

tential) and the corresponding  $pH$  value. The equation for this relationship is

$$\text{Log}_{10} E = -0.0633 pH + 0.4080$$

where  $E$  is the absolute potential of the benzaldehyde electrode.

In contrast to the quinhydrone system, the benzaldehyde system is irreversible. The chemical change involved seems to be the reduction of benzaldehyde to benzyl alcohol; hydrions and electrons both being present, a potential with reference to the other half-cell (calomel) is influenced by the  $pH$  of the solution into which the benzaldehyde is stirred.

DEPARTMENT OF CHEMISTRY  
EASTERN TEACHERS COLLEGE  
RICHMOND, KY.

THOS. C. HERNDON

DEPARTMENT OF CHEMISTRY  
GEORGE PEABODY COLLEGE FOR TEACHERS  
NASHVILLE, TENN.

HANOR A. WEBB

RECEIVED AUGUST 2, 1934

#### THE ATOMIC WEIGHT OF PROTACTINIUM

Sir:

Part of the one tenth gram of protactinium oxide, recently isolated by M. S. Agruss and the writer [THIS JOURNAL, 56, 2200 (1934)] has been used for the first direct determination of the atomic weight of protactinium. An x-ray photograph of this material kindly taken by Dr. W. C. Pierce had shown no impurities.

The classical method of M. C. de Marignac [*Ann. chim. phys.* [IV] 9, 250 (1866)] for tantalum was utilized for this determination. Potassium protactinium fluoride ( $K_2PaF_7$ ) was prepared from the oxide. It crystallizes in beautiful colorless sharp long needles, very insoluble in water containing 0.5% of hydrogen fluoride. It is stable in air and can easily be dried to constant weight at 20 or 100°. This was reconverted into the oxide by fuming with sulfuric acid, diluting with water, precipitating with ammonia, filtering the hydroxide, and igniting and weighing as oxide. All operations were carried out in and with platinum equipment. All the chemicals were highly purified. A very sensitive ultra microbalance [K. W. H. Kühlmann, Hamburg, Germany] was used; all weights were corrected to vacuum. Further details will be given in a subsequent paper.

The first preliminary analysis gave 61.18 parts of the oxide and 39.67 parts of potassium sulfate per 100 parts of potassium protactinium fluoride.

Assuming the formula to be  $K_2PaF_7$  and protactinium to have an atomic weight of 231, 61.29 and 39.40 parts, respectively, should have been obtained. This agreement definitely establishes the pentavalency of protactinium and the formula  $Pa_2O_5$  for the oxide.

The two final determinations gave the following results:

$K_2PaF_7$ , g.	$Pa_2O_5$ , g.	$2K_2PaF_7:Pa_2O_5$	At. wt., Pa
0.091907	0.056274	1.6332	230.4
.070047	.042913	1.6323	230.8

For the atomic weights of the other elements the 1934 values of the International Committee were used [G. P. Baxter, Mme. P. Curie, O. Höningsschmid, P. Lebeau and R. J. Meyer, THIS JOURNAL, 56, 753 (1934)].

The mean value of the atomic weight of protactinium is 230.6, or in whole numbers 231, with an accuracy of about  $\pm 0.5$  unit. This value is in complete agreement with F. W. Aston's results on actinium lead ( $AcD = 207$ ), obtained by means of his mass spectrograph.

For a precision atomic weight determination the analysis of the recently discovered  $PaCl_5$  [A. V. Grosse, THIS JOURNAL, 56, 2200 (1934)] will probably be more suitable; however, the latter can be used to its full advantage only when larger quantities of protactinium will be available. Such a determination is planned in the future.

We are much indebted to the management of the Universal Oil Products Co., Chicago, for placing at our disposal the facilities of their Research Laboratories.

KENT CHEMICAL LABORATORY  
UNIVERSITY OF CHICAGO  
CHICAGO, ILL.

A. V. GROSSE

RECEIVED OCTOBER 3, 1934

#### HALOGENATION INHIBITION BY OXYGEN

Sir:

Bauer and Daniels [THIS JOURNAL, 56, 2014 (1934)] present evidence for the inhibition of the halogenation of cinnamic acid by oxygen and in their last paragraph suggest that the influence of oxygen on reactions of this type may be quite general.

In these Laboratories the inhibiting effect of oxygen on certain halogenation reactions has been observed in many instances, and is the subject of patents granted to this Company.

