

ABSTRACTS.

GENERAL AND INORGANIC CHEMISTRY.

Eukairite from Argentina. ROBERT OTTO.

Berzelius and later A. E. Nordenskjöld analyzed a rare mineral, consisting of an equal number of atoms of silver, copper and selenium. This mineral was found in minute quantities in the copper mine Skrikerum in Smöland, Sweden. Emil Hünicken has found in Villa Argentina, Prov. Rioja, Argentine Republic, in Arnango in the Andes of Famatina and in other places, a peculiar mineral, which was sent for exact analysis to the author. The mineral occurs in veins, some of which have a width of 1 c.m. but at a depth of 14 m. are 35 c.m. broad. The mineral, according to analysis, is the same as Berzelius' Enkairite, and consists of :

Ag = 42, 7 per cent.

Cu = 25, 5 “

Se = 31, 5 “

(*Ber. d. Chem. Ges.*, **23**, 1939.)

L. H. F.

On Spontaneously Inflammable Hydrogen phosphide. L. GATTERMANN and W. HAUSKNECHT.

For the extensive and interesting details of this remarkable research we refer to the original paper. This liquid phosphine was obtained pure from calcium phosphide prepared in an original manner. An analytical determination of phosphorus was not feasible. But the hydrogen was determined by means of combustion with lead chromate. Figures were found agreeing with the formula PH_2 . Also the decomposition by sunlight furnishes figures corresponding to that formula. The attempt to determine the vapor density in V. Meyer's apparatus, below the boiling point of the substance, using methyl iodide as a mantle, was not successful. Quite a number of determinations pointed towards the formula P_2H_4 (66) since values such as: 74, 73 and 77 were obtained.

The boiling point was determined successfully. It does *not* lie at temperatures between 30° and 40° C., as the handbooks state,

but was found to be 57° to 58° C., at 735 m. m. The following figures were found in determining the specific gravity :

(I.) Spec. Grav., 1.016.

(II.) Spec. Grav., 1.007.

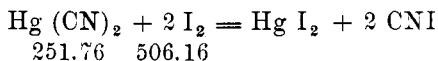
It follows that this hydrogen phosphide is slightly heavier than water, and this fact was confirmed by direct experiment which showed a large drop of the liquid to sink in water. (*Ber. d. Chem. Ges.*, **23**, 1174, 1890.)

L. H. F.

Vapor Density and Melting Point of Cyanogen Iodide.

KARL SEUBERT and WILLIAM POLLARD.

The two above named determinations have heretofore not been performed. The substance is very volatile and strongly poisonous. The cyanogen iodide was prepared in the manner used by Davy and described by Serullas; action of iodine upon mercuric cyanide. The equation :



calls for one part of mercuric cyanide and two parts of iodine, while Serullas recommends exactly the reverse, *i. e.*, 2 pts. Hg (CN)₂ to 1 pt. of iodine. The great excess of the former should prevent volatilization of free iodine. The authors used mixtures according to the above equation or in the proportion of equal parts of the two substances. But they were careful to allow the reaction to take place very slowly and spontaneously, in direct sunlight, during 2 to 3 days, using peculiar apparatus. The product obtained, which cannot easily be analyzed gravimetrically, allowed titration in the simple manner, given by E. v. Meyer. According to the latter, cyanogen iodide and hydriodic acid, *in excess*, decompose as follows :



The liberated iodine is titrated in the ordinary manner. Instead of using a solution of HI, E. v. Meyer proposes to apply a solution of KI acidulated with H₂SO₄. The vapor density obtained by Victor Meyer's method led to the formula CNI, analogous to CNCl and CNBr. The melting point was determined in the ordinary way, in a capillary tube, but this latter had to be sealed

at both ends, the substance volatilizing below its melting point. The bath used was H_2SO_4 . The results obtained were :

	Melting Point.	Congealing Point.
a.....	146,5°	143°
b.....	146,5°	142,5°
c.....	146,5°	142,5°

(*Ber. d. Chem. Ges.*, **23**, 1062.)

L. H. F.

A New Apparatus for Determination of Melting Point.

A. C. CHRISTOMANOS.

This interesting apparatus allows the substance, the melting point of which is to be determined, to float on mercury, which can be heated, while a little mercury rests on top of the substance. An electric bell is connected with the two quantities of mercury, separated from one another by the substance to be tested. When the latter melts, the mercury flows together, the bell rings and the thermometer is read. (*Ber. d. Chem. Ges.*, **23**, 1093.) L. H. F.

