cation. Although the analytical figures obtained with this derivative were satisfactory, its melting point (152°) proved to be higher than that recorded in the literature (128°[2] and 143°[3]). In order to clear up this discrepancy, we have since prepared the phenylhydrazone of synthetic isobutyrylformic acid. The latter melts at 152°, thus confirming our observation on the substance obtained from ergotinine. A mixed melting point showed no depression.

The method of synthesis was essentially that reported by Tschelinzeff[4] with a slight variation in the method of hydrolysis of the intermediate isobutyryl cyanide. It was found necessary to heat the cyanide on the steam-bath for two hours in 1:1 hydrochloric acid in order to effect hydrolysis. The hydrolysis mixture was extracted with ether, the ether extract dried with sodium sulfate and evaporated to a sirup. If this sirup is used to prepare the hydrazone it does not crystallize. However, if the sirup is shaken with a little water, in which it is not completely soluble, and the aqueous layer used to prepare the hydrazone, the product crystallizes nicely. Repeated recrystallizations from dilute alcohol failed to raise the melting point above 152°.

Anal. Calcd. for $C_{11}H_{14}O_2N_2$: C, 64.08; H, 6.84; N, 13.59. Found: C, 64.15; H, 6.74; N, 13.66.

FROM THE LABORATORIES OF
THE ROCKEFELLER INSTITUTE
FOR MEDICAL RESEARCH
NEW YORK, N. Y.

RECEIVED JUNE 28, 1934

---

(2) D. Tschtschenke, *Bull. soc. chim.*, [4] **37**, 623 (1925).

(3) E. Abderhalden and E. Rossner, *Z. physiol. Chem.*, **163**, 261 (1926).

(4) W. Tschelinzeff and W. Schmidt, *Ber.*, **62**, 2210 (1929).

COMMUNICATIONS TO THE EDITOR

ORGANIC REACTIONS WITH LIQUEFIED HYDROGEN CHLORIDE

Sir:

Information is accumulating in our laboratories relative to the reaction of liquefied hydrogen chloride with various types of organic compounds. In the majority of cases the reactions proceed rapidly indeed, partly because of the fact that the liquefied hydrohalides, in particular hydrogen chloride, are excellent solvents for a wide range of compounds. Many of the resulting solutions are good conductors of electricity.

The reactions observed so far are additions to multiple bonds, dehydration, or both; acidolysis appears not to be as frequent as might be anticipated. Reactions of hydrohalides as exemplified by our experiments are interesting in view of theoretical considerations concerned with addition to multiple bonds. As example of these reactions the following are typical: (1) vinyl acetate reacts with liquid hydrogen chloride at atmospheric pressure forming α-chloroethyl acetate in 50 to 70% yields. The literature contains two boiling points for this compound, 119–121° (740 mm.[1]) and 113–116° (740 mm.[2]); different preparations resulted in products which boiled at either one or the other of the two points. This is being investigated. (2) Allyl alcohol (b. p. 96.5–97.5°) is converted to allyl ether (b. p. 91–93°) with a high yield. (3) Acetaldehyde yields α,α′-dichloroethyl ether boiling at 112.5–114° in yields of 70%, n^{25}_{D} 1.4186, d^{25}_{4} 1.106. This compound was identified by hydrolysis to acetaldehyde in the presence of *p*-nitrophenylhydrazine and isolation of the hydrazone. (4) Good yields of ethylene chlorohydrin are obtained from the reaction of ethylene oxide with liquefied hydrogen chloride.

A mixture of one mole of isopropyl acetate and one mole of *n*-butyl alcohol was treated with liquid hydrogen chloride at atmospheric pressure, from which was isolated some isopropyl alcohol and butyl acetate. This is being investigated on a series of such compounds with the purpose of obtaining data relative to negativity of the groups tested.

A number of cases have been found in which no action takes place. Cinnamic acid is a typical example. This work is being extended. A complete report will be made later.

NORTHWESTERN UNIVERSITY ERICH GEBAUER-FUELNEGG
DEPARTMENT OF CHEMISTRY
EVANSTON, ILL.
BORG LABORATORIES EUGENE MOFFETT
CHICAGO, ILL.

RECEIVED JULY 11, 1934

---

(1) Descade, *Ann. chim.*, [7] **29**, 488 (1903).

(2) Ulich and Adams, THIS JOURNAL, **43**, 660 (1921).