The action is made use of as a means of controlling halogenation. The effect is, in many instances, so great that we find it necessary to distil fractionally any chlorine which is to be used for certain investigations of halogenation for the express purpose of removing traces of oxygen.

In addition to the workers quoted by Bauer and Daniels, others have described the influence of oxygen on halogenation reactions. Luther and Goldberg [*Z. physik. Chem.*, **56**, 43 (1906)] describe the inhibition of substitution of chlorine into benzene, toluene, xylene and acetic acid, and conclude that this is a typical phenomenon of all photochlorination; Pease and Walz [*THIS JOURNAL*, **53**, 3729 (1931)] demonstrated the inhibitory effect of oxygen on the thermal chlorination of methane.

In these Laboratories it has been shown that the chlorination of propane, butane and pentanes is similarly inhibited by oxygen irrespective of whether the chlorination is being catalyzed by

light or by the presence of olefins simultaneously reacting. This last-mentioned catalysis of halogen substitution by a simultaneously occurring addition reaction is also the subject of patents issued to this Company [British Patent 399,991, 1933] but has not yet been otherwise published.

Our experiments have failed to show any inhibition by oxygen of the addition of chlorine to olefinic hydrocarbons such, for example, as beta-butylene, which reaction proceeds rapidly in the dark in the absence of catalysts. In view, however, of the observations of Bauer and Daniels on the bromination of cinnamic acid and Dickinson and Leermakers on the photochlorination of tetrachloroethylene, this may be only a matter of degree. The reaction of beta-butylene with chlorine in darkness is so fast that retardation by oxygen or, conversely, acceleration by light is not easy to detect.

SHELL DEVELOPMENT COMPANY  
EMERYVILLE, CALIFORNIA

R. M. DEANESLY

RECEIVED OCTOBER 22, 1934

## NEW BOOKS

**Bilder zur qualitativen Mikroanalyse anorganischer Stoffe.** (Illustrations for Qualitative Microanalysis of Inorganic Substances.) Collected by W. GEILMANN, Professor at the Technical High School of Hannover. Verlag von Leopold Voss, Salomonstrasse 18 B, Leipzig C 1, Germany, 1934. Text + 240 figs. 16 × 23.5 cm. Price, RM. 8; bound, RM. 9.

This assemblage of photomicrographs of crystalline inorganic salts should prove a valuable reference book to micro-analysts. The 240 photomicrographs (many double) show distinctive forms of one or more salts of nearly all the elements, the magnification varying from 55× to 490×. The photomicrographs are very clear and are remarkably free from the confusion of form often found in this sort of illustration. The text consists of short descriptions of each preparation.

LAWRENCE T. FAIRHALL

**Der Zündvorgang in Gasmischungen.** (The Explosion Process in Gas Mixtures.) By DR.-ING. GEORG JAHN, Berlin. Verlag von R. Oldenbourg, Schliessfach 31, München 1, Germany, 1934. vii + 69 pp. 25 figs. 17 × 25 cm. Price, RM. 6.

This booklet is concerned with the velocity of inflammation (flame speed) and the factors which govern the propagation of flame in space. The author attempts to show the validity of the equation for the velocity derived

thermodynamically by Nusselt [*Z. Ver. Deutscher Ingenieure*, **59**, 872 (1915)] by comparing it with velocities determined experimentally by the Bunsen burner cone method. There is no mention of the identical theories of Jouguet [*Compt. rend.*, **156**, 872 (1913); **179**, 454 (1924)] and Daniell [*Proc. Roy. Soc. (London)*, **A126**, 393 (1930)]. All three theories are based on the same fundamentals, namely, that the gas to be burned must be raised to its ignition temperature before combustion ensues and that this rise in temperature is accomplished by the process of heat conduction from the burned gas. The only difference between the three theories lies in the assumption regarding the rate of liberation of thermal energy due to chemical reaction along the *x*-axis between the boundaries of the flame front, that is, from unburned phase to burned phase. While no experimental basis exists for any of the assumptions made, Nusselt arbitrarily assumed that equal amounts of heat are released in unit lengths of the *x*-axis.

In accepting Nusselt's ideas Jahn recognizes the insufficiency of expressing the rate of chemical reaction by the simple mass law and no attempt is made to treat the chemical reactions kinetically. Assuming that the intermediate reactions introduce a factor which is constant throughout the explosive mixture concentration range, he groups everything but the mass law expression for the rate into a single constant which is determined from an experimental flame velocity measurement. The constant having been so determined the agreement between the calculated