

taining possibly some water vapor, is orange red. To now introduce the illuminating gas open the valve *O* for a moment, then close it. The end *C* of the discharge tube is instantly filled with a beautiful greenish-white color characteristic of illuminating gas. This color will diffuse slowly towards *A*, each color paling out, and after three or four minutes the discharge throughout the tube will assume a uniform grayish hue. The rate of diffusion is surprisingly slow and of course depends upon a number of factors, *e. g.*, the gas pressure in the tube, the pressure of the gas that is admitted, the ionization within the tube due to the discharge passing through the tube, the amount of moisture present, etc.

If now the gas connection at *N* be removed and this stem opened to the air the pump and connections may be freed of gas and the inverse experiment performed; namely, that of introducing a small quantity of air. The resulting orange red color and its diffusion through the grayish hue of the illuminating gas is even more striking than the first.

The success of the experiment depends largely upon the skill of the operator in properly proportioning the quantity of gas to be introduced. It is a very simple experiment to perform.

CHAS. T. KNIPP

LABORATORY OF PHYSICS,
UNIVERSITY OF ILLINOIS,
June 2, 1915

THE NEW ORLEANS MEETING OF THE AMERICAN CHEMICAL SOCIETY. III

DIVISION OF PHYSICAL AND INORGANIC CHEMISTRY

G. A. Hulett, *chairman*
R. C. Wells, *secretary*

E. R. WEAVER: *A Colorimetric Determination of Acetylene.*

A new colorimetric method for the determination of very small amounts of acetylene in gas mixtures depends upon the formation of a red colloidal solution of cuprous chloride containing gelatine and alcohol. Comparison is made with a solution of a red dye or a piece of ruby glass. In the gravimetric determination of acetylene it has been found necessary to exclude air during the filtration and washing of the precipitate.

GEORGE W. MOREY: *The Ternary System $K_2O-SiO_2-H_2O$ from 300°-700°.* (Lantern.)

E. C. FRANKLIN: *Rubidium Ammonosodate and Ammonopotassiate.*

R. S. McBRIDE: *Experiments on the Distillation of Liquid Air in a Magnetic Field.*

Preliminary experiments on distillation of liquid air in a strong magnetic field indicate that there is an improvement in the separation of oxygen and nitrogen due to the influence of the magnetic field.

E. P. SCHOCH and DENTON J. BROWN: *A Systematic, Rapid, Electroanalytical Procedure for the Separation and Determination of Silver, Arsenic, Copper, Bismuth, Antimony, Tin, Lead and Cadmium.*

In our earlier work, published elsewhere, we have shown that copper, tin, lead, bismuth and antimony can be determined accurately by electro-deposition out of acidified chloride electrolytes which contain suitable reducing agents such as hydroxylamine or formalin. We have found since that copper, bismuth and antimony can be deposited simultaneously, and can be separated from tin and lead; that tin and lead can be deposited simultaneously and separated from cadmium; that copper or bismuth can be separated from antimony by dissolving alloys of these metals in nitric acid plus tartaric acid and electrolyzing the solutions with a limited cathode potential; that bismuth phosphate can be precipitated quantitatively out of the same solution; that tin may be separated completely from lead by dissolving an alloy of these two metals in nitric acid plus potassium nitrate; and that silver in silver chloride may be determined by dissolving the latter in ammonia, adding ammonium nitrate and electrolyzing.

These facts are all combined in the following systematic procedure for the rapid electroanalytical determination of all the common metals the potentials of which are more noble than that of cadmium.

(A) Dissolve sample in hydrochloric acid or in aqua regia; an insoluble residue—silver chloride—is dissolved in ammonia plus ammonium nitrate, and the silver determined electrolytically.

(B) Treat solution *A* with hydroxylamine—mercury, gold and platinum will be precipitated and can be determined by well-known methods.

(C) Out of filtrate *B*, remove arsenic by distillation with hydrochloric acid, and determine arsenic iodometrically.

(D) Electrolyze *retort residue C*—copper, antimony and bismuth will be deposited with a cathode potential limited to 0.45 volts (against the normal calomel electrode).

(E) Dissolve *metal deposit D* in nitric acid plus tartaric acid, and precipitate bismuth as bismuth phosphate.

(F) Electrolyze *filtrate E* with a limited cathode potential—copper alone will be deposited. Antimony is obtained *by difference*.

(G) Electrolyze *residue D* with a cathode potential limited to 0.7 volt against the normal calomel electrode: tin and lead will be deposited. Treat the deposit with nitric acid plus potassium nitrate: the solution contains all the lead, and this metal may be deposited as lead peroxide, or the residue of tin oxide may be dissolved in hydrochloric acid plus hydroxylamine and the tin determined by electrolysis.

(H) Electrolyze *residue G* to obtain cadmium or other metals.

P. SCHOCH and W. A. FELSING: *The Influence of the Potassium Ion upon the Potential of the Ferrocyanide-ferricyanide Electrode*.

