

GEORGE AUGUSTUS HULETT: FROM LIQUID CRYSTALS TO STANDARD CELL

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Born July 15, 1867 on a farm in DuPage Township in Will County, Illinois, George Hulett (Fig. 1) developed an aptitude for machinery repair in his boyhood. This aptitude served him well in later life, when he became one of the great experimentalists of his time (1). He entered Oberlin College in 1888, then in 1890 transferred to Princeton, from where he graduated in 1892. As an assistant in chemistry during the following four years, he wrote two articles, one on lecture apparatus and the other on the distillation of water. Hulett then traveled to Leipzig, to become one of the succession of American students and associates of Wilhelm Ostwald (1853-1932). Apart from their own later successful careers, these scientists were largely responsible for the growth of physical and analytical chemistry in America (2).

Hulett's project at Leipzig was to study the continuity of phase transitions, especially of liquid crystals (3). In 1888, Friedrich Reinitzer (1857-1927) had found that cholesteryl benzoate melted to a turbid but fully fluid liquid which exhibited double refraction. On further heating, the liquid suddenly became transparent and no longer birefringent (4). In his studies of *p*-azoxyanisole and *p*-azoxyphenetole, which behaved

similarly to cholesteryl benzoate, Otto Lehmann (1855-1922) termed such substances "fliessende Krystalle" (liquid crystals) (5).



Figure 1. George Augustus Hulett

The idea of a critical point for the transition of the turbid-transparent, or anisotropic-isotropic, liquid system arose from the known behavior of a typical liquid-vapor system such as that exhibited by CO₂. The transition of the liquid into its vapor under rising temperature and pressure is characterized by a continuously decreasing difference in the specific volumes of the two phases. Finally this difference vanishes at the *critical point*, where temperature, pressure and specific volume have fixed values for the system. Because the phases become identical at the critical point, the approach to this may be followed by observations of differences in any specific property, e.g., density, entropy, and heat of transition. Ostwald thought that the liquid crystal state had some

connection with critical phenomena and that pressure studies might reveal this connection.

While Hulett's work was in progress, Rudolf Schenck (1870-1906) published his studies of the two azoxy liquid crystals (6). Schenck found that the den-

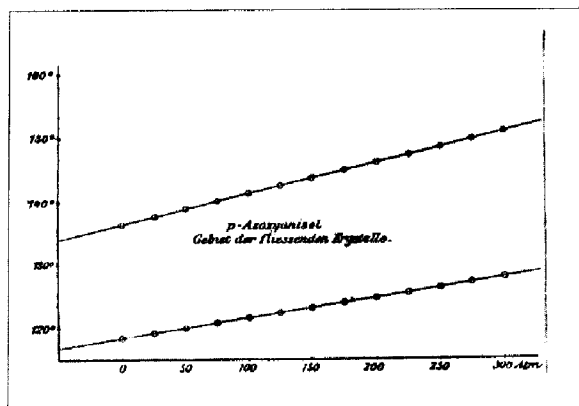


Figure 2. Pressure-temperature curves of *p*-azoxyanisole (Ref. 3)

sity-temperature curves of each of these substances exhibited a break that coincided with the anisotropic-isotropic transition temperature. The presence of an additive such as thymol was found to lower the transition temperature, an effect that Schenck regarded as analogous to the depression of the freezing point of a solvent by the addition of a solute. Using data from various experiments with *p*-azoxyanisole, he estimated that a pressure of 13.2 atm. should cause the transition temperature to rise by one degree.

Using materials contained in carefully cleaned capillary tubes, Hulett determined melting points and transition points at pressures up to 300 atm. Figure 2, reproduced from Hulett's paper (3), summarizes the results obtained with *p*-azoxyanisole. The interval between the melting point and the transition point *increases* as temperature and pressure are raised. Thus any critical point for the transition would lie at a large *negative* pressure. Similar pairs of curves were obtained for *p*-azoxyphenole and, less satisfactorily, for cholesteryl benzoate. We now know that the anisotropic form of the latter compound has properties and structure that are quite different from those of the azoxy compounds, which have rod-like molecules and belong to the *nematic* class of liquid crystal (7).

