

ABSTRACTS OF UNIVERSITY OF DELAWARE THESES
FOR ADVANCED DEGREES

1942

TRAFTON O. BUCHANAN. *An Investigation of a Method of Predicting the Success or Failure of Secondary School Pupils.* S.M.

The primary purpose of this investigation was to determine whether it is possible to predict success or failure of students at secondary school level throughout their four years in school. Also, a secondary purpose was to suggest a possible method for determining to what extent a pupil's achievement of the first year might be used as a basis for prediction. By surveying the first year grades of three separate groups, consisting of 100 pupils each, it was observed that the average grades of the entire first year suggested a most stable basis. Using this, tables were compiled for the prediction of the three remaining years in each group. Conclusions were drawn from a final comparison of all three groups, by means of tables and graphs. The method, as suggested, has been applied to a group of students, and proven to be most satisfactory. However, the real validity can be determined only after a period of years.

CURTIS M. DANN. *The Hydrolysis of Aqueous Titanium Tetrachloride Solutions.* S.M.

Most titanium compounds in aqueous solution hydrolyze readily to form the insoluble titanium dioxide, commercially important as a white pigment. Two previous studies of the speed of this hydrolysis reaction have been reported in the literature, neither of which resulted in conclusions as to the rate-determining factors involved. Fairly extensive investigations have been made of the mechanism of the analogous slow hydrolysis of ferric and of stannic chlorides.

In this study, the rates of hydrolysis of moderately concentrated solutions of titanium tetrachloride have been investigated by allowing the reactions to proceed at constant temperature and determining the amounts of reaction by analysis of the mother liquor contained in samples withdrawn at various times. In all cases, the hydrolysis rate at first gradually accelerated during an induction period, then

became constant during the major portion of the precipitation, and finally fell off as the mixture approached equilibrium. The reaction rates were decreased by the addition of extra hydrochloric acid and were strongly accelerated by the addition of colloidal titanium dioxide. Throughout the course of the reaction, the rate appeared to be proportional to the amount of surface present and to the extent of supersaturation of titanium in solution.

The reaction was studied at temperatures ranging from 70 to 100° C. and found to display an increase in rate with temperature corresponding to an activation energy of 26,600 calories per mol. However, the observed reaction rates were much higher than would be predicted from the collision theory, using this value for the activation energy. This discrepancy was accounted for by the assumptions (1) that contributions of vibrational degrees of freedom were received from the solid surface, thereby increasing the probability of reaction of a colliding molecule or (2) that more nuclei were formed at the higher temperatures, in which case only a portion of the observed temperature coefficient would be due to actual energy barriers.

RICHARD H. GALE. *Potentiometric Titration of Dibasic Acids in Dioxane-Water Mixtures.* S.M.

The general theory of potentiometric titration of dibasic acids and aqueous solutions has been developed and established by several investigators. The general treatments of the problem have been given by Auerbach and Smolczyk (*Z. physik. Chem.*, 110, 65 1924) and Soderback (*Arkiv. Kemi. Min. och. Geol.*, 11A, 1 1934). The effect of employing a solvent of lower dielectric value than that of water involves an extension or modification of the general theory of titration. The object of the research presented in this thesis was to extend the general theory to solvent media of low dielectric value and to test experimentally the relations obtained.

On the theoretical side, general relations were obtained which proved to be identical in form with those obtained by Auerbach and Smolczyk for aqueous solutions, provided that constant ionic environment could be attained by the presence of a supporting electrolyte. The resulting first and second dissociation constants were found to differ from the thermodynamic dissociation constants by a constant factor involving the concentration of the supporting electrolyte.

On the experimental side, potentiometric titrations of the dibasic acids: oxalic, malonic, succinic, and glutaric, were performed in

dioxane-water mixtures containing 50 and 65% dioxane, with a quinhydrone-mercurous sulfate electrode chain. Relatively high concentration of lithium sulfate was employed as supporting electrolyte. These data were used in support of the extended theory of acid-base titration presented.