The potential of the ferrocyanide-ferricyanide electrode is made more noble by the addition of potassium salts to the electrolyte, but the amount of this change in potential is much greater than the amount calculated from the change in the ratio of ferrocyanide to ferricyanide ions when the concentrations of the latter are calculated from the conductivity ratio and with the aid of the rule of mixtures as set forth by Sherrill. It was suggested by Lewis that this extra effect may be due to the potassium ion taking part in the pole reaction. Thus, with the undissociated salts, the reaction would be: $K_3Fe(CN)_6$ plus K-ion plus one electron gives $K_4Fe(CN)_6$ —and it has been shown recently by Mueller that with concentrations of potassium ion ranging from 0.2 normal to 0.8 normal the amount of change in potential corresponds to the amount of change in the potassium ion if the concentration relations of the other substances remains constant. Since the latter is not likely to be true, and since the potassium ion shows the same influence even in the most dilute solutions tried, the authors sought to ascertain whether or no the concentration influence of the potassium ion is constant with a particular power of its concentration. This was found to be the case with the .75 power of the potassium ion concentration, and if the ferrocyanide and the ferricyanide ion

concentrations are calculated from the conductivity ratio and the rule of mixtures. The various mixtures tried present a range of total potassium ion concentration from 7.8 millimol to 395 millimol per liter. In some mixtures the potassium ion was derived wholly from the iron cyanides, in others, almost wholly from potassium chloride, and in others still, partly from both sources. The different potentials thus reduced to unit concentrations present a maximum range of 8 millivolts with this large variation of concentrations, and hence the result may be considered to be constant. Furthermore, it is likely that on repetition measurements will be obtained which will show considerably less variation.

Since the calculations of the above potentials involve the general dilution law of strong electrolytes and the rule of mixtures, it was desirable to test these calculations in some way, hence the conductivities of these mixtures were measured and compared with their calculated values. When allowance is made for the influence of the viscosities of the solutions, then the observed and the calculated conductivities agree to one per cent. and less.

The work is now being repeated with calcium salts in place of potassium salts. Although the immediate result of this work is the establishing of an empiric relation between concentrations and pole potentials, yet it is likely that the results will throw some light on the manner of ionization of salts with polyvalent ions—particularly because other electrodes such as the thallous-thallic, the ferrous-ferric and the mercurous-mercuric, show similar relations.

R. G. VAN NAME and D. U. HILL: *The Rates of Solution of Metals in Ferric Salts and in Chromic Acid*.

The observed rates of solution were lowered by increasing the concentration of free sulphuric acid. In ferric sulphate with 0.5-molar acid the rates differed and were higher the more electropositive the metal. With 10-molar acid the four most electropositive metals tested all gave the same rate. The lowering of the rate with increasing acidity is due to increase in the viscosity, which retards the diffusion. In general all results are in agreement with the diffusion theory of heterogeneous reactions, but the marked dependence upon the nature of the metal, observed at the lower acidity, contradicts Nernst's hypothesis that, where no secondary effects interfere, the rate of the chemical reaction proper (as distinguished from the diffusion process) must always be extremely high.

PAUL M. GIESY and JAMES R. WITHROW: *The Electrolytic Preparation of Solid Alkali Amalgams in Quantity.*

Kerp, by his method, obtained 200 gr. of solid potassium amalgam in 4 to 5 hrs. This method has been modified so as to yield 490 gr. in $\frac{1}{2}$ hr. As previously found, Shepherd's method did not give pure amalgams. Smith and Bennett, by their method, using 3 amp. current, obtained about 180 gr. solid sodium amalgam. By using 20 amp. current, and cooling the cell by an ice-water bath, 680 gr. were obtained in $2\frac{1}{4}$ hrs. It is not necessary to cool the cell in the case of potassium amalgam. After electrolyzing 50 min. with 1,000 gr. mercury and 20 amp. current, 1,015 gr. of solid potassium amalgam were obtained by chilling.

O. L. BARNEBEY: *Permanganate Determination of Iron in the Presence of Fluorides. The Analysis of Silicates and Carbonates for their Ferrous Iron Content.*

In a systematic study of the effect of various reagents toward increasing the accuracy of titrating ferrous iron in the presence of fluorides, boric acid was found to give the best results. Boric acid when added to the ferrous solution preceding titration converts the hydrofluoric acid to metafluoboric acid, HBF_4 , which does not interfere with the permanganate reaction. This use of boric acid is applied in the analysis of silicate and carbonate rocks for their ferrous iron content.

O. L. BARNEBEY: *The Permanganate and Iodimetric Titration of Iodide in the Presence of Bromide and Chloride.*

The Pean de St. Gilles permanganate method of titrating iodide to iodate has been modified by adding manganous sulfate with the ferrous sulfate in removing the excess of permanganate. This prevents the liberation of bromine or chlorine at this stage of the analysis as well as later when titrating the excess of ferrous sulfate with the permanganate. After the completion of the permanganate titration the iodate formed may be determined by adding phosphoric acid and potassium iodide and titrating the liberated iodine with thio-sulfate.

HAL WALTERS MOSELEY: *The Phenomenon of Passivity in Connection with Ferrous Alloys of Different Composition and Structure.*

The author has shown that samples of iron and steel of very different composition and structure

can be made passive with a definite current density when the samples were made the anode in an electrolytic cell. The nature and concentration of the electrolyte are also factors influencing the establishment of the passive state. The current density required is not related in any simple way to the composition or structure of the samples.

The results confirm the view that the phenomenon is perfectly general for all classes of irons and steels, and show that passivating agents as inhibitors of corrosion have a very wide applicability.

WILLIAM C. MOORE: *The Thermo-electric Properties of Carbon.*

Preliminary experiments with various combinations of arc carbons as thermo couples showed that each particular combination had individual thermo-electric characteristics.

More elaborate measurements were then made with various carbon copper couples. The burning of such couples at high temperatures was so serious that the simple carbon copper couple was modified by enclosing the arc carbon rod within a copper tube, the combination serving as a couple, the tube being partially exhausted by a water pump.

