

of ether but for ease of controlling conditions so that the results would be comparable. This accounts for the fact that the yield of phenetole using ethyl sulfate is not as high as that reported by Cade.<sup>3</sup> The yields of phosphates and phenol ethers are given in Table I.

It should be noted that while the yields of phenol ethers from phosphates are low compared with that from the sulfate, they are based on the amount of alkyl radical available. Many of the higher yields from other esters reported in the literature are based on the substance being alkylated, using a large excess of alkylating agent.

<sup>3</sup> Cade, *Chem. Met. Eng.*, **29**, 319 (1923).

CONTRIBUTION FROM THE  
DEPARTMENT OF CHEMISTRY  
STANFORD UNIVERSITY  
STANFORD UNIVERSITY, CALIFORNIA

RECEIVED AUGUST 30, 1932  
PUBLISHED JANUARY 11, 1933

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## COMMUNICATIONS TO THE EDITOR

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### PREPARATION OF KETENE DIETHYL ACETAL

*Sir:*

According to the communication of Snell and McElvain [THIS JOURNAL, **55**, 416 (1933)] these authors were unable to duplicate the preparation of ketene diethyl acetal described by me [Scheibler, Marhenkel and Nikolic, *Ann.*, **458**, 28 (1927)]. This preparation, however, has often been accomplished in my laboratory by several young chemists. The above failure may have been due to two causes. (1) The residue obtained from sodium ethoxide and ethyl acetate after removal of the volatile substances, containing the so-called "primary reaction product of the acetoacetic ester synthesis," may have lost alcohol during the treatment and been transformed into the sodium derivative of acetoacetic ester which, treated with water, of course did not give ketene acetal [Scheibler and Marhenkel, *Ann.*, **458**, 6, 18 (1927)].

The evaporation of ether and the excess ester must be performed quickly at low temperature under diminished pressure. It is not surprising that Snell and McElvain, who dried the residue in a vacuum desiccator over sulfuric acid until it attained a constant weight, only obtained sodio-acetoacetic ester. The weight of the dry residue obtained by them from 23 g. of sodium was only 90–100 g. instead of 125 g. A small amount of ethyl acetate may remain in the residue and be quickly saponified when it is treated with water, in contrast with ketene acetal, which does not undergo any decomposition in aqueous alkaline solution.

(2) The authors may have used too much calcium chloride in shaking

the ether solution for three or four hours with three successive portions of powdered calcium chloride. I only employed a quantity just sufficient to fix the alcohol which was mixed with ketene acetal. When being shaken in this way ketene acetal is held by the great surplus of solid calcium chloride, which is not the case when a concentrated aqueous solution of calcium chloride is used. The separation of alcohol is better performed in such a manner. The directions given by me should be changed as follows.

After drying with anhydrous sodium sulfate, the ethereal solution from the extraction of the "primary reaction product" triturated with water, is distilled through a fractionating column. The residue containing ether only in a little amount is shaken intermittently during six hours with four parts of saturated aqueous solution of calcium chloride. Then it is extracted with ether in a continuous extraction apparatus and the resulting solution is dried with anhydrous sodium sulfate. Observing the precautionary measures mentioned before, ether and finally ketene acetal are distilled; yield, 13 g. or 11.2% of the calculated amount based on 23 g. of sodium used.

The preparation of dimethyl ketene diethyl acetal from ethyl isobutyrate was not successful with sodium ethoxide. It was performed in another manner which will be described later.

TECHNISCHE HOCHSCHULE OF BERLIN  
LABORATORY OF ORGANIC CHEMISTRY  
BERLIN-LICHTERFELDE, GERMANY

HELMUTH SCHEIBLER

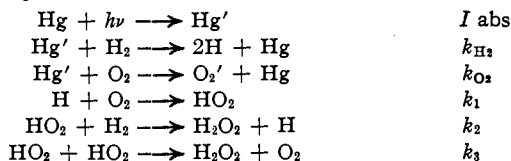
RECEIVED OCTOBER 19, 1932

PUBLISHED JANUARY 11, 1933

## KINETICS OF THE MERCURY SENSITIZED REACTION BETWEEN HYDROGEN AND OXYGEN

*Sir:*

Investigations of the mercury sensitized photo-reaction between hydrogen and oxygen have given rise to a large number of conflicting and unconnected data. These have been used to set up mutually conflicting theories of the mechanism of the reaction of hydrogen atoms with oxygen. It can, however, be demonstrated that almost all the known facts can be correlated and be completely in accord if we assume as the true mechanism:



