Title
THE RESEARCH STYLE OF GILBERT N. LEWIS: ACIDS AND BASES

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Glenn T. Seaborg

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THE RESEARCH STYLE OF GILBERT N. LEWIS: ACIDS AND BASES

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Abstract

My first job after I received my Ph.D. in chemistry at the University of California, Berkeley, in the spring of 1937 was to serve as the personal research assistant of the great physical chemist, Gilbert N. Lewis. I served in this capacity for a term of two years, 1937 to 1939. After I had worked with him for some time on another project, Lewis shifted his attention to the preparation of demonstration experiments for the lecture on "Acids and Bases" that he was scheduled to give at the Franklin Institute in Philadelphia in the spring of 1938. Thus he was returning to the task of obtaining more experimental evidence for his generalized theory of acids and bases, described in his classic 1923 book, "Valence and the Structure of Atoms and Molecules." According to that definition, a basic molecule is one that has an electron-pair which may enter the valence shell of another atom to consummate the electron-pair bond; an acid molecule is one which is capable of receiving such an electron-pair into the shell of one of its atoms. Lewis and I tested many such acids and bases and he used many of these in his demonstration experiments in Philadelphia. Following this, we worked together on experiments to test his theory of primary and secondary acids and bases and on other experiments related to his concept of generalized acids and bases. Towards the end of our collaboration he began his experiments on the relation of energy levels of molecules to their emission of light and he was already beginning to think in terms of the Triplet State.

Presented at 183rd National Meeting of American Chemical Society, Las Vegas, Nevada, March 30, 1982, at a symposium of the Division of Chemical Education on "Gilbert Newton Lewis."

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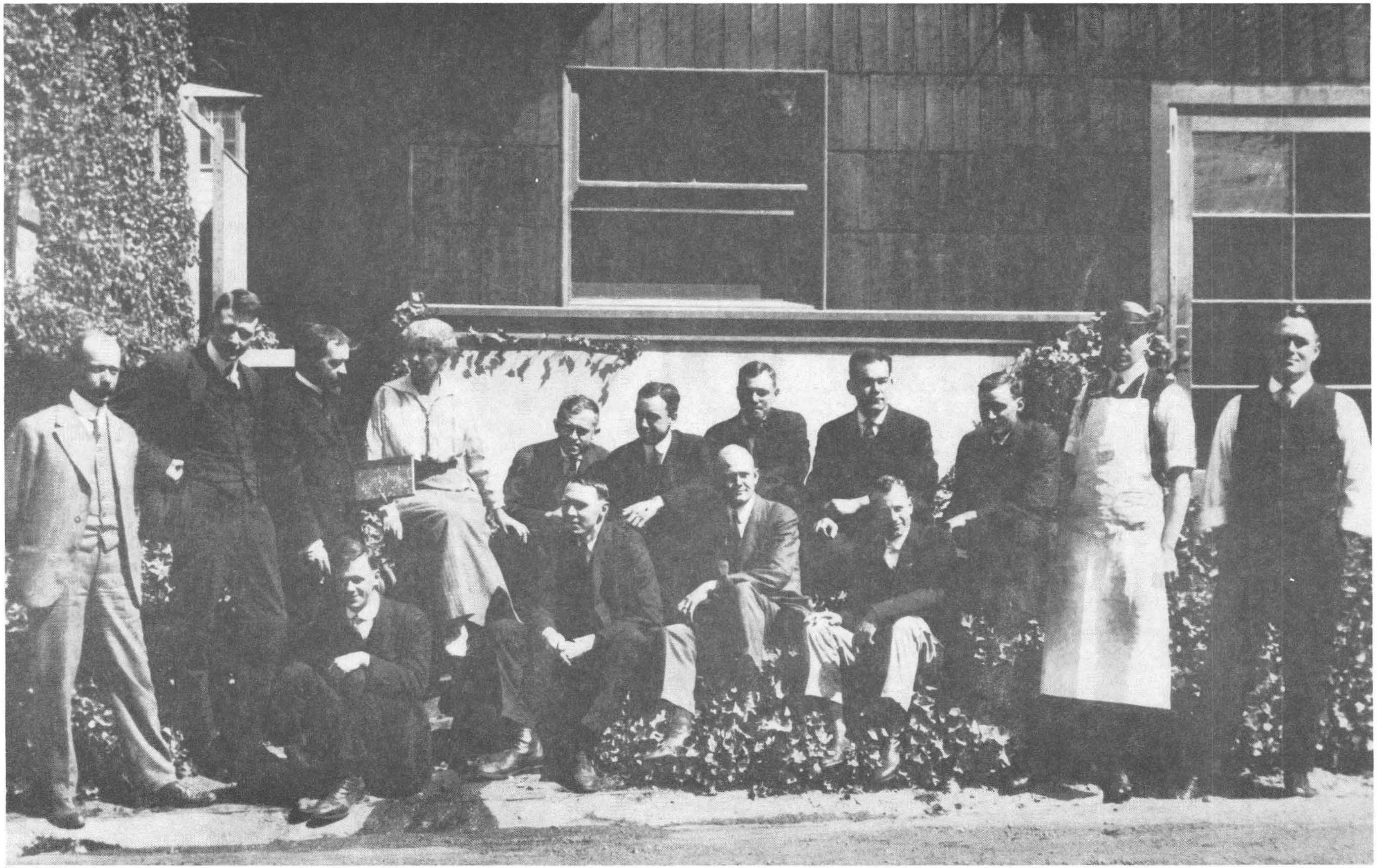
The Research Style of Gilbert N. Lewis:
Acids and Bases

I started my graduate work in the College of Chemistry at Berkeley in the fall of 1934. As an undergraduate at U.C.L.A., I had become acquainted with the 1923 book by Gilbert Newton Lewis "Valence and the Structure of Atoms and Molecules" and was fascinated by it. I wanted to meet and become acquainted with this remarkable man, but I could not then have envisioned that I would be working with him on a daily basis.

I was drawn to Berkeley by my admiration for Lewis and by the presence there of Ernest Orlando Lawrence and his cyclotron, for I was intrigued by the relatively new field of nuclear science. When I arrived and started my classes and research, I found the atmosphere and surroundings exciting to an extent that defies description. It was as if I were living in a sort of world of magic with continual stimulation. In addition to Lewis I met the authors of most of the chemistry textbooks I had used at U.C.L.A.--Joel Hildebrand, Wendell Latimer, William Bray, Walter Blasdale, Walter Porter. I took classes from Axel Olson, Gerald Branch and William Giauque, and I opted to do my graduate research in the nuclear field under Ernest Gibson in a laboratory situated in Ernest Lawrence's nearby Radiation Laboratory. In my thermodynamics class with Olson I was introduced to the classic book "Thermodynamics and the Free Energy of Chemical Substances" by G. N. Lewis and M. Randall, and this book was also used, although augmented by more recent material, in Giauque's more advanced thermodynamics course that I took during the second semester of my graduate work. (The pictures show College of Chemistry staff as of 1917 and 1920.)

Nearly everyone who participated as a member of the College of Chemistry in



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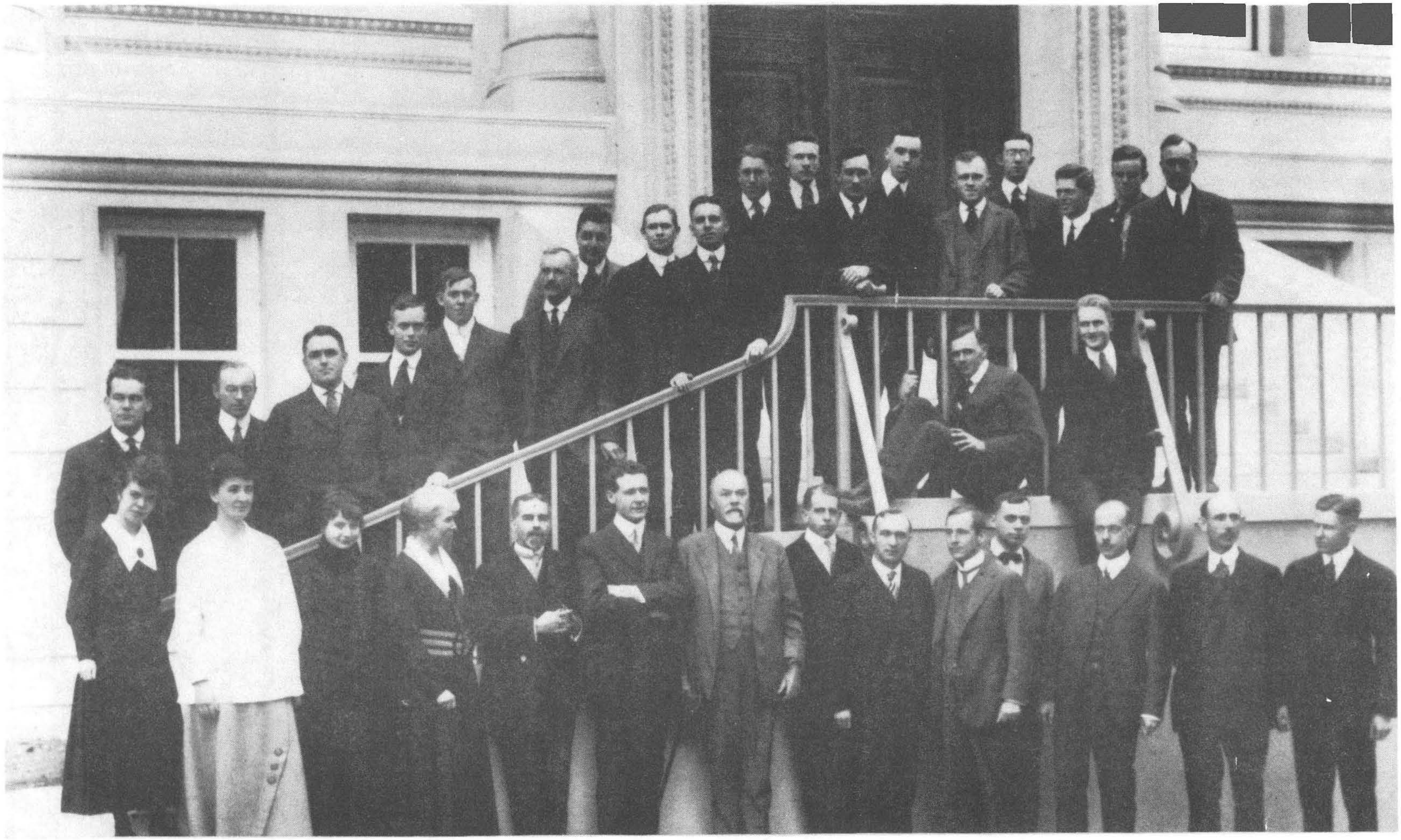
Picture taken on May 14, 1917, in front of Chemistry Annex.
Back Row (Left to Right): William C. Bray, William L. Argo, Gilbert N. Lewis, Miss Constance Gray, Parry Borgstrom, George S. Parks, Merle Randall, Charles S. Bisson, Asa L. Caulkins, Svend Holmstrup (shopman), William J. Cummings (glassblower).
Front Row (Seated Left to Right): Axel R. Olson, Thomas B. Brighton, Orville E. Cushman, Guy W. Clark.