With several of the carbon-carbon couples and some of the carbon-copper couples, a point or a region of maximum electromotive force was found. With one carbon-copper couple this region exceeded from 741°C. to 816°C. ; with another carbon-copper couple, this region exceeded from 514°C. to 565°C. These carbons were of different composition and had different manufacturing histories. The temperature coefficient of the electromotive force of these couples was very irregular before reaching the region of maximum electromotive force; after passing through this region this coefficient became more regular, and the slope of the $de/dT - T$ curve changed. The carbon was negative at the cold end, but in one case became positive at a high temperature. The carbon used in a different carbon copper couple was positive throughout the experiment, an E.M.F. of 2.18 millivolts being reached when the furnace temperature was 878°C. In this case the electromotive force did not pass through a maximum.

The electromotive force of the one carbon-carbon couple reached a value of 14.59 millivolts at a furnace temperature of 707° and a cold junction temperature of 55.5° .

In general, this is higher than that reached by

carbon copper couples. The variations shown by any one couple in general are reproducible. The results show that the thermo-electric properties of carbon depend on the initial composition and the manufacturing history of the carbon.

It is possible that the change in direction of the temperature coefficient-temperature curve indicates that some of the carbon material undergoes a transition into some other material. The results here reported seem to show that ordinary carbon is a mixture of several substances—in all probability several varieties of carbon with various hydrocarbon bodies of high molecular weight, since Moissan² has shown that all forms of amorphous carbon contain hydrogen.

D. A. MACINNES and KARR PARKER: *Potassium Chloride Concentration Cells.*

J. P. MONTGOMERY: *The Precipitation of Lead Chloride in Qualitative Analysis.*

STEWART J. LLOYD: *Radium Content of Water from the Gulf of Mexico.*

Previous Results.—One liter of sea water contains in grams of radium:

Jolly	17.6×10^{-12}
Eve	0.3×10^{-12}
Eve	0.9×10^{-12}
Satterly	1.0×10^{-12}

Seven and one fourth liters of Gulf water evaporated down and measured gave 1.7×10^{-12} . The amount of radium in the ocean is hence probably about 1,400 tons, which implies a content of uranium of 4,200,000,000 tons.

W. A. TAYLOR: *Studies in the Measurement of the Electrical Conductivity of Solutions.*

WILLIAM J. VAN SICKLEN: *Electrolytic Rectification of Alternating Currents.*

A number of cells were devised varying within wide limits several factors affecting the energy efficiency of rectification. The electrodes used were for the most part iron-aluminium, carbon-aluminium, nickel-aluminium. The affect of the following factors on the energy efficiency of rectification were determined: relative area of and distance between electrodes, E.M.F. of the input circuit, resistance in the output circuit, nature and conductivity and temperature of the electrolyte.

² "Electric Furnace," p. 48, 1904 ed.—Lenher's translations.

The alternating current used throughout the determinations was of 60 cycle frequency.

WILLIAM D. HARKINS and ERNEST D. WILSON: *The Changes of Mass and Weight Involved in the Formation of Complex Atoms.*

WILLIAM D. HARKINS and ERNEST D. WILSON: *The Structure of Complex Atoms.*

WILLIAM D. HARKINS and ERNEST D. WILSON: *Nuclear and Valence Electrons.*

WILLIAM D. HARKINS and ERNEST D. WILSON: *A Periodic Table which Plots the Atomic Weights of the Ordinary and the Isotopic Elements.*

ERNEST D. WILSON and WILLIAM D. HARKINS: *A Connection between Planck's Quantum Hypothesis, the Magnetron, and the Balmer Series Formula.*

LLOYD C. DANIELS: *Cuprous Salts of Oxygen Acids and a New Method for Preparing Cuprous Salts.*

References are given to the salts of this class that have been described. They are the sulfite, sulfate, ammoniated sulfate, carbon monoxide compound of the sulfate, acid thiosulfate and acetate.

The brown insoluble product of the action of oxalic acid on cuprous sulfite is shown by its clear colorless solution in hydrochloric acid, by its clear solution in ammonia, and by its formation of calcium nitrate and nitric acid, to be a new salt of this class. Analysis shows its composition to be $\text{Cu}_6\text{H}_2(\text{C}_2\text{O}_4)_4$. The same method is to be applied to the preparation of other cuprous compounds.

M. A. ROSANOFF: *A Relational Process of Fractional Distillation.*

WATER, SEWAGE AND SANITATION SECTION

Earle B. Phelps, *chairman*
H. P. Corson, *secretary*

The following list of officers of the Division of Water, Sewage and Sanitation, were elected for 1915:

Chairman: Edward Bartow.
Vice-chairman: Earle B. Phelps.
Secretary: H. P. Corson.

Executive Committee: Edward Bartow, Earle B. Phelps, H. P. Corson, C. P. Hoover, E. H. S. Bailey.

F. W. BRUCKMILLER: *The Use of Benzdene for Sulfates in Water Analysis.*

EDWARD BARTOW and A. N. BENNETT: *The Determination of Arsenic in Filter Alum.*

European specifications require that filter alum be free from arsenic. This suggested an investigation of filter alum used in the United States. Samples collected from plants in Illinois showed not more than 4 parts per million of As_2O_3 . Since the Illinois plants are supplied from western manufacturing, samples were obtained from plants throughout the east. Larger amounts of arsenic were found in some of the specimens obtained. Only traces of arsenic were found in water treated with alum, containing the highest amount of arsenic found. While this would indicate a strong possibility that the presence of arsenic in filter alum is not significant, the authors would recommend that preference be given to alums with a low arsenic content.

C. P. HOOVER: *The Manufacture of Alum at the Columbus Water Softening and Purification Works.*

The process most generally employed to-day for coagulating and purifying water contemplates applying to the water under treatment a solution of aluminum sulfate. The cost of this chemical varies from \$17 to \$20 per ton.