These give the kinetic expression

$$\frac{d[\text{H}_2\text{O}_2]}{dt} = \frac{k_2[\text{H}_2]}{\sqrt{k_3}} \sqrt{\frac{[\text{H}_2] k_{\text{H}_2} I \text{ abs}}{[\text{H}_2] k_{\text{H}_2} + [\text{O}_2] k_{\text{O}_2}}} + \frac{[\text{H}_2] k_{\text{H}_2} I \text{ abs}}{[\text{H}_2] k_{\text{H}_2} + [\text{O}_2] k_{\text{O}_2}}$$

Assuming  $k_2/\sqrt{k_3} = 10^{-3}$ , this equation fits exactly the data of Marshall [THIS JOURNAL, **49**, 2763 (1927)] on the influence of  $[H_2]$  and  $[O_2]$  on the rate, if we put for  $k_{H_2}$   $1.1 \times 10^7$ ,  $k_{O_2}$   $0.68 \times 10^7$  as determined by Zemansky [Phys. Rev., **36**, 919 (1930)]. The constant ( $I$  abs) so obtained is constant to within less than 3% for all the experiments of Marshall not indicated as uncertain. Furthermore, the value of the quantum yield as calculated, using  $k_2/\sqrt{k_3} = 10^{-3}$  lies between 1 and 2 in those experiments, in close agreement with those experimentally determined (1-2.5). In addition, the discrepancy between the quantum yield measurements of Frankenburg and Klinkhardt [Z. physik. Chem., **15B**, 421 (1931)] and by Marshall [J. Phys. Chem., **30**, 1078 (1926); THIS JOURNAL, **54**, 4460 (1932)] is explained, in that the former used a light intensity a hundredfold greater than the latter. The mechanism postulated calls for a higher quantum yield with lower intensities, which is again in agreement with the experiments. This subject will be given a complete exposition in a paper shortly to be submitted to the JOURNAL.

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF MICHIGAN  
ANN ARBOR, MICHIGAN

JOHN R. BATES

RECEIVED DECEMBER 5, 1932

PUBLISHED JANUARY 11, 1933

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#### FURTHER REMARKS ON THE PREPARATION OF KETENE ACETAL

Sir:

Scheibler [THIS JOURNAL, **55**, 425 (1933)] ascribes our failure to obtain ketene acetal [*ibid.*, **55**, 416 (1933)], first, to too long standing of the "primary reaction product" over sulfuric acid, and second, to the use of excessive amounts of calcium chloride in the purification of the product. The first reason is not valid because we did not use a "primary reaction product" which had attained constant weight over sulfuric acid, but rather the residue left after the evaporation of the reaction mixture at room temperature under diminished pressure in a vacuum desiccator as described by the original investigators [Scheibler and co-workers, *Ann.*, **458**, 28 (1927)]. On account of the second reason Scheibler now revises his original extraction procedure.

In consideration of this revised procedure we have made two further attempts to prepare ketene acetal. The same quantities of materials that were used in our earlier work were employed. The preparation of the "primary reaction product" was carried out in a tared 3-liter round-bottomed Pyrex flask. In this way it was possible to evaporate the ether and ethyl acetate from the reaction mixture and obtain a dry residue in about six hours, whereas evaporation in a vacuum desiccator according to the original procedure required about ten hours. It is not apparent to us how the time for this evaporation can be further decreased without

the application of heat. The weight of the dry residue obtained in our latest experiments was in one case 77 g. and in the other 78 g. instead of 125 g. reported by the original investigators. In fact, intermittent weighings of the tared evaporation flask during the latter period of the evaporation showed that when its contents weighed 125 g. they were still liquid.

On working up these residues according to the revised procedure of Scheibler we obtained in one case 7 g. (A) and in the other 9 g. (B) of product at the point where ketene acetal should appear. In each of these products the amount of ethyl acetate was determined by saponification of an aliquot with 0.1 *N* potassium hydroxide and the amounts of ethyl alcohol and water were estimated by treatment of an aliquot with phenyl isocyanate followed by the isolation of the phenyl urethan and diphenyl urea. The following summary shows the percentages of these substances which were found to be present in the products which we obtained.

