

LEO BREWER (1919–2005)



FOUNDER OF HIGH TEMPERATURE CHEMISTRY AND THERMODYNAMICS

Leo Brewer Career – Main Traits and Achievements

Born June 13, 1919, in St. Louis, Mo., Leo Brewer received his undergraduate degree from the California Institute of Technology in 1940. On the personal recommendation of Linus Pauling, who went on to win two Nobel Prizes, Brewer entered the chemistry graduate program at the University of California, Berkeley (UCB), and only 28 months later, in 1943, completed his thesis work and received his Ph.D. degree under the direction of Professor Axel Olson, the former doctor student of more known Professor Gilbert Newton Lewis. The title of Leo's thesis was "The Iodination of Mesityl Oxide", devoted to the effect of electrolytes upon the rates of aqueous reactions. Immediately afterwards Leo became Research Associate in the Manhattan District Project, Radiation Lab, soon later named Lawrence Berkeley Laboratory (1943–46). He was then appointed to the Faculty of the Chemistry Department at UCB, where he served for 60 years of his 85 years of fruitful life, starting as Assistant Professor in 1946, Associate Professor in 1950, Professor in 1955, and Emeritus in 1989.

Just after finishing his Ph.D. thesis, Leo Brewer was immediately asked to join the top-secret, wartime Manhattan Project with the aim of developing the atomic bomb, and in such respect headed a group that undertook the task of predicting the possible high-temperature properties of the newly discovered plutonium metal, then available only in trace amounts. Their ordered aim was to provide high temperature withstanding materials for a crucible that would contain

molten plutonium without contaminating the latter. To complete such a task, Leo Brewer thoroughly studied the behaviour of all the elements at high temperature, and, being unsatisfied with any existing materials for such a highly defined crucible in rather severe restrictive requirements, he experimented with new sulfides of thorium and cerium, which proved successful. Brewer's new crucibles were ready when the plutonium became available and determined his entire scientific future.

In another characteristic approach to produce extraordinary stable intermetallics, by following his theory of hypo-hyper-d-intermetallic bonding, Leo Brewer attempted Hf and Pd to get a symmetric Laves HfPd_3 intermetallic phase. An unusually high bonding strength has resulted from the huge reaction enthalpy, amounting to more than $620 \text{ kJ}\cdot\text{mol}^{-1}$, the whole process took an explosive course, and consequently the high temperature chemistry and the high temperature thermodynamics were born.

The combination of his theory with experimentation that Brewer created during the World War II work, marked his overall research throughout Leo's extraordinarily distinguished career. Although Brewer's research covered an unusually broad range of subjects and employed unusual array of different techniques in the arsenal of modern chemistry, physics and metallurgy, from basic fundamental theory to spectroscopy in its early age, Leo was always focused primarily on his high-temperature thermodynamics, material science, studies of intermetallic phases and development of his intermetallic bonding theory, though in his scientifically rich career he was at different points therein also involved with astrophysics and ceramics. In such a respect, Brewer systematically attacked many important chemical problems at high temperature by experimental and theoretical means and advanced the understanding of the behavior of materials, an area most in need for improvements, all together leading to his own intermetallic bonding model.



Leo Brewer as Assistant Professor in 1946

Leo Brewer – Honors, Awards and Recognition

Leo Brewer has been a unique figure and an extraordinary scientific personality in many respects worthy of recollection for coming generations. First of all, Leo was a caring and gifted teacher who taught freshman chemistry along with more advanced courses he himself conceived and founded, and for his excellent transferring and widespreading of university knowledge he received the Linford Award for Distinguished Teaching from the Electrochemical Society in 1988. Though Brewer directed 40 doctoral students and nearly two dozens postdoctoral fellows over the course of his career, the entire impact of his work and all his scientific papers Leo has mostly carried out and primarily wrote himself as a single author. Brewer's inventive and unique ideas were always pursued and accomplished prevailingly by himself to completion and mostly published as his very own. His work – published in nearly 200 articles and in his revision of the well-known Thermodynamic textbook by G.N. Lewis and Merie Randall from 1923 – was highly recognized with numerous awards, including election to the National Academy of Sciences in 1959. Leo Brewer was honored with Great Western Dow Fellow (1942), Guggenheim Fellow (1950), the Leo Hendrick Baekeland (1953), E.O. Lawrence Award of the Atomic Energy Commission (1961), W. Coover Awards of the American Chemical Society (1967), the Palladium Medal of the Electrochemical Society (1971), Fellow of the American Physical Society (1973), Distinguished Alumni Award, California Institute of Technology (1974), the William Hume Rothery Award of the American Metallurgical Society (1983), the fellowship in the American Academy of Arts and Sciences (1979), Leo Brewer Special Festschrift Modern High Temperature Science (1984), the American Society for Metals, ASM International (1989), TMS Extractive Metallurgy Science Award (1991), American Chemical Society (1993) and American Association of University Professors (1998), both for fifty-year citation, and with an unusually long list of honorary lectureships named after the most eminent names of American science like G.N. Lewis, H. Eyring, R.S. Williams, O.M. Smith, H. Huffman, W. Coover, W.D. Harkins, Louis Jacob Bircher, etc. Brewer was requested and organized the first Gordon Research Conference of High Temperature Chemistry.