THE APPLICATION OF COLORIMETRY IN THE ULTRAVIOLET TO THE DETERMINATION OF THE STRENGTH OF ACIDS AND BASES

Sir:

The important problem of determining the base strengths of very weak bases (*e. g.*, most organic acids, esters, ketones, aldehydes, ethers, amines, and amides) has been solved by the methods of visual colorimetry for the limited group of bases whose ionization is accompanied by a change in color. Because of the great desirability of obtaining similar quantitative information for uncolored bases, we have investigated the validity of what may be called colorimetry in the ultraviolet as a method of measuring ionization and base strength. For this purpose the ultraviolet absorption spectra of a carboxylic acid (benzoic acid), of a phenolic acid (2,4-dinitrophenol), and of a singly charged acid (anilinium ion, which is the conjugate acid to the simple base aniline) have been measured under the following conditions: (1) in an acid solution in which the ionization of the acid is negligible; (2) in a basic solution in which the acid is completely ionized; (3) in a buffer solution of known acidity in which ionization is approximately half complete. In every case ionization was accompanied by a marked change in the absorption spectrum from which calculation of the extent of ionization was easily possible. The values of acid strength obtained are listed herewith, together with the values (derived from conductivity or hydrolysis measurements) given in the Landolt–Börnstein "Tabellen."

	pK (absorption spectra)	pK (L.–B.)
Benzoic acid	4.16 ± 0.11	4.18
Dinitrophenol	4.09 ± .04	4.10
Anilinium ion	4.62 ± .05	4.62

The deviations represent variations in the pK obtained from different regions of the spectrum.

Having thus demonstrated the validity of the method, we have further investigated the ionization of benzoic acid as a base

$$C_6H_5COOH + H^+ \rightleftarrows C_6H_5COOH_2^+$$

by determining its absorption spectrum in a series of increasingly acid sulfuric acid–water mixtures. A large change took place between concentrations of 70 and 95% sulfuric acid, and very little change in any other range of acidity. From these spectra and the visual colorimetric values of the acidity function H_0 for the sulfuric acid solutions, we obtain the following value for the base strength of benzoic acid

$$pK' \equiv -\log a_B a_{H^+}/a_{BH^+} = -7.25 \pm 0.25$$

The method will be applied to the determination of the base strengths of other colorless organic compounds.

DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK, N. Y.

LOUIS P. HAMMETT
ANDREW DINGWALL
LEO FLEXSER

RECEIVED AUGUST 3, 1934

IRRADIATION OF YEAST ORYZANIN

Sir:

We have found that a one-hour irradiation of a solution containing 24.4 mg. per liter of yeast oryzanin kindly furnished by S. Ohdake and U. Suzuki, at a distance of 4.3 cm. from a Victor quartz lamp, destroyed its ability to alleviate the neurological symptoms of rats maintained on a vitamin B_1 deficient diet in doses as large as 12 γ. The original solution was active in doses of less than 3 γ. The two-peaked absorption of the compound, which resembles that of cytosine [THIS JOURNAL **56,** 1728 (1934)] is rapidly destroyed by the irradiation. On the other hand, irradiation with ultraviolet from which most of the radiations of wave lengths less than 2960 Å. have been filtered out, for a period of thirty minutes produces a transient increase in the characteristic absorption, and even after four hours leaves the absorption bands still present, while the biological potency is

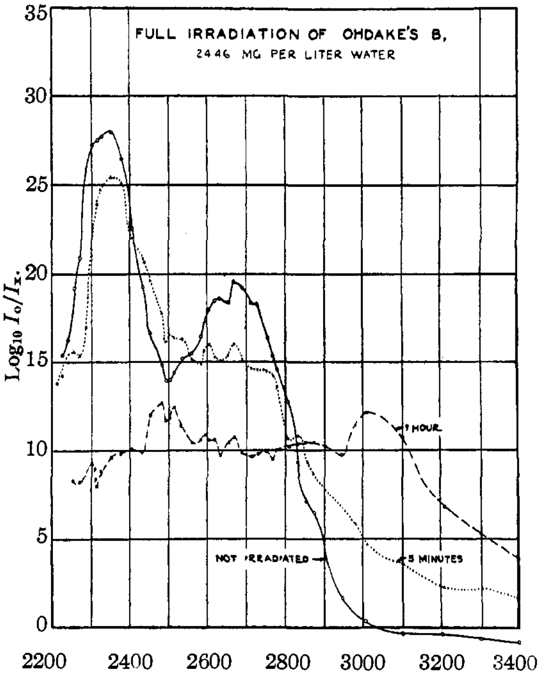


Fig. 1

only slightly, if at all, diminished. Similar results have been obtained with preparations from other sources.