As support for the concept of negative pressure, Hulett cited experiments reported by Marcellin Berthelot (1827-1907) in 1850 (8). A thick-walled tube almost filled with water was sealed to enclose a tiny amount of air, which on warming to 28° C and shaking dissolved. When the temperature had fallen to the ambient 18° C, the water still occupied the entire volume. At the slightest agitation tiny bubbles appeared, and the water regained its original volume. The phenomenon might be

due to some supersaturating effect, or to a *real* increase in the volume of water. Results obtained when the tube was filled under vacuum with air-free water showed that supersaturation was not involved. Even greater effects were obtained with liquids such as ethanol and ether.

Having dealt with liquid crystals, Hulett turned to the effect of pressure on the melting points of *p*-toluidine, camphor, and benzene (3). This followed a report that the temperature-pressure curve of *p*-toluidine exhibited a maximum at 180 atm. (9). Hulett obtained linear curves for the substances that he examined. A later paper described his determination of the compressibility of water at 9° C and 50° C, and of *p*-toluidine at 45° C (10).

Having obtained his Ph.D. in 1898, Hulett became an instructor at the University of Michigan, where he continued the study of negative pressure (11). He pointed out that, if the compressibility coefficient was the same for negative as for positive pressures, Berthelot's experiments indicated negative pressures of approximately 52 kg.cm⁻² for water and 108 kg.cm⁻² for ether. Later workers, notably Osborne Reynolds (1842-

1912), continued the study of negative pressure (12). Reynolds filled a 152-cm. barometer tube with water, then displaced the water by mercury; but this left a film of water on the tube walls. When the tube was turned upright, it remained full of mercury, although the column was *twice* the barometric height. In a device involving centrifugal force on water, Reynolds obtained a negative pressure of 5 atm. To relate volume change to negative pressure, Hulett devised the

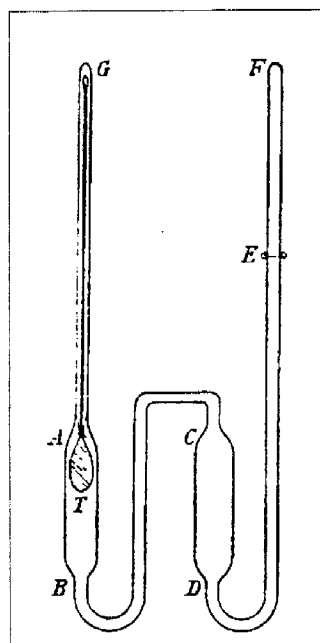


Figure 3. Hulett's pressure-volume apparatus (Ref. 11)

apparatus shown in Fig. 3, where T is the stout bulb of the mercury-containing manometer TG. The entire volume ABCDF was filled with the liquid to be examined. A platinum wire, fused in across the bore of the cali-

brated tube F, was heated to collapse the negative pressure effect. Portion B of the apparatus was kept at constant temperature, while the temperature of portion CD could be varied. The heating of CD applied positive pressure to T, causing the mercury thread in G to rise; the cooling of CD produced negative pressure, indicated by a fall in the thread. With ethanol, Hulett found that the pressure-volume curve was linear over the range +12 atm. pressure to -17 atm. Although these values are large, the actual tenacity, or tensile strength, of a liquid can be much greater. The values refer to the bulk of the liquid, not to the film that remains behind. Theoretical treatments by Josef Stefan (1835-1893) (13) and by Ottokar Tumlirz (1856-1928) (14) indicate that the values can be of the same order as the tensile strength of a metal such as silver.

When added to a solvent, a soluble substance (here regarded as nonvolatile and undissociated) dissolves and, under the influence of osmosis, diffuses to the boundaries of the solution. Here it exerts a force that tends to enlarge the volume of the solution, an effect opposed by the tensile strength of the liquid and by the vapor pressure of the solvent. Hulett regarded the osmotic effect as *negative* pressure; this causes the vapor pressure above the solution to be less than that above the pure solvent at the same temperature. He developed an isothermal cyclic process involving water and an aqueous solution, which led to the relationship:

$$p_1 - p_2 = Dp = -Pj/V \quad (1)$$

where j and V are the molecular volumes of water and of water vapor, respectively, at constant temperature T under vapor pressure p_1 , while p_2 is the corresponding vapor pressure under osmotic pressure P .

Hulett pointed out that Eq. 1 is analogous to that derived for the lowering of the vapor pressure of a liquid when it is compressed (15, 16):

$$p - p = +P\phi j/V \quad (2)$$

Here p is the vapor pressure of the uncompressed liquid and p that when under (positive) pressure $P\phi$. Hulett examined corrections to Eq. 1, to allow for the difference in the densities of the solvent and of the solution. He then used known data of the freezing point of a 0.1 M aqueous solution and of the vapor pressure-temperature relationship of the ice-water system to calculate Dp . The result agreed with that obtained from Eq. 1.

