The Role of Michael Faraday in the Development of Contemporary Chemical Engineering

James W. Gentry
Department of Chemical Engineering
University of Maryland, College Park, Maryland

The origins of contemporary Chemical Engineering (i.e. transport phenomena, thermodynamics, kinetics . ..) lie in the first three quarters of the nineteenth century. Michael Faraday was responsible for more than a half-dozen historically significant studies which were subsequently incorporated into chemical engineering practice and which form the standard chemical engineering curriculum. Here we focus on those traits of Faraday which led to his reputation of the greatest experimental scientist. These traits are illustrated with a discussion of three of his seminal works in the foundations of chemical engineering. These are his papers on heterogeneous catalysis, the manufacture of optical glass, and the liquefaction of gases. In this paper we discuss the background in which Faraday worked, and the consequence which resulted from the study.

Experimental studies utilize three attributes. First the researcher needs to be a careful observer. Many of Faraday's most impressive results including the discovery of the thermal properties of semiconductors and the use of the Faraday -Tyndall effect to detect submicron particles in a colloidal solution directly followed from his acute observations. Secondly the experimentalist must be a gifted technician. Evidence of this trait are the design of definitive experiments and the development of new instrumentation. Finally, the most talented experimentalist are able to formulate bold hypothesis of the underlying science. Faraday's conjectures on the 'condensation theory' of surface catalysis and the role of the critical point in gas liquefaction are examples of his insightful guesses.

Kinetics and Surface Catalysis:

Kinetics is the study of the rate of chemical analysis. Frequently in gas phase reactions, the gaseous components are absorbed on to a solid substrate where they react and then are desorbed. In some cases the properties of surface facilitate the reaction. Such a system is called heterogeneous catalysis. One such reaction is the combination of oxygen and hydrogen to form water. This mixture when ignited by a spark or flame will ignite and explode with violence. Normally, no reaction occurs at room temperature. However the presence of a platinum substrate will serve to catalyze the reaction. In the mid-1 820's, Dobereiner passed hydrogen through a platinum gauze. The hydrogen catalyzed by the platinum combines with oxygen from the air. The mixture ignites and then begins to burn. Dobereiner developed a very successful commercial product - fire lighter - based on this principle. The instrument was eventually replaced by the safety match. The only mechanisms for the catalytic behavior of the platinum surface that were proposed prior to Faraday's study were vague references to electrical forces.

The **important** paper of Faraday on heterogeneous kinetics followed from an unexpected observation that he made during his study of electrolysis. In order to measure the amount of electrical energy passing through his cell, he developed a "Volta electrometer" based on the amount of water decomposed into oxygen and hydrogen. The instrument used a calibrated gauge to measure the volume of water displaced during the electrolysis and hence the extent of the reaction. Unfortunately the oxygen and hydrogen recombined forming water and reducing the volume of the gases which were generated. Thus an accurate determinations of the magnitude of electrical energy produced could be obtained only if this secondary reaction could be blocked.

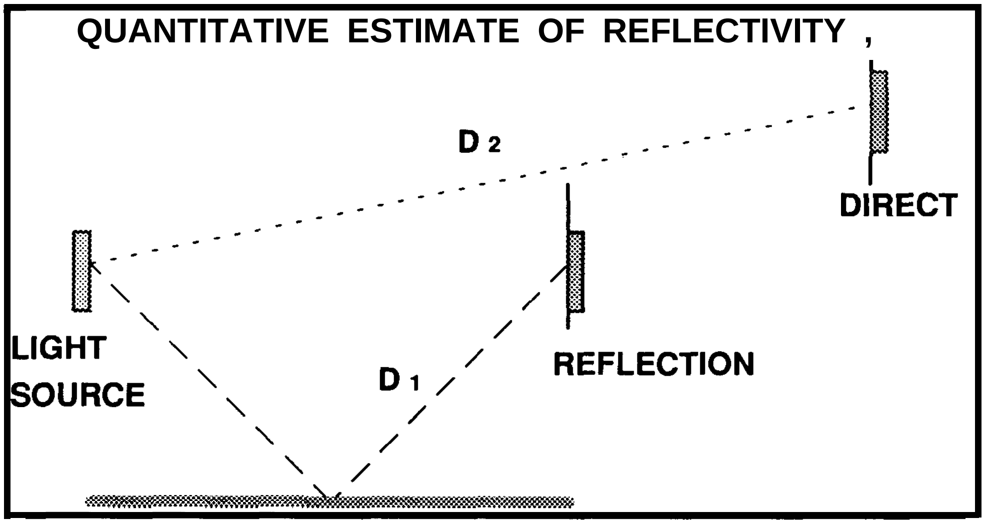
Faraday solved his specific problem by redesigning his cell so that the platinum plates remain immersed under water. About a month later he decided to examine the reaction phenomena more carefully. First, he demonstrated that the reaction occurred in the presence of a clean platinum surface. When the surface became tarnished or contaminated, the reaction rate decreased. He then proposed a " condensation " model as a mechanism of the reaction rate. The most quantitative aspect of this work was the study t of trace contaminants. He showed that 2 % concentrations of CO or C_2H_2 were sufficient to halt the reaction temporarily and that PH_3 or H_2S permanently poisoned the catalyst. This work on catalyst poisoning anticipates the development of catalytic science (191 5-1 940) traditionally associated with work of Langmuir is 1915 almost 80 years after the completion of the Faraday study. **Zangwill** has stated that this study by Faraday was one of the "three notable results of importance to the future of surface science" in the 19th century. **Somorjai** pointed out that " Faraday was the first scientist who studied catalytic reactions". However, the time was not ripe. The impetus for Langmuir's investigations was the study of reaction mechanisms by Bodenstein at the turn of the century not the work of Faraday.