ORGANIC CHEMISTRY.

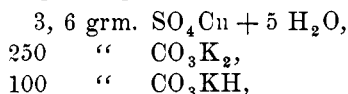
Determination of Different Sugars by Cupro-potassium Carbonate Solution. H. Osr.

This research is based upon the proposition which was made in 1876 by A. Soldaini, to use a solution of copper carbonate in potassium bicarbonate instead of Fehling's solution. This solution has, so far, not been adopted because it is difficult to obtain of constant composition and because its action upon invert sugar is too slow. The author proposes two solutions, which have been useful to him. One consists of :

23, 5 grms.	cryst. copper sulphate,
250	“ potassium carbonate,
100	“ potassium bicarbonate,

per litre. First the potassium salts are dissolved, then the copper solution is gradually added. The action of this solution depends not only upon the presence of copper, but also upon that of potassium carbonates and upon the strength of the sugar solution. It

is available for volumetric as well as gravimetric analysis, and is applicable for titrations of mixtures of sucrose with but little glucose. Fehling's reagent gives very unreliable results for such mixtures. Besides this, the end of the reaction, which is manifested by a yellow coloration when using Fehling's solution, is indicated for the above liquid by a colorless, transparent appearance of the mixture. For sucrose very poor in glucose, as for instance in beet sugar, the above solution is too concentrated, and a solution of the following strength is used :



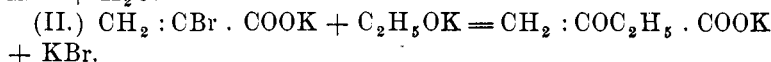
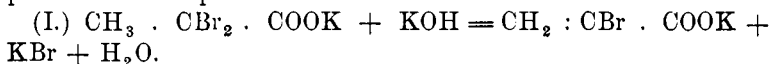
per litre. This solution should only be used gravimetrically. (*Ber. d. Chem. Ges.*, **23**, 1035.)

L. H. F.

Ethoxyacrylic Acid from α -Dichloropropionic Acid.

ROBERT OTTO.

According to W. Merz alcoholic potassium, when acting upon α -dibromopropionic acid forms ethoxyacrylic acid. The reaction performs in two phases :



The author, together with G. Holst has now prepared this same acid from α -dichloropropionic acid. It forms white crystals, melting at 110°C . (*Ber. d. Chem. Ges.*, **23**, 1108, 1890.)

L. H. F.

Friedel-Craft's Synthesis of Ketones from Phenolethers.

L. GATTERMANN, R. EHRHARDT and H. MAISCH.

The results obtained are summed up by the authors as follows :

Phenolethers react very smoothly with acid chlorides, forming ketones of extraordinary capacity of crystallization. Almost all of them may be obtained in measurable crystals. Mineralogists are thus offered splendid material to study the relations between form of crystals and constitution. The law which Leuckart noticed for phenyl cyanate and which Gattermann observed for urea chloride

with hydrocarbons and phenoethers, is illustrated, namely, that, in the case of an unoccupied para position, this is filled out by the acid residue entering. Sometimes, besides the normal ketone, an unsaturated alkylene compound is formed. This latter is generated from one molecule of a normal ketone and one molecule of unattacked phenoether by the joint loss of water. (*Ber. d. Chem. Ges.*, **23**, 1199, 1890). L. H. F.

Action of Ammonia on Di- and Tri- Halogenated Substitution Products of Hydrocarbons. P. GALEWSKY.

It has been shown of late by Udransky and Baumann that diamines may be precipitated almost quantitatively from very dilute, aqueous solutions by treating these with benzoyl chloride and dilute NaOH. The precipitates represent the corresponding benzoyl compounds. The present research was commenced with the intention to learn by means of this benzoylchloride reaction, whether alkylene bromides, treated with alcoholic ammonia in the cold, would yield diamines even in small quantity. Ethylene bromide allowed the formation of the diamine at ordinary temperature, propylene bromide required higher temperature. Tribromallyl yielded neither a di- nor a tri- amine, but as a result of this reaction a brominated monamine was formed :



The amine was proved to be identical with the bromallylamine recently prepared by Paal and Hermann; it may have either of the following constitutional formulæ :

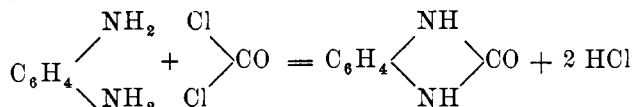
- (a) $CH_2. NH_2. CH: CHBr$
- (b) $CH_2. NH_2. C Br: CH_2$

It should be remarked, that the bromine atom is very closely linked in this compound and does not admit of the formation of a diamine when heated with alcoholic ammonia to 200° C. The yield of bromallylamine according to the above method is not at all a quantitative one. (*Ber. d. Chem. Ges.*, **23**, 1066.) L. H. F.