The material of this thesis has been published under the same title in the *Journal of the American Chemical Society*, 64, 1153, (1942).

S. L. HOPPESTEAD. *Buds as Factors in the Transmission of Fruit Diseases.* S.M.

The paper deals mainly with research conducted in Delaware during 1938-1941. The experiments discussed were designed to study the dissemination and overwintering of fruit disease organisms by means of buds. Major emphasis is placed on the study of the dissemination and overwintering of bacterial spot of peach.

Data obtained through experimental work showed the terminal buds and tips to be the chief host parts in which *Phytophthora pruni* (EFS) Bergey et al survived the winter under field conditions. The lateral buds were shown not to harbor the causal organism during the entire dormant period under field conditions, but *Phytophthora pruni* was found to survive the conditions of nursery stock storage sheds. Lateral buds were also considered to be important means by which bacterial spot is introduced into healthy peach plantings when the budding process is carried out.

Methods of eradicating the disease from peach stock were tested. The most practical procedure tested was to grow the infected stock under arid conditions until freedom from the disease is accomplished followed by resetting the stock in a carefully selected area isolated from all hosts of *Phytophthora pruni*.

A grape pathogen, *Melanospora destruens* Shear, was isolated from dormant grape buds. No pathogenic organisms were obtained in cultures made of dormant apple buds.

H. W. LAWRENCE. *Studies in Eugene O'Neill.* A.M.

The first chapter of this thesis is an attempt to discover in Eugene O'Neill's plays evidence of the two most powerful influences of his life—the sea and religion. A brief biographical sketch is introduced in order to justify the statement that these two influences dominated his early life and work. The influence of the sea is most noticeable

in O'Neill's earlier plays and is discussed with particular emphasis on *Bound East For Cardiff*, the first O'Neill play to be presented before an audience. The analysis of *Bound East For Cardiff* is unavoidably mechanical, since it represents an admitted attempt to trace autobiographical data. The discussion of the religious influence in O'Neill's works is confined to a consideration of three plays, *Dynamo*, *The Fountain*, and *Days Without End*. Although two of these plays, *Days Without End* and *The Fountain*, are relatively unknown, they are discussed because, with *Dynamo*, they serve to illustrate the different approaches used by O'Neill in advancing the case of religion. The approaches are shown to be by implication, by poetic indirection or allegory, and by the use of outright Catholic propaganda.

The second chapter analyzes the extent to which O'Neill borrowed from the Greeks in writing his version of the Electra legend. An attempt is made to measure *Mourning Becomes Electra* by the Aristotelean demand that tragedy produce emotional catharsis, and the suggestion made that O'Neill's failure to achieve extreme pity and terror is an inevitable result of his inability to employ a supernatural impetus in a play written for a modern audience. Next the motivations found in the Greek versions and those found in *Mourning Becomes Electra* are compared. The observation is made that O'Neill's characters are moved by more worldly considerations than are their Greek prototypes. Following this, the parallel incidents and situations found in the Greek versions and in O'Neill's version are noted. The concluding paragraphs express the opinion that O'Neill met his self-imposed requirement, that Electra be given an ending worthy of her tragic character.

The concluding chapter suggests that O'Neill's experimentation in unorthodox methods has provided the American stage with a challenge which should result in the production of more significant and original plays. The criticisms generally made of O'Neill's work are recognized and admitted to be justified; but O'Neill's position as our most eminent playwright is defended.

LILLIAN B. MADEN. *An Analysis of Delaware Old Age Assistance*. S.M.