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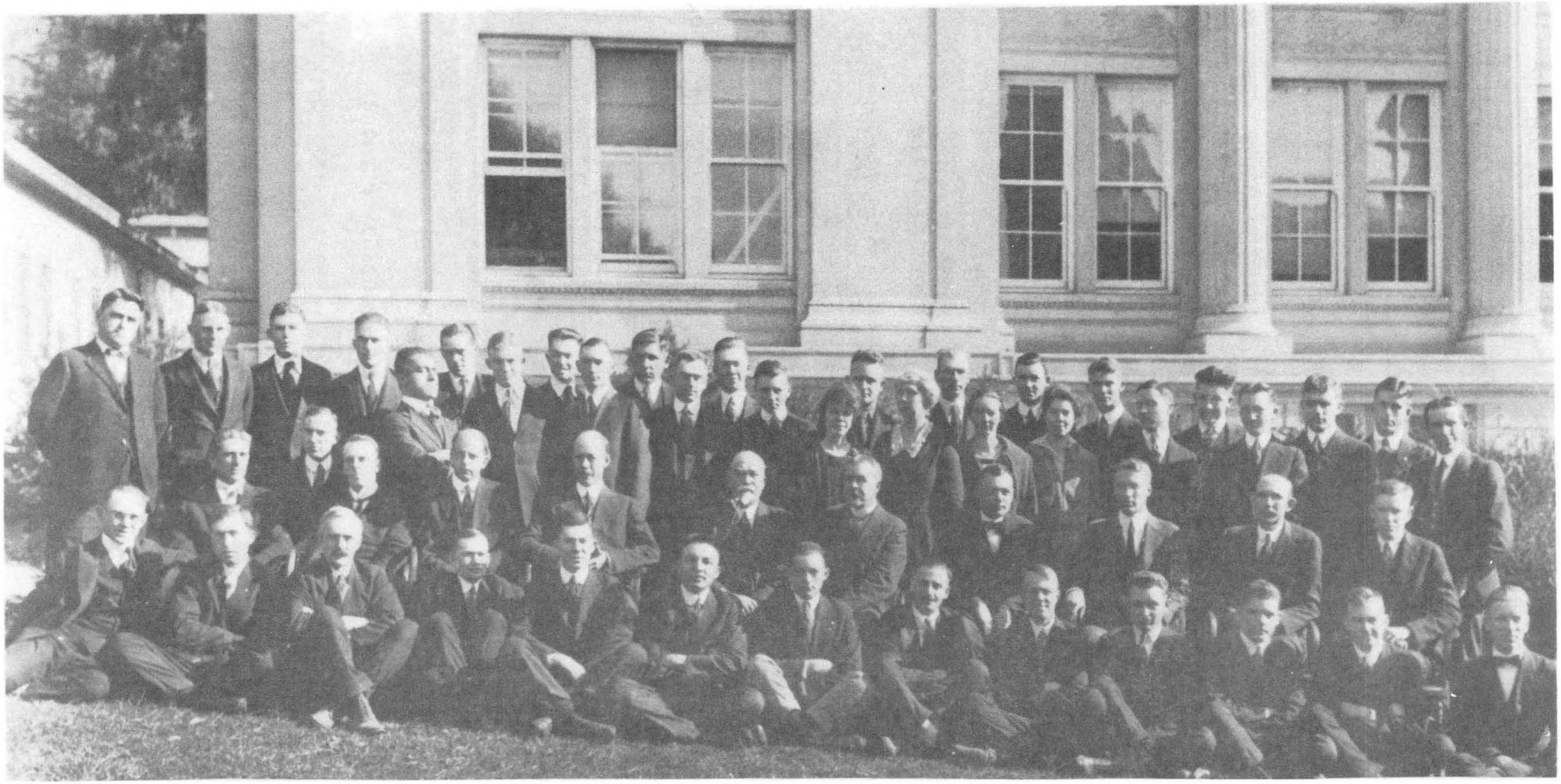
University of California College of Chemistry Staff Members in front of newly constructed Gilman Hall, Fall of 1917.

Front Row (Left to Right): M.J. Fisher, Esther Branch, Esther Kittredge, Constance Gray, Gilbert N. Lewis, William L. Argo, Edmund O'Neill, T. Dale Stewart, C. Walter Porter, G. Ernest Gibson, Merle Randall, William C. Bray, Walter C. Blasdale, Ermon D. Eastman; On Wall: Axel, R. Olson, Angier H. Foster; Back Row: Charles S. Bisson, Wendell M. Latimer, William J. Cummings, Carl Iddings, Reginald B.Rule, James T. Rattray, Charles C. Scalione, Hal D. Draper, William G. Horsch, William H. Hampton, Willard G. Babcock, John M. McGee, George S. Parks, Parry Borgstrom, Albert G. Loomis, George A. Linhart, William D. Ramage, Harry N. Cooper.



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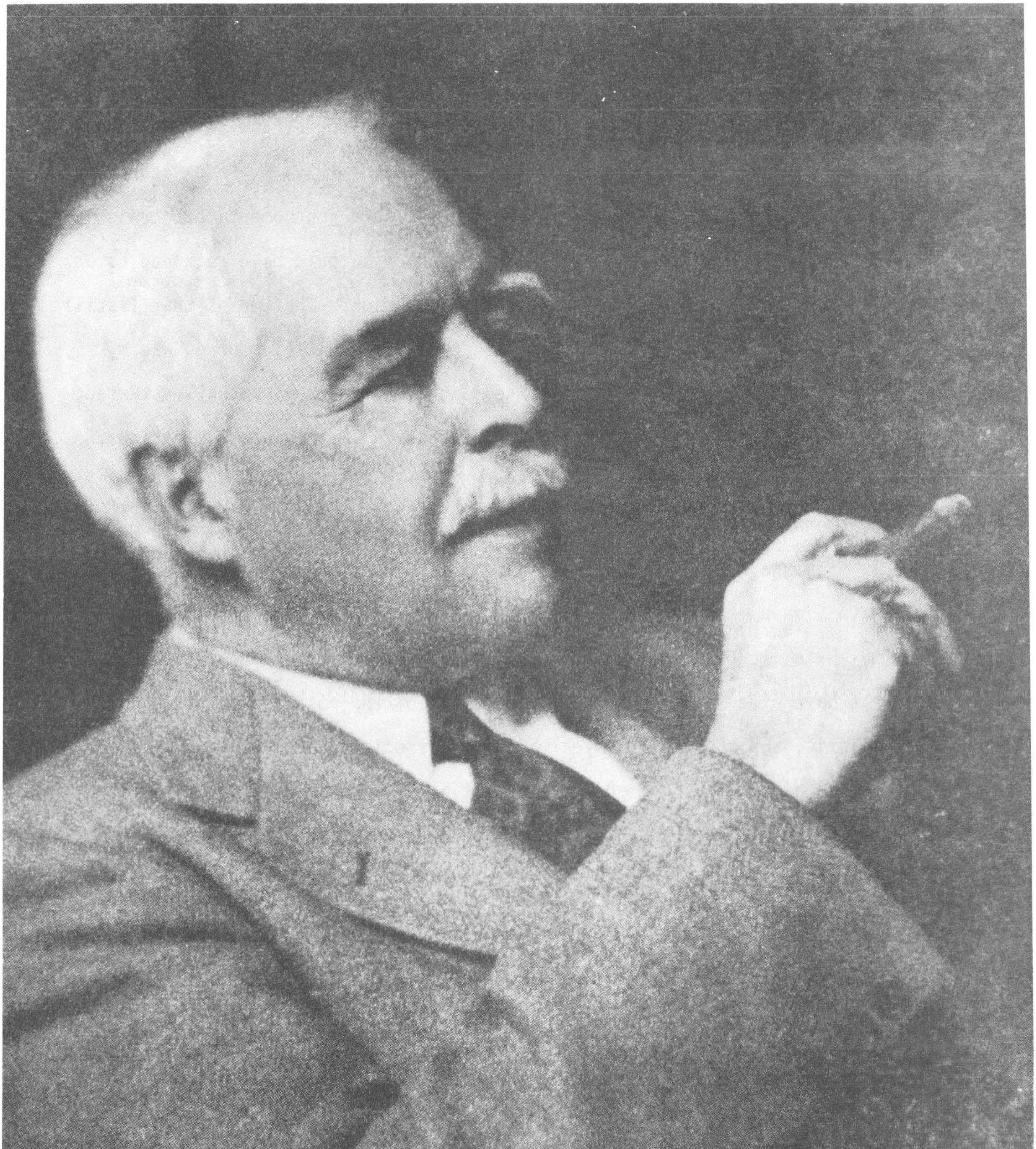
University of California College of Chemistry Staff Members in front of the North End of Gilman Hall, November 1920.
From Left to Right, Seated, First Row: P.S. Danner, H.W. Chapman, J.T. Rattray, H.D. Draper, N.W. Taylor, T.F. Buehrer, A.M. Shaffer, R.H. Gerke, F.R. Bichowsky, R.C. Fuson, T.F. Young, T.E. Phipps, R.M. Bauer; Seated, Second Row: G.F. Nelson, W.M. Latimer, G.E.K. Branch, T.D. Stewart, W.C. Bray, E. O'Neill, G.N. Lewis, M. Randall, J.H. Hildebrand, W.C. Blasdale, E.D. Eastman; Standing, Third Row: E.J. Cuy, R.M. Evans, W.M. Hoskins, R.F. Newton, A.P. Vanselow, M.J. Fisher, C. Gray, E.R. Bishop, A.L. Elliott, C.A. Jenks, G.E. Ostrom; Standing, Fourth Row: W.J. Cummings, J.A. Almquist, R.W. Millar, W.A. Noyes, Jr., A.M. Williams, M.L. Huggins, E. Anderson, D.C. Bardwell, H.K. Ihrig, B.M. Burchfiel, W.F. Giauque, S. Maeser, K.R. Edlund, T.R. Hogness, J.B. Ramsey, and M.L. Zavala.