The Manufacture of Optical Glass:

Throughout the 18th and 19th centuries, the principal uses of optical glass were for navigational and surveying instruments. However the most prestigious application was for the manufacturing of telescopes. By the midpoint of the 18 the century single lens (i.e. "long telescopes") were being replaced by reflectors. This state of affairs was to be reversed by the manufacture of achromatic lens by John **Dollond.** By the turn of the century the new refractors using the achromatic lens had become the telescope of choice, with the objective to build better telescopes by using larger lens. The limiting factor in the manufacture of such lens was the inability to obtain glass blanks of size which were uniform. Uneven cooling resulted in the formation of striate which rendered the blanks unfit for optical use. The inability to produce telescope lens of sufficient quality resulted in a shift of the center for optical glass from England to the continent. In the 1820's a three person Royal commission was appointed to study the manufacture of optical glass and to develop methods for producing high quality optical glass. Faraday, a member of the commission, was assigned the responsibility of developing a method for producing the glass. In 1829 he presented the results of his study in a Baker Lecture to the Royal Society. It was the first of his four Baker lectures.

The Faraday work on optical glass has always been controversial. First, his research **did not** prove to be successful in developing a process for optical glass manufacture which was more economical that the competitive processes on the continent. Secondly, it has become clear that the Faraday contributions to the manufacture of optical glass was outstripped by several other 19th century technicians- particularly P. Guinand and O. Schott. Thirdly his optical work lacks the fundamental discoveries that mark his best work and which reinforces the impact of the kinetics and vapor pressure studies reported here, In contrast the funds provided to the Royal Society to carry out the studies literally saved the institution which was seriously strapped for cash at the time.

The unique feature of Faraday's paper is that it is arguably the best description of a chemical process in the chemical engineering literature. It is essentially a monograph with a length of over 60 pages. The two principal innovations described in the paper are using platinum to construct the molds and stirring rods and in a developing for quantitatively measuring the reflectivity of the surface. Arguably the most significant contribution in the paper was showing that trace gas compositions in the furnace air can lead to tarnishing of the glass surface. Faraday showed that trace amounts of CO reduced the lead oxide at the surface of the glass. The method used by Faraday for measuring the reflectivity is shown in the figure below. The intensity of the shadow from a lights source at a distance D2 is matched with the intensity of the shadow from the light source reflected from the glass measured at distance D1. Faraday showed that 8.5 % of the light was reflected for his optical glass consisting of silica, boric acid, and lead oxide compared to 3.8% for plate glass.



The composition of the glass used in the Faraday studies is compared below with the composition of flint glass and the optical glass produced by Guinand. Glasses of high density are necessary for optical glass. These were traditionally made by using comparatively high concentrations of lead oxide. The glasses developed by Faraday were much denser using lead oxide concentrations of more that 70%. Such glasses tarnish easily. Faraday found this tarnishing could be circumvented by insuring that the glass contained no alkali (i.e. potash). This required the development of glasses with over 17 % boric acid. What is novel in this approach by Faraday is the emphasis placed on the chemistry of the glasses. In the manufacture of glasses as in other scientific endeavors Faraday took the modern view point. Because of this aspect the subsequent work of Schott is closer in its viewpoint to Faraday than to Guinand.