A plant for making alum has recently been built and put in service at the Columbus Water Purification Plant. This is the first plant of its kind ever built at a water purification works for making alum to coagulate water, and, although it has only been in operation a short time, it has been a success both technically and economically. The process is short, simple and inexpensive, because it consists simply in boiling bauxite with sulfuric acid and applying the resultant solution to the water under treatment, thus eliminating five distinct steps in alum-making, namely: filtering, concentrating, crystallizing, grinding and redissolving. An investment of \$12,000 was required for its construction, and it has been conservatively estimated that \$6,000 per year will be saved the city in the cost of alum. Between 800 and 1,000 tons of alum will be manufactured during the coming year at a cost of about \$10.50 per ton.

ARTHUR LEDERER: *Determination of the Biochemical Oxygen Demand by the Saltpeter Method in Stockyards, Tanneries and Corn Products Waste.*

The saltpeter method was originally described by Lederer in the *Journal of Infectious Diseases*, 14:

482 (1914). In short, the method depends upon the denitrification of a sodium nitrate solution when incubated for a definite period (10 days at 20° C., or 5 days at 37° C.) with sewage or polluted water. The residual nitrite-nitrate oxygen is determined analytically. The method permits a comparison of the strength of sewages from the deoxygenation standpoint. The oxygen demand of domestic sewages usually varies between 100 and 300 p. p. m. of oxygen. The method can be applied to slaughteringhouse wastes without modification. The oxygen consumption of the Chicago stockyards waste in the Center Av. sewer fluctuates around 1,000 p.p.m., 20 per cent. of which is consumed during the first twenty-four hours. The oxygen demand of combined corn products waste fluctuated between 400 and 1,200 p.p.m., approximately 7 per cent. of which was used up in the first twenty-four hours. In this and in tannery waste the presence of lime or acid should be guarded against. If free lime is present it must be neutralized with dilute hydrochloric acid previous to incubation with sodium nitrate. If acid is present neutralize with sodium bicarbonate. The oxygen demand of a calfskin tannery waste investigated fluctuated between 400 and 1,000 p.p.m., 7 per cent. of which was used up in the first twenty-four hours. If a waste is sterile or devoid of sewage bacteria "seed" it with a few c.c. of sewage or polluted water. The general principles brought out in the work with the wastes mentioned can be applied to other wastes.

EARLE B. PHELPS: *Ventilation Studies.*

EDWARD BARTOW and F. W. MOHLMAN: *Purification of Sewage by Aeration in the Presence of Activated Sludge.*

Domestic sewage from the city of Champaign has been treated according to the method suggested by Ardern and Lockett.³ When raw sewage is aerated without the addition of sludge ammonium nitrogen is replaced by nitrite nitrogen, the nitrite nitrogen in turn being replaced by nitrate nitrogen. In the presence of sludge, the nitrite nitrogen is never present in large quantities. Ammonium nitrogen is apparently changed directly to nitrate nitrogen. The time of nitrification is reduced from fifteen days to four hours. The predominant organism in the sludge is an annelid worm, known as *Aeolosoma hemprichi*, although other microscopic animals are present. The sludge

³ *Jour. Soc. Chem. Ind.*, 33: 523-39; 1,122-24.

does not have an unpleasant odor, although it will putrefy if kept for a long time in a moist condition without air. The dried material contains 6 per cent. of nitrogen; 1.44 per cent. of phosphorus. These figures would indicate its value as a fertilizer, which fact has been confirmed by pot cultures. Portions of the dried sludge showed excellent growths of wheat at the end of 18 days. The experiments are being continued on a larger scale.

RAY C. WERNER: *Sanitary and Mineral Properties of the Water Supplies of Georgia.*

A sanitary water laboratory was established by the Georgia State Board of Health in May, 1910, and a sanitary survey of public water supplies undertaken. The work has been limited, due to lack of funds, but about thirty water works plants have been inspected and analyses have been made from most public supplies of the state. The interest of superintendents and other officials of water works is growing and some water works laboratories are being installed in the state. Mismanagement and lack of understanding of technical features of purification leads to poor filtering results in some cities.

Supplies of the state are in general: Filtered stream waters in northern half and deep wells in southern section. The stream waters are usually turbid and more or less colored, but are not grossly contaminated. These waters are soft. The deep well waters are excellent in appearance and sanitary quality, and are fairly high in mineral contents, but few if any are treated for softening before use.

W. L. STEVENSON and others: *Analytical Methods for Sewage Works Operation.*

JOHN L. PORTER: *The New Orleans Water Purification Works.*

H. P. LETTON: *Rat Proofing of Wharves as an Anti-plague Measure.*

H. E. HALE and T. W. MELIA: *A Comparison of Methods for Determining Putrescibility or Oxygen Demand.*

E. J. TULLY: *A Sanitary Survey of Lake Michigan together with a Study of Stream Pollution along the Wisconsin Shore.*

It is established as a result of this investigation that the water of Lake Michigan along the Wisconsin shore is not a uniformly safe source of supply. The water is polluted and at times quite heavily so,

not only in the immediate vicinity of sewer outfalls, but throughout the entire littoral area studied, even to a distance of seven miles from shore, and municipal supplies are frequently more or less polluted.

It is therefore recommended that all public water supplies be purified and it is advised that sewage be subjected to adequate treatment before disposed by dilution.

DIVISION OF ORGANIC CHEMISTRY

F. B. Allan, *chairman*

C. G. Derick, *vice-chairman and secretary*

The division of organic chemistry held its meetings in Parlor "E" of the Grunewald Hotel, Friday, April 2, 1915, with Vice-chairman C. G. Derick presiding. Of the thirty-two papers listed, fifteen were given by the authors, eleven by abstracts and the remaining six by title only. Each paper was very freely discussed although the average attendance at morning and afternoon meetings was only fifteen.