BASIC SCIENCE RESEARCH LABORATORY F. F. HEYROTH
UNIVERSITY OF CINCINNATI J. R. LOOFBOUROW

RECEIVED AUGUST 2, 1934

THERMAL DIFFUSION OF GASES NEAR A HOT METAL SURFACE

Sir:

In an experimental study of the equilibrium of molten iron and steam [THIS JOURNAL, **55**, 3131 (1933)] the only criterion of equilibrium was the fact that the oxygen content of the iron reached a constant and reproducible value at a constant steam–hydrogen ratio. The surprising results of Emmett and Shultz [*ibid.*, **55**, 1376 (1933)], in which a thermal separation of steam and hydrogen was observed even in a flowing system, raised the question as to whether such a phenomenon could have occurred in our experiments. This suspicion was heightened by the fact that for a given oxygen content of the liquid iron the observed ratio of steam to hydrogen was consistently a little higher than that calculated from the ratio CO_2:CO found by Vacher and Hamilton [*Trans. Am. Inst. Mining Met. Eng.*, **95**, 124 (1931)].

It should be possible to diminish the temperature gradient and thereby also the amount of thermal separation by preheating the gas stream as it approaches the hot metal surface. The preheating due to radiation from the liquid iron will be the more efficient the lower the lineal velocity of the gases. In the earlier experiments the gases were introduced through a 3-mm. tube at 250 to 450 cc. per minute, whereas Vacher [*Bur. Standards J. Res.*, **11**, 541 (1933)], using a larger tube and lower rate of flow, obtained a lower ratio of steam to hydrogen.

A series of experiments has been conducted in which the steam–hydrogen mixture was admitted through a 7-mm. tube containing an electrically heated spiral of platinum wire. In another series this preheating was supplemented by a cast chromium sleeve which fitted over the top of the crucible containing the melt and which was heated by induction to a temperature approximating that of the liquid iron. The results of these experiments at 1600° and 0.065% oxygen in the liquid iron are given in Table I. The temperature recorded for the platinum coil is its average determined by its resistance. The end nearest the exit was several hundred degrees hotter. The recorded sleeve temperatures are estimates.

TABLE I

THE EQUILIBRIUM: $FeO\ (\text{in } Fe) + H_2 = Fe(l) + H_2O$ AT 1600°

Expt.	$\frac{p_{H_2O}}{p_{H_2}} \times \%O$	Flow cc./min.	Coil temp., °C.	Conditions
1–18	4.75	300	..	3-mm. tube
33	4.58	300	..	7-mm. tube
34	4.33	300	1170	No sleeve
35	4.23	300	1320	No sleeve
51	4.20	300	1170	Sleeve about 1500°
52	4.04	300	1170	Sleeve about 1600°
53	3.94	200	1170	Same as 52
55	4.20	450	1050	No sleeve

The results substantiate the hypothesis of partial thermal separation of the cold gases near the hot metal surface, which results in a diffusion of steam away from the surface and a low oxygen content of the liquid iron. In experiments 52 and 53 the preheating is believed to have been sufficient to largely eliminate this source of error. These two experiments are also in very good agreement with calculations from similar data on the system Fe:C:O.

DEPARTMENT OF ENGINEERING RESEARCH JOHN CHIPMAN
UNIVERSITY OF MICHIGAN M. G. FONTANA
ANN ARBOR, MICHIGAN

RECEIVED AUGUST 9, 1934

MAGNETIC SUSCEPTIBILITY OF METAL KETYLS

Sir:

We have recently made an investigation on the magnetic susceptibilities of some of the metal ketyls in solution by the Gouy method. The root mean square permanent magnetic moment per molecule was calculated from the molal susceptibility χ_M of the solute by means of the Langevin relation

$$\mu = 2.83\sqrt{T(\chi_M - N\alpha)}$$

μ being in Bohr magnetons. The values of $N\alpha$ were found by Pascal's rule from values in the "International Critical Tables." The percentage dissociation of the metal ketyls under the conditions given in the table below was calculated from the relation

$$D = 100\,(\mu^2/3)$$

which follows from the assumption that the radicals have a magnetic moment of $\sqrt{3}$ Bohr magnetons.

