COMMUNICATIONS TO THE EDITOR

THE ACTION OF ARSINES WITH HALOARSINES

Sir:

In a recent publication by F. F. Blicke and L. D. Powers [THIS JOURNAL, **54**, 3353 (1932)] on the interaction of phenylarsines with phenylhaloarsines, these workers have found that the data of Steinkopf and Smie [*Ber.*, **59**, 1459 (1926)] are not correct, but overlooks that I myself have rectified this mistake more than two years ago, when investigating in cooperation with H. Dudek [*Ber.*, **62**, 2494 (1929)] the action of diphenylarsine with phenyldichloroarsine and phenylarsine with diphenylchloroarsine. I obtained the same data as recently published by F. F. Blicke and L. D. Powers.

Furthermore, I stated that owing to these new facts I could not uphold any more the existence of all other compounds published with Smie in *Ber.*, **59**, 1459 (1926).

DRESDEN, GERMANY WILHELM STEINKOPF

RECEIVED FEBRUARY 1, 1933 PUBLISHED MAY 6, 1933

THE ACTION OF ARSINES WITH HALOARSINES

Sir:

We wish to express our deep regret at our failure to read thoroughly the article of Steinkopf and Dudek, "Zur Kenntnis organischer Arsenverbindungen. XV. Ueber die Existenz der Arseno-azo-bindung und ueber das Phospho-arseno-benzol," *Ber.*, **62**, 2494 (1929). It should, however, be pointed out that while the alleged discovery of six new types of arsenicals was clearly stated in the title of the original article [Steinkopf and Smie, "Zur Kenntnis organischer Arsenverbindungen. IX. Darstellung neuer Typen organischer Arsenverbindungen," *Ber.*, **59**, 1453 (1926)], the correction of this work appeared in an article whose title—"Ueber die Existenz der Arseno-azo-bindung und ueber das Phospho-arseno-benzol"—gave no hint of this important matter.

In this connection it might also be mentioned that no reference to this correction occurs in *Chemical Abstracts* for 1930, although the material dealing with arseno-azo- and phospho-arseno compounds was abstracted.

The information in our articles [THIS JOURNAL, **54**, 3353 (1932); **55**, 316 (1933)] does not duplicate that presented by Steinkopf in his retraction. We have investigated in detail each of the six reactions by means of which Steinkopf and Smie thought they had obtained six new types of arsenicals and have recorded experimental procedures by means of which the mixtures of previously known arsenicals—which are actually formed in place of Steinkopf's new types—can be separated. Steinkopf reinvestigated only two of the six reactions and merely waives his claim to the discovery of the new compounds which he originally thought had been formed in the four other reactions.

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F. F. BLICKE
L. D. POWERS

RECEIVED APRIL 3, 1933 PUBLISHED MAY 6, 1933

THE CALCIUM CHLORIDE MODIFICATIONS OF MANNOSE AND GULOSE

Sir:

The writer previously reported [*J. Bur. Standards*, **8**, 615 (1932)] that α- and β-*d*-mannose, on oxidation with bromine in the presence of barium carbonate yield δ-lactones, which indicates that these sugars have 1,5 ring structures. Application by the writer of the same method to the labile calcium chloride compound of mannose reported by Dale [THIS JOURNAL, **51**, 2225 (1929)] shows that this substance gives largely mannonic γ-lactone. This is evidence that *d*-mannose·$CaCl_2 \cdot 4H_2O$ has a 1,4 ring structure rather than a normal 1,5 ring.

A quantitative oxidation of the labile mannose compound is not possible because, in solution with water, it is converted rapidly into normal α-*d*-mannose. If the oxidation period is short the oxidation product is largely γ-lactone, but with longer periods considerable δ-lactone is formed. Presumably the γ-lactone is derived from the original product, while the δ-lactone arises from normal α-*d*-mannose, formed by the mutarotation reaction.

