NATIONAL ACADEMY OF SCIENCES

WILLIAM CROWELL BRAY

1879—1946

A Biographical Memoir by JOEL HENRY HILDEBRAND

Any opinions expressed in this memoir are those of the author(s) and do not necessarily reflect the views of the National Academy of Sciences.

Biographical Memoir

Copyright 1951 National Academy of sciences Washington d.c.



WILLIAM CROWELL BRAY

1879-1946

BY JOEL HENRY HILDEBRAND

William Crowell Bray was born September 2, 1879, at Wingham, Ontario, Canada, of good English stock. His grandfather, William Bray, born in Portsmouth in 1814, had served for eighteen years in the Royal Navy before settling in Ontario, Canada, where he engaged in business, and, late in life, became a chemist. He was described by his eminent grandson as "active in mind and body, a lover of music, and, although quiet and retiring, a natural leader in municipal, church and military affairs." One of his four sons, William Thomas Bray, the father of William C., was born in Adelaide, Ontario, in 1847. He became a pharmacist. He was characterized as "able, energetic, interested in chemistry and literature, and a social favorite." When he was but 35 years old, he contracted pneumonia following his rescue of a friend from drowning, and died, leaving a widow and two children, William Crowell, 3 years old, and Ethel Kathleen (now the wife of Professor Otto Mathey-Zorn, of Amherst College).

William Crowell's mother was a Willson, descended from a family of Cromwell supporters, who came from England His great-great-grandfather, Crowell Willson, a in 1660. "United Empire Loyalist," left the states for Canada in 1777 and settled in the Niagara peninsula. He served as a member of the parliament for Ontario. The grandfather of William Crowell Bray, who was also named Crowell Willson, served for 32 years as a member of parliament, both before and after the Confederation. He was a manufacturer and financier. After the untimely death of young William Crowell's father, mentioned in the preceding paragraph, this grandfather came to live with the widowed mother and her two little ones. He has been remembered with great respect and gratitude by them both.

Nine years later the mother died, and the 12-year-old lad went to London, Ontario, to live with a great-uncle and aunt, where he became a day pupil at the Collegiate Institute of that city. He was able to matriculate in Toronto University in 1897, but was persuaded to remain in the Collegiate Institute for a postgraduate year because he was an "immature, shy lad." In the University, the following year, he came under the influence of the distinguished and stimulating chemist, Professor W. Lash Miller. Bray proved to be an apt student; he graduated with honors in 1902 and was awarded a traveling fellowship. His first publication, in 1903, entitled "The rate of reactions in solutions containing potassium iodide, potassium chlorate, and hydrochloric acid," describing work done while still an undergraduate, is notable in that it set the course he was to follow during a lifetime of research devoted mainly to the kinetics of inorganic reactions, especially those involving compounds of the halogens.

His traveling fellowship took him to Leipzig, to the school of Wilhelm Ostwald, where physical chemistry had been receiving its main impulse. Here he came chiefly under the influence of Professor R. Luther, under whose direction he worked his thesis for the Ph.D. degree, awarded in 1905. A long paper on the hydrogen halides was published in four parts in the Zeitschrift für physikalische Chemie, in 1906, and, in the same journal and year, a study of the reactions of chlorine dioxide with the chlorine acids.

In Leipzig, he met a number of American students, including Arthur B. Lamb, who later achieved professional distinction. Although at that time he was very much a Canadian, he joined the "American Colony Club." These contacts opened the way for an invitation in 1905 to join the remarkable group of young physical chemists, including such men as Gilbert N. Lewis, Richard C. Tolman, Edward B. Washburn, and Charles A. Kraus, gathered by Arthur A. Noyes at the Massachusetts Institute of Technology. No less than eleven papers bear witness to his activity during the seven years which he spent in the laboratory at the Institute. Doubtless the most notable fruit of this period was the System of Qualitative Analysis which he worked out in partnership with A. A. Noyes and E. B. Spear, and published in four long papers in the Journal of the American Chemical Society. In this comprehensive work, qualitative analysis was lifted, as never before, from the level of pure empiricism to a firm theoretical basis in the Mass Law and the Ionic Theory.