EDWARD KREMERS: *The Classification and Nomenclature of Organic Compounds.*

VICTOR P. LEE: *Dimethylsulfate as a Methylating Agent.*

Many methyl ethers have been prepared with the object of determining their value, if they possess any, either as perfume substances, or as diluents or softeners when mixed with other synthetic perfume substances. The use of dimethylsulfate for this purpose is not new but has not been used much until quite recently. As dimethylsulfate is now a comparatively cheap reagent, and as its use as an alkylating reagent is very simple, it is replacing methyl iodide to a great extent. A table of the compounds prepared is given and the method used is outlined.

FRANCIS D. DODGE: *Some Derivatives of Coumarin.*

The author has prepared addition compounds of coumarin with the acid sulphites of sodium and potassium. These are well crystallized salts, and are to be regarded as sulphonates of hydro-coumarin. On heating, they decompose smoothly into coumarin, alkaline sulphite and sulphurous anhydride. They combine quantitatively with one molecule of alkaline hydroxide, yielding sulphonates of ortho-hydro-coumaric acid.

The latter are very soluble salts, showing little tendency to crystallize, and by the action of strong alkaline hydroxides, at 100°, are converted into

salts of ortho-coumaric acid. These reactions afford a very convenient method for converting coumarin into coumaric acid.

By the action of acetic anhydride at the ordinary temperature, the sulphonate of hydro-coumaric acid reverts to the hydro-coumarin sulphonate, so that by this series of smooth reactions it is possible to pass at will from coumarin to coumaric acid, or *vice versa*.

An analogous compound of Limettin (dimethoxy-coumarin) with sodium bi-sulphite is described.

The author also calls attention to the characteristic behavior of the coumarins on hydrolysis, which may be of diagnostic value for compounds of unknown constitution.

L. F. AUGSPURGER: *The Isolation of a Blue Hydrocarbon from Milfoil Oil.*

The blue color of certain volatile oils has long attracted attention, but thus far appears to have escaped rational chemical investigation. Thanks to the distillation of more than a liter of volatile oil of *Achillea millefolium* by Professor E. R. Miller last summer, the writer had several hundred cubic centimeters of the high boiling intensely blue fraction placed at his disposal. Thanks also to the observation made by Mr. A. E. Sherndal in the laboratory of Dodge and Olcott, that an artificial blue oil combines with phosphoric acid to form a labile addition product from which the blue hydrocarbon oil can be recovered by the addition of water, it became possible for the first time to isolate the blue substance of a natural oil in a pure state.

Analysis of the compound thus isolated revealed the composition $C_{16}H_{18}$. It will be seen at once that whereas this hydrocarbon has the same number of carbon atoms as have the sesquiterpenes, $C_{15}H_{24}$, its hydrocarbon content is much lower, hence it is less saturated. The most interesting observation of the investigation thus far is that the blue color is lost upon additions to the molecule. Apparently it makes no difference whether hydrogen is added (reduction with palladium hydrogen), phosphoric acid, or possibly other substances still to be tested.

NELLIE WAKEMAN: *A Possible New Terpene from Monarda Punctata.*

Although Schumann in 1896 reported the presence of cymene, and Hendricks in 1899 that of limonene as results of the preliminary investigation of this oil, the subsequent study of larger amounts seemed to add to the complexity of the

chemical study of the oldest of the *Monarda* oils.

A large amount of the non-phenol constituents of horsemint oil having been placed at the disposal of the writer, a more careful study was made of the hydrocarbon fractions than before. All endeavors to make the hydrocarbon which yields a nitroso chloride correspond with one of the known terpenes have failed. The melting point of its nitrol piperidine differs by 103 and 87 degrees respectively from that of limonene and dipentene and by 78 degrees from that of pinene. The benzylamine base shows no such striking differences. With aniline, however, it does not react as does limonene but resembles pinene.

As soon as new material that is now being prepared for further nitroso chloride experiments is ready, a third attempt to identify this hydrocarbon with known terpenes will be made. For a summary of the chemical studies of the *Monarda* see Bulletin 448 of the University of Wisconsin.

C. H. HERTY and D. H. KILLEFFER: *The So-called Alpha and Beta Isomeric Resin Acids.*

OLIVER KAMM and C. G. DERICK: *The Structure of Certain Hydronaphthoic Acids.*

The evidence previously advanced for the structure of the isomeric dihydro- β -naphthoic acids was based upon the reactions of their dibromides. A study of the oxidation products from these unsaturated acids has verified the conclusions previously advanced.

C. G. DERICK and OLIVER KAMM: *The Correlation of Ionization and Structure in Unsaturated Acids.*

Conclusions are drawn chiefly from acids having the unsaturation in a ring structure, thus eliminating the possibilities of cis-trans isomerism. The effect of conjugation of double unions is shown and the method of determining the constitution of acids of unknown structure is indicated. The possibility of obtaining a quantitative expression for conjugation of Thiele's partial valences is expressed.

OLIVER KAMM: *Some Tests for Qualitative Organic Analysis.*

Several tests used in the courses in qualitative organic analysis at the University of Illinois are mentioned.

1. The identification of the volatile fatty acids by means of a method based upon that advanced by Duclaux for quantitative work.

2. A test for aromatic amines based upon the fact that the oxalates of most primary aromatic amines are only sparingly soluble in water while those of secondary and tertiary amines are soluble. Many of these oxalates may be titrated quantitatively, thus assisting in the identification of the amines.

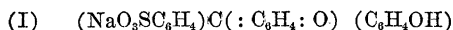
3. A rapid test for the nitro group by reduction with sodium amalgam is discussed.

