The authors wish to thank Dr. Guy W. Clark and Dr. Merton C. Lockhart of Lederle Laboratory for help in large scale preparation, and the Milton and Proctor funds of Harvard University and the Rockefeller Foundation for financial assistance.

Department of Biochemistry
Harvard Medical School
Boston, Mass.
Department of Physiology
Duke Medical School
Durham, N. C.

Received March 29, 1938

COMMUNICATIONS TO THE EDITOR

COMPARISON OF X-RAY PHOTOGRAPHS TAKEN WITH X AND Y BUILT-UP FILMS

Sir:

Some time ago Mr. Clifford Holley and I reported [*Phys. Rev.*, **52,** 525 (1937)] that X films of calcium stearate have approximately the same grating-space as Y films of barium–copper stearate. In Figs. 1 and 2 are shown some of the photographs taken with films built by Dr. Katharine Blodgett on the basis of which this statement was made. They show Lα and Lβ lines of tungsten in the first three observable orders on both sides of the direct beam. Figure 1 was taken with an 1100 layer Y film of barium–copper stearate, Fig. 2 with a 300 layer X film of calcium stearate. In both cases the direction of dipping was parallel to the axis of rotation of the film. It can be seen that the photograph taken with the X film is essentially the same as the one taken with the Y film with respect to both the grating-space and the relative intensities of the various orders. The grating-spaces of these films, corrected for refraction and based upon the ruled grating wave length scale, are: Y film of barium–copper stearate, 50.47 Å.; X film of calcium stearate, 50.12 Å.

Porter and Wyman have shown [This Journal, **59,** 2746 (1937)] that the contact potentials of X films increase with the number of layers, whereas those for Y films remain constant. The X-ray photographs, however, seem to be independent of the contact potential. The potentials of an X and a Y film of calcium stearate were measured, after which photographs of the kind shown here were taken. The photographs were much the same as those shown, despite the difference in the contact potentials of the films before exposure. The apparent grating-spaces of the two films in the first order differed by about 1%, the X film having the greater spacing. The two films were built from 10^{-4} molar solutions of calcium chloride. Castor oil was used as piston oil for the X film, and oleic acid for the Y film.

Fig. 1.—Three orders of tungsten L-spectra from Y film.

Fig. 2.—Three orders of tungsten L-spectra from X film.

Ryerson Physical Laboratory
University of Chicago
Chicago, Illinois
Seymour Bernstein

Received April 22, 1938

PRESSURE–AREA RELATIONS OF MONOLAYERS AT THE SOLID–LIQUID INTERFACE

Sir:

While the pressure $F = \gamma - \gamma'$ of a monolayer on water may be determined by a film balance, no method has been known for obtaining F at a solid–liquid interface. In order to determine this value the contact angle θ_1 between the plane surface of the solid and the pure liquid is found by an improved form of the tilting plate method, so arranged that the surface of the liquid can be kept clean by sweeping. Then the pure liquid of surface tension γ_l, *e. g.*, water, is replaced by a solution of the desired solute, of tension $\gamma_{l'}$ and the new contact angle θ_2 is determined. Then

$$\gamma_s = \gamma_{sl} - \gamma_l \cos \theta_1 \quad (1)$$

$$\gamma_s' = \gamma_{sl}' - \gamma_{l'} \cos \theta_2 \quad (2)$$

where s indicates a solid.

Tests seem to indicate that the contamination of the interface solid–vapor with the solute can often be made so small that $\gamma_s = \gamma_{s'}$ so in this case (1) − (2) gives $\gamma_{s1} - \gamma_{s1'} = F = \gamma_1 \cos \theta_1 - \gamma_{1'} \cos \theta_2$ where the quantities in the right hand term can be measured. Now since

$$\left(\frac{\partial F}{\partial a}\right)_T = -\left(\frac{\partial \gamma'}{\partial a}\right)_T$$

where a is the activity of the solute, the adsorption may be obtained by the equation of Gibbs. This gives the area a per molecule adsorbed. The area A, which refers to the total number of molecules of solute in the monolayer, is slightly less than a, since some molecules are already present.

Of the measurements made thus far, only those in which butyl alcohol is a solute are cited here. The relations are given in Fig. 1 for films of this substance at (1) the water–vapor, (2) the water–solid paraffin, and (3) the water–stibnite interface.

For a film which acts as a perfect gas $FA/kT = 1$. Since at a film pressure of 40 dynes per cm. the pressure per sq. cm. is of the order of 700 atmospheres, high pressures are involved.

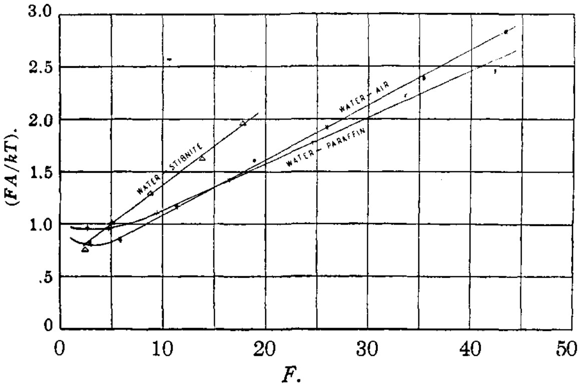

Fig. 1.—Pressure-area relations of films at the solid-liquid interface.

