

## ABSTRACTS OF UNIVERSITY OF DELAWARE THESES FOR ADVANCED DEGREES

1946

EDWARD MINKA. *The Annexation of Hawaii.* M.A.

In most cases the causes for any single event of historical importance are remote and often hidden. This is particularly true in the study of the factors leading to the annexation of Hawaii by the United States. It has been necessary to turn back to the first contact made by the Hawaiians with Europeans. Without them, there would have been no unified government, and the islands would have become the property of the first maritime nation that realized their commercial and strategical importance in the Pacific Ocean. At the time of their discovery by Captain Cook, Kamebawsha the Great was engaged in uniting the four districts of the island of Hawaii. It is doubtful whether, without the firearms and strategy introduced by the traders who followed Cook, he could have brought the islands together under his suzerainty. By the time that their great value became apparent to the sea powers, the monarchy had grown strong. Moreover, it was protected by the mutual jealousy and distrust that existed between the powers that hoped to acquire sovereignty over them. The question of annexation became a live international problem. At one time or another early in the nineteenth century, various world powers made abortive bids to annex the islands. Very early the State Department of the United States made it clear that the Hawaiian Islands constituted a sphere of special interest to the United States. So determined was our attitude in regard to the maintenance of the sovereignty of the Hawaiian Government, and so predominant were our economic interests there, that toward the end of the century it became apparent to the world powers that annexation to the United States was inevitable. The sole uncertainty was the means by which this would be accomplished in view of our reiterated declarations of recognition of sovereignty. This study elaborates upon the interests of other nations in the islands, their attempts at annexation, and the conditions that resulted in the territorial status of the islands.

DOROTHY LEVIS MUNROE. *Emulsion Copolymerization of Styrene and Isoprene.* M.A.

This investigation reports the emulsion copolymerization of isoprene and styrene in proportions by weight of 40% isoprene to 60% styrene. Studies were made of the technique of carrying out the polymerization, the method of isolating the product, and the effect of various conditions on the properties of the product.

The polymerizations were carried out in aqueous emulsions at 40°. The products were most satisfactorily isolated by acid coagulation followed by reprecipitation from a toluene solution with methyl alcohol. The yield of a polymerization reaction was determined on the acid coagulum, and the composition of the polymer in terms of percentage styrene content was ascertained by iodine analyses of the purified product. In the later runs, intrinsic viscosity determinations were made on samples removed at varying time intervals in order to give some indication of the relative size of the polymer molecules formed up to a particular conversion point.

The study of the effect of reaction time on the percentage conversion showed that the maximum conversion, about 74%, was reached after eighteen to twenty hours of polymerization. At this time the per cent of styrene in the product reached a minimum value, which corresponded to the weight present in the original charge of monomers.

The presence of a modifier in the emulsion recipe was shown to result in slightly higher yields and in products of slightly higher styrene content than when it was omitted. However, small variations in the amount of the modifier used were shown to produce no appreciable effect.

Variations in the physical nature of the product were produced by varying the time of polymerization and the method of isolating the polymer. Products were observed to become more rubbery as the styrene content decreased with increasing time of polymerization. In general, the polymers resulting from methyl alcohol coagulation were very much softer and more sticky than those obtained from acid precipitation, which were usually quite tough and elastic. Products prepared for analyses by the frozen benzene technique were generally tough and somewhat translucent.

The increase in the molecular weights of the polymer with the



time of polymerization was indicated by the increasing intrinsic viscosities obtained at varying intervals.

Fractionation of the polymer in several instances made it possible to demonstrate by analyses that the polymer was of a uniform composition.

HARRY G. STAULCUP. *Notes on the Early Stalcop Family in Delaware.* M.A.

Johan Anderson Stalkofta, a Swedish soldier stationed in New Sweden, was the progenitor of the Stalcop family in America. The surname Stalkofta, a Swedish nickname for steel-coat, was anglicized to Stalcop, and became the family surname down through its succeeding generations.

The Stalcops were not important leaders in the colony that was New Sweden until it became incorporated under English Rule in 1664. From that time on they assumed a rather prominent role in the community. Though mixed up in the Long Finn Rebellion against the English in 1669, the Stalcop family became one of the first large land owners, by a grant from the English, in Wilmington. Their land holdings were subsequently increased by both grant and purchase.

They were all members of the Swedish Lutheran Church. For the most part, they participated prominently and freely in all the Church activities. It was through their generosity that the Church obtained the land on which the Old Swedes' Church in Wilmington now stands. Their homes were used for Church social gatherings. They participated in the founding of the first school in Wilmington, and saw to it that their children attended the school.

Most of the Stalcops were land owners and farmers. However, they helped to establish one of the first gristmills in Wilmington. At least one of them gained his livelihood by milling grain. Another of them became the second owner of the Market Street Ferry in Wilmington, and for four generations they were its proprietors.