the Lewis era recalls and comments on the Research Conference presided over by Lewis with his inimitable style. This was held each Tuesday afternoon during the school year, starting at 4:10 p.m. and lasting until about 5:30 p.m. in Room 102 at the extreme south end on the first floor of Gilman Hall. (Lewis' office was only a few doors away in Room 108, with its door usually open. His and the College of Chemistry's secretary, Mabel Kittredge (Mrs. Wilson), was located next door to him in Room 110.) At the Research Conference, Lewis always occupied the same place at the central table--the first chair on the right side facing the speaker and the blackboard. Members of the faculty sat at the table and the others (graduate students, post docs, research fellows, etc.) sat in chairs set at two levels at the two sides and back of the room. Lewis always had one of his Alhambra Casino cigars in his hand or mouth and several more in his upper coat pocket. The first of the two speakers, a graduate student giving a report from the literature, started when Lewis gave his inevitable signal: "Shall we begin!" The second speaker--a faculty member, research fellow or advanced or finishing graduate student--then reported on research that had been conducted in the College. Although Lewis dominated the scene through sheer intellectual brilliance, no matter what the topic, anyone was free to ask questions or speak his piece; in the latter instance, prudence suggested that the comment had best not be foolish or ill-informed. If Lewis had any weakness, it was that he did not suffer fools gladly--in fact, his tolerance level here was close to zero.

During my three years as a graduate student and the subsequent years until the war, Lewis always attended the Nuclear Seminar held on Wednesday evenings in Room 102, Gilman Hall. This seminar was run by Willard Libby, together with Robert Fowler (until he left Berkeley in 1936), and was also attended regularly by Wendell Latimer, William Bray and Ermon Eastman.

Lewis also conducted some research with neutrons during 1936-1937. He was always highly supportive of my nuclear research, some of which was conducted



Lewis with his cigar as he was typically seen at the Tuesday afternoon Research Conference in Room 102, Gilman Hall.

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in my spare time during the period that I served as his personal research assistant.

With this background in mind, let me now proceed to a description of my work with Lewis as a research associate. I'll never forget how this got started. I had completed my graduate research in the spring of 1937, my Ph.D. degree had been awarded, and it was time for me to go and find a job someplace. Lewis didn't recommend me for a position anywhere, which I could have regarded as a bad sign. Actually, in this case, it was a good sign. That meant that I still had a chance to stay at Berkeley in some capacity--which, of course, was my objective. One day in July after the next academic year had actually started, (so I was technically without any salary), Lewis called me into his office and asked me if I would like to be his research assistant. (Lewis was unique in having a personal research assistant, whose salary at that time was $1800 per year.) Although I was fervently hoping to stay in some capacity, I was flabbergasted to find he thought me qualified for this role and I expressed my doubts to him. He smiled, indicated that if he didn't think I could do the job, he wouldn't have offered it to me. My acceptance of the position he offered was enthusiastic, and thus our two-year intimate association began.

Lewis had suffered some disappointment in his previous research with neutrons. In fact, I had played a role in frankly advising him where he was going wrong, an act that took some courage on my part, and this may have influenced him in his decision to undertake the risk of having me as his research assistant. He told me that he had decided to forego research for a time, during which I would be free to continue the nuclear research that I had underway. As I have already indicated, I continued a rather substantial effort in the nuclear field, with his blessing, during the entire two-year period that I was associated with him.

In the late fall of 1937, Lewis resumed his research. He decided to try to separate the rare earths praseodymium and neodymium using a system involving repetitive exchange between the aqueous ions and their hydroxide precipitates.

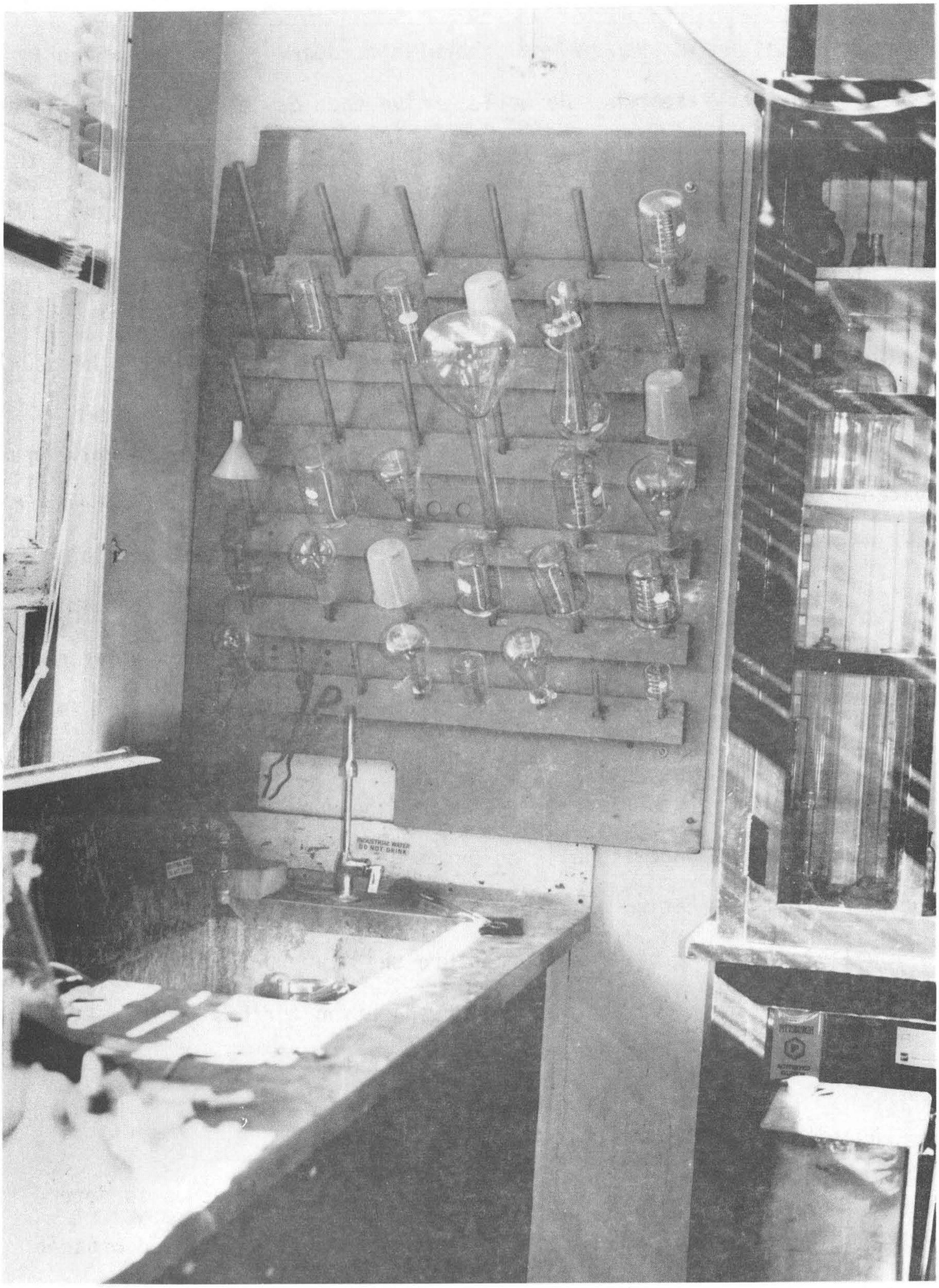
He employed a long, tubular, glass column extending from the third floor to the basement at the south end of Gilman Hall. The column was constructed with the help of Bill Cummings, the long-time glass blower in the College, who worked in Room 210 of Gilman Hall, and erected with the help of George Nelson, the irascible head of the machine shop, located in Room 7 in the basement of Gilman Hall. (He was irascible from the standpoint of graduate students, but very polite to Lewis and now to me in my prestigious role as the assistant to the "Chief.") The long column was serviced by a machine-driven system for agitating its contained solution in order to keep the hydroxide precipitates suspended along the column's length. It was my duty to keep this operating, which I did with only limited success. Lewis, with no help from me, measured the degree of separation of the praseodymium from neodymium with the spectroscope in the dark room off Room 301, Gilman Hall. For whatever reason, including possible shortcomings in my performance, no detectable separation of praseodymium from neodymium was achieved.

In the early spring of 1938, Lewis returned to his former interest in acids and bases--the theme of this essay. If I recall correctly (this was 44 years ago!) he was, at least in part, motivated by the need for an interesting topic, supported by feasible experimental demonstrations, for a talk that he was scheduled to give at the Franklin Institute in Philadelphia in May on the occasion of his receiving a Doctor of Science degree and Honorary Membership in the Franklin Institute in connection with the Dedication of the Benjamin Franklin Memorial (i.e., the large new building housing the Institute's activities, including the science museum). In any case, much of our first work in this area was directed toward such demonstration experiments.

Our experiments were directed toward his generalized concept of acids and bases. In his 1923 book "Valence and the Structure of Atoms and Molecules" Lewis had proposed a very general definition of acids and bases. According to that definition, a basic molecule is one that has an electron-pair which may enter the valence shell of another atom to consummate the electron-pair bond, and an acid molecule is one which is capable of receiving such an electron pair into the shell of one of its atoms. Lewis wanted, with my help, to find a broad base of experimental evidence for this concept.

We worked in Room 119, at the north end of the first floor of Gilman Hall, a laboratory that Lewis had used for a number of years previously. It was here that he did his work with Ronald McDonald and others during 1933-1935 on the isolation of deuterium by the electrolysis of water and the determination of a number of its properties. The apparatus used for this work was still there in the east side of the room, a part of the room that we didn't use at this time. We used the laboratory bench extending along the west side of the room, flanked in the back by a row of windows. The sink, at which I washed and cleaned our glassware each evening, was at the extreme right (north) end of the bench and our writing desk adjoined the opposite end of the laboratory bench against the south wall. Our indicator experiments were performed on the laboratory bench top at the ambient room temperature in ordinary test tubes. For later, more sophisticated (but still basically simple) experiments, which I shall describe presently, we used a low temperature bath which consisted of a large, wide-mouthed Dewar filled with acetone which was cooled by the addition of chunks of dry ice (solid carbon dioxide). Our vacuum bench, used in later experiments, was in the center of the room, opposite and parallel to the laboratory bench.