Mention should also be made of his work on the tri-iodide equilibrium, the effect of salts on the solubility of other salts, the hydrolysis of iodine and bromine, ionization in molten salt solutions, and a particularly notable paper on "The General Relation between the Concentration and the Conductance of Ionized Solutions in Various Solvents," with C. A. Kraus, published in 1913.

In 1912, he joined the group of enthusiastic young chemists gathered by Gilbert N. Lewis at the University of California at Berkeley. Here, in addition to continuing his research activity, he played a prominent part in developing the methods in both undergraduate and graduate instruction which have had wide influence throughout the United States. It was the conviction of Lewis, eagerly adopted by his young colleagues, that research and teaching should be regarded as allies, not enemies, that one must begin right in the freshman course in order to develop graduate students eager and able in research.

The laboratory manual for the freshman course, under the title, "A Course in General Chemistry," was first published in 1915, under the authorship of W. C. Bray and L. Rosenstein. It was revised and published in 1921 and subsequently, down to the present, under the authorship of W. C. Bray and W. M. Latimer. The pioneering nature of the efforts of these authors can only be appreciated by comparing the experiments in this book with those found in the average laboratory manual a generation ago, which too often consisted merely in verifying descriptive statements. The very different aims of Bray and Latimer were stated, in part, in these words, "This course in General Chemistry has been developed with the conviction that it is the duty of a university to train its students to meet new problems. and that it is more important to give the student a scientific training than it is to sort out for him those facts which may have a special bearing on the particular line of work that he is intending to follow.

"In the laboratory the effort is made constantly to throw the student upon his own responsibility especially in observing accurately and in drawing conclusions from his experiments. He is often called upon to predict results of untried experiments. Numerous questions and problems are introduced to draw attention to essential points which the inexperienced or the careless student might pass over. The problem of 'keeping the gifted student busy at his level of achievement' may be partly solved by allowing him to work slightly ahead of the rest of the class, for he welcomes the opportunity of overcoming the difficulties by his own efforts even though this involves more work than if he had waited for the class discussion."

Bray practiced what he preached. Like the other professors in the same department, during his stay at Berkeley he regularly took charge of a laboratory and quiz section of freshmen, and labored over them with a zeal which some probably did not fully appreciate till long afterwards. He was strict in his standards of industry and accuracy and he spent no time joking with students, or discussing their personal affairs, but serious students came eventually to appreciate what he had done for their minds, as illustrated by one of them out of many who later achieved distinction, Professor Don M. Yost, who dedicated his "Systematic Inorganic Chemistry" "To William C. Bray, Able Scientist, Inspiring Teacher."

Bray's first publication out of the Berkeley laboratory was a paper with G. E. K. Branch on "Valence and Tautomerism," concerning which G. N. Lewis wrote, "Out of the haze of valence theory two separate ideas stand forth prominently. Bray and Branch have performed an important service to theoretical chemistry in differentiating these two ideas and in suggesting a terminology which adequately expresses the distinction."

On the outbreak of World War I, Bray and several associates began to work upon the pressing problem of devising a gas mask to absorb carbon monoxide, which was claiming many victims of incomplete combustion in battleship turrets and in machine-gun pits. The joint efforts of Bray, Lamb, Frazer, Almquist and others, in connection with the Defense Research Section, Chemical Warfare Service, led to the preparation of "hopcalite," (Hopkins-California) an effective mixed-oxide catalyst for the low temperature oxidation of carbon monoxide.

Bray was naturalized in 1913. He was promoted to associate professor in 1916 and to full professor in 1918. In 1919, he served as Associate Director of the Fixed Nitrogen Research Laboratory.