A 0.025-mole sample of crystalline mannose·$CaCl_2 \cdot 4H_2O$ was added to 100 cc. of ice water containing 5 cc. of bromine and 15 g. of barium carbonate. After five minutes the reaction was stopped by shaking with olive oil. The aqueous solution contained 0.0127 mole of unoxidized sugar and 0.0123 equivalent of lactone (estimated by titration). Hence the oxidation was 49% complete. The specific rotation of the product based on the above analysis, after eighteen minutes, was +42.6°; (60 min.), +37.9°; (180 min.), +35.2°; (48 hrs.), +26.7°. Since the rotation of the δ-lactone is +111°, the γ-lactone +52°, and that of the unoxidized sugar about +20°, changing to +14.7°, it is estimated that the oxidation product contained 76% γ-lactone and 24% δ-lactone.

The writer is applying his Barium Carbonate Oxidation Method to the sugars and their solutions to obtain data as to the isomeric changes accompanying mutarotation and the effect of salts on the equilibrium existing in solutions. It was previously shown [*Bur. Standards Jour. Res.*, **5**, 748 (1930)] that the equilibrium between the various forms of gulose in solution may be altered by the addition of calcium chloride. The experiments on mannose indicate that the changes in the compositions of the solutions may involve changes in the proportions of the ring isomers. Rapid measurements at 0° of the optical rotations of α-*d*-gulose·$CaCl_2$·H_2O show that the mutarotation previously reported is preceded by a short period in which the change in rotation is less rapid than later on. This is evidence that the mutarotation is more complex than the reversible interconversion of only two isomers. It is noted that a new gulose calcium chloride compound has been separated. It corresponds to the formula $(C_6H_{12}O_6)_2CaCl_2$, and gives $[\alpha]_D^{20}$ $+34°$ (1.4 minutes after solution in water), constant $-167°$ (3.3292 g./100 cc.).

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RECEIVED MARCH 27, 1933 PUBLISHED MAY 6, 1933

CONCENTRATION OF THE HEAVY HYDROGEN ISOTOPE

Sir:

In connection with investigations on some commercial chromium plating baths, the writers have determined the specific gravities of the water contained therein.

The waters from nine baths give specific gravities varying from 1.00002 to 1.00064. These baths have been operated for varying periods of time, the maximum being about three years.

Increases in specific gravity on prolonged electrolysis of water have been reported by Washburn and Urey [*Proc. Nat. Acad. Sci.*, **18**, 496 (1932)] and Lewis [THIS JOURNAL, **55**, 1297 (1933)] and by them attributed to the concentrating of the heavier isotopes of hydrogen. On this basis the highest specific gravity (1.00064) observed by us indicates the presence of about 0.6% of water containing the heavier hydrogen isotope in one of the samples examined.

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RECEIVED APRIL 3, 1933 PUBLISHED MAY 6, 1933

THE PREPARATION OF CRYSTALLINE β-*l*-ALLOSE, A NEW ALDOHEXOSE, FROM *l*-RIBOSE BY THE CYANOHYDRIN REACTION

Sir:

In the extension of our studies with *l*-ribose, the synthesis of which from *l*-arabinose through *l*-arabinal was recently announced [THIS JOURNAL, **54**, 4749 (1932)], we have undertaken the preparation of the unknown aldohexoses, *l*-altrose and *l*-allose, by the cyanohydrin reaction. Our investigations have been guided in large measure by the valuable contribution of Levene and Jacobs [*Ber.*, **43**, 3141 (1910)], who prepared the crystalline calcium salt of *d*-altronic acid and the crystalline lactone of *d*-allonic acid after the addition of hydrogen cyanide to *d*-ribose. After formation and reduction of the sirupy lactone of *d*-altronic acid and the crystalline lactone of *d*-allonic acid, Levene and Jacobs obtained sirups which were shown to contain *d*-altrose and *d*-allose.

After applying the cyanohydrin reaction to 30 g. of *l*-ribose we were able to isolate 17 g. of the crystalline calcium salt of *l*-altronic acid and 14.5 g. of the crystalline lactone of *l*-allonic acid. The recrystallization of the lactone of *l*-allonic acid to constant properties gave 13 g. with m. p. 130° and $[\alpha]_D^{25}$ +6.3°, in water. Levene and Jacobs found $[\alpha]_D^{20}$ −6.8° for *d*-allonolactone.

