



Jannik Bjerrum (5 April 1909—29 August 1992). Photograph from 1986.

Jannik Bjerrum was born in 1909 in Copenhagen. As grandson of the world-famous ophthalmologist Jannik Bjerrum and son of the outstanding chemist Niels Bjerrum, he was born into a strong scientific tradition. The influence both of his family and of his inspiring teachers was of great importance for the young Bjerrum, who opted for a scientific career even before taking his final school examination, “studentereksamen”, in 1927.

Bjerrum obtained his masters degree in chemistry at the University of Copenhagen in 1932, specializing in physical chemistry. During his studies he profited not only from the influence of outstanding teachers, especially E. Biilman and J.N. Brønsted, but also from contact with his father's friends, in particular Niels Bohr who helped to mould Bjerrum's scientific development and strengthen his exceptional scientific instinct.

After completion of his masters degree and a short period of study abroad, Bjerrum pursued his scientific career at the University of Copenhagen. He became scientific assistant in 1933, dr. phil in 1941 and professor in 1948. He was vice chancellor from 1965–1967 and Master of “Regensen” from 1967–1978. As professor at the University of Copenhagen he also directed Chemical Laboratory A at the Polytechnic (later the Technical University of Denmark) from 1948–1960. He was president of the Danish Chemical Society from 1954–1956. During his career he published some 150 papers. Bjerrum was elected a fellow of the Royal Danish

Academy of Sciences and Letters in 1948, and he became a member of the Danish Academy of Technical Sciences in 1958, member of the Royal Norwegian Scientific Academy in 1960, member of the Royal Swedish Scientific Academy in 1969 as well as of several other foreign academies. He was awarded the Augustinus prize in 1958, and he received the Royal Danish Knighthood of the 1st order in 1963 and the Commander order of Dannebrog in 1977. He received honorary doctorates from the Universities of Debrecen (Ungarn) and Lund (Sweden) in 1979 and 1987, respectively.

In 1937 he married Grethe Ehlers. They had seven children. Bjerrum enjoyed having a large family, and he always tried to divide his time between family and science.

A CELEBRATION OF INORGANIC LIVES

A survey of Jannik Bjerrum's life and scientific work based upon his private notes and adapted to the present form by the authors

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Shall we begin by asking you about your childhood?

My father, Niels Bjerrum, was very occupied by his many duties so it was mainly my mother, Ellen Bjerrum, neé Dreyer, who took care of me and my three younger sisters Bodil, Marianne and Kirstine. My mother was a capable housewife and a caring mother for all of us. She loved and admired my father, and her devotion probably made our father an example and an authority for us children more than a person to whom we could entrust and confide our small worries and secrets. Later, when I learned to know him better, I realized that behind his apparent strictness was a great and noble person.

During the first ten years of my life I spent long periods with my grandfather, Professor Jannik Bjerrum, in Hellerup, a suburb of Copenhagen. I enjoyed the delightful outdoor life in the large old garden of his house near The Sound (Øresund). My grandparents were very hospitable and their home was the centre for a large circle of acquaintances, so that numerous people contributed to my development. Especially my nine year older uncle Hans Adolf Bjerrum, who later became a civil engineer, was always willing to let me participate in his many interesting activities. The constructive play he initiated was important for my development. My grandfather's sister, the physicist Kirstine Meyer, also had a great influence on my life as she had an unusual gift for fascinating children. She was the one who taught me early on to appreciate sedentary work. After the death of my grandfather in 1920 my grandmother continued the family traditions of hospitality, but in a smaller house, and her oldest daughter, Aunt Dede as we called her, dedicated herself to us children during those years.

My mother came from a wealthy family. Her father, Peter Dreyer, was a wine merchant and consul. Every second Christmas was spent in their home in Randers where my uncle, Carl Dreyer, who at that time was a bachelor and who was a clever amateur conjurer, took care of me. His magic tricks particularly fascinated me and stimulated my imagination. Shortly before the end of the First World War my grandparents moved from Randers to an apartment in Copenhagen just a few minutes walk from my parents' somewhat smaller apartment. During the next years my sisters and I were frequent visitors in their home, and my mother's youngest brother, Jørgen Dreyer, was of especial importance to me during this period and continued to be a fatherly friend over the years. When my uncle moved abroad, I took over his room and lived with my grandparents until my father and mother moved to a bigger apartment in 1924, when I finally got my own room at home.