From his return to the University in 1920 till his death, in 1946, he and his coworkers published no less than forty-five papers. One deserving special mention was a second piece of comprehensive work on chemical analysis with A. A. Noyes, "The Systematic Detection of the Rarer Chemical Elements," in 1924. This was published in 1927 in book form. Other contributions included studies in the catalytic decomposition of hydrogen peroxide by halide-halogen couples, the oxidation of hydrogen peroxide by halide-halogen couples, the oxidation of hydrazine, a rare fourth-order reaction, ferryl ion, the hydrolysis of ferric ion and the standard potential of the ferrousferric electrode, the interaction of ozone and hydrogen peroxide, and a general discussion of mechanisms in which he stressed the important, but often neglected, distinction between "steady states" and true equilibria.

Bray was a singularly modest, unself-seeking man. He made little effort to attract graduate students to do research under his direction, but rather emphasized to them the difficulties and discouragements involved. Some of his colleagues had to offset this by pointing out to students the rare privilege open to them of working under one of the great masters of inorganic chemistry. A limited number were intelligent enough to take advantage of the opportunity, and as a result, the average quality of the men who worked with him has been very high. Among them may be mentioned Professors J. A. Almquist, R. E. Connick, H. A. Young of the University of California; Professor J. B. Ramsev of the University of California at Los Angeles; Dr. H. A. Liebhafsky of the General Electric Company: Professor R. D. Livingston of the University of Minnesota; Dr. B. Makower of the United States Department of Agriculture Western Regional Laboratory; and Professor H. Taube of the University of Chicago.

He married Nora Thomas in 1914. They have a daughter, Margaret.

He was elected to the National Academy of Sciences, the American Academy of Arts and Sciences, and was a member of the American Chemical Society, the American Electrochemical Society, and the American Association for the Advancement of Science.

Bray took sabbatical leave from May to December, 1934, spending his time with Mrs. Bray and Margaret in European travel, and in residence for a period in Vienna, where he found congenial relations with another eminent chemist interested in kinetics, Professor Emil Abel, of the Technische Hochschule.

During the difficult war years from March 1943 till March 1, 1945, when he resigned for reasons of health, he served as Chairman of the Department of Chemistry.

He suffered a heart attack late in 1945 and was immobilized for several months. He gradually improved, and visited his office and lunched, as was his wont, at the Faculty Club, but on February 24, 1946, he was suddenly and fatally stricken. The loss of Lewis, Bray and Eastman, all within a short time, was a sore blow to the Department of Chemistry.

Professor Bray had a calm, dignified personality, but he was none-the-less good company in his quiet way. Although he took serious matters very seriously, he had a fine sense of humor. One evening, for example, at a small dinner of intimate friends at his home, he remarked almost out of a clear sky, "You know, Joel Hildebrand is the most cordially hated member of the faculty." I rejoined, "Look here, Will, isn't that putting it on pretty thick. Do I have no rival in all the faculty?" "No," he replied, "when Joel and Mrs. Joel go camping in summer in the High Sierra, Joel does all the cooking and the other faculty wives have found it out."

He belonged to a congenial group of faculty members and laymen who, in the summers of 1925 and 1926, built a lodge at 7000 feet at Donner Summit in the Sierra Nevada. The group called itself "the Sierra Ski Club," but the members took good fellowship and good conversation far more seriously than good skiing, and their chief activities were intellectual and gastronomic, around the great fireplace, rather than muscular, upon the snow. Bray was a welcome member of this group, one who always remained quite sober without being solemn.

His keen powers of observation and analysis were not exhausted in the laboratory but were further exercised as a spectator to a football game or as a "kibitzer" at a card game. Gilbert Lewis once remarked that "even if you made a 'grand slam' Bray would tell you how you could have made one more trick." And he looked upon a football game with the cold but all-seeing eye of a pure connoisseur, oblivious to the hysteria of the crowd. I once repeated to the great football coach, "Andy" Smith, an observation Bray had made to me regarding tactics in a certain game. Andy listened attentively and then said, "That man must know a lot about football."