I was immediately struck by the combination of simplicity and power of the research style of Lewis and this impression grew during the entire period of my work with him. He disdained complex apparatus and measurements. He revelled in uncomplicated but highly meaningful experiments. And he had the capability to deduce a maximum of information, including equilibrium and heat of activation data, from our elementary experiments. I never ceased to marvel at his reasoning power and ability to plan the next logical step toward our goal. I learned from him habits of thought that were to aid continuously my subsequent scientific career. And, of course, working--and apparently holding my own--with him, boosted my self-confidence, which was not at a very high level at this stage of my life.



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Sink area in Room 119, Gilman Hall, where Seaborg serviced the experiments he performed with Lewis.

Starting at this time, I worked with Lewis on a daily basis, interspersed with intervals when he was otherwise occupied and during which I pursued my nuclear research. He would arrive each day between 10 and 11 a.m. in his green Dodge car, which he would park on the road (South Drive) between the Chemistry buildings and the Men's Faculty Club. When I spotted his car, I knew that it was time to join him in Room 119. We then usually would work together until about noon or 1 p.m., when he went to the Faculty Club to play cards with his friends (he didn't eat any lunch) while I went to lunch. He usually returned to our laboratory at about 2 p.m. and we would work together until late afternoon (4:30 p.m. to 6 p.m.). This gave me time to work on my other research projects before he came, during the noon break, and after he left in the afternoon. However, he often gave me assignments to assemble materials, prepare solutions, etc., over the noon hour or overnight, or when he left town for a day or two. These assignments were usually unrealistically demanding for such a time scale, and I had to scramble to meet his demands. This was not for the purpose of keeping me busy, but because he underestimated the size of the tasks. Sometimes we worked in the laboratory during the evening after dinner, often on Saturday morning, and occasionally on Sunday. We did most of the work on writing up our work for publication on Sunday afternoons in our laboratory (room 119).

I believe that the best way to capture the flavor of my experiments with Lewis on generalized acids and bases in preparation for his lecture at the Franklin Institute is to quote from my journal of that period:

<u>Thursday, March 17, 1938</u>

Today we performed exploratory indicator experiments to determine the color of a number of indicators (that is, colored organic molecules or dyes), dissolved in about 75 cc dioxane. Lewis plans to work with these indicators. They are:

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Chemistry Building, Gilman Hall, LeConte Hall and Campanile with South Drive in foreground, 1941.

1. crystal violet
2. bromcresol green
3. methyl red
4. chlorphenol red
5. alizarin
6. bromthymol blue
7. cyanin orange
8. thymol blue
9. phenolphthalein

Friday, March 18, 1938

Professor Lewis and I continued the joint experiments that we began yesterday. We added 4-5 drops of $SnCl_4$ solution (10% in CCl_4) to approximately 1 cc of each of the nine indicators (in dioxane) prepared yesterday. In each case we observed the color change, or lack of change, as this generalized acid ($SnCl_4$) was added. In other experiments, we added 2-3 drops of pyridine solution (15% in dioxane) to approximately 1 cc each of the same indicators--there was very little color change (if any) in most cases.

Saturday, March 19, 1938

Continuing our experiments of yesterday and the day before, Lewis and I added 2-3 drops of triethylamine solution (approximately 10% in dioxane) to approximately 1 cc of each of the nine indicators (in dioxane) that we prepared on Thursday; this is for the purpose of observing the change in color (or lack of change in color) when this generalized base (trimethylamine) is added to the indicators. These are exploratory experiments to get the feel for the way generalized acids and bases react to change the colors of indicators.

Monday, March 21, 1938

Today Lewis and I added 2-3 drops of BCl_3 solution (10 grams per 500 cc of CCl_4) to approximately 1 cc of each of the nine indicators (in dioxane) prepared last Thursday. The color changes produced by this generalized acid were observed in order to compare them with the color changes produced by the generalized acid $SnCl_4$ in our experiments last Friday. In general, the color changes, or lack of color changes, are strikingly similar for the two acids.

Thursday, March 24, 1938

I prepared indicators for Professor Lewis by dissolving a few tenths of a gram of each of the following in about 75 cc of acetone--bromcresol purple, bromthymol blue, aurin, neutral red, phenol red, cyanin, tropaeolin 00, and thymol blue. We passed the acid SO_2 into small portions of each of these solutions and observed the color changes (or lack of color changes).

Friday, March 25, 1938

In our experiments today Professor Lewis and I added 3-4 drops of the base triethylamine (10% in dioxane) and in separate experiments again passed the acid SO_2 into portions of each of the indicator solutions prepared yesterday and observed in each case the color change. We then added the acid BCl_3 to portions of a number of these solutions and in separate experiments the acid $SnCl_4$ to some of these solutions (tropaelin 00 and thymol blue) and noted similarities in the color changes. The effects of the bases triethylamine and pyridine on tropaelin 00 and thymol blue were also noted.

Monday, March 28, 1938

Today Lewis and I set up and practiced a number of demonstration experiments on generalized acids and bases that he will use in his lecture at the Franklin Institute in May. We observed the color changes when bromcresol purple, bromthymol blue, neutral red, and thymol blue (all in acetone) were treated with the base triethylamine and after that with the acid SO_2. Similar experiments with the acid BCl_3 and the base pyridine with tropaelin 00 (in acetone) were also performed.

Wednesday, April 20, 1938

Today Lewis and I experimented with the indicator thymol blue (in acetone) to which a few drops of the acid $AgClO_4$ (in benzene) were added. The color change was observed, and then 1-2 drops of the base pyridine (in dioxane) were added and the color change again noted. We found we could titrate back and forth successfully with this acid and this base. Similarly we found we could do this with the indicator tropaelin OO (in acetone).

Thursday, May 5, 1938

Lewis and I experimented with the acid BCl_3 (in CCl_4) added to 2-3 cc methyl red (in dioxane). We found that the heavy precipitate which formed could be redissolved with the base pyridine (in dioxane).

Friday, May 13, 1938

Today I helped Professor Lewis pack his suitcase for his demonstration lecture at the Franklin Institute next Friday morning. He is travelling to Philadelphia by train. I was pleased to see him bring into our laboratory and place on the bench two suitcases, because I felt this would give me ample room to pack the material for his demonstration experiments. However, he told me that he would need much of this space for his cigar boxes. (He smokes "Alhambra Casino" cigars incessantly and will need a good supply to keep him going during his visit to Philadelphia.)

He filled one entire suitcase and part of the other with cigar boxes, which meant that I had to exercise some ingenuity in order to get the equipment, chemicals, etc., into the remaining space.

Lewis gave his talk at the Franklin Institute in Philadelphia on Friday morning, May 20, 1938, as scheduled. During his talk he performed the demonstration experiments that we had developed. So far as I know, his talk was well received. However, the main impact came from his publication, based on the talk, which appeared in the September issue of the Journal of the Franklin Institute (226, 293 (1938)). In the preparation of this paper, which was written entirely by Lewis without my help, he used additional data that we developed in subsequent experiments. However, the main thrust of the paper was his beautiful exposition of his concept of generalized acids and bases, which had a worldwide impact and became the "bible" for workers in this field. His primary acids and bases are characterized by their instantaneous neutralization reactions, which occur without any heat of activation. He also introduced here his concept of secondary acids and bases, whose neutralization requires a heat of activation. I soon found that I was destined to work with him on a program of experimental verification of this idea.

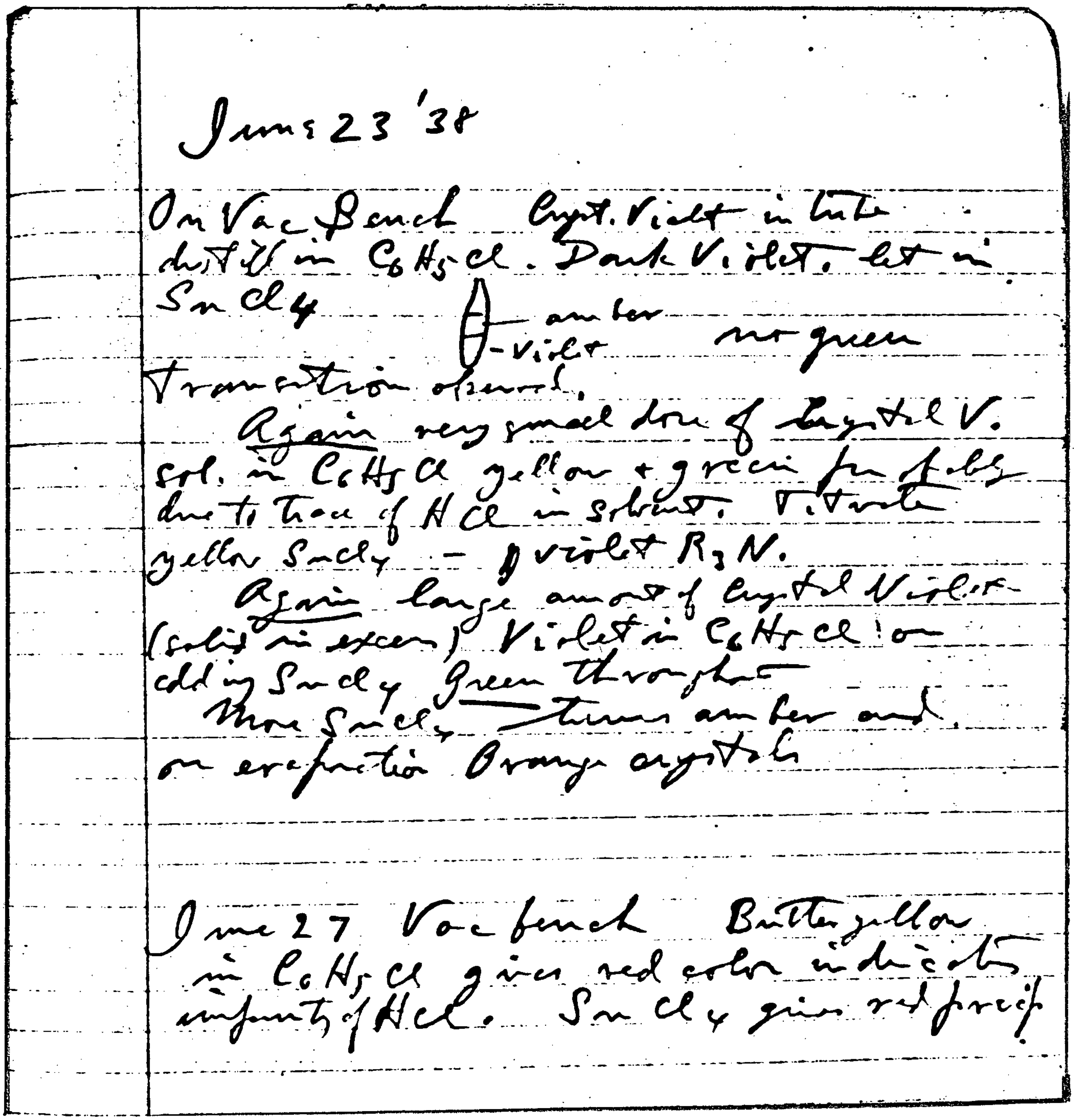
Lewis and I resumed our experiments on generalized acids and bases during June and early July, 1938, after he returned from his trip to Philadelphia. We found many cases where, with one solvent and one indicator, the colors obtained seemed to be dependent only upon the acid or basic condition of the solution and not at all upon the particular acid or base. By means of the color changes the solutions could be titrated back and forth as in aqueous solution. For example, with thymol blue dissolved in acetone, the color was yellow with either pyridine or triethylamine, while the acids $SnCl_4$, BCl_3, SO_2, and $AgClO_4$ gave an apparently identical red color. With crystal violet in acetone, the color changes successively from violet to green to yellow upon the gradual addition of $SnCl_4$ or BCl_3, after which the original violet color could be restored upon the addition of an excess of triethylamine.