While at the University of Michigan, Hulett carried out various other investigations. These included the purification of mercury and a study of the electrical con-

ductivity of saturated gypsum solution ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). He found that, when finely divided gypsum was added to this solution, the conductivity first rose, then slowly declined. This is analogous to the "Ostwald ripening" of analytical precipitates, brought about because small particles have a greater solubility than larger ones. Returning to Princeton in 1905, Hulett became its first professor of physical chemistry in 1909. He was already involved in a lifelong interest, the study and development of standard potentiometric cells, work that required measurements of the highest precision and hence great skill and care.

In the decades that followed the invention of voltaic electricity in 1800, the need arose for a standard of electromotive force. The cell invented by John Frederic Daniell (1790-1845) in 1836 filled this need for over a quarter of a century (17). This $\text{Cu} | \text{CuSO}_4(\text{satd}) :: \text{ZnSO}_4(\text{aq}) | \text{Zn}$ cell was simple and had negligible temperature coefficient. However, because of the interdiffusion of the solutions, the cell lacked long-term stability (18). The single-solution cell $\text{Hg}, \text{Hg}_2\text{SO}_4(\text{s}) | \text{ZnSO}_4(\text{satd}) | \text{Zn}$, introduced by Latimer Clark (1822-1898) in 1872, was much more satisfactory (19). Major improvements by Lord Rayleigh (1842-1919) and Eleanor Mildred (Mrs. Henry) Sidgwick in 1884 were replacement of zinc by zinc amalgam and an H-shaped container which kept the amalgam well away from the Hg_2SO_4 -covered mercury cathode (20). In 1892, Edward Weston (1850-1936) patented the cell that still bears his name (21). This cell, consisting of a cadmium amalgam anode and CdSO_4 solution as electrolyte, and the Clark cell were the subjects of Hulett's extensive investigations.

Henry Smith Carhart (1844-1920) joined the faculty of the University of Michigan in 1886. His specialty was voltaic cells; in 1893 he described a modified Clark-type cell with an electromotive force (emf) of almost exactly

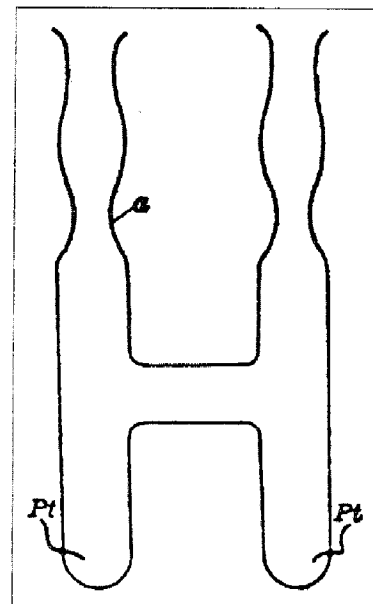


Figure 4. The Carhart-Hulett H-form cell (Ref. 23)

one volt (22). It is possible that association with Carhart triggered Hulett's interest in standard cells. In fact, Carhart and Hulett jointly authored a 1904 account of ongoing work in the preparation of standard cells (23). The purification of mercury and of the salt $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$, as well as the preparation of cadmium amalgam and of the "depolarizer" Hg_2SO_4 , was described. The H-form cell that they adopted (Fig. 4), with limbs shorter than those in the cell described by Rayleigh and Sidgwick (20), was sealed off at the necks after filling; it became generally adopted. The emfs of four sets of 6 to 10 cells maintained at 20°C were measured

at intervals. Figure 5 shows the emf-time curve of cell D6, one of a set made with HgSO_4 precipitated from HgNO_3 . A cell from a set made with electrolytically prepared Hg_2SO_4 behaved as indicated by curve D1. The immediate and continued stability of this type of cell was attributed to the use of nitrate-free Hg_2SO_4 .

Hulett was the sole author of a second 1904 paper (24). This dealt with the purification of Hg_2SO_4 , which can undergo hydrolysis, an effect minimized by addition of H_2SO_4 . He next described a cadmium-cadmium amalgam cell with a stable emf close to 50 mV (25). A further study concerned amalgams and the purification of mercury (26).