The services of Professor Bray transcended the Department of Chemistry and reached throughout the University. He served on numerous important faculty committees as chairman and as member. The same qualities which made his work so effective in chemistry made his service effective to the University. His colleagues respected him for his wisdom and loved him for his human qualities. As stated by one of his friends in the department, "his character and university service, like his scientific achievements, have appeared the finer the more intimately they have come to be known."

KEY TO ABBREVIATIONS USED IN BIBLIOGRAPHY

Chem. Rev. = Chemical Reviews

J. Am. Chem. Soc. = Journal of the American Chemical Society

- J. Indus. Eng. Chem. = Journal of Industrial and Engineering Chemistry
- J. Phys. Chem. = Journal of Physical Chemistry
- Proc. Nat. Acad. Sci. = Proceedings of the National Academy of Sciences
- Trans. Am. Electrochem. Soc. = Transactions of the American Electrochemical Society

Z. anorg. Chem. = Zeitschrift für anorganische Chemie

Z. physik. Chem. = Zeitschrift für physikalische Chemie

BIBLIOGRAPHY

1903

The Rate of Reactions in Solutions Containing Potassium Iodide, Potassium Chlorate and Hydrochloric Acid. J. Phys. Chem., 7, 92.

1905

On the Use of the Differential Equation in Calculating the Results of Kinetic Measurements; The Reaction between Arsenic Acid and Potassium Iodide near the Equilibrium. J. Phys. Chem., 9, 573.

1906

Beiträge zur Kenntniss der Halogensauerstoffverbindungen. Parts I-IV. Z. physik. Chem., 54, 463-97, 569-608, 731-49.

Einige Reaktionen des Chlordioxyde und der chlorige Saüre. Z. anorg. Chem., 48, 217.

1907

A System of Qualitative Analysis for the Common Elements. Parts I and II (with A. A. Noyes). J. Am. Chem. Soc., 29, 137.

1908

The Same. Part III (with A. A. Noyes and E. B. Spear). J. Am. Chem. Soc., 30, 481.

1909

The Same. Part IV. J. Am. Chem. Soc., 31, 611.

The Ionization Relations of Ortho- and Pyrophosphoric Acids and their Sodium Salts (with G. A. Abbott). J. Am. Chem. Soc., 31, 729.

1910

The Conductance and Ionization of Potassium Tri-iodide and the Equilibrium between Iodine and Polyiodides in Aqueous Solution (with G. M. J. MacKay). J. Am. Chem. Soc., 32, 914.

The Hydrolysis of Iodine and of Bromine. J. Am. Chem. Soc., 32, 932.

- A Volumetric Method of Determining Iodide in the Presence of Chloride, Bromide or Free Iodine (with G. M. J. MacKay). J. Am. Chem. Soc., 32, 1103.
- A Source of Error in Permanganate Titrations: Preliminary Note. J. Am. Chem. Soc., 32, 1204.
- The Equilibrium between Solid Cuprous Iodide and Aqueous Solutions containing Cupric Salt and Iodine (with G. M. J. MacKay). J. Am. Chem. Soc., 32, 1207.

1911

- The Conductance of Aqueous Solutions of Sodium Chloride, Hydrochloric Acid and their Mixtures (with F. L. Hunt). J. Am. Chem. Soc., 33, 781.
- The Effect of Salts on the Solubility of Other Salts. I. (A) Introduction. (B) Preliminary Note on the Effect of Salts on the Solubility of Uni-bivalent Salts (with A. A. Noyes). J. Am. Chem. Soc., 33, 1643.
- The Same. III. Solubility of Thallous Chloride in Solutions of Potassium Nitrate, Potassium Sulfate and Thallous Sulfate at 25° (with W. J. Winninghoff). J. Am. Chem. Soc., 33, 1663.
- The Same. IV. Quantitative Discussion of the Solubility of Uni-univalent Salts in the Presence of Other Salts. J. Am Chem. Soc., 33, 1674.