Action of Phosgen upon o-Diamines. A. HARTMANN.

Heretofore this action has only been mentioned by Michler and Zimmermann in regard to m-phenyldiamine. It has now been

studied further and it is found that a ring-formed, closed chain of ureas is obtained under the influence of phosgen, which occurs in general according to the following equation for phenylendiamine :

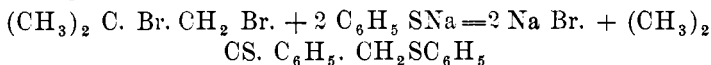


(*Ber. d. Chem. Ges.*, **23**, 1046.)

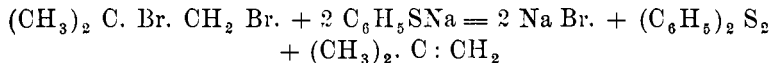
L. H. F.

Behavior of Sodiumphenyl mercaptide with Isobutylene-bromide. ROBERT OTTO.

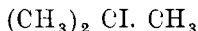
This reaction did not take place in a normal manner, according to the equation :



but, apparently quantitatively, in the following manner :



yielding sodium bromide, phenylene disulphide and *isobutylene*. This latter, under the influence of hydriodic acid, was easily transformed into the iodide of tertiary butylic alcohol :



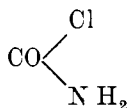
boiling at 98° to 99° C.

(*Ber. d. Chem. Ges.*, **23**, 1051.)

L. H. F.

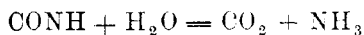
A Modification of the Urea chloride Synthesis. L. GATTERMANN and A. ROSSOLYMO.

About two years ago a method was described by Gattermann, Schmidt, Hess and Harris, according to which



reacting with aromatic hydrocarbons and phenoethers in the presence of aluminium chloride effects a synthesis of carbo acids. Urea chloride is formed from phosgene and ammonium chloride.

Large quantities of liquefied phosgene gas are necessary for this reaction. In order to simplify the method, it was attempted to avoid the use of phosgene. Since urea chloride at the higher temperatures at which these syntheses were performed dissociates into cyanic acid and hydrochloric acid, the use of a mixture of these two was indicated. Cyanic acid may be prepared from cyanuric acid, which furnishes three molecules of the former, when heated carefully. It should be remarked, that although it was found that the mixture of cyanic acid and hydrochloric acid allowed a synthesis in the above mentioned sense for *small* quantities of carboacids, the old method, using urea chloride has to be resorted to when larger quantities are desired. Cyanuric acid was prepared by the action of bromine upon potassium ferricyanide. It has to be applied in a perfectly anhydrous state, because *cyanic* acid, when brought in contact with water decomposes, according to the equation.



The following table shows the hydrocarbons or phenoethers used in this manner and the melting points of the acid amides obtained :

Hydrocarbons or Phenoethers.	Melting Point of the Acid Amide.
Benzol	127° C
Toluol	156 "
o-Xylol	165 "
m-Xylol	180 "
p-Xylol	186 "
Pseudocumol	200 "
Durol	173 "
Naphthalene	202 "
Acenaphthene	198 "
Anisol	163 "
Phenetol	202 "
α -Naphthylmethylether	234 "
α -Naphthylethylether	244 "
β -Naphthylmethylether	186 "
β -Naphthylethylether	161 "

(*Ber. d. Chem. Ges.*, **23**, 1190, 1890.)

L. H. F.

Aldehydes of the Hydrocinnamic Acid Series. W. VON MILLER and G. ROHDE.

According to the preceding communication, the data found in the literature of hydrocinnamic aldehydes are to be stricken out. The authors have now prepared some genuine representatives of this series, which offer, besides the other well known characteristics of *aldehydes*, the following special ones :

1. They possess a very characteristic and agreeable odor, suggestive of lilac or jessamine ;

2. With concentrated or slightly diluted sulphuric acid they furnish liquids which, in transmitted light, are more or less intensely rose or carmine colored.

These aldehydes were prepared by means of destructive distillation of the calcium salts of the corresponding acids with calcium formate. (*Ber. d. Chem. Ges.*, **23**, 1079.) L. H. F.