The purpose in writing this paper was to give a complete, composite picture of the organization and operation of one very limited form of public assistance. It is felt that it will be helpful to students of social welfare to have under one cover, the facts pertaining to the

foundations upon which a welfare agency administering categorical relief¹ is built; the actual construction of that agency; and a survey of that agency at work. Most material on this subject is scattered through texts, articles and reports and is, therefore, disjointed and without coherence. This paper has the advantage of having come from inside the agency itself, being based on two years of experience in the Social Service Department of the Old Age Assistance Unit of the Delaware Old Age Welfare Commission.² For this reason, it may not be as objective as many other studies along the same lines, but should demonstrate some of the stresses and strains within agencies that hinder efficient functioning. Such material, recorded by a person outside the agency, is likely to lay the emphasis on outside factors which disrupt the work. The writer feels that both inside and outside factors should be taken into consideration.

However, as a unit in the Social Welfare Program of the State and the Nation, such an agency can, and should, provide the means for dealing with one group of the many which form our democratic (in theory, at least) society. That the Agency is not functioning in a broad social sense will be apparent. Vested interests, such as wealth, politics, prestige, family and the like, all play a part in corrupting agency practices. In this respect, Delaware is no exception.

This paper attempts to illustrate these points in their proper perspective in relation to the whole state and national programs for social welfare and points out the Social factors which have given rise to the need for Old Age Assistance.

THEODORE D. MCKINLEY. *A Multipurpose Integrating Spectrophotometer.* S.M.

The optical properties of a large number of materials are of importance from the viewpoint of both fundamental investigation and commercial application. This is especially true of light-scattering materials, such as pigments, paints, paper, and opal glasses, where reflectance, absorption, total transmission, scattered transmission, and non-scattered transmission are properties of prime importance.

¹ Categorical relief is that form which gives assistance under certain classifications, as, Old Age Assistance, Mother's Pension, Aid to the Blind, and Unemployable Relief. This practice is fast falling into disrepute. The newer and more satisfactory plan is to administer public aid generally. This eliminates overlapping of agencies' functions, jealousies between agencies, differences in personnel standards and agency policies; and makes for more efficient rehabilitation work with the persons receiving help.

² The Old Age Welfare Commission administers Old Age Assistance and the Relief Unit, which are entirely different forms of categorical relief.

This study had as its object the design, construction, and calibration of a simple, precise, and inexpensive integrating spectrophotometer for making such optical measurements on relatively non-selective light-scattering materials. The construction of this instrument was prompted by the fact that no single integrating instrument with such a diversity of uses was commercially available.

A high pressure mercury arc light source together with a series of filters and a plane diffraction grating provides monochromatic illumination at seven wave-lengths in the visible and near-ultraviolet spectra. The optical system of the instrument is designed for parallel illumination of the sample at normal incidence and a twelve-inch integrating sphere is provided to collect the reflected or transmitted light.

The light measuring system consists of a cesium phototube of the vacuum type mounted in a housing on the integrating sphere and in series with a variable set of resistors and a battery which operates the cell at slightly greater than saturation voltage. An electrometer measures the voltage drop across the resistors and, by means of a calibration chart, this voltage drop can be directly converted to percent reflectance or transmission. The sensitivity may be varied over a four-hundred-fold range. At highest sensitivity, the instrument will detect a flow of 10^{-13} ampere in the phototube circuit which corresponds approximately to 5×10^{-12} times the output of a ten-watt Mazda lamp.

Reflectance measurements made by this instrument on a number of opal glasses were in close agreement with independent measurements made by two General Electric recording spectrophotometers. Measurements of the reflectance, absorption, total transmission, and non-scattered transmission of various materials were made to illustrate the utility of the instrument as a scientific tool.

JACQUELIN H. SMITH. *Education in Delaware Since 1917*. S.M.

The purpose of this thesis is to trace the development of education in Delaware from 1917 to the present time. The background states the conditions existing before 1917. The factors which brought about changes in the school system include associations and organizations and surveys which were made. The most important survey was made by the General Education Board of New York City and gave suggestions and recommendations for improvement. The problems taken up are the change in the conception of the meaning of educa-

tion, teacher education and certification, reorganization of the curriculum, and the improvement in school buildings, all contributing to an improved educational system in Delaware.