During my early childhood I liked to draw and paint but stamp collecting soon became my great interest. As a teenager I was fascinated by amateur photography and building small radio receivers. Collecting wild flowers became a hobby that I much enjoyed during my summer holidays, and in 1923–1925 I established a large herbarium of wild plants found in the area around Blokhus in Northern Jutland where my parents rented a house for the summer.

Can you tell us about your school days and when you first realized your interest in chemistry?

I started school (H. A. Adlers Fællesskole) at the age of six. I was a dreamer and it was difficult for me to learn to read. I still clearly remember how my mother did her best to practise with me while I was longing for play and experimentation. I was much better at maths but it was not until I had history that I showed any real interest in my school work. My teachers in mathematics and physics in high school were very inspiring, and I think they strengthened my interest in natural sciences.

I became interested in chemistry at an early age by reading books in my father's library, for example Jöns Jacob Berzelius' "Stoichiometrische Untersuchungen" from 1812, and of course I could ask my father questions. I can't say my father prompted me; it was more an indirect influence. I did my first experiments at home in the kitchen but it was soon too much for my mother, who complained about the smell when I was precipitating metal ions with hydrogen sulfide. At the age of 15 I was allowed to work in my father's laboratory at The Royal Veterinary and Agricultural University. After having obtained some experience in qualitative and quantitative analysis I started to verify some of Berzelius' experiments, and I obtained reasonable atomic weights for more than 10 elements. All the experiments are carefully described in a school exercise book which is dated 1925. I later used it to show to my children when they complained about the exercises they had to conduct at school. My father's assistant, later Professor Carl Faurholt, took good care of me during this period.

Can you tell us about your time as an undergraduate and graduate student?

In 1927, 18 years old, I began to study chemistry at the University of Copenhagen. I had chosen to study for "magisterkonferens" which made it possible for me to determine my own timetable since I wanted time to do my own research. I studied chemistry the first year together with engineering students. I quickly passed the obligatory courses in analysis and synthesis. The lectures were given by the chemistry Professors Julius Petersen, Einar Biilman and Johannes N. Brønsted. Julius Petersen's lectures in inorganic chemistry were distinguished by their excellent experiments. These experiments later formed the basis for my own lectures in inorganic chemistry at the Polytechnic. Einar Biilman's lectures were of interest because of his eloquence and his many historical anecdotes, while Brønsted's lectures were prominent because of his ability to make difficult fields of physical chemistry simple (sometimes so simple that the difficulties were not realized until the problems were studied at home). Among the young assistants at the institute I became acquainted with Stig Veibel and Hakon Lund, both of whom later became professors. The latter was my teacher in organic synthesis. We had many fruitful discussions and my first research project was done with Hakon Lund on a method for producing anhydrous alcohol. The project resulted in a publication in *Ber. Deutsch. Chem. Ges.* (1931). This was the first time my name appeared in the literature.

My father was obviously of great importance to my development during this period, and our conversations provided me with a lot of chemical insight and many a good piece of advice. However, he influenced me most of all by his example, and I took great pleasure in reading his scientific work. During these years I also became more closely acquainted with my father's friends, especially Holger Hendriksen, Ole Chiewitz and Niels Bohr, and I spent many pleasant hours in their company on Sunday walks and sailing the boat they owned together. Scientific and political problems were discussed, and I learned a lot from being present during these conversations. The boat's log book, which is still in existence, reflects in part those happy days.

My studies and my interest in my parents' circle of acquaintances did not impede my normal life as a student, during which I met and became friends with several other students of the same age. They were often invited home so my younger sisters could benefit from their company. Among my friends from this period were the actuary Paul Johansen and the physician Johannes Ipsen Jr. (later professor at Harvard).

I took up my own research at the Veterinary and Agricultural University quite early in my studies. During the course in qualitative analysis I had noticed that copper-ammonia solutions (supposed to contain the tetraammine complex) underwent a colour change from violet to blue on increasing the ammonia concentration. Studying this phenomenon I was able to show that the colour change was

caused by the formation of a pentaammine complex having a very low formation constant and a spectrum clearly different from that of the tetraammine.