1912

- Geschmolzene Salze als Lösungsmittel. Die Ionization darin gelöster Salze. Z. physik. Chem., 80, 251-3, 378-80.
- A General Law of Ionization for Solutions of Binary Electrolytes. Trans. Am. Electrochem. Soc., 21, 143-54.

1913

- The General Relation between the Concentration and the Conductance of Ionized Solutions in Various Solvents (with C. A. Kraus). J. Am. Chem. Soc., 35, 1315.
- Valence and Tautomerism (with G. E. K. Branch). J. Am. Chem. Soc., 35, 1440.

1916

A Laboratory Manual of General Chemistry, Lederer, Street and Zeus Publishers, Berkeley, Cal.

- Experiments with Nitrogen Trichloride (with C. T. Dowell). J. Am. Chem. Soc., 39, 896.
- The Reactions between Chlorine and Ammonia (with C. T. Dowell). J. Am. Chem. Soc., 39, 905.

1919

The Volumetric Determination of Hydroxylamine (with M. E. Simpson and A. A. MacKenzie). J. Am. Chem. Soc., 41, 1363.

1920

- The Removal of Carbon Monoxide from Air (with A. B. Lamb and J. C. W. Frazer). J. Indus. Eng. Chem., 12, 213.
- The Preparation of Iodic Acid and its Anhydride (with A. B. Lamb and W. J. Geldard). J. Am. Chem. Soc., 42, 1636.

1921

A Periodic Reaction in Homogeneous Solution and its Relation to Catalysis. J. Am. Chem. Soc., 43, 1262.

1923

- The Catalytic Decomposition of Hydrogen Peroxide in a Bromine-Bromide Solution and a Study of the Steady State. J. Am. Chem. Soc., 45, 1251.
- A Course in General Chemistry (with W. M. Latimer). The Macmillan Company, New York.
- The Catalytic Decomposition of Hydrogen Peroxide in a Bromine-Bromide Solution. II. Rate Measurements in Dilute Solutions and in the absence of Sulfate, and their interpretation as a Function of the Activity Product of Hydrobromic Acid (with R. S. Livingston). J. Am. Chem. Soc., 45, 2048.
- The Catalytic Oxidation of Carbon Monoxide. I. Efficiency of the Catalysts Manganese Dioxide, Cupric Oxide and Mixtures of these Oxides (with J. A. Almquist). J. Am. Chem. Soc., 45, 2305.

- The Oxidation of Hydrazine. I. The Volumetric Analysis of Hydrazine by the Iodic Acid, Iodine, Bromine, and Hypochlorous Acid Methods (with E. J. Cuy). J. Am. Chem. Soc., 46, 858.
- The Oxidation of Hydrazine. II. The Effect of Oxygen on the Decomposition of Hydrazine. The Reactions with Ferricyanide in Alkaline Solution and Dichromate in Acid Solution (with E. J. Cuy), J. Am. Chem. Soc., 46, 1786.
- The Oxidation of Hydrazine. III. The Limiting Reaction of Permanganate and Manganic Salts in Acid Solution with Hydrazine (with E. J. Cuy and M. E. Rosenberg). J. Am. Chem. Soc., 46, 1796.
- The Standardization of Thiosulfate Solution by the Permanganate-Iodide and Dichromate-Iodide Methods (with Harry East Miller). J. Am. Chem. Soc., 46, 2204.
- The Systematic Detection of the Rarer Chemical Elements (with Arthur A. Noyes). Chem. Rev., 1, 277-201.

1925

The Catalytic Decomposition of Hydrogen Peroxide in an Acid Chlorine-Chloride Solution (with R. S. Livingston). J. Am. Chem. Soc., 47, 2069. A Correction, ibid., 48. (1926).