Because similar effects could also be obtained by HCl, and since we had been working in the open with reagents that had not been especially dried, we were afraid that some of the similarities in color produced by the different acids could be due to small impurities of H-acids in the reagents. We therefore conducted experiments with very dry solvents, given to us by Dr. C. H. Li, with indicators which themselves contain no labile hydrogen, such as butter yellow, cyanin and crystal violet, and upon the vacuum bench to prevent the pick-up of water. These experiments gave the same results as those performed in the open with ordinary reagents. Again a couple of quotations from my journal can give the flavor of this work:

> <u>Thursday, June 9, 1938</u>
>
> Professor Lewis has returned from his trip to Philadelphia, and we recommenced our experiments on generalized acids and bases in Room 119. Today we did experiments in which we added the acid BCl_3 (in CCl_4) to crystal violet (in acetone) and observed a succession of color changes (blue, green, and yellow). We then added the acid $SnCl_4$ to another, identical solution of crystal violet and observed the same succession of color changes. Lewis is writing his paper "Acids and Bases" for publication in the Journal of the Franklin Institute. This is based on his demonstration lecture at the Franklin Institute last month and will include information from additional experiments that we will now perform in order to round out his story.
>
> <u>Friday, June 17, 1938</u>
>
> Lewis and I continued our experiments on our new vacuum line. We observed the color change when the acid BCl_3 was added to a solution of crystal violet in ether which had been thoroughly dried by Dr. C. H. Li. We also added the acid BCl_3 to crystal violet in acetone (very thoroughly dried by Dr. C. H. Li) and again observed the successive color changes; then we added triethylamine (thoroughly dried) and noted the color change sequence back to the original color. Our titrations thus gave the same results when water was thoroughly excluded as our original work with ordinary reagents conducted openly on the laboratory bench.

Toward the end of June, Lewis gave me leave to go to San Diego to give a talk on my nuclear work at a meeting of the American Physical Society. During my absence he conducted vacuum bench experiments to observe the color changes when $SnCl_4$ and triethylamine were added to a solution of crystal violet in thoroughly dried chlorobenzene, when $SnCl_4$ or HCl were added to a solution of butter yellow in chlorobenzene, etc.

I reproduce here his notes covering one of these experiments as he recorded them in my notebook:



June 23 '38

On Vac Bench Cryst. Violet in tube distill in C_6H_5Cl. Dark Violet. let in $SnCl_4$ amber violet no green transition observed.

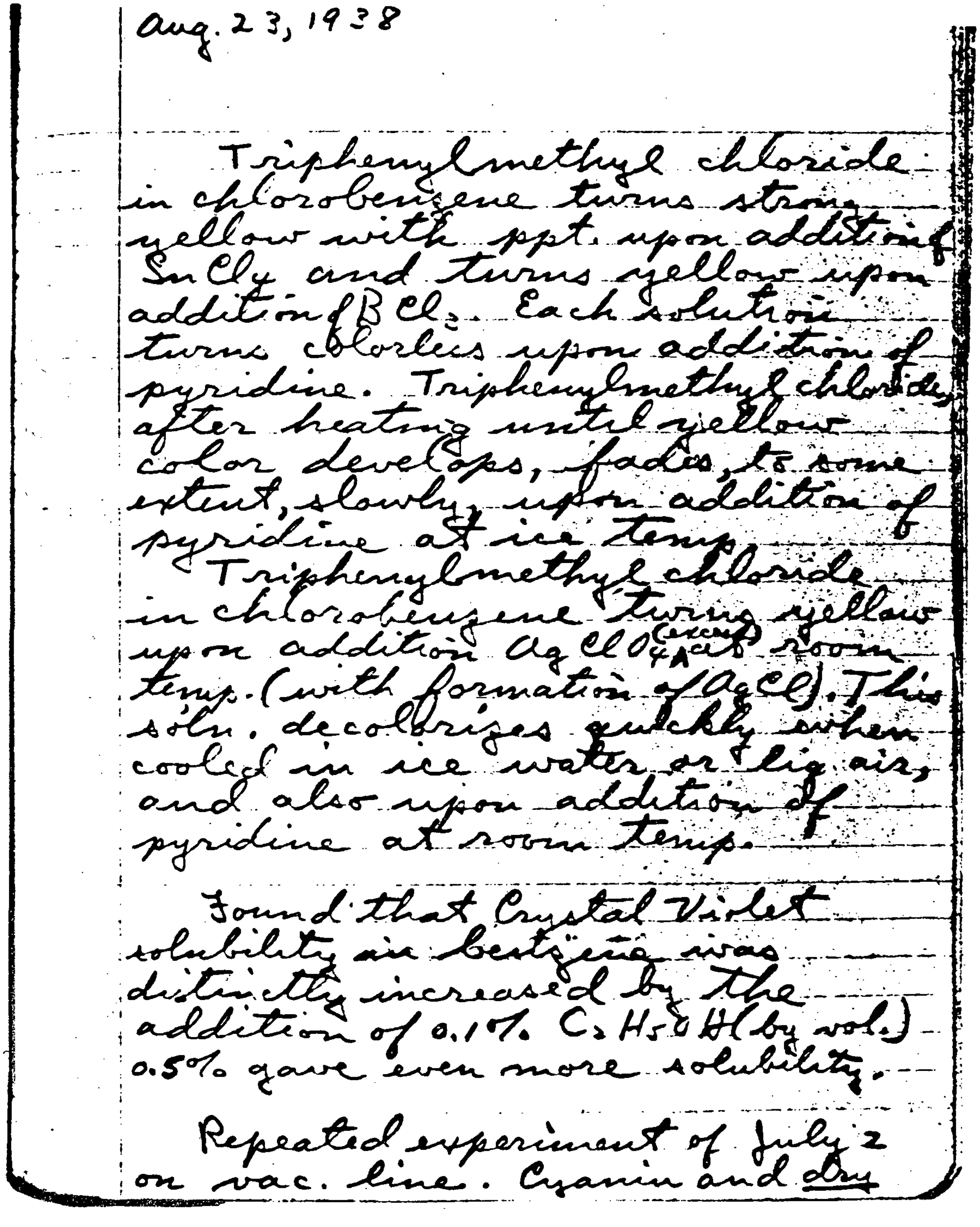
Again very small dose of Crystal V. sol. in C_6H_5Cl yellow + green [illegible] due to trace of HCl in solvent. Titrate yellow $SnCl_4$ – [illegible] violet R_3N.

Again large amount of Crystal Violet (solid in excess) Violet in C_6H_5Cl: on adding $SnCl_4$ Green throughout

More $SnCl_4$ turns amber and on evaporation Orange crystals

June 27 Vac bench Butter yellow in C_6H_5Cl gives red color indicating impurity of HCl. $SnCl_4$ gives red precip.

In addition to taking some vacation during the summer of 1938 with his family at their cottage in Inverness, he spent a good deal of time on his paper "Acids and Bases," which he was getting ready to send to the Journal of the Franklin Institute. The process of formulating his thoughts and setting them down on paper suggested to him many little confirmatory experiments which we then performed. I reproduce here a sample page from my journal (notebook) of this period:



Aug. 23, 1938

Triphenylmethyl chloride in chlorobenzene turns strong yellow with ppt. upon addition of $SnCl_4$ and turns yellow upon addition of BCl_3. Each solution turns colorless upon addition of pyridine. Triphenylmethyl chloride after heating until yellow color develops, fades, to some extent, slowly, upon addition of pyridine at ice temp.

Triphenylmethyl chloride in chlorobenzene turns yellow upon addition $AgClO_4$ (excess) at room temp. (with formation of $AgCl$). This soln. decolorizes quickly when cooled in ice water or liq air, and also upon addition of pyridine at room temp.

Found that Crystal Violet solubility in benzene was distinctly increased by the addition of 0.1% C_2H_5OH (by vol.) 0.5% gave even more solubility.

Repeated experiment of July 2 on vac. line. Cyanin and dry

In September Lewis turned to his next project--experiments related to his concept of secondary acids and bases--and from the latter part of September until Christmastime, I worked with him on a daily basis on much the schedule that I outlined earlier. We did some broadly based experiments which led to the publication of our background paper "Primary and Secondary Acids and Bases" (J. Am. Chem. Soc. 61, 1886 (1939)), and a detailed investigation of a specific secondary and primary base, which was published as a companion paper entitled "Trinitrotriphenylmethide Ion as a Secondary and Primary Base" (J. Am. Chem. Soc. 61, 1894 (1939)).

It was in the course of this detailed investigation of this secondary and primary base that I was to see first hand a master researcher at work and to be privileged to be a participant. Here was a prime example of simple experiments leading to interesting and fascinating interpretations and in my description I shall do my best to capture the flavor of the process.

As background for understanding these experiments, we should recall that Lewis had suggested that there is a large group of acids and bases, called primary, which require no energy of activation in their mutual neutralization, and there is another group, called secondary, such that a secondary acid does not combine, even with a primary base, nor a secondary base with a primary acid, except when energy, and frequently large energy of activation, is provided.