At Princeton, Hulett compared the performances of the Clark and of the Weston cells (27, 28). After gentle rotation, a Weston cell showed a long-term upward drift of emf, an effect attributed to nonequilibrium conditions at the cathode ($\text{Hg}-\text{Hg}_2\text{SO}_4$). After similar treatment, the emf of a Clark cell rapidly stabilized. At this stage, Hulett favored the Clark cell as a standard of emf, despite its much higher temperature coefficient. In fact, until 1908, this cell was generally accepted as the standard. Two papers of 1906 concerned materials for the construction of Weston cells and a further examina-

tion of the effects of cell rotation (29, 30). That oxidation of Hg_2SO_4 by air was not the cause of emf drift was demonstrated by passage of hydrogen through the solution. Two opposing effects, hydrolysis of Hg_2SO_4 and a slow reaction of the products with the mercury surface, were suspected. In null-point potentiometry, the drift in

emf of conventional working batteries necessitates frequent adjustment of the calibration resistor. Hulett developed the enlarged Weston cell shown in Fig. 6 to eliminate this nuisance (31). The paraffined cork of the 8-cm diameter bottle carries tubes for making contact with the

mercury pool K and the contents of shallow dish A, which contains cadmium amalgam and mercury. Current from an external source was used to form Hg_2SO_4 on the surface of K. Discharging through a 10 KW resistor, the emf changed by only about 0.1 mV from the open-circuit value.

In 1908 Hulett reviewed the progress that he and others had made toward the establishment of a reliable standard of emf; the problem was an international one (32). He noted that solid cadmium amalgam was an isomorphous mixture of composition dependent on that of the liquid phase. Nevertheless, the emfs of cells made with amalgams of 10% and of 7% total cadmium differed by only 7 ppm. The

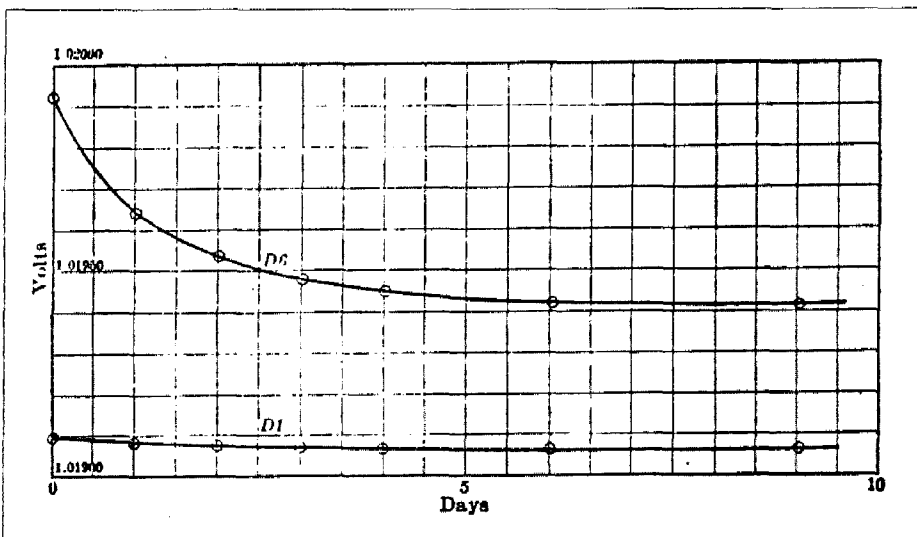


Figure 5. Emf—time curves of cells made with precipitated (D6) and electrolytically prepared (D1) Hg_2SO_4 (Ref. 23)

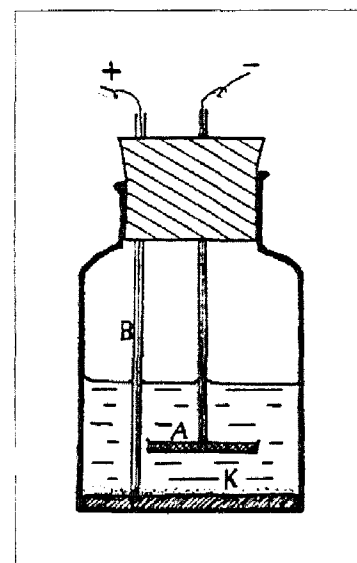


Figure 6. Weston-type cell for use as supply source in potentiometry (Ref. 31)