Leo Brewer's family tree of scientific descendants has been dispersed over several hundreds of people. It would be an exhausting task and almost impossible to list all great honours, scientific and honorary memberships, and professional activities Leo Brewer experienced and earned during his long and creatively rich life. Such listed data is proudly treasured by the Department of Chemistry, University of California at Berkeley. As an example, let us just mention his critical review of the data for the gaseous monoxides of all the

elements and tabulation of their thermodynamic functions between room temperature and 3,000 K, to get an impression of the thorough and highly exhaustible approach of his to all high temperature chemistry and thermodynamic problems.

Our first meeting was in May 1977, when Leo Brewer presented his annual report on Mo-Co intermetallic phases for LBL authorities in the "Leo Brewer room" audience of MMRD (Molecular and Materials Research Division, well known bldg. 62, LBL), where Leo served as Head of the former Inorganic Materials Research Division (IMRD) for more than a decade (1961–75).

Intermetallic Hypo-Hyper-*d*-Interelectronic Bonding and Electrocatalysis for Hydrogen Electrode Reactions

The stability dependence on the atomic ratios of these two metals, Mo and Co, turned out that, as a function of the alloying composition along their phase diagram, closely correlates with the electrocatalytic activity for the hydrogen evolution reaction (HER), that I have already published: MoCo₃ has been both the most stable and electrocatalytically the most active. When I requested to read the literature on the Brewer intermetallic bonding theory, Leo first introduced me to papers of some physical scientists disputing the latter with an extremely formidable opposition, to warn me to avoid eventual being misled!

The Brewer intermetallic bonding theory [1–3], as a generalized Lewis acid–base reaction model [4], thermodynamically predicts that whenever metals of the left half of the transition series or hypo-*d*-electronic elements, having empty or half-filled vacant *d*-orbitals (bonding *d*-band, lower *d*-valence, d^1-d^5), are alloyed with metals of the right half of the transition series or hyper-*d*-electronic elements (or anti-bonding *d*-band, upper valence, d^6-d^{10}), having internally paired *d*-electrons not available for bonding in the pure metal, there occur symmetric Laves type intermetallic phases and stoichiometric compounds usually of extraordinary stability, the latter increasing from 3*d* to 5*d* level and in general with the exposure of *d*-orbitals in space. The correlation between interactive cohesive bonding (Gibbs free enthalpy of formation), and therefrom resulting rather high stability of hypo-hyper-*d*-interelectronic transition metal intermetallic phases and their electrocatalytic activity [5–10], for both cathodic HER and its anodic oxidation (HOR) has immediately been recognized and established: the electrocatalytic synergism results as the effect of further expanded and more exposed *d*-orbitals while establishing an hypo-hyper-*d*-interelectronic phase, that implies, according to Brewer, a partial delocalization of paired *d*-electrons from hyper-*d*- to empty or half filled hypo-*d*-band, which is now strongly supported by many XPS measurements.