For the most part they were prosperous and moderately successful. Most had large families. However, but for one or two Stalcops, they all left Delaware by or in the fifth generation. Two Stalcops migrated to New Jersey. The rest migrated first south to Virginia, West Virginia, North Carolina, Tennessee, and Kentucky. Their children eventually migrated to Indiana, Ohio, Missouri, and Texas.

HAROLD F. BOGARDUS. *The Ternary Systems Barium Chloride-Dioxane-Water and Calcium Chloride-Dioxane-Water.* M.S.

A phase study of the ternary systems barium chloride dioxane-water and calcium chloride-dioxane-water at 25° has been presented. The system barium chloride-dioxane-water showed no immiscibility and the only solid phases found were barium chloride dihydrate and unsolvated barium chloride. From vapor pressure equilibria in this system, it has been shown that the solid phases of this system are  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  up to 99.58% dioxane and anhydrous barium chloride above this concentration of dioxane. The system calcium chloride-dioxane-water showed immiscibility at high concentrations of dioxane. Two solid phases were encountered: calcium chloride hexahydrate and a new solvate to which the formula  $\text{CaCl}_2 \cdot (\text{C}_2\text{H}_4)_2\text{O}_2 \cdot 2\text{H}_2\text{O}$  has been assigned.

Note: Essential material taken from the above thesis has been published in an article by the same title in the *Journal of Physical Chemistry*, Vol. 47, No. 9, December, 1943.

ANTOINETTE JOAN DEMARIE. *The Initrogen Status in Delaware Soil Types.* M.S.

#### *Losses Through Leaching:*

Lysimeter experiments were conducted for a period of six months (October to March inclusive) to study the nitrate nitrogen losses during the dormant months, using three Delaware soil types: Sassafras Loam, Sassafras Loamy Sand, and Pocomoke Loam. The surface six inches, with manure, fertilizer and lime applications, were studied, using cropped (winter wheat and crimson clover) and uncropped soils. The rainfall, 43.7 inches, was applied artificially.

The heaviest nitrate nitrogen losses took place in October. It was found under Delaware climatic conditions that losses through leaching occurred throughout the six months. The winters here are very open, freezing taking place during only about two weeks of the whole dormant season.

The total recovery of nitrate nitrogen in the leachate during the winter months exceeded somewhat the amount of nitrate nitrogen present in the soils at the beginning of the experiments, thus showing that some nitrification took place during the dormant period, from October to March inclusive.



Contrary to general thought, more nitrates were recovered in the leachate from the cropped soils than from the uncropped soils. Leachate was greater in the cropped soils than in the uncropped soils. Probably the shading of the crop prevented some evaporation in the cropped soils, thus increasing the amount of leachate. Evidently a cover crop planted as late in the season as October failed to hold down nitrate nitrogen losses. To receive full benefits from a cover crop in conserving plant nutrients, it is quite evident that the crop should be planted much earlier, probably in August or early September.

#### *Nitrification:*

The nitrifying capacity of the three soil types during a six-month growing period was determined in the laboratory under optimum growing conditions. Soils with treatments of manure, fertilizer, and lime (treatments applied as in lysimeter soils) and without treatments were studied.

In the treated soils nitrification was rapid and the amount of nitrate nitrogen at the end of the six-month period greatly exceeded the amount present at the beginning. The untreated soils showed a much slower rate of nitrification, and far less nitrate nitrogen was formed during the six months. The treated subsoils produced nitrate nitrogen which greatly exceeded the amount nitrified in the untreated subsoils. In all but one case the nitrifying capacity of the treated subsoils was greater than in the untreated surface soils. This indicates the importance of manure, fertilizer, and lime treatments in soils to increase the nitrifying capacity.

These data show that many of the soil types of Delaware are so depleted in organic nitrogen and nitrifiable nitrogen that maximum crop yields cannot be expected.

Not all the nitrate nitrogen nitrified by a soil would reach the crops, since losses by leaching reduce the amount of nitrogen in the available nitrate form.

Probably flora utilization of considerable amounts of nitrate nitrogen was a factor in all these treated soils. This fact may account for the marked fluctuations in the amount of nitrate nitrogen shown during the first three months. This period was followed by a uniform increased nitrate accumulation.

Nitrate nitrogen is constantly being washed from the soils by

heavy rainfalls, as is indicated by the presence of large amounts of nitrate in the water tables of Delaware.

HOWARD A. NEIDIG. *Studies on the Preparation and Oxidation of 1,2,2,2-tetraphenyl-1-ethanol.* M.S.

The reduction of aromatic ketones to aromatic pinacols using magnesium subiodide and a photochemical reaction was studied.

A tentative mechanism was advanced for the formation of an iodomagnesium addition complex of aromatic ketones.

Benzopinacol was converted into beta-benzopinacolone by using glacial acetic acid and iodine. The effect of such reducing agents as aluminum isopropoxide, Grignard reagents and catalytic hydrogenation on beta-benzopinacolone was observed.

1,2,2,2-Tetraphenyl-1-ethanol was oxidized with chromic oxide and glacial acetic acid, yielding beta-benzopinacolone. However, triphenylcarbinol and benzaldehyde were isolated from the reaction mixture. The formation of the latter showed the unusual behavior of a secondary hydroxyl attached to a carbon holding a neo carbon when subjected to oxidative attack.