The reduction of the 13 g. of *l*-allonolactone was accomplished in the usual manner with sodium amalgam. After evaporation of the solution, removal of sodium sulfate by precipitation in hot 85% alcohol, and evaporation of the filtrate, the unchanged *l*-allonolactone was removed by conversion to the barium salt of *l*-allonic acid and precipitation of the latter from hot 90–95% alcohol. During the evaporation, under reduced pressure, of the final alcoholic filtrate the *l*-allose began to crystallize in rosets of very slender prisms. These crystals were filtered out and combined with other portions of the sugar, obtained by further evaporation, to give 9.2 g. of white crystalline *l*-allose. By one recrystallization of this quantity of *l*-allose from 93% alcohol there was obtained 7.2 g. of the purified sugar, with m. p. 128–129°. A 4% aqueous solution of the *l*-allose gave the following values of $[\alpha]_D^{20}$: −2.88°, four minutes after solution; −8.13°, thirty-four minutes after solution; and −13.88° (constant), twenty hours after solution. By the usual unimolecular equation $1/t \log [(r_0 - r_\infty)/(r - r_\infty)] = k_1 + k_2$ we have determined that the velocity coefficient at 20° of the mutarotation, $(k_1 + k_2)$, is 0.0094 (minutes and decimal logarithms), and that the calculated $[\alpha]_D^{20}$ value at zero time is −1.9°. This crystalline form of the sugar is to be designated *β*-*l*-allose according to the nomenclature proposed by Hudson [THIS JOURNAL, **31**, 66 (1909)], since it is the less levorotatory form of a sugar of the levo configurational series. Crystalline *l*-allose is the sixth crystalline aldehexose of the sixteen possible stereoisomers in the series of aldohexoses. The other known crystalline aldohexoses are *d*- and *l*-glucose and galactose, and *d*-mannose.

These investigations, which were facilitated by a Grant-in-Aid from the National Research Council, will be extended to the reduction of the *l*-altronolactone and more fully described in a future publication in THIS JOURNAL. Thanks are expressed to Dr. C. S. Hudson, of the National Institute of Health, Washington, D. C., for his interest and valuable suggestions.

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RECEIVED APRIL 18, 1933 PUBLISHED MAY 6, 1933

REACTION VELOCITY AND THE "EQUI-VALENCE-CHANGE PRINCIPLE"

Sir:

For some time I have been searching for cases of oxidation-reduction reactions suitable to test an hypothesis concerning a factor which it is thought may be an important one affecting reaction velocity, and which appears not to have been considered heretofore. The hypothesis, which may be called the equi-valence-change principle—if it prove to be a principle—may be briefly stated in simplest form as follows. It is reasonable to suppose that chemical reactions are more likely to result from bi-molecular collisions (or a sequence of such), than from simultaneous collisions of larger number. True tri-molecular or higher order reactions, if such occur, would be expected to be much slower processes because such collisions are statistically less probable events. If, then, in the case of oxidation-reduction reactions, a reductant molecule in an active state collides with an active oxidant molecule, reaction will occur if there results a decrease of free energy, and provided the *number* of electrons which the reductant *may* lose (or share) is the same as the number the oxidant may accept or share. It is assumed that only certain valence states, represented by known compounds, are "possible." If the number of electrons which may be lost or shared is not the same as the number required by the oxidant—if the possible valence change of reductant does not satisfy a possible valence state of oxidant—it would seem logical to expect that bi-molecular reaction could not occur, regardless of activity or free energy decrease, except as a result of less frequent tri-molecular collisions. (The idea is perhaps not applicable to some gaseous reactions.) According to this view "permissible" equivalence of valence change should be a factor affecting the fraction of collisions which are successful. And, where this factor inhibits reaction velocity, the introduction of third reactants able to mediate the first "odd" reaction into consecutive "even" steps should markedly catalyze the process.