Based on the results of some preliminary experiments and Lewis' intuition and analysis, we decided that the intensely blue 4, 4', 4" trinitrotriphenylmethide ion should be a base that could exist in the primary and secondary forms and be a good material for experimentation to give support for and information on this concept. Our first experiments, performed in open test tubes, are described in my journal:

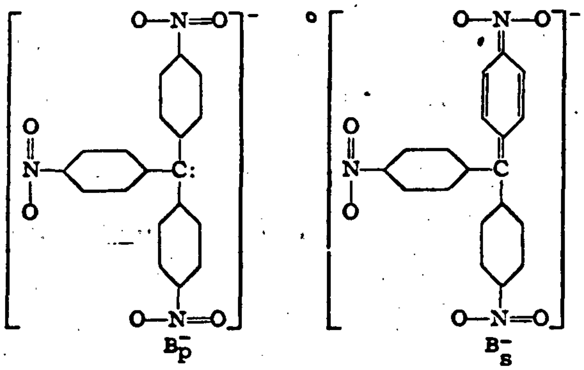
Wednesday, September 21, 1938

Lewis and I began test-tube experiments with 4, 4', 4" trinitrotriphenylmethane which we believe can be used to test our ideas about primary and secondary bases. We titrated trinitrotriphenylmethane in toluene at room temperature with sodium hydroxide (.02 M in absolute alcohol) to form an instantaneous blue color and then with HCl (0.02 M in absolute alcohol) to form an instantaneous colorless solution. The blue color is due to trinitrotriphenylmethide ion while the colorless form is trinitrotriphenylmethane. When the experiment was repeated at ice temperature, we observed the same color changes except that it took 4-5 seconds for the blue solution to turn colorless upon the addition of HCl. At the temperature of liquid air (near the freezing point of the solution), there was very slow development of the blue color and of the colorless solution (order of minutes). Addition of more HCl to the blue basic solution gave a bright "orange-yellow" solution which slowly faded to colorless. When we repeated the experiment at ice temperature, the "orange-yellow" color formed upon the addition of the excess HCl. We also experimented with a solvent of three parts ethyl alcohol and one part toluene and found that we could titrate back and forth between the blue (with NaOH) and orange (with HCl) colors at low temperatures.

Thursday, September 22, 1938

Today Lewis and I did test-tube experiments with trinitrotriphenylmethane in a solvent containing three parts ethyl alcohol and one part toluene. We titrated with NaOH and acetic acid HAc (in absolute alcohol). We found that, with the acid HAc at liquid air temperature (freezing point of toluene), the "orange-yellow" color did not appear. We also found that this is true when we used toluene with no alcohol. The fading of the blue color to colorless was quite fast upon the addition of HAc at ice temperature but slow at the lower temperature. Apparently HAc has a different effect than HCl. We measured the solubility of crystal violet chloride in various concentrations of phenol in toluene. We plan to use this blue solution as a comparison standard in our experiments to measure the rate of fading of the blue color of trinitrotriphenylmethide ion; this ion apparently acts as a secondary base, and we wish to investigate the kinetics of its transformation to the colorless form which seems to be the primary base. A set of standard color comparison solutions will be prepared by diluting the crystal violet solutions successively by factors of two.

Lewis soon deduced that the action of the HCl was not our main concern and our first interest should be in the secondary base (B_s^-) in the blue form that requires a heat of activation to be converted to the primary form (B_p^-) in which it reacts instantaneously with the HAc. Thus he deduced that the two forms would have these formulae:



We launched into a series of kinetic experiments to measure the rate of fading of the blue B_s^- upon the addition of acetic acid or other acids which combined instantaneously with the small proportion of B_p^- that was present. This mechanism, for any acid HY, can be summarized as follows:

$$B_s^- \overset{(a)}{\rightleftharpoons} B_p^-$$

$$B_p^- + HY \xrightarrow{(b)} BHY^- \xrightarrow{(c)} HB + Y^-$$

He suggested that (b) is the rate determining step, and that the concentration of B_p^- depends upon the concentration of B_s^-, the temperature and the difference in energy between B_p^- and B_s^-. On this basis, the reaction should be bimolecular and the measured heat of activation should be the same with all acids (HY) of sufficient strength.

To test this we measured the rates of reaction (rate of fading of the blue color) over a range of temperatures in order to determine the heat of activation. The experimental method was simplicity itself. The first experiments were performed in open test tubes, but it was found that trinitrotriphenylmethane was sensitive to oxygen under the conditions used, and therefore the reaction vessels were evacuated. Our solvent was 85% ethyl alcohol and 15% toluene, and our first series of experiments were with acetic acid. The reaction vessel, in the form of an inverted Y, with the alkaline blue methide ion solution in one limb and the acid in the other, was placed in the low temperature bath (of acetone cooled with dry ice). When the temperature equilibrium was attained, the vessel was tipped rapidly back and forth until the contents were thoroughly mixed. The reaction (rate of fading of the blue color) was then followed by comparing the color with a set of standard color tubes. (The set of standard color tubes consisted of solutions of crystal violet, which had blue colors nearly identical to those of the blue methide ion, made by successive two-fold dilutions to cover the entire range of diminishing blue colors.) After the experiments had indicated that the reaction was always of first order with respect to the colored ion, the procedure was simplified further. The time was taken merely between the mixing and matching of a single color standard, which corresponded to one-sixteenth of the original concentration of the blue methide ion (i.e., the color standard was made by four two-fold dilutions of the original matching crystal violet solution.)

We made measurements with acetic acid at four temperatures: -53°, -63°,

-76°, and -82°C and from these we could calculate that the reaction was first order with respect to the acid and the heat of activation for the reaction of fading of the blue methide ion was 8.6 kcal. According to our interpretation, then, this is the energy difference between the secondary form B_s^- and the primary form B_p^- of the methide ion. We then measured the heat of activation for the same reaction for five additional acids, for which the reaction also proved to be bimolecular, and found the same value for the heat of activation within the limits of our experimental value--an average of 9.1 kcal. Such a result is to be expected from our interpretation that the heat of activation should be equal to the difference in energy between the primary and secondary forms of the base. If the activation occurred only at the moment of collision between the reacting molecules, it would be hard to explain why the heat of activation or, in other words, the potential barrier in the activated complex should be the same for such very different substances as alcohol (for which we also measured the heat of activation, indirectly, as described below) and our other acids--chloroacetic, furoic, alpha-naphthoic, lactic, and benzoic, as well as acetic acid.

I have recounted here in some detail only the central conclusions from this research. Lewis made many other deductions that are too involved to be easily described here in detail, but which can be enjoyed by reading the paper reporting this work. I shall merely sketch some, by no means all, of these conclusions. From some other of our measurements he was able to deduce the equilibrium constant for the reaction in which the blue methide ion is formed from the reaction of the hydroxide (or ethylate) with the trinitrotriphenylmethane, and the heat of activation, from which he found that the heat of activation for the reverse reaction (B_s^- plus ethyl alcohol), corresponding to the difference in energy between the primary and secondary forms of the base, is 8.9 kcal., in good agreement with our direct determination for the six acids (9.1 kcal.). He could deduce from our measurements that only one eighth of the trinitrotriphenylmethane was in the form of the blue methide ion under the conditions of our kinetic experiments. He also concluded that our kinetic measurements with such weak acids as phenol and boric acid suggest that these displace the solvent alcohol from the nitro groups in the blue methide ion to an extent depending upon their concentration, and that the ion with the phenol attached is less reactive than the corresponding alcohol compound.

Earlier on, I have alluded to the orange color produced immediately upon the addition of the strong acid HCl to a solution of the blue methide ion. We also found this upon the addition of the relatively strong trichloroacetic acid. Lewis found a ready explanation for this. When the blue ion has been formed and the central carbon has lost its power of acting immediately as a base, the basic power has, in a certain sense, been transferred to the three nitro groups. Therefore, a sufficiently strong acid should attach itself at one or more of the nitro groups and in this process the blue ion should act as a primary base.

We finished these experiments just before Christmastime in 1938. After a diversion in January to test experimentally another of his ideas, we began in February the process of writing our two papers on primary and secondary acids and bases for publication in the Journal of the American Chemical Society. Writing a paper with Lewis was a very interesting process. We did most of our work on this, extending sporadically over several months, on Sunday afternoons in our laboratory, Room 119 in Gilman Hall. The process consisted of Lewis, while pacing back and forth with cigar in hand or mouth, dictating to me. I recorded his thoughts in longhand. However, his output was interspersed with discussions with me and even with experimental work when he wanted to check a point or simply wanted a break. His sentences were carefully composed and the result was always a beautiful and articulate composition.

After we had finished the two papers up to the point of the summary of the second paper, he said to me that he was tired of this process, and suggested that I write this summary by myself. By this time I was familiar enough with his thought processes to make this feasible. I wrote the following, which he accepted after no more than a glance at it and without changing a word:

> Trinitrotriphenylmethide ion was expected and has proved to be a secondary base. In alcohol when this blue ion is added to any weak acid

at temperatures between -30 and -80° the formation of the corresponding methane is slow and can be followed colorimetrically. The rate of neutralization was studied with numerous acids and under like conditions the rates diminish with diminishing acid strength. With the weakest acids the rates are not proportional to the concentration of acid, and this fact is explained. With the six acids of intermediate strength the rates were found proportional to the concentrations of blue ion and of un-ionized acid, and unaffected by neutral salts. In these cases the heat of activation was calculated from the temperature coefficient of the rates and was found approximately constant with a mean value of 9.1 kcal. By indirect methods the rate of neutralization by alcohol itself was determined. Here the heat of activation is found to be 8.9 kcal. The constancy of the heat of activation over the great range from chloroacetic acid to alcohol can hardly be explained by the theory of an activated complex. The value obtained is taken as a measure of the difference in energy between the primary and secondary forms of the base. The small departures from this constant value are attributed in part to experimental error, but especially to differences in the actual composition of the reacting ion. Several kinds of evidence are adduced to show that the actual composition of the blue ion depends not only upon the solvent but in several cases upon the presence of other solutes.

While the trinitrotriphenylmethide ion is a secondary base with respect to addition of acid to the central carbon, it is a primary base with respect to addition of acid to the nitro groups. In the presence of strong acids an orange substance is thus formed which contains more than one free hydrogen ion per molecule. The very slow rate of fading of the orange compound is studied, and an explanation is suggested for the large catalytic effect of water. Mono-and dichloroacetic acids give mixtures of the orange and blue substances and the rate of fading in these solutions leads to some of the conclusions already mentioned.