W. F. MONCREIF, JR., and J. T. MCGILL: *Qualitative Organic Analysis*.

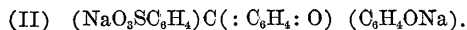
An account is given of the development of systematic qualitative organic analysis; the methods used by some of the workers in this subject are compared; and the status of the subject in the curricula of a number of American colleges and universities is discussed. Emphasis is laid upon its advantages as a supplement to the usual organic preparation work.

E. C. WHITE and S. F. ACREE: *Recent Progress in the Study of the Quinone Phenolate Theory of Indicators*.

By the use of phenosulphonaphthalein it has been possible to show that a solution of the monobasic salt of the structure



is not deeply colored as compared with that of the dibasic salt



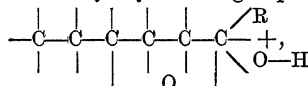
The monobasic salt has precisely the same color as the free acid, as is shown by titrating the acid with alkali (experiment performed at the meeting) as well as by a study of the adsorption spectra of solutions of the acid, the monobasic salt, and the dibasic salt (spectrophotographs shown at the meeting). The acid and the monobasic sulphate are orange colored in solution, whereas the dibasic salt is purple. The former two substances already have a quinone group, but as the intense color does not appear until the dibasic salt is formed, it is clearly demonstrated that not the quinone alone, but the combination of quinone and phenolate groupings is the cause of the intense color.

The effects of substituent groups on the acidity of the phenol and sulphonic acids, and the relations of these effects to color in the acids themselves and their salts are being studied. The results secured up to this time with the tetrabrom

and tetranitro derivatives indicate that the significant color changes are associated with the formation of the complex *quinone phenolate anion* $\text{RC}(:\text{C}_6\text{H}_4:\text{O}) (\text{C}_6\text{H}_4\text{O})$.

S. F. ACREE: *A Theory of the Unsaturation of Sugars and their Derivatives by Acids and Alkalies*.

In the mutarotation of sugars and their derivatives, the catalytic activity of the hydroxyl ion depends upon the formation of an anion of the characteristic lactonyl hydroxide group



analogous to $\text{R}-\text{C}-\text{O}-\text{H}^+$ which all sugars possess

if they show mutarotation by alkalies. When this lactonyl hydroxyl is used up in glucoside formation such anions can not form and no mutarotation by alkalies occurs.

The catalytic activity of the hydrogen ion is believed to be due to the formation of an oxonium salt of the lactonyl hydroxide group or its alkyl, corresponding anilide, etc., derivatives. That a di- or tri-basic, etc., oxonium salt is not the *active* salt in mutarotation by acids is shown by the fact that the increased velocity of the reaction is proportional to the first power of the concentration of the hydrogen ion instead of the second, third, etc., powers.

This theory has been extended to the Walden inversion, the rearrangement of such substance as δ and l menthone and many cases which logically follow as details of this theory.

S. F. ACREE: *On the Reactions of both the Ions and Molecules of Acids, Bases and Salts. A Reinterpretation of the Reactions of Sodium Methylate and Sodium Ethylate with 1, 2-Dinitrobenzene, 1, 2, 4-Dinitrochlorbenzene and 1, 2, 4-Dinitrobrombenzene*.

The data of Hedlit, Conrad and Brueckner, and of Bruyn, Steger and Lulofs on the reactions of sodium methylate and sodium ethylate with aliphatic and aromatic alkyl halides and nitro derivatives can be reinterpreted on the basis of the writer's theory that both the ions and the molecules of acids, bases and salts are chemically active. When the reaction velocities obtained by these workers and our conductivity data are applied to our equation $K_N = K_i\alpha + K_m(1 - \alpha)$ we se-

cure excellent constants for K_i and K_m , the activity of the ethylate or methylate ion, and the non-ionized sodium ethylate or methylate respectively.

G. D. BEAL and H. F. LEWIS: *Studies on Alkaloidal Salts. I. Strychnine Salts.*

Preliminary notice of the work being done at the University of Illinois, under the auspices of the Pharmaceutical Research Fund.

Methods of alkaloidal assay by the use of immiscible solvents are being studied. Salts of strychnine with tartaric, hydrochloric and sulphuric acid have been made and their solubilities investigated. Solvents used were ether, chloroform, water-saturated chloroform, alcohol and water. The distribution coefficient was determined using the formula $C'/C'' = d$, C' being the concentration of the salt in the chloroform layer, C'' the concentration of the salt in the aqueous layer. This was done with both neutral and acid solutions of the salt with chloroform.

C. S. HUDSON and J. K. DALE: *A Comparison of the Optical Rotatory Powers of the Alpha and Beta Forms of Certain Acetylated Derivatives of Glucose.*

After careful purification, the alpha and beta forms of glucose pentacetate (molecular weight 390) were found to have the specific rotations $+102^\circ$ and $+4^\circ$, respectively, in chloroform. The corresponding alpha and beta forms of tetracetyl methylglucoside (m. w. 362) showed $(\alpha)_D^{20} = +131^\circ$ and -18° . The sum of the molecular rotations of the alpha and beta forms is thus 41,300 for the glucose pentacetates and 40,900 for the tetracetyl methyl glucosides. The agreement conforms to theoretical considerations. The paper appears in full in the *Journal of the American Chemical Society*.