Many cases seemingly in support of this idea have been surveyed in a preliminary way, and will be reported in due time, though few cases are found which are not open to several interpretations. The following case, called to my attention by Dr. P. W. Preisler, appears to be free from this objection, and is here recorded from the desire of securing criticism of my interpretation of it, and of the hypothesis.

Ceric–cerous sulfates, and thallous–thallic sulfates are known to be reversible, electromotively active couples, both the oxidants and reductants being almost instantly reactive with many substances in *N* sulfuric acid solution at room temperature. If a half cell is made of each couple in any finite ratio, using platinum electrodes, the potential difference between them is promptly registered and determinable by potentiometer, and corresponds with that expected from their recorded normal potentials

($Tl^{3+} - Tl^{1+}$, 1.2 v.; $Ce^{4+} - Ce^{3+}$, 1.5 v.)

It is therefore surprising to find that when ceric sulfate and thallous sulfate in *N* sulfuric acid are mixed, there is virtually no reaction, even on boiling. At 25° the half period is longer, perhaps much longer, than a thousand hours. The observed potential difference indicates the possibility of reaction and performance of work *when separated*, but when together reaction fails to take place. Mellor's Treatise (Vol. V, p. 662) cites the existence of a double salt of thallous ceric sulfates, $2Tl_2SO_4 \cdot Ce(SO_4)_2$. The most probable explanation of this unreactivity is that oxidation of thallous ion requires the loss of *two* electrons (Tl^{2+} being unknown) while ceric ion can accept only *one* (Ce^{2+} being unknown).

The addition of $MnSO_4$ (0.001 *M*) to a mixture of ceric and thallous sulfates (0.01 g. atomic in *N* H_2SO_4 at 25°) so catalyzes the reaction that the half period is about one hour. The probable mechanism of the catalysis follows from the facts that (a) ceric sulfate rapidly oxidizes Mn^{++} to Mn^{3+} and then to Mn^{4+} (MnO_2), and (b) MnO_2 oxidizes Tl^+ to Tl^{3+}. Platinum black, also, rather more rapidly catalyzes the reaction. The halide ions show slight catalytic activity.

These and other reactions, including oxidations involving oxygen, and their catalysis are being studied from the point of view of the hypothesis stated. There are many apparent contradictions, some of which already appear capable of resolution; whether it will be possible to establish the hypothesis as a general rule, future work will decide.

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EXCHANGE ADSORPTION AND ITS INFLUENCE UPON THE SOLUBILITY OF PRECIPITATES WITH IONIC LATTICES IN ELECTROLYTE SOLUTIONS

Sir:

In a previous communication [I. M. Kolthoff and Charles Rosenblum, THIS JOURNAL, **55**, 851 (1933)] it was reported that in the adsorption of the sodium salt of Ponceau 4R only dye ions were adsorbed, no sodium ions being removed from the solutions. Other experiments have shown that this "exchange" adsorption at the water–solid interface of pure ionic precipitates may occur quite generally. Finely divided calcium oxalate monohydrate was precipitated and purified by intermittent shaking and washing for several months. In the determination of the adsorption of alkali iodates, sulfates and sodium hydroxide, it was found that only the anions were adsorbed, or at least ten times more strongly than the alkali ions. On shaking with very dilute barium and manganese chloride solutions only the cations were adsorbed. Therefore cation as well as anion exchange occurs

$$\begin{array}{llllll} \text{CaOx} & + \ \text{SO}_4^{=} & \longrightarrow & \text{CaSO}_4 & + \ \text{Ox}^{=} \\ \text{Solid} & \text{Solution} & & \text{Interface} & \text{Solution} \\ \text{CaOx} & + \ \text{Ba}^{++} & \longrightarrow & \text{BaOx} & + \ \text{Ca}^{++} \end{array}$$

An important conclusion which can be drawn from the occurrence of exchange adsorption is that the solubility of an ionic precipitate in an electrolyte solution is a function of the amount of solid present or, more precisely, of the amount of surface exposed by the solid in those cases in which cation or anion exchange takes place. Experimentally this was shown to be true. The solubility of calcium oxalate monohydrate was determined by shaking small and large quantities of precipitate with various solutions until equilibrium was attained; the saturated solutions were analyzed for oxalate or calcium by micro methods.