Product	Ethyl acetate, %	Alcohol, % <sup>a</sup>	Water, %	Total % found
A	13.0	72.5	2.2	87.7
B	0	87.5	1.5	89.0

<sup>a</sup> Analyses of a known mixture of alcohol and ethyl acetate, containing 85% of the former and 15% of the latter showed that only 85-90% of the alcohol could be recovered as the phenyl urethan, m. p. 52°.

These results show that the products which we obtained were mainly alcohol containing small amounts of water and ethyl acetate. It is our opinion that the failure of the found values to total 100% is due to the limitations of the procedure used for the determination of alcohol.

On the basis of our experiences, we believe that our failure to prepare ketene acetal is traceable to the discrepancy between the results reported by Scheibler and those obtained by us in connection with the formation of the so-called "primary reaction product" from ethyl acetate and sodium ethoxide. The results which we report now confirm our earlier conclusion that there is not only no evidence for, but definite evidence against, the existence of such a reaction product.

LABORATORY OF ORGANIC CHEMISTRY  
UNIVERSITY OF WISCONSIN  
MADISON, WISCONSIN

JOHN M. SNELL  
S. M. McELVAIN

RECEIVED NOVEMBER 12, 1932

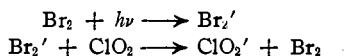
PUBLISHED JANUARY 11, 1933

## BROMINE SENSITIZED PHOTO-DECOMPOSITION OF CHLORINE DIOXIDE

*Sir:*

Chlorine dioxide is decomposed by light with production of  $\text{Cl}_2\text{O}_6$ , light in the blue and ultraviolet being equally effective [Finkelnburg and Schumacher, *Z. physik. Chem.*, Bodenstein Band, 704 (1931); Spinks, *THIS JOURNAL*, 54, 1689 (1932)]. Since the region of predissociation in

$\text{ClO}_2$  does not extend above 3750 Å., it was thought that further investigation would prove interesting. It is found that the quantum efficiency at 4360 Å. is only slightly less than that at 3650 Å.  $\text{ClO}_2$  does not absorb at 5460 Å. and no photoreaction is obtained on isolating  $\text{ClO}_2$  with light of this wave length using a mercury arc and glass filter. On adding a small percentage of bromine a sensitized photoreaction takes place using 5460 Å., the quantum efficiency being practically equal to that at 3650. The equal efficiency of 3650 and 4360 Å. is explicable by the scheme suggested by Schumacher in which predissociation or the activation of  $\text{ClO}_2$  molecules leads eventually to the production of  $1\text{ClO} + 1\text{ClO}_3$  by one quantum of light. Apart from differences in energies of these groups one would expect any chains resulting to be of the same length. The equal quantum efficiency of 5460 Å. could be explained by



and then as before. It would be necessary that practically all the activated bromine molecules should be deactivated only by  $\text{ClO}_2$  molecules under our conditions.

UNIVERSITY OF SASKATCHEWAN  
SASKATOON, SASK., CANADA

J. W. T. SPINKS

RECEIVED DECEMBER 5, 1932

PUBLISHED JANUARY 11, 1933

### ROTATORY DISPERSION IN THE VISIBLE AND THE ULTRAVIOLET RANGE OF CONFIGURATIONALLY CORRELATED CARBINOLS, HALIDES AND ACIDS

Sir:

High precision dispersion measurements in the visible and in the ultraviolet to about 2300 Å. have been made on the following substances, the configurations of which have been correlated by Levene and Marker.

Compounds	Sign of observed rotation in the visible	Sign of contribution of the functional group	Sign of contribution of the rest of the molecule
2-Methylbutanol	+	+	-
1-Bromide-2-methylbutane	-	+	-
1-Iodo-2-methylnonane	-	+	-
$\beta$ -Methyl- <i>n</i> -valeric acid	-	+	-

It may be seen from this table that individual substances of this group vary in the direction of their rotation in the visible. An explanation of the differences in the direction of rotations of the correlated substances has been found by the analysis of their rotatory dispersion curves.