1926

- Capillary Condensation and Adsorption (with H. D. Draper). Proc. Nat. Acad. Sci., 12, 295.
- The Catalytic Oxidation of Carbon Monoxide. II. The Adsorption of Carbon Dioxide, Carbon Monoxide and Oxygen by the Catalysts, Manganese Dioxide, Cupric Oxide, and Mixtures of these Oxides (with W. M. Hoskins). J. Am. Chem. Soc., 48, 1454.
- The Catalytic Oxidation of Carbon Monoxide. III. Catalytic Efficiency of Mixtures of Dry Manganese Dioxide and Cupric Oxide (with G. J. Doss). J. Am. Chem. Soc., 48, 2060.

1927

"Qualitative Analysis for the Rare Elements" (with A. A. Noyes). The Macmillan Company, New York.

1928

The Rate of Oxidation of Hydrogen Peroxide by Bromine and its Relation to the Catalytic Decomposition of Hydrogen Peroxide in a Bromine-Bromide Solution (with R. S. Livingston). J. Am. Chem. Soc., 50, 1654.

1930

- The Autocatalytic Reduction of Bromate by Hydrogen Peroxide in Acid Solution (with Paul R. Davis). J. Am. Chem. Soc., 52, 1427.
- An Oxide of Iodine, I₂O₂. An Intermediate Compound. J. Am. Chem. Soc., 52, 3580.

1931

- Reactions Involving Hydrogen Peroxide, Iodine and Iodate Ion. I. Introduction (with H. A. Liebhafsky). J. Am. Chem. Soc., 53, 38.
- II. The Preparation of Iodic Acid. Preliminary Rate Measurements (with A. L. Caulkins). J. Am. Chem. Soc., 53, 44.

- The Mechanism of Reactions in Aqueous Solution. Examples Involving Equilibria and Steady States. Chem. Rev. 10, 161.
- Ferryl Ion, a Compound of Tetravalent Iron (with M. Gorin). J. Am. Chem. Soc., 54, 2124.
- The Rate of the Fourth Order Reaction Between Bromic and Hydrobromic Acids. The Kinetic Salt Effect (with H. A. Young). J. Am. Chem. Soc., 54, 4284.

A Course in General Chemistry (with W. M. Latimer). Revised Edition (159 pages). MacMillan and Company, N. Y.

1933

- The Simultaneous Reduction of Vanadic Acid and Oxygen by Iodide. Induced Catalysis of Oxygen Reactions (with J. B. Ramsey). J. Am. Chem. Soc., 55, 2270.
- The Rate of Oxidation of Hydrogen Peroxide by Chlorine in the Presence of Hydrochloric Acid (with B. Makower). J. Am. Chem. Soc., 55, 4765.

1934

The Hydrolysis of Ferric Ion. The Standard Potential of the Ferric-Ferrous Electrode at 25° . The Equilibrium Fe⁺⁺⁺ + Cl⁻ = FeC 1⁺⁺ (with A. V. Hershey). J. Am. Chem. Soc., 56, 1889.

1935

The Kinetic Salt Effect in the Fourth Order Reaction $BrO_3^- + Br^- + 2H^+ \longrightarrow$. Ionization Quotients for HSO⁴⁻ at 25° (with H. A. Liebhafsky). J. Am. Chem. Soc., 57, 51.

1936

Kinetic and Equilibrium Measurements of the Reaction $2Fe^{+++} + 2I^-$ = $2Fe^{++} + I_2$ (with A. V. Hershey). J. Am. Chem. Soc., 58, 1760.

1938

The Interaction of Ozone and Hydrogen Peroxide in Aqueous Solution. J. Am. Chem. Soc., 60, 82.

- A Course in General Chemistry (with W. M. Latimer). Third edition (206 pages). MacMillan and Company, New York.
- Chain Reactions in Aqueous Solutions Containing Ozone, Hydrogen Peroxide and Acid (with H. Taube). J. Am. Chem. Soc., 62, 3357.