Copper–ammonia solutions with less than four ammonia molecules per copper(II) ion are unstable and give basic precipitates. When I found that it was possible to make homogeneous solutions of all the complexes from the aqua copper to the tetraammine complex in the presence of ammonium salts in high concentration, I took up a study of the equilibrium conditions as a function of the concentration of free ammonia. This was done by measuring the ammonia vapour pressure over the solutions. The salt medium was 2 M ammonium nitrate, which at the same time constitutes a constant salt medium. The very low ammonia vapour pressures over some of the solutions were measured by passing up to 100 l of purified air slowly through the solutions and titrating the transferred ammonia with 0.01 M HCl. In this way I determined the average number of ammonia molecules bound per copper atom (now internationally known as $\bar{n}$) as a function of the free concentration of ammonia. Analysis of the data showed the existence of all the intermediate complexes and the consecutive formation constants were determined. The results were confirmed by solubility measurements using the slightly soluble basic copper nitrate (Gerhardtite) in 2 M ammonium nitrate. The spectra of the copper–ammonia solutions were measured in the visible region, and spectra of the individual copper ammine species were calculated from a knowledge of the stability constants. The work was followed up by a study of the equilibrium between copper amalgam and the copper(I) and copper(II) amines by EMF measurements. This study gave an independent confirmation of the results obtained for the copper(II) amines and made it possible to calculate the stepwise formation constants for the diammine copper(I) ion. The copper ammine work was published in German in *The Royal Danish Academy of Science and Letters (Det Kgl. Danske Videnskabernes Selskab, Matematisk-fysiske Meddelelser)* during the years 1931–1934, and for this reason it is not so well known as my later work. In 1932 I finished my university studies in physical chemistry with Brønsted as my teacher.

Can you tell us about your time after graduation?

Just after finishing my master's degree I went to Germany and studied for six months with Kasimir Fajans in Munich. The scientific impact of my studies in Professor Fajans' laboratory was small but the stay had a great influence on my personal development. The international student life, as reflected at the University of Munich in the last days of the Weimar Republic, gave me a feeling of the importance of international collaboration in science — and some ability at drinking beer. The latter facilitated my later rôle as Master for the oldest student hall of residence in Denmark, "Regensen". During my return trip to Denmark I visited several of my father's friends and colleagues at German universities. I remember especially the hospitality of Professor Georges de Hevesy in Freiburg and Professor

Fritz Weigert in Leipzig. After my return from Germany I was determined to pursue a scientific career. However, the job situation at that time was difficult, so I had to wait some months before I could continue my studies on copper ammine formation as a guest in Professor J. A. Christiansen's laboratory at the Polytechnics. In 1933 Professor Valdemar Henriques offered me a position at the Institute of Physiology in the Medical Faculty, University of Copenhagen, and since no other position was available I jumped at the offer. Here I was occupied with biochemical studies (the metabolism of copper in the blood of rabbits) and I developed a method for determining small amounts of copper in serum. I benefited personally from the collaboration with Henriques, and, more importantly, these studies lead to a Rockefeller Fellowship in biochemistry. Professor Biilmann promised me a position as a teacher at his department of chemistry on my return — which was unusual at that time.

In 1934 I went to study with Professor Leonor Michaelis at the Rockefeller Institute for Medical Research in New York. Due to his interest in coordination compounds Michaelis was the biochemist at that time with whom I shared most research interests. It became apparent to me that if it was possible to measure pH in ammoniacal metal salt solutions with sufficiently high accuracy, it would be an easy matter to extend my copper–ammonia studies to all ammine-forming metal ions. The electrodes which could be considered for such studies were the hydrogen gas electrode, the quinhydrone electrode and the glass electrode. However, the hydrogen gas electrode is of limited use, and the quinhydrone electrode can only measure the hydrogen ion concentration in solutions with $\text{pH} < 7$. Only the glass electrode is universal in its application. So when I learned that MacInnes' laboratory in the Rockefeller Institute had succeeded in making reliable and accurate glass electrodes of Corning glass 015, I realized that this electrode with the theoretical pH-dependence would be ideal for metal complex studies. After publishing a short paper with Michaelis, he was kind enough to let me continue my own studies with the glass electrode. The glass electrode set-up used in Michaelis' laboratory was placed in the professor's own working room, and for this reason I did most of my measurements in the evenings. Much later I acquired my own electrodes and these and the other equipment were then placed in a thermostated room. I worked hard during the week but I normally kept Sundays for relaxation and went for walks in the surroundings of New York with colleagues from the Rockefeller Institute. I particularly remember walks with the physical chemist MacInnes, the biochemist Hotchkiss and the Danish–Swedish physician Jørgen Lehmann. I also visited colleagues at Princeton and Yale, and went on skiing trips to the Green Mountains and Adirondacks. In the summer holidays I went to Woods Hole, as did many other people in the natural sciences. I also especially recall sailing to Maine with Dr. Webster from the Rockefeller Institute. At Christmas I went to St. Marguerite, close to Montreal. The sudden death of my mother shortly before I left for New York was a great loss to me. However, in spite of this, the year I spent at the Rockefeller Institute in New York was among the best in my life.