On Sulphocyanogen and Selenocyanogen Compounds. L. HAGELBERG.

Buff and Sonnenschein discovered ethylene rhodanide almost simultaneously in the year 1855. In 1874, Lermontoff prepared the methylene rhodanide. No other dirhodanides of the formula $C_n H_{2n} (SCN)_2$ are known in the fatty series. The author has now prepared :

Trimethylene rhodanide= $NCS. CH_2. CH_2. CH_2. SCN$

Propylene rhodanide= $CH_3. CH. SCN. CH_2. SCN$

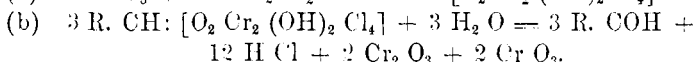
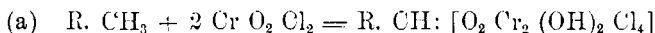
Propylene selenocyanide= $CH_3. CH. Se. CN. CH_2 Se CN$

and derivatives of these compounds. (*Ber. d. Chem. Ges.*, **23**, 1083.) L. H. F.

Contributions to a Knowledge of Etard's Reaction. W. VON MILLER and G. ROHDE.

The authors intended to perform the synthesis of indene derivatives starting from cinnamic aldehydes. This synthesis would have implied the assumption of a formation of hydrocinnamic aldehydes. According to Etard, hydrocinnamic aldehyde can be prepared from propylbenzol by the action of chromyl chloride. He maintained that, as with the other homologues of benzol, the re-

action was accomplished according to the following two equations:



The authors, in treating propylbenzol in this way did *not* obtain hydrocinnamic aldehyde but its isomere, benzylmethylketone together with benzaldehyde. When the mixture of these two latter was treated with oxidizing reagents, stilbene resulted. Hydrocinnamic aldehyde alone, or mixed with benzaldehyde, when subjected to a condensation experiment does *not* furnish stilbene.

Thus Etard's reaction, which formerly was considered as one leading to aldehydes, had in this case generated a ketone. A series of critical experiments, performed with cymol and ethylbenzol in the same manner, showed that also in these cases ketones are formed, contrary to Etard's data; phenylethylaldehyde is formed only in case of ethylbenzol. (*Ber. d. Chem. Ges.*, **22**, 1070.)

L. H. F.

Researches on Diazo Compounds. LUDWIG GATTERMANN.

Experiments which were performed with the intention of forming diphenyl from diazobenzol chloride by the action of metals, such as zinc dust, iron or copper powder, showed that copper at 0° C. reacts very strongly, but that no diphenyl but only chlorbenzol was formed. Following up this observation it may be stated, that in this manner also the amido group of aniline and of its homologues was replaced by bromine, cyanogen, the nitro and the sulphocyanogen groups. A fortunate accident finally showed that when diazobenzol sulphate was acted upon by powdered copper in the presence of alcohol, diphenyl was formed and *not* phenolether as anticipated. The cheaper zinc and iron *in the presence of alcohol*, react in the same manner to form diphenyl. (*Ber. d. Chem. Ges.*, **23**, 1218, 1890.)

L. H. F.

On Ethanedichinolyline. A. M. COMEY.

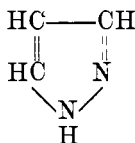
In order to give a wider application to Skraup's reaction, the author made paradiamidodibenzyl, nitrophenol, sulphuric acid

and glycerol react together. The base obtained crystallizes in colorless, hexagonal plates of melting point 124° C. The analysis led to the formula $C_{20}H_{16}N_2$. Since the two amido groups of diamidodibenzyl are in para position, the new base must be parathanedichinolyline, isomeric with Bulach's ethanedichinoline, melting at 106.5° . (*Ber. d. Chem. Ges.*, **23**, 1115, 1890.)

L. H. F.

Synthesis of Pyrazol. L. BALBIANO.

This body resulted from the reaction between hydrazinhydrate and epichlorhydrine. The analysis confirmed the formula C_3H_4N . Pyrazol crystallizes in hard, colorless needles. It dissolves in water to form a neutral solution. The odor is faintly suggestive of pyridine. Melting point: $69.5-70$ C. Boiling point: $186-188^{\circ}$ C., at 757.9 m. m. The properties of pyrazol correspond with those of a body prepared by Buchner from acetylenedicarbo-diazoacetic acid. This latter substance when heated to $230-240^{\circ}$ C. decomposes into CO_2 and $C_3H_4N_2$, the latter probably having the constitution :

(*Ber. d. Chem. Ges.*, **23**, 1103, 1890.)