C. S. HUDSON and J. M. JOHNSON: *The Isomeric Alpha and Beta Octacetates of Maltose and of Cellose.*

By heating the beta octacetate of maltose, of m.p. $159-60^\circ$, with acetic anhydride and zinc chloride, it was transformed to the new isomeric crystalline alpha maltose octacetate of m. p. 125° . The specific rotations in chloroform are $+122^\circ$ for the alpha form and $+63^\circ$ for the beta. After careful purification, the known alpha and beta octacetates of cellose show $(\alpha)_D^{20} = +41^\circ$ and -15° , respectively, in chloroform. The difference of the rotations of the alpha and beta forms is

thus 59° for maltose octacetate, 56° for cellose octacetate, and 57° has been found previously for the forms of lactose octacetate. From the rotation of the glucose pentacetates, the value 56° may be calculated. The four pairs of substances are thus in excellent agreement with theory. The paper will be published in full in the *Journal of the American Chemical Society*.

C. S. HUDSON and J. K. DALE: *The Isomeric Pentacetates of Mannose.*

The expected form of mannose pentacetate has been prepared in a crystalline state by the method described in the preceding abstract. The new isomer melts at 64° and shows dextro-rotation $(\alpha)_D^{20} = +55^\circ$, in chloroform. Fischer found the beta pentacetate to melt at 117.5° and to show $(\alpha)_D^{20} = -25^\circ$, in chloroform, which we have confirmed. The difference between the rotations of the two isomers is thus 80° in comparison with the value 98° found for the two forms of glucose pentacetate. Full paper will be published in the *Journal of the American Chemical Society*.

C. S. HUDSON and H. O. PARKER: *The Isomeric Pentacetates of Galactose.*

By the same method (see preceding) galactose pentacetate has been transformed to a crystalline isomer of m. p. 96° and specific rotation $+106^\circ$ in chloroform. The new substance is evidently the alpha galactose pentacetate, since the earlier discovered form rotates $+23^\circ$, and is thus the beta pentacetate. The difference between the rotations of the two isomers is 83° , which differs somewhat from the value in the case of the glucose pentacetate (98°), and agrees with the value found for the mannose pentacetates.

C. S. HUDSON and D. H. BRAUNS: *Crystalline D-Fructose Pentacetate.*

By acetylating very pure fructose with acetic anhydride and sulphuric acid below 0° , a beautifully crystalline pentacetate of fructose has been prepared. It melts at $109-09^\circ$ and shows levorotation $(\alpha)_D^{20} = -121^\circ$ in chloroform. Paper in full will be published in the *Journal of the American Chemical Society*.

C. S. HUDSON: *The Existence of a Third Pentacetate of Galactose.*

It is found that the acetylation of galactose with acetic anhydride and sodium acetate yields in addition to the well-known first pentacetate of the

sugar a fair amount (10 per cent.) of another crystalline substance melting at 98° and showing levorotation $(\alpha)_D^{20} = -41.6^\circ$ in chloroform. Analysis shows it to be a new pentacetate of galactose. There are accordingly three isomeric forms of the pentacetate. Full paper to appear soon in the *Journal of the American Chemical Society*.

FRIEND E. CLARK and SAMUEL F. COX: *Some Derivatives of Chlor-methyl Ether*.

NORMAN A. DUBOIS: *Hop-seed Oil*.

CARL O. JOHNS: *Researches on Purines: On a New Synthesis of Purines. On 2-Oxy-8-Thiopurine, 2-Oxy-8-Methyl Mercaptopurines, 2-Oxy-8-Methyl Aminopurine and 2-Oxy-6-, 9-Dimethyl-8-Thiopurine*.

Mercaptopurines when treated with methylamine yield methyl-aminopurines and methyl mercaptan. The change of 2-oxy-8-methyl mercaptopurine into 2-oxy-8-methylaminopurine is offered in substantiation of this statement and the preparation of these products is described.

CARL O. JOHNS: *Researches on Thioamino Acids. On Thiohippuric Acid and Phthalyl-aminothioacetic Acid*.

Thiohippuric acid (m. p. 104°) was prepared from hippuryl chloride and potassium hydrogen sulfide. Upon hydrolysis with warm water hydrogen sulfide and hippuric acid resulted. With iodine in alkaline solution it gives dithiohippuric acid—a reaction characteristic of the thio acids. The anilide of hippuric acid is described.

Similarly, phthalyl- α -aminothioacetic acid was prepared from phthalylglycyl chloride and potassium hydrogen sulfide. It crystallizes from benzene in plates which melt at 112°. The anilide of phthalyl- α -aminoacetic acid is described.

B. G. FEINBERG: *Citral, and its Determination*.

C. G. DERICK: *The Preparation of Trimethylene Oxide*.

Since the commercial product "Blizzard" offers a cheap source for trimethylene glycol, trimethylene bromide was prepared in large quantities very cheaply from the action of 48 per cent. HBr with subsequent saturation with gaseous HBr; yields better than 90 per cent. being obtained. Trimethylene bromide heated to its boiling point with PbO gave monomolecular trimethylene oxide boiling at 52.3° under 745 mm. pressure. From the

reaction flask a polymeric form of the oxide was isolated which boils at 183° under 55 mm. pressure.

Silver oxide acts with almost explosive violence upon the bromide if 100 grams of the latter is employed and only traces of the oxide are obtained.

Mercuric oxide appears to act best of all, giving mainly the monomolecular form.

C. G. DERICK and E. H. VOLLWEILER: *The Use of Trimethylene Oxide in the Grignard Reaction. The Synthesis of Normal Primary Hexyl Alcohol*.

The polymeric form of trimethylene oxide was treated with magnesium propyl bromide in ether solution. The reaction is fairly rapid, generating heat. Upon distillation with steam the *n*-primary hexyl alcohol distills and is extracted with ether from the aqueous layer saturated with potassium carbonate.