In February 1936 after my return to Denmark I took up position in the Department of Chemistry at the University of Copenhagen. In the beginning I was Professor Biilman's private assistant. However, he soon gave me a free hand to do my own research. The next year was a period with quiet working hours in the laboratory combined with a reasonable amount of teaching — a period which provided me with satisfactory conditions for my scientific work. I taught chemistry for medical students, but I was also lecture assistant for Biilman. This was quite a difficult task, as Biilman got very upset if a lecture experiment failed! In spring 1940 I became teaching assistant for the organic laboratory course at the Chemistry Department, a demanding but also more satisfactory job than teaching medical students. It gave me a deeper understanding of organic chemistry that was of great help later in my career.

Despite my teaching duties I made rapid progress in my scientific work. The metal complex studies were continued after my return to Denmark, and the result of this work: "Metal Ammine Formation in Aqueous Solution. Theory of the Reversible Step Reactions" was published as my "Habilitationsschrift" (Ph.D.thesis) in the beginning of 1940. The thesis was in Danish and I am deeply grateful to my father for advising me to have it translated into English, otherwise it would probably never have been noticed outside Scandinavia. In the beginning of 1941, during the German occupation of Denmark, I succeeded in sending about 50 copies to the U.S.A. before the attack on Pearl Harbour, so that it became known in America during the war. The results contained in the thesis are well known, and I shall only mention that besides providing a large body of data, fundamental formulae and general methods for treating complex systems with monodentate ligands, it also opens up the field of quantitative chelate complex formation with ethylenediamine as an example. My discovery that charcoal catalyzes equilibration between the inert cobalt(III) amines also made it possible to determine the stability constants for these complexes, besides being of importance for preparative purposes. In the preliminary experiments I found that colloidal palladium in the presence of low concentrations of the labile cobalt(II) system had a catalytic influence on the equilibration. However, when charcoal was used as catalyst the presence of cobalt(II) was not necessary, even though it was found that cobalt(II) also had a promoting influence in this case. The reason for this is that charcoal to some extent reduces cobalt(III) to cobalt(II) on the surface of the carbon. This was not taken into consideration when I found that charcoal had no catalytic influence in the analogous chromium(III) systems, and it was one of my co-workers, Claus Schäffer (my successor in the chair of inorganic chemistry), who in 1961 discovered that charcoal in the presence of chromium(II) is a good catalyst for the chromium(III) systems. This catalytic approach to the study of chromium(III) systems has been developed further and utilized during the seventies in my laboratory by Professor Peter Andersen.

My scientific work after the publication of my thesis continued in the field of solution chemistry. In 1943 I made a contribution to the theory of simple association

of molecules in gas and liquids. The paper was written in Danish, but the thermodynamic formulae given were also derived in the same year by Josef Kreuzer (*Z. Phys. Chem. B*, 53 (1943) 213), so my work was never published in an international journal. In 1944 I introduced a new method for the investigation of stepwise equilibria making use of the "principle of corresponding solutions", and I showed how it is possible to make a semi-quantitative treatment weak complex formation [such as that of copper(II) chloride] in a solvent with high and varying concentrations of a complex-forming electrolyte. Further studies of this kind [with cobalt(II) chloride and chromium(III) chloride] were continued many years later with Leif Skibsted and with my youngest son, Morten J. Bjerrum.

I continued my research during the war to the extent that it was possible to get chemicals and instruments. In 1944 I applied for a professorship in chemistry at the Polytechnic. It was common at that time for applicants for a professorship to give several lectures in a competition judged by the other professors, and since I had not had much practice in giving lectures the competition was won by R.W. Asmussen. This was a great disappointment, since it was impossible at that time to have graduate students without being a full professor. However, I continued research by myself, and my work was well received at the Sixth Nordic Chemistry Meeting in Lund, Sweden, at which I gave my plenary lecture "Om metalioners tilbøjelighed til kompleksdannelse" (On the Tendency of Metal Ions Towards Complex Formation). The discrepancy between the Brønsted and Lewis definitions of acids and bases also occupied my time. While their definitions of a base agree well, this is not the case for their definitions of an acid. For historical reasons I felt that the name "acid" should be reserved for the proton acids, and I pointed out that the proton itself cannot be considered as an acid. Therefore, instead of using two different acid definitions, I proposed the term antibase for Lewis acids such as BF_3 , SO_2 and the proton itself, expressing their ability to neutralize bases without being acids. However, this nomenclature has only found limited use in Denmark and Germany.