COMPOSITION OF VARIOUS GLASSES

COMPOSITION	FLINT GLASS	GUINAND	FARADAY		
Silica	51.9	44.3	36	10.5	
Potash	13.8	11.8			
Lead Oxide	33.3	43.1	64	73.7	82.3
Boric Acid				15.8	17.7
DENSITY	3.29	3.62		5.44	6.39

Vapor Pressure - Temperature and Thermodynamics:

In 1822-23 two seminal contributions were made in experimental thermodynamics- Faraday demonstrated a general procedure for liquefying gases by simultaneous cooling and pressurization and Cagniard de La Tour showed the existence of the critical temperature. These two discoveries established the view that there was continuity between the liquid and gaseous states and set the agenda for research in vapor-liquid phenomena for the next century. After 1924 the prevailing view was that other suitable conditions all gases could be liquefied. Between 1823 and 1845 Thilorier developed a commercial process for obtaining solid C02. He used the design of Faraday replacing glass with cast iron. On vaporization liquid C02 froze forming solid C02 or dry ice. Now researchers could reach temperatures lower than -100° C. In 1845 Faraday perfected a technique for controlling the pressure and temperature of the cooling bath. He reached the lowest temperatures there-to-fore obtained.

This 1845 paper illustrates the attribute of Faraday as an unrivaled technician. I view the major contributions of this paper as (1) developing a protocol which allows temperatures as low as -100 ^{0}C to be reached, (2) controlling the temperature of the bath at intermediate values resulting in vapor pressure temperature data below the freezing point of water for compounds which are normally gases, (3) obtaining vapor pressure data for substances with critical temperatures below O ^{0}C, and proposing the cascade process for reaching still lower temperatures. The trick of reaching low temperatures was to cool the solution with solid C02 in an ether bath. The temperature is lowered still further by pulling a vacuum on the ether. The evaporation of the ether at low pressures cools the system still further. More important the temperature of the bath can be controlled by adjustment of the vapor pressure of the ether- C02 bath.

The net result of this study was that about a half dozen compounds were solidified and another half-dozen compounds liquefied for the first time. For the first time vapor pressures as a function of temperature for temperatures well below freezing were obtained for compounds which were gases at ambient temperatures. It can be argued that these were the first cryogenic measurements. The vapor pressure data obtained by Faraday were the oldest data used in developing the correlations for vapor pressures of cyanogen, H2S, H Cl, and BF3 that are still used in the Handbooks of Chemistry and Chemical Engineering. Comparison of the vapor pressure data obtained by Faraday with more up-to-date correlations (i.e. Reid et. al.) show that the Faraday measurements and the correlations are in remarkable agreement. The largest discrepancies occurred when the temperature was in the range of 10-30 “C. Apparently the temperature control for Faraday's measurements near or above the ambient was not as accurate as for the lower temperature.

The 1845 paper is famous for its conjecture that gases could not be liquefied at temperatures above their critical point, no matter what the pressure. Faraday seems to be the first to make this conjecture linking gas liquefaction with the critical point. This conjecture was strengthened by Natterer who showed that liquefaction of oxygen did not occur even when the pressure exceeded 1000 atmosphere. It was not until the mid-seventies of the nineteenth century that oxygen and nitrogen were liquefied by Pictet and Cailletet. These two investigators used completely different methods reported their success within 24 hours of each other. The liquefaction of oxygen, the definition of the critical point by Andrews and the development of the equation of state by Van der Waals in the years between 1869 and 1877 represent a burst of innovation in vapor liquid thermodynamics approached only by the earlier studies of Faraday and Cagniard de la Tour and a flurry of activity in the last decade of the nineteenth century where the inert gases, hydrogen, and finally helium were liquefied. With these studies the agenda implicit in the Faraday papers of 1823 and 1845 was concluded.

Faraday, M., (1830), "On the Manufacture of Glass for Optical Purposes", **Experimental Researches in Chemistry and Physics,** P. 231-291.

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Faraday, M., (1845), "On the Liquefaction and Solidification of Bodies Generally Existing as Gases", **Experimental Researches in Chemistry and Physics,** P. 96-124