The dispersion curves of all these substances may be expressed by the two-term Drude formula

$$[M] = \frac{a}{\lambda^2 - \lambda_0^2} - \frac{a'}{\lambda^2 - \lambda_0'^2}$$

for rotatory dispersion. In our case the higher  $\lambda_0$  value has a definite physical significance corresponding to a known absorption band (2050 Å. for COOH, 2560 Å. for I in 2-methyl-*n*-nonyl iodide). The contribution of the functional group (first term of above formula) is of opposite sign to the contribution of the rest of the molecule (second term). The direction of the first term is to the right and that of the second is to the left. It follows from this that in the levorotatory substances the sign of the contribution of the first band is opposite to the sign of the rotation of the substance observed in the visible. Thus, the sign of the rotation in the visible of the two halides is opposite to the sign of the contributions of Br and of I, which is contrary to the view expressed by W. Kuhn [*Ber.*, **63**, 191 (1930)], whereas in the secondary halides as well as in 1-bromo-3-methylpentane and in 1-iodo-4-methylhexane the direction of the contribution furnished by the halides determines the direction of the rotation in the visible.

The most striking example of the first band exerting a minor influence on the rotation in the visible is given by  $\beta$ -methyl-*n*-valeric acid. With decreasing wave lengths, the rotation increases slowly, reaches a maximum at 2850 Å., decreases sharply to a zero value at 2450 Å. and increases in the opposite direction for still smaller wave lengths. The molecular rotation in heptane is accurately represented ( $\pm 1\%$ ) by the equation

$$[M]^{25} = + \frac{8.088}{\lambda^2 - 0.042} - \frac{11.68}{\lambda^2 - 0.034}$$

The details of this study as well as the results dealing with the influence of the distance of the functional group on the sign of its contribution will be discussed in full in the near future.

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

P. A. LEVENE  
ALEXANDRE ROTHEN

RECEIVED DECEMBER 7, 1932

PUBLISHED JANUARY 11, 1933

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## AN ABSOLUTE METHOD FOR ESTABLISHING ORIENTATION IN THE FURAN SERIES

*Sir:*

Identification of the simpler substitution products of furan, such as the methylated and halogenated furans, is not readily accomplished on account of the difficulty of obtaining solid derivatives from them. The observation that addition of maleic anhydride to furan and certain substituted furans<sup>1</sup> gives rise to crystalline solids, has led us to investigate this reaction as a general method for the identification of furan derivatives.<sup>2</sup> We have found that addition of maleic anhydride occurs with a variety of substituted

(1) Diels and Alder, *Ber.*, **62**, 554 (1929); Rinkes, *Rec. trav. chim.*, **50**, 1127 (1931).

(2) We are indebted to Professor Diels for his courtesy in permitting us to investigate this application of the maleic anhydride reaction.

furans but is hindered by the presence of certain substituents. Crystalline solids were obtained from 2-bromofuran (m. p. 116°), 3-bromofuran (m. p. 131.5–132°), furfuryl methyl ether (m. p. 97°), furfural diacetate (m. p. 126.5–127°), furfurylacetone (m. p. 86–87°) and several others. We have not succeeded in obtaining addition products from compounds containing a carbethoxyl, cyano, nitro or ethylenic group attached directly to the ring.

A study of the effect of hydrolytic agents upon the addition products (substituted 3,6-endoxo- $\Delta^4$ -tetrahydrophthalic anhydrides) has shown that they can be converted directly into the corresponding phthalic acids (or anhydrides).<sup>3</sup> Since the orientation of the substituents in the resulting phthalic acids (or anhydrides) is known, this transformation constitutes an absolute method for establishing the position of substituents in the furan ring. Thus, the substituted 3,6-endoxo- $\Delta^4$ -tetrahydrophthalic anhydrides from 2-methylfuran, 2- and 3-bromofuran on heating with hydrogen bromide in glacial acetic acid gave, respectively, 3-methylphthalic anhydride (m. p. 111–113°), 3-bromophthalic anhydride (m. p. 134–135°), and 4-bromophthalic anhydride (m. p. 108–110°). We are now engaged in extending the observations reported here.

(3) Diels and Alder [*Ann.*, **490**, 243 (1931)] have shown that the addition product from furan and maleic acid can be converted into phthalic acid by a series of five reactions, involving four intermediate products.

DEPARTMENT OF CHEMISTRY  
CORNELL UNIVERSITY  
ITHACA, N. Y.