When did you become full professor? What can you tell us about your students?

In 1948 I became professor at the University of Copenhagen and director of the Laboratory of Inorganic and Analytical Chemistry (A) at the Polytechnic in Copenhagen, and the same year I had the honor of being elected a fellow of The Royal Danish Academy of Sciences. Until then I had to do all experimental work myself, but after my appointment as professor I could continue my studies with the help of students. Among these were Carl Johan Ballhausen, Christian Klíxbüll Jørgensen, Claus Schäffer and Flemming Woldbye, all of whom have become internationally known chemists and professors. Much work was also done by visitors such as Fred Basolo, Arthur Adamson and Mihály Beck.

Together with my first graduate student, Svend Erik Rasmussen (now professor at Århus University), I studied the acid-base, cis-trans and complex equilibria in



Jannik Bjerrum together with his associates during a lunch break in 1956 at Chemistry Department A. From left to right: Flemming Woldbye, Carl J. Ballhausen, Jannik Bjerrum, Arthur W. Adamson, E. Rancke-Madsen, Niels Hofman-Bang, Ingeborg Poulsen, Knud Georg Poulsen, Claus Schäffer and Christian Klíxbüll Jørgensen. The photograph was taken by Fred Basolo.

the cobalt(III)-ethylenediamine system. During this study it was found that even acidic solutions of the diaquabis(ethylenediamine) ion became more acid on prolonged standing in closed bottles, and it was assumed that this was due to polymerization reactions. More than 20 years later, in collaboration with Eva Porzsolt, the same influence of ageing was found with the diaquacobalt(III)-tren complex. However, in the meantime Dasgupta and Harris (*J. Am. Chem. Soc.*, 97 (1975) 1733) had found that such cobalt systems have an extremely high tendency for uptake of carbon dioxide and release of hydrogen ions. The pH lowering was therefore understandable, and an orange-red compound which separated from our solutions was identified as the carbonato-tren complex. Another promising student, Chr. Klíxbüll Jørgensen (now professor at the University of Geneva) was interested in spectroscopy and drew my attention to the fact that the sharp band of the neodymium ion at 427.5 nm in aqueous solution became shifted to 429.5 nm in ethanol. This observation was utilized in following the formation of the neodymium aqua ion in ethanolic solution. Jørgensen subsequently continued these studies with other aqua ions.

Together with Knud Georg Poulsen I studied the kinetics of the slow complex formation in the chromium(III) thiocyanate system. One day I discussed with him the possibility of doing similar kinetic studies with those transition metal ions which

at that time were considered to attain equilibrium instantaneously, and I suggested that he should investigate whether cooling was sufficient to slow down the reaction between ferric ions and thiocyanate ions. Both reactants were cooled in methanol solutions, and we were surprised to find that the formation of the red thiocyanate complex was completely inhibited at the temperature of solid carbon dioxide. In this way it was discovered that most of the reactions of the transition metal ions could be followed by classical methods at temperatures down to -100°C using methanol as solvent. These experiments showed for the first time the connection between rates of complex formation and valency and electronic configurations of the metals in the transition series. Thus: (i) for ions with the same electronic configuration, for example Fe^{3+} and Mn^{2+} , higher valency is associated with lower rate and higher complexity; (ii) in cases of equal valency, ions with half-filled and filled (or nearly filled) shells show a much higher rate of complex formation than the remaining ions in the transition series (compare, for example, Fe^{3+} with Cr^{3+} and Co^{3+} , or Mn^{2+} , Cu^{2+} and Zn^{2+} with Fe^{2+} , Co^{2+} and Ni^{2+}). By estimating half-lives for dissociation of the complexes in acidic solution at two temperatures the activation energies were calculated, and in this way values of the activation energies for the formation and dissociation of the nickel(II) and copper(II) ethylenediamine complexes were obtained which were in fair agreement with results obtained later by the relaxation methods developed by Eigen and co-workers. This pioneering work, which was published only in *Nature* (169 (1952) 463) and as a symposium paper (Symposium on Co-ordination Chemistry, Copenhagen, August, 1953, 51–56) has not achieved the recognition it deserves, and I have often regretted that the experiments were not continued and published in more detail.