With small quantities of solid present, the normal solubilities were found ($[\text{Ca}^{++}] = [\text{Ox}^{=}]$ in saturated solution). Some data are given herewith.

$[\text{Ca}^{++}]$ AND $[\text{Ox}^{=}]$ IN SATURATED SOLUTIONS OF $\text{CaOx}\cdot\text{H}_2\text{O}$ AT 25°

Electrolyte	Concn., *M*	Normal solubility in millimoles per liter Ox	Ca	Solubility with 12 to 15 g. of CaOx per 250 cc. Ox	Ca
Water		0.067	0.067	0.067	0.067
$(\text{NH}_4)_2\text{SO}_4$	0.01	.112	.115	*.31*	.05
NH_4IO_3	.01	(.090)	.090	(.13)	.058
NaOH	.01	.126	(.126)	*.30*	(.052)
BaCl_2	.001	.078	(.078)	.03	(*.21*)

The saturated solutions of calcium oxalate contain an excess of oxalate ions in the experiments with alkali sulfates, iodates and sodium hydroxide, but an excess of calcium ions with barium and manganese chloride, the absolute values being a function of the amount of solid present.

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I. M. KOLTHOFF
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RECEIVED APRIL 21, 1933 PUBLISHED MAY 6, 1933

DIELECTRIC POLARIZATION IN SOLIDS

Sir:

In a study of the relation between dielectric properties and chemical constitution, in progress at Bell Laboratories for several years, some observations of interest in connection with recent communications on rotation of molecules or groups in crystalline solids [Hitchcock and Smyth, THIS JOURNAL, **55**, 1296 (1933)] deserve reporting. A transition in the solid state accompanied by a change of heat capacity and dielectric constant, ϵ, as predicted by Pauling for HCl has been observed for camphor, borneol and isoborneol.

d-Camphor shows a change of ϵ between −37 and −32° larger than that reported for HCl or H_2S. *d-l*-Camphor shows a change of the same magnitude between -70 and $-80°$. Borneol and isoborneol show changes of ϵ, though not as large as for camphor, between 70 and 80° and 25 and 45°, respectively. The curves of ϵ *vs.* T for camphor and isoborneol show a hysteresis effect at the transition point and the change for isoborneol is so spread out as to suggest the presence of impurities in the unpurified commercial materials used.

Some facts of interest about the change of dielectric properties at the transition point are the following. (1) The time of relaxation of the polarization to which the high value of ϵ above the transition point is due is less than 5×10^{-7} sec. (2) n^2_D at 20° for camphor is approximately equal to ϵ below the transition point. (3) There is no dispersion of either ϵ' or ϵ'' over a wide range of temperatures, including the transition range, for frequencies to 10^5 cycles for borneol, isoborneol or *d*-camphor. (4) There is a distinct low frequency dispersion for *d*-*l*-camphor occurring just below the transition point and dependent on the purity of the material. (5) Preliminary data show that above the transition point ϵ does not decrease with increasing T sufficiently to cause the polarization to vary linearly with $1/T$. (6) Measurements on solutions of camphor in hexane over a range of temperatures including the transition range show that P_∞ *vs.* $1/T$ is linear for higher temperatures but departs from it at low.

The absence of dispersion in the transition range distinctly differentiates the polarization which is responsible for the high ϵ in these materials from that observed in many polar substances which form glasses on cooling. The temperature variation of ϵ of these solids indicates that the additional polarization present above the transition point is a different function of temperature than that for free orientation of dipoles. The temperature variation of polarization of the solutions may be interpreted either as a change of electric moment with temperature or as evidence of the existence of an atomic polarization or group rotation which depends upon temperature. Further study of the change of polarization of the solids with temperature is being made.

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