M. G. VAN CAMPEN, JR.  
JOHN R. JOHNSON

RECEIVED DECEMBER 9, 1932

PUBLISHED JANUARY 11, 1933

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### VAPOR PRESSURE AND HEAT OF VAPORIZATION OF GRAPHITE

*Sir:*

A large amount of experimental work has been carried out in the past decade to determine the vapor pressure and heat of vaporization of graphite and very discordant values are given in the literature. We have recently investigated this problem, determining vapor pressure from the rate of loss in weight of carbon rings heated by high frequency induction in a vacuum [reported to April, 1932, Meeting, American Philosophical Society]. The interpretation of the results is complicated by the fact that carbon vapor exists in both monatomic and diatomic forms, the relative amounts being determined by the total pressure and the temperature. Vaughan and Kistiakowsky [*Phys. Rev.*, **40**, 457 (1932)] have independently made calculations, using the equations of quantum statistical mechanics, which support this conclusion.

It is possible to reconcile our results in the temperature range 2350–2800°K. with those of Kohn and Gückel [*Z. Physik*, **27**, 305 (1924)] on the vapor pressure of carbon in the arc.

They have taken the value of 4200°K. as the temperature of the positive

crater at 1 atmosphere pressure. This value is due to Benedict [*Ann. Physik*, **49**, 144 (1916)]. The method used by her has been adversely criticized by others and a careful search of the literature shows that this temperature may be 200° too high.

The following values are the heats of reaction for the two processes involved:



The rate of loss in weight in g./sq. cm./sec. as a function of temperature is given by the formula

$$\log m = -\frac{177,000}{4.58T} + 2 \log T + \left(\frac{F^\circ - E_0^\circ}{4.58T}\right)_{\text{graphite}} + 3.174 \quad (3)$$

This equation applies only to the carbon evaporating to form monatomic vapor. In the temperature range 2300–2800°K. this is 92–96% of the total carbon evaporating. The vapor pressure can be calculated from the rate of loss in weight by the equation

$$\log p = \log m + 1/2 \log T - 2.187 \quad (4)$$

where  $p$  is expressed in atmospheres. The equation for the variation of the equilibrium constant of reaction (2) as a function of temperature is

$$\log \frac{(P_c)^2}{(P_{c_2})} = -\frac{150,000}{4.58T} + 3/2 \log T + \log(1 - e^{-2340/T}) + 1.462 \quad (5)$$

When this equation is applied to the results of Kohn and Gückel the following values are calculated for the partial pressures of monatomic carbon vapor

$T$ , °K.	Total pressure	$P_c$ (atm.)	$P_c$ (extrap.)
4200	1	0.21	0.17
4705	5	1.23	1.50

The fourth column gives the values extrapolated by equations (3) and (4) from the results in the temperature range 2350–2800°K. In making the extrapolation it was assumed that the latent heat of fusion of graphite was 8000 cal.

RESEARCH LABORATORY  
GENERAL ELECTRIC COMPANY  
SCHENECTADY, N. Y.

A. L. MARSHALL  
FRANCIS J. NORTON

RECEIVED DECEMBER 9, 1932      PUBLISHED JANUARY 11, 1933

#### A SIMPLE TEST FOR STREAMING IN THE POROUS DIAPHRAGM DIFFUSION CELL

Sir:

The diffusion cell of Northrop and Anson [*J. Gen. Physiol.*, **12**, 543 (1929)] as further standardized by McBain and Liu [THIS JOURNAL, **53**, 59 (1931); see also M. E. Laing McBain, THIS JOURNAL, in press (1933)]



is now widely used in this country and abroad as a highly convenient and accurate method. These authors eliminated bulk streaming of liquid through the sintered glass or other porous membrane by careful leveling of the membrane which separates the denser liquid above from the lighter liquid beneath. Several workers have obtained erratic results when using membranes that were too coarse.

We find that it is simplest to test all cells for streaming by using them once tilted at an angle such as  $30^\circ$ . If the pores are too coarse, the values for diffusion may be increased as much as four-fold as compared with either the same cell used horizontally or with a cell of fine pores. Such cells should be discarded because those with finer pores such as glass sintered membranes "G3" ( $2-5 \times 10^4 \text{ \AA}$ ) are scarcely affected by tilting.

DEPARTMENT OF CHEMISTRY  
STANFORD UNIVERSITY, CALIF.