Metal ketyl	Solvent	Concn., wt. %	Temp., °C.	Molal susceptibility of solute, χ_M	D, %
p-Biphenyl phenylketone sodium	Benzene	9.4	27	-152×10^{-6}	1.7
p-Biphenyl phenylketone sodium	Dioxane	3.0	26	+339	41
Benzophenone sodium	Benzene	1.7	25	−195	<1.0

A result for *p*-methoxybenzophenone sodium of $D = 33\%$ at 25° and a concentration of 1.0% with benzene as the solvent was also obtained, but, because of the fact that only a small concentration of the metal ketyl could be obtained coupled with the fact that a relatively large excess of the ketone was necessary to cause reaction with the sodium, a large correction thus being made necessary, the results were considered to be not very significant. We found that α-naphthyl phenyl ketone would not form a metal ketyl in benzene solution even though sodium, potassium and sodium amalgam were tried.

Schlenk and Thal [*Ber.*, **46**, 2840 (1913)] advance as evidence that the metal ketyls are completely dissociated (at least in ether solution) the results of certain boiling point measurements. The boiling point reading of the thermometer was taken first for the pure solvent, then after the addition of a small amount of *p*-biphenyl phenyl ketone, and finally after the addition of some potassium metal. The solution was kept in contact with an atmosphere of nitrogen. Schlenk and Thal state that they observed no fall in boiling point after the addition of the potassium. We have repeated their work as nearly as possible, but have obtained quite different results. We made two runs, in each of which there was a fall in boiling point after the addition of the potassium of approximately one-half of the total rise caused by the addition of the ketone. The fall took place over a period of about an hour, and the final reading was a steady one. The fall in boiling point indicates a decrease in the number of moles of dissolved material; this decrease presumably corresponds to the formation of undissociated molecules of the sodium salt of the pinacol. We attempted the experiment also with dioxane as the solvent, but at the boiling point of this solvent (101°) the metal ketyl would not go into solution, but merely formed a protective coating on the surface of the potassium, although the latter was molten.

Sugden [*Trans. Faraday Soc.*, **30**, 18 (1934)] has recently published some results for the magnetic susceptibilities of benzophenone potassium and *p*-biphenyl phenyl ketone potassium in dioxane which show that these metal ketyls are very highly dissociated in the solutions used. His results are in qualitative but not in quantitative agreement with ours. The difference may be due to the fact that the potassium rather than the sodium salt was used. We are not continuing the work because Sugden has promised to furnish more details soon.

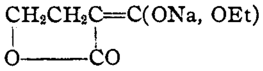
GATES CHEMICAL LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA
R. N. DOESCHER
G. W. WHELAND

RECEIVED AUGUST 9, 1934

THE FORMATION OF ENOLATES FROM α-LACTONIC ESTERS

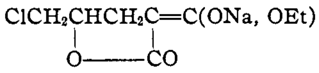
Sir:

Traube and Lehmann [*Ber.*, **34**, 1977 (1901)] treated an alcoholic solution of sodium enol malonic ester with ethylene oxide and obtained a sodium derivative of α-carbethoxybutyrolactone. In continuation of an investigation on the synthesis of lactones from malonic acid and related substances [Michael and Ross, THIS JOURNAL, **55**, 3684 (1933)] we deemed it important to prove experimentally its enolate structure, (I) [Meyer-Jacobson "Lehrb. org. Chem.," I², 641 (1913)]. We find that it can be reformed from the lactone and sodium ethoxide, that it reacts with methyl iodide to form the C-α-methyl derivative, and that treatment with iodine yields a mixture of two stereomeric dilactonic esters. These results definitely prove its enolate structure.



$$\begin{array}{l}\mathrm{CH_2CH_2C{=}C(ONa,\ OEt)}\\ \mathrm{|\qquad\quad\ |}\\ \mathrm{O\text{———}CO}\end{array}$$

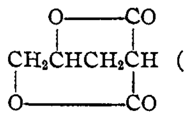
(I)

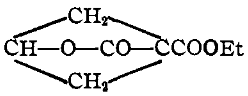


$$\begin{array}{l}\mathrm{ClCH_2CHCH_2C{=}C(ONa,\ OEt)}\\ \mathrm{\qquad\ |\qquad\quad |}\\ \mathrm{\qquad O\text{———}CO}\end{array}$$

(II)

With epichlorohydrin, Traube and Lehmann [*loc. cit.*] isolated the enolate of α-carbethoxy-δ-chlorovalero-γ-lactone (II). On heating this compound with alcohol, and the formed viscous organic product with hydrochloric acid, Leuchs [*Ber.*, **40**, 307 (1901)] obtained a small yield of the γ,δ-dilactone (III). We find the first phase to be an intramolecular C-alkylation, leading to the cyclic tetramethylene lactonic ester (IV), which, on boiling with hydrochloric acid is converted into the γ-δ-dilactone.