phase rule indicated that the potential of the anode (amalgam) system is invariant at fixed temperature. Hulett confirmed the indifference of the cathode system to dissolved oxygen and further examined the hydrolysis of Hg_2SO_4 . He carefully analyzed the electrolyte solutions, to some of which H_2SO_4 had been added. Thus he was able to determine the solubility of Hg_2SO_4 at various acidities, both for the Weston (cadmium) and the Clark (zinc) systems (Fig. 7). In saturated CdSO_4 solution the rapid solubility decrease in the region up to 0.08 M H_2SO_4 is striking; such an effect is absent in ZnSO_4 solution. When cells were prepared with "neutral" CdSO_4 solution, efforts were made to remove all H_2SO_4 from the Hg_2SO_4 , such as by washing with alcohol or CdSO_4 solution. However, the Hg_2SO_4 then undergoes hydrolysis, an effect accelerated by contact with mercury. Nevertheless, the emf of a cell with solution made 0.2 M in H_2SO_4 remained constant to within 0.03 mV over a three-year period. The only defect was very slow evolution of hydrogen.

To meet an objection to his assumption that the hydrolysis of Hg_2SO_4 was accelerated by mercury, Hulett rotated a tube containing Hg_2SO_4 , CdSO_4 , and the saturated solution (33). Portions of the liquid were withdrawn at intervals and tested on a clean mercury surface against a cadmium amalgam, thus forming a complete cell. The emf, 1.01800 V after one day, rose to 1.01870 V after 12 days, then remained unchanged. After addition of mercury, rotation of the tube was resumed. Cell measurements made after 18 days showed that the emf had risen to 1.01955 V, indicating an increase of dissolved mercury. Presumably the basic salt, $\text{Hg}_2(\text{OH})_2\text{Hg}_2\text{SO}_4$, formed by hydrolysis, first remains in solution and then begins to precipitate. Then the concentration of dissolved mercury, increasing up to this point, begins to fall. Equilibrium is not reached until the hydrolytically formed H_2SO_4 reaches a concentration of 0.08 M. Extreme precautions were taken in an

experimental study of equilibrium in the mercury-cadmium sulfate-water system (34). The hydrogen-filled cell system (Fig. 8) contained CdSO_4 solution and five cadmium amalgams of accurately known composition. Platinum wires *a* through *e* led to the amalgams. With the saturated (5.902 % cadmium) liquid amalgam *a* as

reference, the potentials of amalgams *b* through *e* were measured, sometimes for 70 days. In the range 1% to 1×10^{-6} % of cadmium, potentials agreed with the theoretical values.

In 1911, Hulett again reported on the construction of Weston cells (35). He described alternative electrolytic methods for the

preparation of Hg_2SO_4 and its incorporation into a paste. Modified designs of the Clark cell and the construction of an electrically heated 100-L kerosene thermostatic bath were also described. Other 1911 papers dealt with the clarification of a misunderstanding of the hydrolysis of Hg_2SO_4 (36) and the carryover of metallic contaminants when mercury is distilled (37). Also included were methods for the purification of mercury and details of an electrically heated mercury still.

Several years elapsed before the appearance of other papers on standard cells. This is not surprising, for Hulett and his students were occupied with many other projects, such as the electrolytic determination of metals, silver coulometry, determination of the atomic weight of cadmium, and the use of cadmium amalgam for the reduction of iron (III). Eventually, however, a study on the use of the double salt $\text{K}_2\text{SO}_4 \cdot \text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ in the Clark cell appeared in 1916 (38). The addition of one or the other of the constituent single salts elucidated the conditions under which the double salt is the solid phase. The specific heats of the reacting substances are necessary for thermodynamic calculations on standard cells applicable to temperatures below the usual range (39). The specific heats of $\text{CdSO}_4 \cdot 8/3 \text{H}_2\text{O}$ and of $\text{CdCl}_2 \cdot 5/2 \text{H}_2\text{O}$ were determined as functions of temperature be-