In 1951 Ilse and Hartmann were the first to apply the crystal-field theory to explain the absorption spectrum of a transition metal ion (the titanium(III) ion, with one d-electron). Their paper (*Z. Phys. Chem.*, 197 (1951) 239), which I handed over one morning to Carl Ballhausen (who was already familiar with quantum mechanical calculations) had a decisive influence on the research in my laboratory, and in collaboration with Ballhausen and Klíxbüll Jørgensen the theory was applied to the spectra of the copper(II) ammonia complexes and provided an explanation for the so-called pentaammine effect discovered in my first paper on the subject. I participated in the research in this field until 1956. During the following years my former co-workers, together with Claus Schäffer, made important experimental and theoretical contributions to the development of the ligand-field theory.

For a number of years I had collected data on complex formation in solution, and as early as 1947 I published a paper in Danish "On the Tendency of Metal Ions Towards Complex Formation" which was later published, in somewhat extended form, in English. In this paper I discussed the average affinities of the relatively few metal ion complex systems for which formation constants were known at that time. On the basis of these data I was able to point out some general rules for complex formation, and without using a specific nomenclature I distinguished between what

Ahrland and Chatt in 1958 denoted as Class (a) and Class (b) and Pearson in 1963 denoted as hard and soft metal ions and ligands. This work led I.M. Kolthoff (then president of "The Commission on Physico-Chemical Data of Analytical Interest") in 1951 to invite me to collaborate on a publication of "Tables of Stability Constants". I undertook this task, but it was soon obvious that it was more than I could manage owing to the almost explosive development of the field during the fifties. I was therefore glad to have assistance from Lars G. Sillén and Gerold Schwarzenbach in compiling data for the inorganic ligands and the organic ligands, respectively, and by our combined efforts we succeeded in getting the tables published by The Chemical Society in two parts in 1957–1958. I had then become tired of this kind of compilation and withdrew from the collaboration in connection with the later editions of the tables.

Until 1955 I had used mainly potentiometric methods to determine stability constants and their temperature coefficients. Some thermochemical measurements were therefore made in collaboration with Ingeborg Poulsen, and these measurements confirmed my estimate from the measurements of temperature coefficients that the heat evolved per step was approximately constant up to the characteristic coordination number for complex systems with non-charged ligands, such as the amines. This showed directly that the fall in the consecutive constants (the statistical effect) is an entropy effect in these systems.

Studies have also been made with monoamines other than ammonia, especially methylamine, butylamine, the ethanolamines and pyridine. These studies have extended our knowledge of the errors introduced by the presence of the ligand in the salt medium, and procedures have been developed to correct for the sometimes considerable salting-out (e.g. with aliphatic amines) and salting-in effects (e.g. with pyridine) which are observed even at relatively low concentrations of the ligand. However, ammonia and ethylenediamine have been my favourite ligands, and my interest in these ligands has continued over the years. In 1961 a kinetic study of the formation of the monoammine nickel(II) ion was made together with Clifford Garner, and in 1974 a study of gold ammines (which until then were practically unknown) was undertaken together with Leif H. Skibsted (now professor at the Royal Veterinary and Agricultural University in Copenhagen). In this study, data were obtained on the stability and acidity of the weakly robust gold(III) tetraammine ion, and the standard potentials of the gold(III) and gold(I) ammine complexes were determined. In connection with this study, the standard potentials of the gold aqua ions were also estimated.

As early as 1948 I proposed in a paper with E. Juhl Nielsen that one ethylenediamine ligand in the tris(ethylenediamine) copper(II) ion in solution is monodentate, and in 1959 Erik Jørgensen and I were able to demonstrate on the basis of kinetic data in the literature the existence of a chromium(III) complex with a monodentate ethylenediamine. Platinum(II) complexes with protonated monodentate ethylenediamine ligands can be prepared, and in 1968 the stability and rate of chelation of such

complexes were studied together with Ole Mønsted. These measurements provided, as one of the first studies of this kind, quantitative information about the kinetics of the ring closure for 5-membered rings (ethylenediamine) and 6-membered rings (trimethylenediamine). The formation of bis(diamine)chromium(III) complexes by direct reaction in acidic solution between the hexaaqua ion and 2,2'-bipyridine or *o*-phenanthroline was demonstrated in a paper with Richard G. Inskeep. The kinetics were studied, and the bis(ligand) complexes were isolated and suggested to have the trans configuration. However, later work in the laboratory (Josephsen and Schäffer, *Acta Chem.Scand.*, 23 (1969) 2206) has shown that they are cis and that there is steric hindrance to formation of the trans complexes.