C. G. DERICK and R. W. HESS: *The Synthesis of γ -Acetylvalerianic Acid*.

Trimethylene bromide dissolved in absolute methyl alcohol is treated with one molecule of potassium cyanide. The γ -bromobutyronitrile formed is purified by fractional distillation under diminished pressure. Yield of pure product 25 per cent. It then condensed with acetoacetic ester and the resulting γ -cyanopropylacetoacetic ethyl ester is purified by distillation under 1 mm. pressure. Upon hydrolysis with 20 per cent. HCl it gives the desired acid.

C. G. DERICK and ST. ELMO BRADY: *The Ionization Constants of Certain Ketoparaffine Monobasic Acids*.

After careful preparation and purification the following acids have been measured by the conductivity with the following results: pyroracemic acid, $k_a^{22^\circ} = 3.643 \times 10^{-3}$ (below 0.005N); levulinic acid, $k_a^{22^\circ} = 2.436 \times 10^{-3}$ and γ -acetylvalerianic acid, $k_a^{22^\circ} = 2.295 \times 10^{-5}$.

The criterion "calculated Δ_0 " shows these results to be accurate to one tenth of one per cent.

M. A. ROSANOFF and M. M. HARRISON: *On the Decomposition of Tertiary Amyl Esters*.

G. B. FRANKFORTER and LILLIAN COHEN: *Equilibrium in the Systems of Methyl Alcohol, Ketones, Water and Inorganic Salts, Part I*.

G. B. FRANKFORTER and STERLING TEMPLE: *Equilibrium in the Systems of Propyl Alcohols, Water and Salts*.

DIVISION OF PHARMACEUTICAL CHEMISTRY

F. R. Eldred, *chairman*A. P. Sy, *secretary*WILBUR L. SCOVILLE: *The Stability of Nitroglycerin Tablets.*

Of 22 different lots of nitroglycerin tablets kept under observation $2\frac{1}{2}$ to $3\frac{1}{2}$ years, those made with a nitroglycerin paste (20 per cent. nitroglycerin absorbed in 80 per cent. sugar of milk) maintained their strength except the $\frac{1}{150}$ gr. and $\frac{1}{200}$ gr. tablets. All tablets made with an alcoholic solution of nitroglycerin deteriorated.

Deterioration may be due to one or both of two conditions; *i. e.*, a finer attenuation of the nitroglycerin when tablets are made from an alcoholic solution, or a more desirable isomeric form of the nitroglycerin as obtained in the paste form. Further experiments will be made to determine which factor may be the more important.

JAMES H. BEAL: *Some Reasons for the Variation Clause of the Food and Drugs Act.*

The United States Pharmacopœia appropriates titles devised and used in the arts and industries and attaches to them special meanings and standards which, though sufficient for pharmaceutical purposes, are not applicable to the arts and industries in which the greater proportion of chemical products are consumed. Only by virtue of the variation clause can these products be lawfully dealt in under their own names when they comply with other than pharmacopœial standards.

The variation clause is necessary to permit improvement of medicinal products in accordance with progress in pharmaceutical knowledge. Improvements are made in these products constantly. Without the existence of the variation clause such products could not be offered under their appropriate titles until after the improvements had been recognized by a revised pharmacopœia, which might be ten years distant.

The continuance of the variation clause as a part of the food and drug law is essential to reasonable freedom in industrial and pharmaceutical chemistry, and the demand for its unconditional repeal should be resisted.

FRANCIS D. DODGE and ALFRED E. SHERNDAL: *The Composition of Oil of Cassia.*

The authors have observed that oil of cassia contains a small amount of substances soluble in alkaline hydroxide solutions, and among these have identified salicylic aldehyde, coumarin, cinnamic acid, salicylic acid, benzoic acid, and an acid, not yet identified, apparently an unsaturated one, possibly of the acrylic series.

Though small in amount, salicylic aldehyde and coumarin undoubtedly participate in the composite aroma of the oil, and it is remarkable that their presence has not been previously observed.

H. A. LANGENHAN: *The Chemistry of the Daturas.*
II. The Alkaloidal Content of Datura Leaves.

The study of the *Daturas* having been assigned by the Bureau of Plant Industry to its northern station at Madison as a special subject for investigation, the garden at Madison has in recent years raised, under the direction of G. A. Russell, the government expert, as many as fifteen to twenty species and varieties of *Daturas*. Much of the material thus produced has been assayed by the writer, and the results of the assays have recently been published as a Bulletin (No. 192) of the University of Wisconsin.

The collected results of all assays published by different experimenters seemed to show that little or nothing could be expected by working along old lines. Hence the cooperation of Professor Leon J. Cole, professor of experimental breeding in the College of Agriculture, and his assistant, Mr. C. M. Woodworth has been secured for a series of breeding experiments. As a result of last summer's work Messrs. Cole and Woodworth have germinated the collected seeds and are studying the results in the greenhouse. As in previous years, the writer has determined the alkaloidal content of the leaves of the plant studied by the breeders. The results thus obtained in greenhouse and laboratory will determine the selection of the seeds to be planted in the experimental garden this coming spring.

N. R. MUELLER: *A Possible Explanation of the Reduction Phenomena Observed in Elixir of Phosphates of Iron, Quinine and Strychnine when Exposed to Light.*

By process of elimination the study of at least one of the basal problems has resolved itself to an investigation of the action of ferric iron in the form of hydroxide on citric acid under the influence of sunlight. Under these conditions the ferric iron is reduced to ferrous iron, at least in part, and goes into solution; a very small amount of the iron appears to be reduced to metallic iron, which is deposited in a very fine state of division. While the iron is reduced, the citric acid is oxidized in part with the formation of carbon dioxide. The colorless solution of iron salt or salts which thus results under the absolute exclusion of atmospheric oxygen becomes colored at once when exposed to the atmosphere, the solution turning greenish.

CHARLES L. PARSONS, *Secretary*