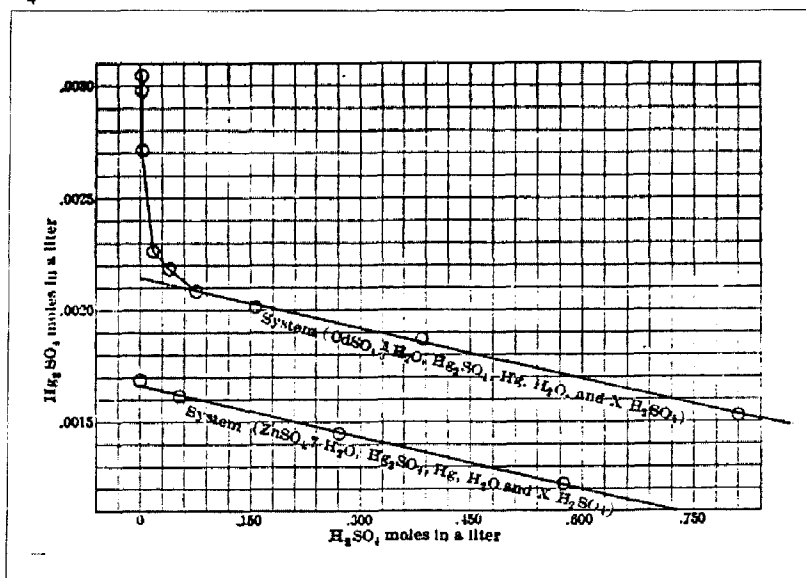


Figure 7. Effect of H_2SO_4 concentration on the solubility of Hg_2SO_4 (Ref. 32)

tween the limits 87° K and 274° K. Along with available data on other cell constituents, the results provided a means for a test of the Nernst heat theorem. Calculations led to an estimate of 1.072 V for the emf of the Weston cell at 291 K; while the observed value was 1.071 V. The calculated and observed values for the chloride-salt cell were 0.7426 V and 0.7236 V, respectively.

More than a decade was to elapse before Hulett resumed work on standard cells. Hulett took a leave of absence to spend a year as chief chemist at the US Bureau of Mines and then returned to Princeton in the fall of 1913. He remained as consultant on the chemistry of coal and other carbonaceous materials. In 1917, when the US entered World War I, Hulett crossed the Atlantic, to provide service (later, highly commended) as consulting chemist to the US Army in Europe. After his return he organized a research unit at Princeton for the Chemical Warfare Service, which led to a continuation of studies on carbonaceous materials, especially charcoal. In 1920 a fall resulted in a crippling concussion that handicapped him as an experimentalist (40). Nevertheless, his research continued; and in 1929 he had returned to the study of standard cells.

Other workers had shown that Weston cells prepared by working in an atmosphere of hydrogen or nitrogen exhibited enhanced constancy, although no proof was offered that the presence of oxygen causes irregularities. Hulett decided to search for any effect of oxygen on cell emfs (41). He set up approximately 40 cells, using various preparations of the Hg_2SO_4 depolarizer. In some cases, oxygen was bubbled through the electrolyte solutions, and these were sometimes acidified with H_2SO_4 . After observations of emf over a one-month period, Hulett concluded that the presence of atmospheric oxygen during the preparation of the cells had no noticeable effect. The abnormalities of the emfs of cells with oxygen-saturated solutions disappeared after about a month. Hulett believed that the hydrolysis of the depolarizer was more detrimental than any effect of

atmospheric oxygen. The hydrolysis of Hg_2SO_4 , evidence for which appeared in the early 1800s, had been examined by others, as well as by Hulett. He decided to examine the changes in the composition of the solid phase and in pH when a vessel that contained mercury,

Hg_2SO_4 , and saturated CdSO_4 was rotated for extended periods (42). The experiments led to the conclusion that the washing of the Hg_2SO_4 with water previously equilibrated with this salt and mercury enhances the constancy of a Weston cell. If this liquid is used to make the saturated CdSO_4 solution, it is slightly acidic and retards the hydrolysis of the depolarizer. In jointly authored papers,

Hulett reported on polarization (43) and hysteresis (44) in standard cells. Overheating during cell construction may be the cause of emfs that are initially high but decrease during a month or so. In 1930 Hulett examined the Weston cells that he and Carhart had constructed in 1903-4 (23). The emfs dropped slightly in the few years up to 1906 but since then had remained constant (45).

