilibria between the crystalline and liquid states of matter penetrated so deeply that even now the problems that interested him are still unsolved.

As Ostwald indicated to Tammann in 1889, it is, in general, most remunerative when investigators work in close contact with the scientific background of the time. It is rare that work carried out in partial isolation has the good fortune that befell the researches of both Willard Gibbs and Hittorf, which good fortune was so well merited. It would appear, in general, that the changing language of scientific thought makes it uneconomic to absorb work done ahead of the time. It is therefore problematical whether the theoretical investigations of Tammann will have any better success with a future generation of scientists than they have had with his contemporaries. Although they had a by no means negligible influence at the time, their importance would rather seem to lie in the fact that his theoretical investigations suggested to him unique methods of experimental approach. Many of the ideas applied to practical problems appear to many of us to be disconnected flights of genius, probably because their point of origin lies beyond our ken. To Tammann his own work was a unified conception, although he has stated that he had "manches Figurchen auf Elfenbein geschnitzt."

His most important work was concerned with heterogeneous systems, and in many directions we find that he has taken the first scientific steps and has laid down the pattern of investigation or the basic idea, which his successors have accepted and further developed. His work on high pressures preceded that of Bridgman by ten years and his most striking achievements in this field were the discovery of the different forms of ice, and his interpretation of polymorphism. By his discovery of thermal analysis he made possible the construction of accurate phase diagrams and thereby initiated the rapid advances by his own students and others in the development of metallography.

Essentially his own was the formulation of the laws for systems not in equilibrium, such as those governing nucleation and the rate of crystallisation. He successfully applied these fundamental ideas to the understanding of the phenomena arising in the cold working of metals and their recrystallisation. He clarified our knowledge of the amorphous state and particularly of glasses. It is surprising how much of his work lies at the basis of the modern approach to geochemistry. By the study of chemical resistance limits, he discovered "superlattices." He employed the interference colours, formed on metals under the action of gases, to study the kinetics of heterogeneous reactions. He laid down the basis for the study of the interaction

between solid phases and showed the dependence of reactivity on diffusion in the solid state, for which he established limiting temperatures.

Tammann saw very clearly the ways in which a complicated problem could be broken down into its elements. A line of enquiry usually started in his private laboratory with an investigation with his own hands and with very simple apparatus. The problem was then handed over to his research assistants and students for further development. He had normally some 20 to 30 students working in his laboratory at Göttingen, following the lines of investigation developed first in his private laboratory. Periodically he would summarise the work of this army of investigators in papers or in monographs, and thereby make clear what had been achieved and what still remained to be done.

One of his greatest contributions to science lay in the men he trained for University and industrial research, who spread his ideas and teaching far and wide. By means of these men his impact on the development of physical chemistry was immediate in its action and at the same time was long-range in its influence. Some idea of the extent of his influence can be gathered from the Tammann "Festschrift" in the *Zeitschrift für anorganische und allgemeine Chemie*, 1926, in which over 100 students and colleagues commemorated his sixty-fifth birthday by their greetings and records of work which owed much to his inspiration.

Although Tammann lived for his work and concentrated his efforts in making the greatest possible penetration into the unknown within his life's span, he was very human in his relations with his staff and students. He was unconventional and disliked formality. His humanity showed itself during the First World War in his care for the numerous Russian students in Göttingen, whose poverty was outstanding. He had an irrepressible sense of humour which showed itself in his daily visit round the laboratory, in the Ph.D. examination, and in all kinds of unlikely places. When he was leaving Dorpat he was introduced to Archbishop Agafangel, who held out his hand to him to kiss; Tammann shook this hand vigorously, much to the amazement of the Archbishop. On the occasion of the Ph.D. examination of an American student, this student sent in his visiting card as was customary, and on entering was received with hearty roars of laughter. He had inadvertently sent in a card, on the back of which was written a couplet which he had copied from the walls of an inn the previous Sunday. Tammann, however, expected the utmost from his collaborators, and only the best would satisfy him.

He received many honours. He was honorary member of the Bunsen Gesellschaft, of the Deutschen Gesellschaft für Metallkunde, of the British Institute of Metals, an Honorary Fellow of the Chemical Society, and was the recipient of the Bunsen, Heyn, and Karl Lueger Prizes. He was a member of many Academies. At the age of 75 he was awarded by Adolf Hitler the Adlerssheld of the Deutsches Reich.

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