FRANK G. CARPENTER. *Studies of the Effect of Vapor Velocity on Condensing Heat Transfer Coefficients.* M.Ch.E.

Large industrial condensers employing high vapor velocities are in common use today, and, although it is known that the heat transfer coefficients found in these units are larger than those predicted by the usual Nusselt equation, very little is known about the effect of vapor velocity on condensing film coefficients. Nusselt (*Z. Ver. deut. Ing.* 60, 541, 569 [1916]) treated the effect of a constant vapor velocity on condensate film thickness, but the resulting relationship for heat transfer coefficient still does not explain results obtained in practice. The present study was undertaken to measure the effect of vapor velocity on condensing film coefficients for vapors of water, ethanol, and methanol; and to evaluate the results in terms of various theoretical approaches.

The apparatus consists of a single vertical copper tube, 0.459 in. I. D., 8 ft. long, which is cooled by water flowing in a surrounding narrow annular space. Forty thermocouples in the annular space are used to trace the temperature rise of the cooling water. A traveling thermocouple in the vapor space is used to determine the end



of the condensing zone. The amount of heat flowing from the condensing vapor to the cooling water is measured and from this the overall heat transfer coefficient is calculated. The annular water film heat transfer coefficient was determined experimentally and the results were published under the title of "Heat Transfer and Friction of Water in an Annular Space" by Carpenter, Colburn, Schoenborn, and Wurster in *Trans. Am. Inst. Chem. Engrs.*, 42, 165-187 (1946).

The observed values of heat transfer coefficients are compared with the usual Nusselt equation for the case of negligible vapor velocity and are found to be generally higher (up to 700%) and considerably scattered.

By analogy with flow through tubes, it is shown that turbulence can begin at a Reynolds number as low as 270 when there are high vapor velocities flowing past the condensate film. The relation for heat transfer coefficient which results from this assumption is compared with the experimental results and, although the steam data agree with the theory, the methanol and ethanol data are somewhat higher, the latter being up to three times too high.

CARL GAZLEY, JR. *The Effects of Turbulence on the Size and Stability of Burner Flames.* M.Ch.E.

In spite of the importance of combustion in modern industry, relatively little is known of the fundamentals. In recent years the advent of the gas turbine has intensified the need for research into the basic principles of combustion. Of the many factors affecting the burning process, the controlling ones seem to be the physical processes of mixing and heat transfer. Therefore these processes were studied in the relatively simple case of gas combustion.

The factors affecting the size and stability of laminar burner flames are rather well defined; however, little research has heretofore been done on the size and stability of turbulent flames. In the present investigation the height and limits of stability of open flames were determined in both laminar and turbulent flow for three city gas-air mixtures: 100% gas, 50% gas, and 18.65% gas (stoichiometric mixture). The effects of tube diameter, flow rate, and composition on flame height were rationalized through considerations of molecular and eddy diffusion and of burning velocity. The effect of various types of turbulence promoters on flame height was determined.

The limits of open-flame stability (flash-back and blow-off) were found to be dependent on the gas-velocity gradient at the stream boundary in turbulent as well as in laminar flow. The limits of stability of enclosed (i.e., exclusion of secondary air) flames were also determined. The effect of turbulence promoters on the stability of both open and enclosed flames was found.

ALBERT F. LENHART. *Shadowgraph Investigations of Gas Mixing and Flame.* M.Ch.E.

Rapid and complete mixing of the fuel and air in the combustion chamber of a jet-turbine engine is the decisive factor in securing a flame which is concentrated in a small space and in which combustion is complete. However the complicated flow conditions in combustion chambers make it difficult to improve operations on the basis of direct burner experiments alone, so burner models, in which the mixing of two non-reacting gases can be studied, are very useful. In the present investigation fundamental data on simpler cases of mixing were obtained to be used in understanding the phenomena observed in burner models.

The shadowgraph method was used in this study. Light from a point source, projected through the gas beams to be studied, was refracted when passing through these regions of different density, and thus shadows of these beams were cast on a screen and the mixing could be studied. By substituting photographic film for the screen, the gas streams were photographed. By using an electric spark of a few-millionths of a second in duration for illumination, instantaneous pictures of the streams were obtained. Average pictures of the streams were made by using a  $\frac{1}{100}$  sec. flash of light from a carbon arc lamp for illumination. Many of these photographs and many sketches of the streams are included.

A study was made of the mixing of a free jet with the surrounding air, the size and the velocity of the jet being varied. The effect of increasing the turbulence of a jet independently of the velocity by using turbulence promoters was then determined. Next the mixing of two gas streams with each other was investigated, supplemented by a study of the penetration of a high-velocity gas stream into the glass-walled duct of a lower-velocity stream when the two ducts were opposed.

The shadowgraph method was also applied to the study of flames to bring out the regions of steep temperature gradients not visible in direct photographs.