C. R. DAWSON

RECEIVED DECEMBER 14, 1932

PUBLISHED JANUARY 11, 1933

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#### THE RADIOACTIVITY OF LANTHANUM, NEODYMIUM AND SAMARIUM

*Sir:*

In view of the note in *Nature* [130, 846 (1932)] by Hevesy and Pahl regarding the radioactivity of samarium, we wish to report an independent investigation on this subject. In October of this year we discovered radioactivity in a sample of samarium and since that date we have examined samples of lanthanum and neodymium which are also radioactive.

The method employs the Geiger-Müller counter set-up as described by Libby [*Phys. Rev.*, 42, 440 (1932)]. The salts investigated have been deposited as a thin film on the inside of a glass tube. This is placed around the counter which is in the form of a long wire enclosed in a metal screen cylinder. In a typical run 20 g. of potassium chloride deposited on the tube increased the zero count of 15 per minute to 160.

The activities of the samples of lanthanum and neodymium are not appreciably screened by 0.07 mm. of aluminum, whereas that of samarium is very largely, if not completely, screened, indicating that the activities of the former are mainly of the beta type and that of the latter alpha. We have used two different samples of neodymium, one sulfate and the other oxalate. Both show an activity which is approximately 2.5 times that of potassium per mole. The lanthanum activity per mole is about 8 times that of potassium and the samarium approximately 3 times. A careful examination of a very pure sample of gadolinium sulfate prepared by Professor B. S. Hopkins gave results which are negative to at least 2% per mole of the activity of potassium.

We believe that the radioactivity of these elements is due to the

presence of unstable isotopes, but have not completely eliminated the possibility of actinium as an impurity in the lanthanum and neodymium samples. This point is under investigation.

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF CALIFORNIA  
BERKELEY, CALIFORNIA

W. F. LIBBY  
W. M. LATIMER

RECEIVED DECEMBER 27, 1932

PUBLISHED JANUARY 11, 1933

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## NEW BOOKS

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**A History of Chemistry.** By F. J. MOORE, Ph.D., Late Professor of Chemistry in the Massachusetts Institute of Technology. Second edition. Revision prepared by William T. Hall. McGraw-Hill Book Company, Inc., 370 Seventh Ave., New York, 1931. xxiii + 324 pp. Illustrated. 14.5 × 21 cm. Price, \$3.00.

The revision of this serviceable book has not involved a departure from the general plan of the first edition. The essential change, apart from restatements necessitated by recent discoveries, is the inclusion of biographical sketches of two groups of chemists, *viz.*, (1) brilliant chemists who died during the last twelve years and (2) deceased American chemists who contributed material to the development of chemistry in this country. It is to be regretted that the bibliography at the end of the chapters has not been enlarged, particularly since so many admirable articles on the history of chemistry have appeared during the last ten years in the *Journal of Chemical Education*. The chapter devoted to chemistry in the United States would be more in harmony with the rest of the book, and certainly more useful to American students, if the growth was described as a connected narrative rather than in the form of disconnected biographies. However, the book as revised is an excellent example of books in its field and a faithful expression of the scholarship of the author, whose life as a scientist and as a teacher is briefly recounted in the introductory portion.

LYMAN C. NEWELL

**Elementary Qualitative Analysis for College Students.** By J. H. REEDY, Associate Professor of Chemistry in the University of Illinois. Second edition. The McGraw-Hill Book Co., Inc., 330 West 42d St., New York, 1932. x + 163 pp. 13 figs. 14 × 21 cm. Price, \$1.50.

"The changes consist mainly in the inclusion of new procedures based upon reagents recently developed, and the extension of older methods to more difficult combinations. . . . Practically the whole book has been rewritten. . . . If the book has a distinctive feature, it is the emphasis placed upon interpretative work on the part of the student."

Preliminary experiments, notes, and exercises following each group will convince the student that the reagents and conditions as specified are well planned to separate the ions sharply and to detect them with certainty.

The theoretical treatment is clear and helpful. Greater stress might have been laid upon the fact that the whole of qualitative analysis can be formulated in terms of a very limited number of equilibria, and displacements of the same.

Here and there are statements which could be revised to advantage, and without appearance of pedantry. Thus ionic precipitates (p. 2) appear to be produced from