The outstanding Brewer intermetallic bonding theory correlates phase composition, its stability limits, crystal structure and average electronic configuration along with reliable thermodynamic data for their characterization of transition metals including lanthanides and actinides. Since electrocatalysis unequivocally defines the optimal d -electronic configuration for the HER and HOR, as the main electrochemical processes, Brewer multi-component and multi-phase diagrams enable us *a priori* to tailor synergistic electrocatalysts. Once when Leo Brewer was awarded with the Palladium medal, as an extremely humble scientist, he remarked of being unaware of his electrochemical contributions. In fact the entire Brewer high temperature thermodynamics has been developed on the basis of the Nernst equilibrium potentials in corresponding molten salts, while at Leo Brewer retirement symposium I myself made such fundamental statements of his high temperature thermodynamics that made possible to define electrocatalytic conclusive formulations both in theory and practice. Ever since I have interconnected the Brewer intermetallic bonding theory with electrocatalysis for the HER at the First International Conference on Electrocatalysis, Neunkirchen am Brandt, Germany, 1983 [5], and inferred on the consequences of the former on the resulting crystal structure and electronic configuration, the latter always being substantially defining electrode kinetics, all we have and face now in the literature as electrocatalysts for hydrogen electrode reactions, besides few exceptions (RuPt, PtSn), are the Brewer type hypo-hyper- d -intermetallic phases, like MoPt₃, MoNi₃, ZrNi₃, TiNi₃, LaNi₅, etc.

Leo Brewer Intermetallic Bonding Theory – Its Main Properties and Disputes

What is the substance of the far-reaching Brewer individual transition metals and more so the intermetallic bonding theory upon which Leo made his great name in the science and indebted us with the broader scientific knowledge and experience for rather far ahead? Brewer uses spectroscopic data in a more quantitative manner by employing the experimental promotion energies required to achieve each of the proposed electronic configurations, together with the experimental enthalpies of sublimation, to determine the bonding energies that result from an exact thermodynamic Haber-Born cycle, when the gaseous atoms in the corresponding valence state are condensed to the solid metal [1–3]. Therefore, the bonding energy is obtained thermodynamically by adding the promotion energy to the enthalpy of sublimation. The net cohesion is the result of the difference between the promotion energy required to produce the atom in its bonding valence state and the resulting bonding energy in the solid state. Conversely, the net atomisation enthalpy is the difference between the valence-state bonding enthalpy and the promotion energy.

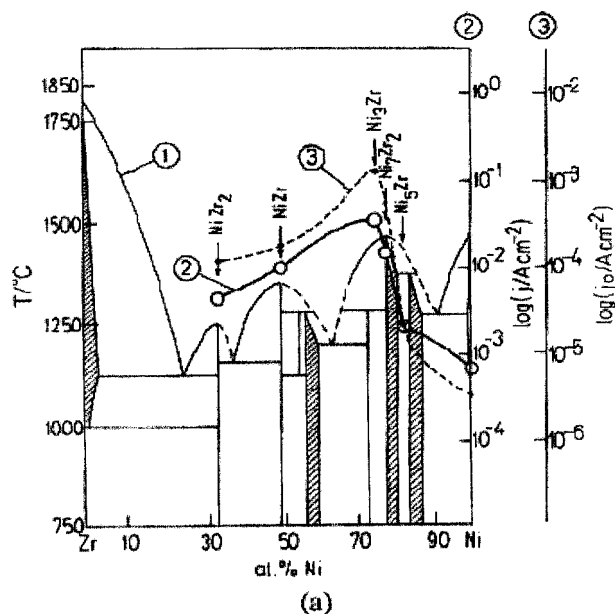


Figure 1b. Extrapolation of Tafel plots to $j = 0.2 \text{ mA}\cdot\text{cm}^{-2}$ and to the exchange current density, j_0 , axis to bring in the common natural correlation of intermetallic bonding effectiveness and electrocatalytic activity for hydrogen evolution, or the Brewer hypo-hyper- d -intermetallic bonding theory and the theory of electrocatalysis (HER) [5,6].