The rather complicated equilibria in the mercury(II) ethylenediamine system were studied together with Erik Larsen (now professor at the Royal Veterinary and Agricultural University in Copenhagen). In this system, as in the analogous silver system studied by Schwarzenbach et al. (*Helv.Chim.Acta*, 35 (1952) 2337) there exists a large number of different species because of the tendency of the metal ions to linear coordination. The formation constants in both systems are now relatively well-known, but there is some doubt about the degree of polymerization of the mono-ethylenediaminesilver ion. My most recently published paper with Eva Bang (in 1979) describes a study of this problem by solubility measurements with mono-ethylenediaminesilver perchlorate in solutions with varying perchlorate concentration at constant salt concentration. Magyar and Schwarzenbach (*Acta Chem.Scand. A*, 32(1978) 943, dedicated to me on the occasion of my 70th birthday and published after the death of Schwarzenbach) provided much evidence to indicate the dimer $\text{Ag}_2\text{en}_2^{2+}$ as being the final polymerization product, but our own measurements are most consistent with continued polymerization beyond the dimerization stage. The problem is therefore still open to discussion.

My copper(II) ammine work in the thirties was performed at sufficiently high ammonium ion concentrations to suppress hydroxo complex formation. With B.V. Agarwala I have continued this work at low ammonium ion concentration, and the results from this study show the existence of μ -dihydroxodicopper(II)ammine complexes, and that it is the tetraamminehydroxo complex and not the triamminehydroxo complex which is formed in strongly alkaline copper(II) solutions at sufficiently high ammonia concentrations.

Though most of my work has been performed with amine systems, I have also made studies with other ligand systems. Besides the studies of the chloride systems of copper(II) and cobalt(II) already mentioned, I have also worked with cyanide and thiocyanate systems. With Mihály Beck I studied the tendency of tetracyanonickelate(II) to form higher complexes, and with Russell Paterson and Ole Mønsted I investigated the stability, spectrum and redox reactions of the unstable tetracyanocuprate(II) ion. Together with Renato Barbieri the organo-monohalogeno- and thiocyanatomercury(II) complexes and their tendency to further complex formation were studied, and the formation of bridged complexes between

thiocyanate bound to chromium(III) or cobalt(III) and silver ions was investigated with D.N. Purohit. The inner-sphere perchlorato complex formation of chromium(III) in concentrated perchloric acid was studied with Kenneth Jones, and the spectrum and half-life for dissociation of the pentaquamonoperchlorato ion in aqueous solution were estimated.

Sten Ahrland, Joseph Chatt and co-workers (*J. Chem. Soc.*, 264(1958) 276) were the first to prepare a water-soluble phosphine ligand (diphenylphosphinobenzene-*m*-sulphonate) and to study its behavior towards silver ions. They found that instead of giving rise to a stop after uptake of the two ligands, the ligand showed a stop in the formation curve after uptake of one, and then again after uptake of three phosphine ligands (in contrast to what is observed with amines and most other ligands). Joseph Chatt informed me of this result at the "Dixième Conseil de Chimie Solvay" in Brussels in 1956. I became very interested, and in the period 1962–1972 I made, together with a number of co-workers, a systematic study of the complex-forming ability of this ligand towards mercury(II), bismuth(III), copper(I), gold(I), palladium(II), and *cis*- and *trans*-diammineplatinum(II) ions. The complex formation of unsubstituted triphenylarsine towards silver ions in alcoholic solution was also studied, and in close cooperation with Sten Ahrland studies with this ligand in dimethylsulfoxide have been continued in Lund and Copenhagen. Phosphines are extremely soft ligands, and these studies have given important information about the stepwise formation of phosphine complexes.

In connection with these studies I have discussed advantages and disadvantages in using Pearson's classification of the reactants as hard and soft acids and bases. One softness parameter for the ligand and one for the metal ion are not sufficient to correlate complex chemical data. However, the use of Edwards' equation (*J. Am. Chem. Soc.*, 76 (1954) 1540), employing a linear combination of a nucleophilic parameter for the ligand and a parameter for its base strength towards the hydrogen ion, permits the correlation of data for the metal ions with ligands of very different type.

The physical chemistry of electrolyte solutions has always been of great interest to me. I have contributed to solving the problems connected with activity coefficients, the usefulness and limitations of a constant ionic medium and the problem of distinguishing between ion-pair formation (outer sphere association) and chemical complex formation (inner sphere association).

It is clear from what you have told us that you devote much of your time to your scientific work. Can you tell us about the other important side of your life, namely your family?