(III)


(IV)

Evidently, the negative carbethoxy and lactonic groups have so loosened the affinity of the tetramethylene α- and β-carbon atoms that the linkage between them is hydrolyzed by the acid and the formed δ-hydroxy-carboxylic acid group undergoes lactonization. Results with other α-lactonic esters and dilactones, containing mobile α-hydrogens, indicate that enolate formation is a general property of such derivatives.

Recently, Tschelinzev [*Ber.*, **67**, 960 (1934)] assumed that enolates containing an α-hydrogen react with carbonyl derivatives by intermolecular aldolization, involving the respective hydrocarbon and carbonyl groups. In accordance monoalkylated malonic and acetoacetic ester enolates do not condense with ethylene oxide. Tschelinzev overlooked that the surmized aldolization process was proved experimentally years ago and that his generalization is untenable. Enolates with an α-hydrogen unite with phenyl isocyanate with intermolecular migration of that hydrogen, forming well neutralized enolates [Michael, *Ber.*, **38**, 22 (1905); *Ann.*, **363**, 64 (1908)]: with sodium enol methyl acetoacetic and methyl malonic esters deep-seated decompositions occur, giving the well neutralized salt of a complicated acid [*loc. cit.*, p. 24]. Sodium enol methyl malonic ester adds to $\Delta^{-\alpha,\beta}$-esters by migration of the methyl group to the $\Delta^{-\alpha}$ carbon atoms [Michael and Ross, THIS JOURNAL, **52**, 4592 (1930); **53**, 1633 (1931)] and, finally, Bennett [*J. Chem. Soc.*, **127**, 1278 (1925)] found that ethylene oxide condenses with (I), which contains no α-hydrogen to give bis butyrolactone α,α-spiran. The subject is evidently complicated, but the reactions always proceed with the maximal possible neutralization of the metal.

CONVERSE MEMORIAL LABORATORY ARTHUR MICHAEL
HARVARD UNIVERSITY NATHAN WEINER
CAMBRIDGE, MASS.

RECEIVED AUGUST 22, 1934

THE POSSIBILITY OF SEPARATING HEAVY WATER BY FRACTIONAL FREEZING

Sir:

On the basis of the fact that D_2O has m. p. 3.8°, the possibility of separating it from H_2O by fractional freezing was taken into consideration. Admitting that the two oxides are isomorphous and form a continuous series of solid solution, the possibility of the separation clearly depends on the relative positions of the *liquidus* and *solidus* curves.

Some graduated fractional freezings were executed, on my suggestion, by Dr. M. Strada, starting from ordinary distilled water. From density measurements made by Dr. Strada it was deduced that the final fractions contained up to 4 per mille of D_2O. Similar results were found from water obtained from old electrolytic cells of a hydrogen plant. A short paper was consequently published by myself and M. Strada in *Rend. Accad. Lincei*, **19**, 433 (1934).

Doubts having arisen of the reliability of the above experiments, I asked my friend and Assistant Professor A. Quilico to repeat the whole operations, during which the greatest care to eliminate sources of error, or to estimate their influence, was taken. Professor Quilico started again from 4000 liters of common water, which, by a nine-step fractional freezing, he reduced to 280 cc. To the water 6% of sodium chloride was added each time in order to obtain ice as minute crystals and at each step about one-third of the whole was sharply separated by centrifugation, as ice. The final fraction was distilled eight times in quartz apparatus, four times alone and four with the usual chemical reagents.

On the liquid thus obtained nine independent density measurements were made, every time in comparison with the original water and four times also with the water coming from the fifth freezing. The influence of temperature was particularly considered. The uniform result was that the former determinations were entirely untrustworthy. The density differences now found were in both directions and never exceeded the possible error of the measurement.