What are the reproaching (disputable) remarks of contemporary physics? The unusual fractional electronic configurations resulting from such exact thermodynamic calculations and based on reliable spectroscopic data, as a general physical view on all chemical structural formulas always imagined for something of rather static properties. However, these are *statistical values* like a prevailing amount and not the decisive core of the Brewer model. The essential contribution is confined in the high temperature thermodynamics and therefrom an *a priori* reliable prediction of the stability degree and limits of hypo-hyper- d -interelectronic transition metal Laves phases. One knows from the Brewer model that any combination of hypo- d -element with the right half of transition series, and *vice versa*, leads to volcanic dependence in the bonding effectiveness, while the strength of interaction and the stability of resulting Brewer type intermetallic phase increases from $3d$ towards $5d$ level. Such state of knowledge led us straightforward to the conclusive statement that every hypo-hyper- d -interelectronic phase diagram reflects volcanic features both in the bonding effectiveness and corresponding electrocatalytic activity for the HER, alike the part of the Periodic Table between two periods of interacting constituents, and therefrom resulting in their mutual correlations. In such a respect Fig. 1 in a sound illustrative manner interconnects the Brewer intermetallic bonding effectiveness and electrocatalytic activity along the Zr-Ni phase diagram. Quite recently, still during the life of Leo Brewer, there has been an extension of the Brewer intermetallic into Brewer interionic bonding

theory, to encompass interatomic, interionic and atomic-ionic bonding pairs, with broader consequences in electrocatalysis [10].

The other disputing remarks even of chemical nature concern the Brewer's paired electron transfer in hypo-hyper-*d*-interelectronic interactive combinations of transition metal intermetallic phases, which occurs in the opposite direction relative to the Pauling electronegativities, otherwise governing all chemical reactions. However, XPS measurements confirm with more than 90 percent effectiveness the predicted Brewer trend in paired *d*-electron delocalization for the reactions with hypo-*d*-electronic elements. The exceptions arise only in highly prevailing percentage of the latter in combinations with hyper-*d*-electronic metals.

Leo Brewer's Struggle for Science and Life

Leo Brewer was a mild-mannered man, primarily born and gifted scientist, a matter-of-fact person, helpful and compassionate for everybody, the personality of courage, incredible enthusiasm and persistence, of unpredictably enormous human energy, vitality and capacity, always optimistic and never seen angry. A rather humble and a down-to-earth scientist with great inventive human magnitude of creativity, never in contradiction, and always kept in full harmony and balance. As one of his successors, Paul W. Gilles stated, Brewer was a scientist whose creativity, courage and intuition were beautifully linked: "What his intuition and creativity led Leo to believe or even to suspect, his courage enabled him to state".

It is almost unknown any similar case of a human being, who has been in such frequent serious health troubles and faced so many physical problems, but never permitted them to damage his emotional stability, always entering in his life struggle mentally quite prepared, cool and stable, and permanently exiting as a winner with no exception. Leo faced the first serious attack on his health and entire life in 1960, when in a New York hospital, after the removal of his right eye and a substantial portion of the bone structure in his face, the first day after surgery he was clammering for a typewriter so that he could work, and a few days latter was cheerful proceeding with full capacity to his professional work, impressing the entire medical staff. His pernicious decease has been attacking unaccountable number of his organs, but Leo won all his life struggle giving an great example to all of us, and finally died of natural causes at the age of 85, old and exhausted.

Leo Brewer used to say: Hildebrand has written more scientific papers after retiring than before! Let us keep such a trend...

Leo Brewer is survived by his three children, Roger Brewer of Portland, Ore.; Gail Brewer of La Canada, Ca.; and Beth Gaydos of Cupertino, Ca., and six grandchildren.

His wife, Rose Strugo Brewer, with whom Leo was leaving within the warmth of a sweet home located opposite to the University and on the other side of Berkeley hills, in Orinda, and who was organizing entire his entire life, died in 1989, and since then nothing has been as before. Leo's creative capacity sharply decayed.

Last but not least, beyond the physical science, Brewer was passionately interested in native California plants and even had a manzanita named after him. As a hobby of his, Leo nurtured hundreds of different plants in his one-acre yard wilderness. Once his Kansas farm growing friend told him: "Leo, why don't you get out there and cut all those weeds?" Leo's plaintive response was: Oh, Helen those aren't weeds, those are native California wild plants". Leo's accompanying love of nature.

The writer of this obituary has never been any regular student or postdoctoral fellow of Leo Brewer, but remote follower with plentiful and continuous support of him for almost two decades, and whose scientific life and contributions would be incomparable reduced and poorer in achievements without the Brewer intermetallic bonding model and high temperature thermodynamics. I always use to say that I made my theory on the founds of Brewer theory, and my own name, on the Leo Brewer name (Appendix).

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This article is based in part on an obituary published by Jane Scheiber, Asst. Dean, College of Chemistry, University of California, Berkeley.

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