L. H. F.

A New Lutidine. E. DÜRKOPF and H. GÖRTSCH.

This base was obtained from dimethylpyridine carbo acid by splitting off CO_2 . It is dried over KOH and boils then at $169-170^{\circ}$ C. The analyses corresponded to a lutidine C_7H_9N . It is a clear, strongly refractive liquid of a mild, pleasant odor, characteristic of the β -compounds. It is more easily soluble in cold than in warm water. Spec. Grav. referred to water of $+4^{\circ}$ C, is 0.9614, at 0° C. A two per cent. solution, oxidized in the cold furnished dinicotinic acid. This lutidine is therefore $\beta\beta'$ -dimethylpyridine. (*Ber. d. Chem. Ges.*, **23**, 1113, 1890.)

L. H. F.

On the Formation of the Quinolin Ring ; a Contribution to the Benzol Theory. W. MARCKWALD.

v. Baeyer's researches (*Ann. Chem., Liebig*, **245**, 103; **251**, 257) show that the only three formulæ to be considered in regard to the constitution of benzol are, his own centric formula, Kekulé's and Dewar's.* It was to be expected that the study of quinoline derivatives formed from aromatic diamines by one of the known synthetical methods, would lead to a decision in favor of one of these formulæ. All of the syntheses which the author has performed lead to phenanthrene ring formations, which speaks in favor of Kekulé's formula. (*Ber. d. Chem. Ges.*, **23**, 1015.)

L. H. F.

On Indian Geranium Oil. F. W. SEMMLER.

Fractional distillation at 17 m. m. pressure furnished 92 p. ct. of an oil boiling at 120.5 to 122.5 C. The analysis gave correct figures for a compound $C_{10}H_{18}O$, which proved to be geraniol. It does not congeal at $-20^{\circ}C$. The odor, which is still more agreeable in the refined than in crude oil, suggests the perfume of the pear or the rose. It is colorless and of Spec. Gr. 0.8900 as $15^{\circ}C$. The alcoholic nature of geraniol has been shown by Jacobsen. The optical methods, as well as the behavior toward iodine and bromine, indicate two ethylene linkings, and consequently this compound $C_{10}H_{18}O$ cannot have a ring-formed constitution. It belongs to the fatty series, $C_nH_{2n-2}O$. Potassium permanganate oxidizes it to isovaleric acid. Under the influence of P_2O_5 terpenes and polyterpenes are formed. (*Ber. d. Chem. Ges.*, **23**, 1098, 1890.)

L. H. F.

The Curves of Boiling Temperatures a Function of the Chemical Nature of Compounds. M. WILDERMAN.

A simple rule for the determination of the boiling points of organic compounds at reduced pressure. Considering the great number of boiling point determinations at different pressures,

* In regard to this assertion see *Ber. d. Chem. Ges.*, **23**, 1276. It is expressly mentioned there, that Dewar's formula need not be considered.

L. H. F.

recorded by Regnault, Schumann, Anschütz and others, the author endeavored to find out whether the relation between pressure and boiling point of a substance has any connection with its chemical nature. About twenty homologous series were arranged and the following result was shown: Within tolerably wide limits of pressure, as between 1500 m. m. and 50 m. m., or, 760 m. m. and 12 m. m. the proportion of the absolute boiling point at M m. m. pressure to that of N m. m. is very nearly constant for all members of the homologous series. The tables given show that the *calculated* boiling points of a compound for an arbitrary pressure of N m. m. differ from the observed boiling point merely by a fraction of *one* degree. This is a difference which lies within the limits of error with which a boiling point can really be determined.

For members of the homologous series the following formula is an approximate expression :

$$\frac{T a p}{T a P} = \frac{T b p}{T b P} = \frac{T c p}{T c P} = D_1 \text{ (I)}$$

in which a , b , c signify different members of the homologous series, p and P lower and higher pressures.

From this main formula five others of importance are derived. It follows from all of them, that the change of boiling point of a compound at a different pressure is really a function of its chemical nature. Bodies containing atoms of the same kind, and having the same constitution, which, consequently, are chemically equal, give the same numerical value. Different homologous series show considerable deviation. This is of great practical importance, particularly for compounds which decompose at ordinary pressure when the attempt to boil them is made. The formula given require merely the knowledge of *one* boiling point. (*Ber. d. Chem. Ges.*, **23**, 1254, 1890.)

L. H. F.