During January, 1939, Lewis and I worked to make an experimental test of an old, rather far out, idea of his. This is far afield from acids and bases, but is, I believe, worth mentioning as a further illustration of the breadth of his intellect and interests. A number of years ago (1930) he had published an article in Science magazine (Science 71, 569) on "The Symmetry of Time in Physics." A consequence this theory, as it applies to radiation, is that we must assign to the emitting and the absorbing atom equal and coordinate roles with respect to the act of transmission of light. A consequence of this, Lewis told me, is that the receiver or observer of the light (for example, the apparatus used for this purpose) is of importance equal to that of the emitter of the light and exhibits its own influence upon how the light manifests itself.

Lewis told me he wanted to test this hypothesis by setting up a Michelson interferometer to detect the interference fringes with different receivers or detectors of radiation and to thus determine if some properties of the radiation depend on the receiver or detector as it should if it conformed with his theory on the symmetry of time. He asked me to set up a Michelson interferometer in the darkroom off Room 301 at the southwest corner of the third (attic) floor of Gilman Hall. This room contained a spectrograph with which Lewis had made his spectrographic measurements on rare earth samples. (These were the samples that emanated from our attempts, about a year earlier, to make separations using the column with its equilibration mixture of rare earth hydroxide precipitates and ions in solution.)

I went to the Department of Physics and borrowed a Michelson interferometer which was ordinarily used for demonstration experiments in some of the physics lecture courses. In order to make this operate correctly I had to prepare some "half-silvered" surfaces on glass with a silver layer of such thickness that about one half of the incident light would be reflected and the other half transmitted through the layer. Since Professor Axel Olson had some experience with this "half-silvering" process, I enlisted his help on this. Lewis and I detected the interference fringes with each of a number of different types of photographic film in order to see if we could detect any gross differences in the way the films reacted. We found some peculiar effects, which excited Lewis for a time, but my skepticism prevailed when I was able to explain these as due to rather prosaic failures in our techniques and which we could correct to eliminate the effects. These negative results then convinced Lewis to go on to something else.

During the period from January to June, 1939, Lewis and I did scouting experiments with a wide range of indicators, acids, and bases. Many interesting observations were made that are not susceptible to summarization in a reasonably brief fashion. As always, there were moments of excitement. I recall a series of experiments, conducted with test tubes immersed in our acetone-carbon dioxide bath, on the development of color when trinitrobenzene and sodium phenolate were reacted in absolute ethyl alcohol over a range of temperatures below room temperature. We found that large excesses of NaOH were needed to produce the indicator color. This elicited some bizarre interpretations from Lewis. However, when these experiments were repeated on the vacuum line the action of NaOH was more reasonable. Apparently, in our open test tube experiments, large amounts of CO_2 were absorbed in the alcoholic solution (coming from the steady evolution of CO_2 from our CO_2-cooled acetone bath)!

Our research during this period did result in one coordinated project from which some interesting conclusions could be drawn. We made observations on the degree of development of color (a measure of the degree of reaction between these acids and bases) when each of the bases ammonia, methylamine, dimethylamine, triethylamine or hydroxide is reacted with each of the acids m-dinitrobenzene and symmetrical trinitrobenzene, trinitrotoluene, trinitroxylene, and trinitromesitylene (twenty-five combinations in all). At any point in the table corresponding to a given base and a given nitro compound the sign + indicates the formation of color.

COLOR PRODUCTION IN MIXING SEVERAL BASES WITH NITRO COMPOUNDS

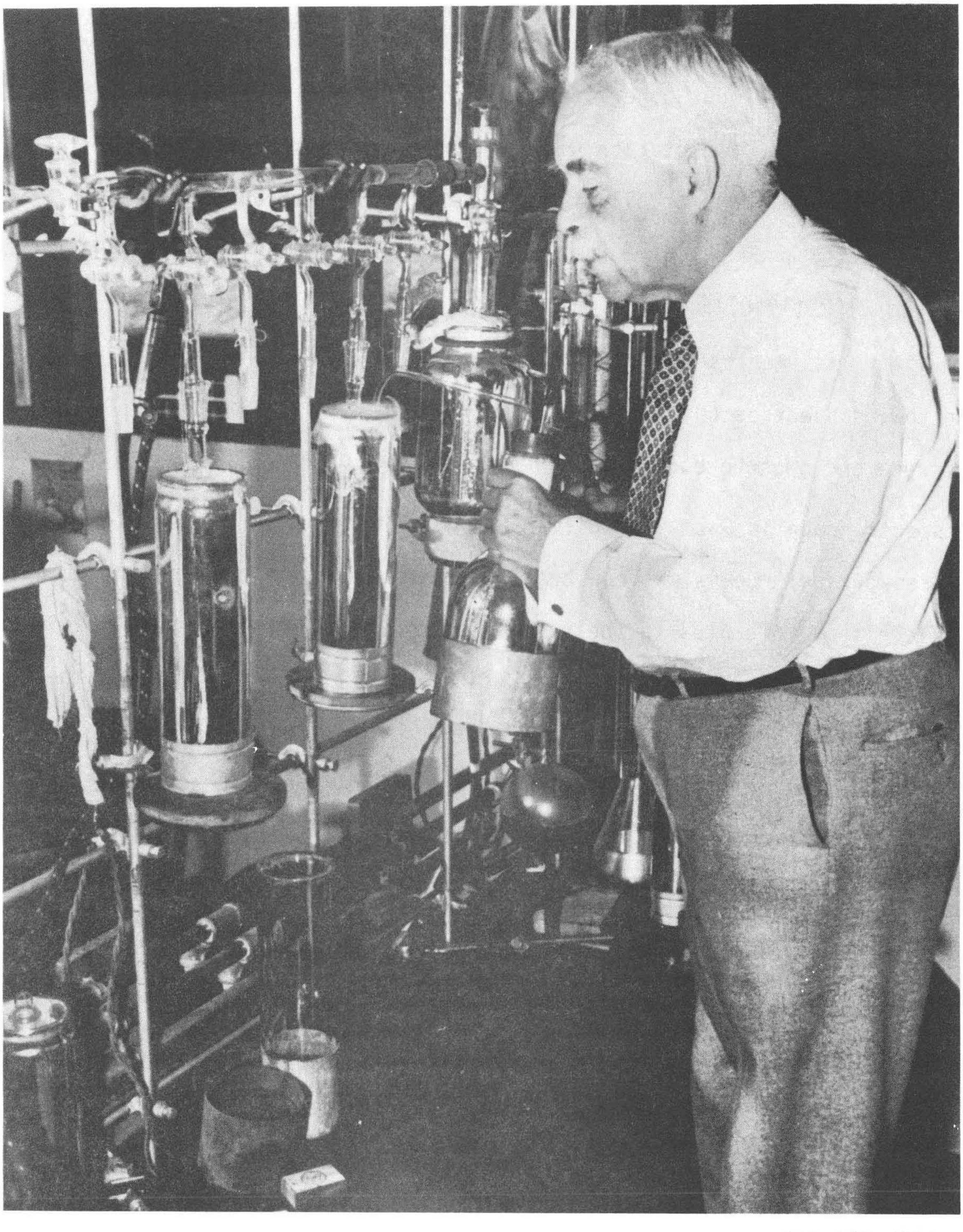
	DNB	TNB	TNT	TNX	TNM
NH_3	+	+	+	+	
NH_2R	+	+	+	+	
NHR_2		+	+		
NR_3		+	+		
OH^- or OR^-		+	+	?	

We found with trinitrobenzene the intensity of color is least with triethylamine, greater with dimethylamine, and still greater with methylamine and ammonia. For the direct addition of the base to one of the ring carbons that is not attached to a nitro group, there is the possibility of double chelation of hydrogen atoms to nitro groups in the case of methylamine and ammonia, thus strengthening the acid-base combination. With the weaker acid, m-dinitrobenzene, methylamine and ammonia--which are capable of double chelation--give good colors, while the two stronger bases, dimethylamine--which is capable of only one chelation--and triethylamine, where no chelation is possible, give no color at all. Thus our conclusion was that the stability of the colored compounds is greatly enhanced by chelation, and especially double chelation, in which the hydrogens of an aliphatic amine are attached to oxygens of the nitro groups. Simlarly, we could deduce that the chief effect of introducing methyl groups into symmetrical trinitrobenzene is to diminish resonance between the nitro groups and the ring, and that this effect, which is very strong when the nitro group is ortho to two methyl groups, as in symmetrical trinitroxylene becomes weak when only one ortho methyl is present, as in symmetrical trinitrotoluene. Trinitromesitylene, in which each nitro group lies between two methyl groups, showed no color with any base.

Lewis and I didn't write up this work for publication until about a year later due to the press of our other activities. When we did, of course, it was done by the same method of dictation with me serving as a scribe. Our publication, which included explanations for all of our observations, was entitled "The Acidity of Aromatic Nitro Compounds toward Amines. The Effect of Double Chelation" (J. Am. Chem. Soc. 62, 2122 (1940)).

During my last months with Lewis, April, May and June, 1939, he turned part of his attention toward spectroscopic observations on light absorption and the observations of fluorescene and phosphorescence in various colored organic substances. For this we used the spectrograph in Room 310, Gilman Hall, where Ted Magel, then a graduate student, was working. Lewis was now beginning his experimentation on the relation of energy levels in molecules to their emission of light and was already beginning to think in terms of the Triplet State. Besides Magel, we were helped in these measurements by Otto Goldschmid, a volunteer research fellow and Ed Meehan, an instructor in the College of Chemistry. Melvin Calvin, and Michael Kasha deal with this subject in their talks at this Symposium.

Also during this time Lewis was working with Melvin Calvin putting the finishing touches on their review paper "The Color of Organic Substances," which they mailed soon thereafter (in August) for publication in Chemical Reviews. Lewis had been interested in the color of chemical substances for a long time and, in fact, this was the subject of his acceptance address in New York on May 6, 1921, when he received the Nichols Medal of the New York Section of the American Chemical Society. He had been working with Calvin, off and on, during much of the last year; I can recall looking in on them in Room 102, where they had their writing sessions, and finding them totally immersed in their piles of reference journals and notes.