ARCHIBALD P. STUART.* *Barbiturates Containing Large Radicals.*
S.M.

Since the discovery, in 1904, of the hypnotic action of veronal, the derivatives of barbituric acid have been studied rather thoroughly by many investigators. Of the hundreds of derivatives prepared and tested, about thirty find commercial application in modern medicine.

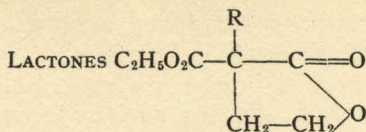
In spite of the rather large amount of information concerning the barbiturates, it is difficult to relate their chemical structure to their physiological action in an absolute fashion. From a general consideration of the field, however, it was felt advisable to synthesize derivatives containing, in the five position, large alkyl radicals which it was hoped would assist in anchoring the compound to the fatty tissues of the brain. On the other hand, since the body fluids are aqueous in character, some water solubility is required. This was to be accomplished by the introduction, also in the five position, of the beta-bromoethyl group [Skinner, *J. Am. Chem. Soc.*, 59, 322 (1937)], with the expectation that the resulting compound would be used by a later investigator to introduce water-solubilizing groups.

Lauryl bromide was prepared from the alcohol, and the lauryl group introduced into malonic ester in the customary manner. By reacting ethylene bromide with the sodium derivative of lauryl malonic ester, there was formed lauryl beta-bromoethyl malonic ester which, on distillation, evolved ethyl bromide to yield α -lauryl- α -carbethoxy- γ -butyrolactone. This lactone, on condensation with urea in the presence of sodium ethoxide, yielded 5-lauryl-5-(2-hydroxyethyl)-barbituric acid. On treatment with fuming hydrobromic acid, the hydroxy derivative yielded 5-lauryl-5-(2-bromoethyl)-barbituric acid.

In a similar fashion 5-n-hexadecyl- and 5-n-octadecyl-5-(2-bromoethyl)-barbituric acids were prepared. A table follows:

* Research done under the direction of Dr. Glenn S. Skinner, Department of Chemistry, University of Delaware. Published in *J. Amer. Chem. Soc.*, 63, 2993 (1941).

TABLE I



R—	B. p.,		M. p., °C.	Yield, %	Found, %		Calculated,	
	°C.	Mm.			C	H	C %	H %
<i>n</i> -C ₁₂ H ₂₅ - ^a	192–194		43.5	81	70.5	10.6	70.1	10.5
<i>n</i> -C ₁₆ H ₃₃ -	225–230	0.3	49	84	72.3	11.1	72.3	11.1
<i>n</i> -C ₁₈ H ₃₇ -	233–238	0.4	55–56	73	72.4	11.3	73.1	11.3

^a *d*₄²⁵ 0.9680 (supercooled liquid); *d*₄⁵⁰ 0.9505; *d*₄⁷⁵ 0.9325.

TABLE II

5-ALKYL-5-β-HYDROXYETHYL BARBITURATES

Alkyl	M. p., °C.	Yield, %	Found N, %	Calcd. N, %
<i>n</i> -C ₁₂ H ₂₅ -	145	82	8.29	8.23
<i>n</i> -C ₁₆ H ₃₃ -	147	83	7.06	7.07
<i>n</i> -C ₁₈ H ₃₇ -	150	81	6.62	6.60

TABLE III

5-ALKYL-5-(β-BROMOETHYL) BARBITURATES

Alkyl	M. p., °C.	Yield, %	Bromine, %	
			Calcd.	Found
<i>n</i> -C ₁₂ H ₂₅ -	101.5		19.72	19.66
<i>n</i> -C ₁₆ H ₃₃ -	102.5	65	17.01	17.08
<i>n</i> -C ₁₈ H ₃₇ -	104.5	70	16.40	16.33