I was still living with my parents when my mother suddenly died from hypertension in 1934. It came as a shock to all of us, and it cast a shadow over my departure to the U.S.A. After my return from New York I continued to live with my father

and my sisters for some time. In November 1937 I married Grethe Ehlers, whom I had known for just six months. She was a student of medicine and we met during a chemistry course which I taught. She gave up her studies after finishing her first year to dedicate herself to our home and our children. Grethe has always had an understanding for my deep devotion to science and consequently she has courageously taken care of the household so it always functioned, irrespective of whether I was present. Thus, I have never been involved in cooking or other domestic activities. It has been a privilege to have her by my side. Furthermore, our children took over the gardening, house repairs, etc. at an early stage. These conditions have allowed me to continue until now with the habits of the past. In that respect I have been very lucky, and I am most thankful to Grethe. For the next generation the situation has greatly changed. I regret that modern lifestyle does not allow my scientifically active children to devote as much of their time to science as I did. In spite of these circumstances, I feel that they have maintained the family traditions for science. Thus my eldest son, Niels Janniksen Bjerrum (born 1940), is Ph.D and associate professor in Inorganic Chemistry at my old department at the Technical University, as it is called nowadays. Ole Jannik Bjerrum (born 1944) is an MD, Ph.D. and Research Director in the pharmaceutical industry and associated with the Technical University as adjunct professor. Elsebeth Baslev Clausen (born 1945) is a graduate in law. Poul Jannik Bjerrum (born 1948) is an MD, Ph.D. and Chief Physician in Clinical Chemistry, Kirstine Bjerrum (born 1951) is a pharmacist. Hans Jannik Bjerrum (born 1953) is an MD and psychiatrist and Morten Jannik Bjerrum (born 1957) is a Ph.D. and associate professor at my father, Niels Bjerrum's, old chemistry department at the Royal Veterinary and Agricultural University.

I tried more to be an example to my children than to be actively involved in their upbringing. Just being there, they came to me and showed their various work for appraisal. However, I have always enjoyed leisure hours with them individually or together, for example on Sunday walks, museum visits or on journeys. Especially the summer holidays, which have always been spent in our summerhouse at Skagen in Northern Jutland have given me many happy days with the family. In more recent years my grandchildren (now numbering 24) have kept me busy.

What have you been doing since your retirement?

When I retired, I was fortunate that circumstances allowed me to continue at the institute with my own laboratory facilities, so I again could conduct experiments with my own hands. In fact, doing experiments at my own pace was actually a kind of relief. During this period I had several guests in the laboratory, including Michal Wilgocki, Predrag Djurdjevic and Ivan Lukes with whom I had fruitful collaborations. This happy situation continued until 1984 when I developed problems with my hip joints due to osteoarthritis so I could hardly walk. After two operations

and a period of convalescence I was again able to work in the laboratory, although not without difficulties.

During the period from 1979 to 1991 I investigated several problems that had aroused my interest during the years. I also took up earlier work which had had to be set aside because my administrative duties as professor did not allow me time to pursue these studies. A problem of particular interest to me was weak complex formation and whether it is possible to determine small stability constants in aqueous solution. I took up this problem in connection with a study of the copper(II) and cobalt(II)chloride complexes in collaboration with my last Ph.D student, Leif Skibsted, and I continued these studies for several other systems, by myself or with co-workers. The use of a constant salt medium with a strong electrolyte in a dominant concentration works well in the case of strong complex formation but not in the case of weak anion complex formation. Instead of maintaining a constant ionic strength, I have chosen to study weak complex formation in solutions with increasing concentrations of a single highly soluble anion, e.g. solutions of HCl, LiCl, LiBr or KSCN. It is possible in this way to obtain semiquantitatively reliable results for weak complex formation up to very high ligand concentrations. This is a consequence of the simple activity relations which apply in strong electrolyte solutions with ion normalities higher than 3 M. Under these conditions the logarithm of the activity coefficient for each electrolyte increases linearly with the concentration, and the electric charges on the ions are practically without influence on the activity coefficients.

A mild stroke in 1990 and a progressing cancer of the prostate slowed my activities so that it was impossible for me to continue my scientific work. However, it gave me great pleasure that my last papers concerning weak complex formation in the chromium(III)-chloride and -bromide systems were published together with my youngest son Morten.

Thus my scientific career, which lasted 60 years, has given me a life full of happy memories.

Postscript

Jannik died on 29 August 1992.

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