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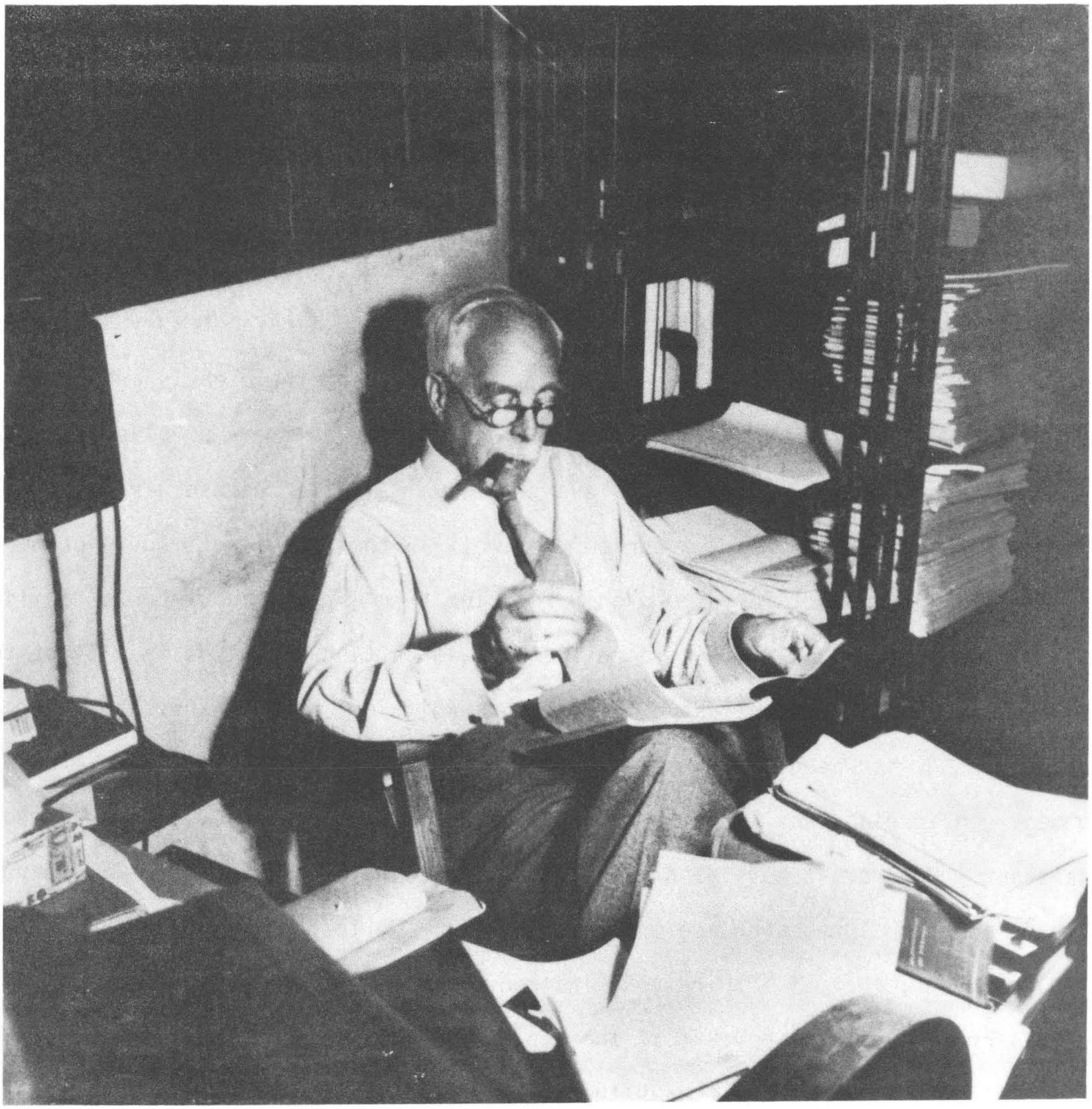
Lewis at vacuum line in the laboratory on the third floor of Gilman Hall at the time in the 1940s when he was conducting research on color and the Triplet State.

During all of the time that I was working with Lewis he was, of course, serving as Dean of the College of Chemistry and Chairman of the Department of Chemistry These positions would ordinarily entail heavy administrative duties, but he did not allow himself to be burdened by them. Nevertheless, I believe, he discharged his responsibilities very well. He was efficient and decisive, highly respected by the faculty members in the College, and eminently fair in his dealings with them. To a large extent he ran the College from his laboratory. I recall that his efficient secretary, Mabel Kittredge, would come into our laboratory, stand poised with her notebook until she commanded his attention, describe clearly and briefly the matter that required his attention or decision. Lewis would either give his answer immediately or ask her to come back in a little while, after he had given the matter some more thought. This system worked very well in those days but might not be adequate today and certainly could only function then with a man of Lewis' ability.

Sometime in June, Lewis told me that he was putting me on the faculty of the College of Chemistry as an instructor. In his whimsical way he expressed the opinion that he had been taking up "too much of my time." This was a revealing comment considering that I was supposed to be serving as his full-time research assistant. However, I have good reason to believe that he was not at all unhappy with my additional research and writing projects. He told me my salary would be $2200 per year, that of a third-year instructor. Thus, to my delight, he was giving me full credit for my two years in the capacity of his research assistant.

In conclusion, I want to say that I regard it as extraordinarily good fortune that I was granted the privilege of spending this time working so closely with Gilbert Newton Lewis.



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Lewis at work in his office, room 108, Gilman Hall

The College of Chemistry
in the Gilbert N. Lewis Era

Gilbert N. Lewis of the Massachusetts Institute of Technology (MIT) accepted the position of Dean of the College of Chemistry and moved to Berkeley in the fall of 1912. This was the beginning of a new and brilliant era of chemistry at Berkeley that continued until Lewis' death in 1946. From MIT he brought with him William C. Bray, Merle Randall, and Richard C. Tolman (who left in 1916) to join the chemistry faculty, in addition to a few graduate students. George Ernest Gibson from Germany and England and Joel H. Hildebrand from the University of Pennsylvania joined the faculty in 1913. Walter C. Blasdale (who retired in 1940), Edmund O'Neill (retired in 1925), Henry C. Biddle (left in 1916), and Edward Booth (who served until his death in 1917) were faculty members at Berkeley before Lewis' arrival and continued on the staff.

From 1913 until 1937, all the newly appointed permanent faculty members received their PhD degrees from the College. William C. Argo (who died of pneumonia in France in 1918) and Gerald E. K. Branch, who received their PhD degrees under Lewis in 1915, were added to the faculty at that time. C. Walter Porter (who received his degree in 1915 under Biddle) was added in 1917. T. Dale Stewart (Tolman, 1916), Ermon D. Eastman (Lewis, 1917) Axel R. Olson (Lewis, 1918), Wendell M. Latimer (Gibson, 1919), Thorfin R. Hogness (Hildebrand, 1921), William F. Giauque (Gibson, 1922), and Gerhard K. Rollefson (Lewis, 1923) were each appointed to the faculty at the time of receipt of the PhD degree. (Stewart actually started in 1917, Olson in 1921; Hogness left in 1930). The last permanent faculty appointments by Lewis were Kenneth S. Pitzer (PhD with Latimer, 1937) in 1937, Melvin Calvin (PhD, University of Minnesota, 1935) in 1937, and Glenn T. Seaborg (PhD with Gibson, 1937) in 1939.

The accompanying photographs are notable in that they are among the very few substantial ones of the College of Chemistry faculty, including Lewis, that were taken during the Lewis era. Soon after the Chemistry Annex was completed in 1912 a number of people moved there from the Chemistry Building (completed in 1890), leaving the remainder of the College staff in the older, larger building. The first picture, taken on May 14, 1917, shows a number of occupants in front of the Chemistry Annex. This photograph includes Lewis and his graduate students Argo (at this time an instructor); Olson; Thomas B. Brighton; Parry Borgstrom; Asa L. Caulkins; Orville E. Cushman; Guy W. Clark; and George S. Parks; Randall and his graduate student, Charles S. Bisson; Bray; Constance Gray, secretary to Lewis; William J. Cummings, glassblower; and Svend Holmstrup, shopman.

The second picture was taken in front of Gilman Hall in the fall of 1917, apparently at about the time this newly constructed building was first completed. This photograph includes faculty members Eastman, Blasdale, Bray, Randall, Gibson, Porter, Stewart, O'Neill, Argo, and Lewis (Branch was away in the Canadian Armed Services while Hildebrand was apparently out of town); Lewis' secretary, Miss Constance Gray, and clerk Mrs. M. J. Fisher; graduate students Esther Kittredge, Esther Branch (wife of Gerald Branch), Charles S. Bisson, Wendell M. Latimer, Charles C. Scalione, William G. Horsch, William H. Hampton, John M. McGee, George S. Parks, Parry Borgstrom, Albert G. Loomis, Angier H. Foster and Axel R. Olson; undergraduate students Carl Iddings, William D. Ramage, Willard G. Babcock, Hal D. Draper and Reginald B. Rule; assistant George A. Linhart; glassblower William J. Cummings, woodworker James T. Rattray and curator Harry N. Cooper.

The third picture was taken in front of the north end of Gilman Hall in November, 1920. Seated in the second row front are George F. Nelson (chief machinist), and faculty members Latimer, Branch, Stewart, Bray, O'Neill, Lewis, Randall, Hildebrand, Blasdale, and Eastman (Gibson, Olson, and Porter are missing). Also included are Miss Gray (secretary to Lewis), Mrs. Maybelle J. Fisher (clerk), Rattray (woodworker), Cummings (glassblower), H. W. Chapman (machinist), postdoctoral fellows Francis R. Bichowsky and W. Albert Noyes, Jr., and Roy F. Newton (instructor). All the others are graduate students--Philip S. Danner, Hal D. Draper, Nelson W. Taylor, Theophil F. Buehrer, Allyn M. Shaffer, Roscoe H. Gerke, Reynold C. Fuson, T. Fraser Young, Thomas E. Phipps, Roy M. Bauer, Eustace J. Cuy, Robert M. Evans, William M. Hoskins, Albert P. Vanselow, Miss Edna R. Bishop, Miss Anna L. Elliott, Clarence A. Jenks, Gustav E. Ostrom, John A. Almquist, Russell W. Millar, Albert M. Williams, Maurice L. Huggins, Evald Anderson, Dwight C. Bardwell, Harry K. Ihrig, Bruner M. Burchfiel, William F. Giauque, Sherwin Maeser, Karl H. Edlund, Thorfin R. Hogness, James B. Ramsey, and Manuel L. Zavala.

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