To eliminate the doubt that the chemical treatment might originate total or partial destruction of D_2O, five more density determinations were made on samples purified by distillation only. The results were the same.

The conclusion to be drawn is that *if* a fractionation takes place, it amounts certainly to less than 1/10,000, and probably less than 1/100,000 when the original mass is reduced to 1/14,300.

This behavior is probably due to the fact that the crystal lattice of both D_2O and H_2O is substantially formed by the O-atoms while the H-resp. D-atoms do not materially affect its dimensions and both waters thus practically crystallize as a single body. This circumstance had formerly been pointed out by myself, but the absolute impossibility of a stepwise fractionation could not be postulated *a priori*.

LABORATORIO DI CHIMICA GENERALE
R. POLITECNICO
MILANO, ITALY
G. BRUNI

RECEIVED AUGUST 23, 1934

OXYGEN A FACTOR IN THE BROMINATION OF CINNAMIC ACID

Sir:

We have found that bromine and cinnamic acid combine rapidly in the dark at room temperature when dissolved oxygen has been removed from the solution. When the oxygen has not been removed, the reaction is very slow in the dark, but it proceeds rapidly in the light. Apparently the many previous investigators of the photobromination of cinnamic acid, including ourselves [Bauer and Daniels, THIS JOURNAL, **56**, 378 (1934)] have been dealing with an oxygen-inhibited reaction.

The experimental apparatus and materials were as described before, except that a side arm containing a magnetic hammer and a sealed-off bulblet of bromine was fused to the quartz reaction cell. The cell was filled with a solution of cinnamic acid in carbon tetrachloride and boiled under reduced pressure at room temperature. The cell was then chilled and sealed off. When the cell had reached 20°, the bromine cell was broken in the dark. In every case the bromine reacted and the solution became colorless so rapidly that the rate of reaction could not be measured conveniently.

Under the same conditions, when a bulblet of oxygen was broken before the bromine bulb was broken, the solution retained its reddish color until exposed to bright light, behaving qualitatively as observed in the earlier investigation when air had not been removed.

Similar results were obtained using simpler apparatus and unpurified materials. An inverted U-tube of Pyrex was provided with a stopcock and tilted in such a way that one leg was partially filled with a carbon tetrachloride solution of cinnamic acid and the other with a carbon tetrachloride solution of bromine, care being taken to prevent bromine from getting into the cinnamic acid solution. Evacuation was continued until the solutions had boiled away to about half of their volumes. The stopcock was closed and on mixing the two solutions the bromine faded out within a few minutes. Admission of air practically stopped the reaction.

These results are in agreement with the findings of Kharasch [Kharasch and Mayo, THIS JOURNAL, **55**, 2468 (1933)] that peroxides affect the addition of hydrobromic acid to the double bond, with those of Schultze [*ibid.*, **56**, 1552, (1934)] that the rate of bromination of cyclopentadiene is affected by oxygen, and with those of Dickinson and Leermakers [*ibid.*, **54**, 3852 (1932)] that oxygen inhibits the photochlorination of tetrachloroethylene.

Experiments in this Laboratory indicate that the influence of oxygen on reactions of this type may be quite general.

LABORATORY OF PHYSICAL CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WIS.
WALTER H. BAUER
FARRINGTON DANIELS

RECEIVED AUGUST 24, 1934

NEW BOOKS

A Comprehensive Treatise on Inorganic and Theoretical Chemistry. By J. W. MELLOR, D.Sc., F.R.S. Vol. XIII. Iron. Longmans, Green and Co., 55 Fifth Ave., New York, 1934. ix + 948 pp. 559 figs. 15.5 × 25 cm. Price, $20.00.

This volume continues the discussion of iron and its compounds. Specifically it covers the physical and chemical properties of the free element and the occurrence, preparation and properties of its oxides.

There are many special chapters of great interest and merit; for instance (18) The Mechanical—(19) The Thermal—(20) The Optical—(21) The Electrical—and (22) The Magnetic Properties of Iron and Iron Carbon Alloys; (24) The Corrosion of Iron and Steel; (26) The Passivity of Iron; (31) and (32) Hydrated Ferric Oxide-Hydrosol and-Hydrogel.

An extraordinary amount of information has been assembled in this volume in compact and accessible form, and as tested in a few restricted fields familiar to the reviewer, this information appears to be surprisingly complete. There is certainly no other treatise on this subject in our language which can compare with it in these respects.