Five short coauthored papers were Hulett's final contributions to the study of standard cells. The preparation of crystalline Hg_2SO_4 by reduction of HgSO_4 by SO_2 was described (46). The hydrolysis of Hg_2SO_4 was further examined, with the conclusion that, to prepare the normal (i.e., unhydrolyzed) depolarizer, a concentration of at least 1 M of H_2SO_4 was necessary (47). In a Weston cell, dissolved mercury species slowly diffuse from cathode to anode (48). To examine this, typical cells were unsealed, so that a tiny amalgamated platinum probe could be inserted. This permitted the determination of mercury concentrations at various points in the solution. A distinct concentration gradient was found in a four-year old cell but none in a cell that had been aged for 18 years. Presumably a steady state had been reached in the older cell. On equilibrating electrolytically prepared Hg_2SO_4 with saturated CdSO_4 solution and mercury in bulk, a mercury (I) \ mercury (II) concentration ratio of 55.3 was found (49). If very finely divided mercury was used, the ratio was larger. Thus the emf of a cell made with "very black mercurous sulfate" (i.e., containing micron-range mercury particles)

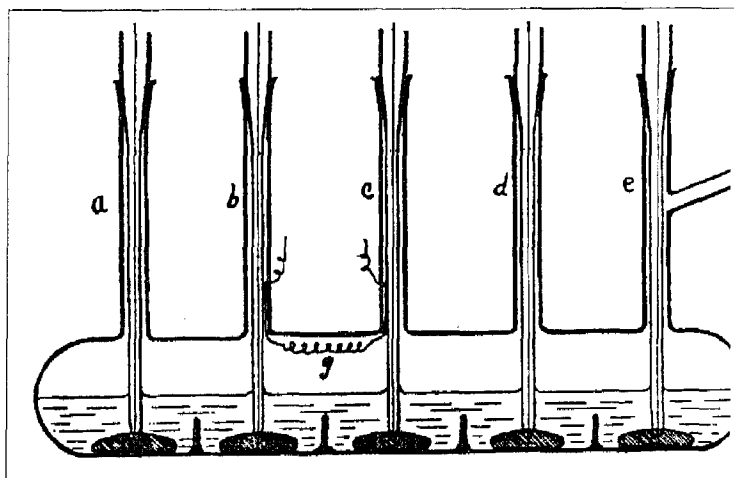


Figure 8. Cell system for the study of cadmium amalgams (Ref. 34)

should be initially abnormal. A cell thus constructed had an emf of 1.017366 V, but this had risen nearly to normal after 32 days. As previously mentioned, Hulett had found evidence for the enhanced solubility of tiny particles, which dissolve and then enhance the size of the larger particles. Presumably a similar effect was operating here. Hulett's final work with the Weston cell was, in a sense, an update on the use of such a cell as the working source in potentiometry (31), in which he described a cell that contained 5.4 L of solution and 5 kg of mercury. Such a cell could supply a current of 1mA with a voltage drop of only 0.5 mV (50).

Although Hulett retired in 1935, he continued to direct research until increasingly bad health curtailed his activities. He died on September 6, 1955. Apart from his superb experimental skill and great scientific ability, he was highly revered by colleagues and students.

ACKNOWLEDGMENT

This work was partially carried out under the Research Fellowship Program of the Science Museum, London.

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LETTER TO THE EDITOR

February 25, 2000

Louis Rosenfeld's excellent article, "Otto Folin and Donald D. Van Slyke: Pioneers of Clinical Chemistry" [*Bull. Hist. Chem.* **1999**, *24*, 40-47], did not include any mention of the pioneering electrophoretic method used by Drs. Van Slyke and Dole to study blood during World War II. Vincent P. Dole was the first person noted among those who had worked with Van Slyke and who later had achieved prominence. During 1943-1944, I was Dr. Dole's technical assistant at the Rockefeller Institute for Medical Research.

Using electrophoresis apparatus to analyze blood supplied by Van Slyke from malaria patients (mostly military personnel attacked by the disease in the Pacific theater of war), we attempted to find out whether the blood of those with relapsing malaria was different from "normal" blood. Separation of proteins in the blood was achieved because of their different mobilities in an electric field. In evaluating the results, we concluded that the severity of the disease in patients with relapsing malaria might be reflected in measurements of the total protein concentration and the albumin:globulin ratio. These and other studies were published in the *Journal of Clinical Investigation*.

The Nobel Prize in Chemistry was awarded to Arne Tiselius in 1948 for his contributions to the development of the electrophoresis apparatus and its applications. Developed by 1937, it was first used in 1939 in the study of diseases. The early versions of the apparatus were very large; I recall they were about 3 meters x 1.5 meters x 1 meter. Each analysis required a day for completion. Today, 12-cm glass tubes can produce separation in 1 - 2 hours; capillary tubes in 10 minutes. *Esther B. Sparberg, Professor Emerita of Chemistry, Hofstra University, Hempstead, Long Island, NY 11550*