Obviously from Fig. 1 the films are gaseous at low pressures. If solid or liquid at high pressures there should be a vertical drop in the curve for the transition region, and then an ascending straight line which extrapolates through the origin. Thus, even though these monolayers are adsorbed on a solid they are nevertheless gaseous. Acetic acid films between water and solid paraffin are also gaseous.

George Herbert Jones Laboratory
University of Chicago
Chicago, Ill.
William D. Harkins
Frederick M. Fowkes

Received April 22, 1938

STEROLS. XXXIV. THE ISOLATION OF HEXAHYDRO-OESTRADIOLS FROM HUMAN NON-PREGNANCY URINE

Sir:

While no investigations of the steroid content of non-pregnant female urine have been reported, it is known that very little oestrogenic material is present [Loewe and Lange, *Klin. Wochschr.*, **5**, 1038 (1926)]. We have now isolated from this source, after removal of a small amount of pregnanediol, two isomeric diols, $C_{18}H_{30}O_2$, the more insoluble melting at 242° and giving a good depression in melting point with pregnanediol and *allo*-pregnanediol. *Anal.* Calcd. for $C_{18}H_{30}O_2$: C, 77.6; H, 10.9. Found: C, 77.4; H, 10.8. The diacetate melted at 160°. *Anal.* Calcd. for $C_{22}H_{34}O_4$: C, 72.9; H, 9.5. Found: C, 73.2; H, 9.7. The second isomer melted at 204°. *Anal.* Calcd. for $C_{18}H_{30}O_2$: C, 77.6; H, 10.9. Found: C, 77.6; H, 10.8. It gave a diacetate melting at 160°, which gave a good depression in melting point with the first diacetate. *Anal.* Calcd. for $C_{22}H_{34}O_4$: C, 72.9; H, 9.5. Found: C, 72.8; H, 9.5. These compounds are present in non-pregnancy human urine, but they do not appear present in pregnancy urine for their easy mode of isolation makes it extremely unlikely that they would have been overlooked in our extensive investigation of the steroid content of this material. Both diols are hexahydro-oestradiols, for they yield equilenin on heating with platinum black. Furthermore, the less abundant lower melting and more soluble isomer is identical with a diol obtained by the catalytic hydrogenation of oestrone according to the method of Dirscherl [*Z. physiol. Chem.*, **239**, 53 (1936)]. This latter diol yields a diketone m. p. 148° (*Anal.* Calcd. for $C_{18}H_{26}O_2$: C, 78.8; H, 9.5. Found: C, 79.0; H, 9.6), different from the diketone m. p. 124° (*Anal.* Calcd. for $C_{18}H_{26}O_2$: C, 78.8; H, 9.5. Found: C, 79.2; H, 9.8) obtained from the diol, m. p. 242°, so the two carbinols must be stereoisomers, differing at least in regard to the configuration at C-5 or C-10. Neither diol is precipitated by digitonin, and both are saturated to bromine.

Since these diols, which evidently arise from the biochemical reduction of oestrone, are not present in pregnancy urine, their presence in non-pregnancy urine indicates that they are not merely enzymatic reduction products, but are associated with the use of oestrone when it functions as a hormone, arising from the latter by reductive processes as do the various carbinols and ketones, from progesterone and androstenedione [Marker, THIS JOURNAL, in press (1938)]. The details of this work will be published in a forthcoming issue of THIS JOURNAL.

We wish to thank Dr. Oliver Kamm and Parke, Davis and Company for their generous help and assistance in various phases of this work.

SCHOOL OF CHEMISTRY AND PHYSICS
PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PENNA.
RUSSELL E. MARKER
EWALD ROHRMANN
EUGENE L. WITTLE
ELMER J. LAWSON

RECEIVED MAY 21, 1938

KINETICS OF THE EXPLOSIVE REACTION BETWEEN HYDROGEN AND OXYGEN SENSITIZED BY NITROGEN PEROXIDE

Sir:

In a recent paper, von Elbe and Lewis [THIS JOURNAL, **59**, 2022 (1937)] propose a scheme of reactions for the above process, having concluded that "the evidence rules out a mechanism based on oxygen atoms." In arriving at this conclusion these authors did not discuss the relevant work of Norrish and Griffiths [*Proc. Roy. Soc.* (London), **A139**, 147 (1933)], and of Foord and Norrish [*ibid.*, **A152**, 196 (1935)] in which new evidence based on the study of the induction period and the effect of irradiation by light is presented.

Without dogmatizing about the precise nature of the chain mechanism we concluded in the light of the new facts that a mechanism involving oxygen atoms is by no means excluded. Such a scheme is indeed capable of giving a fair description of the facts and no other scheme has yet been advanced which has been shown to take our new facts into consideration.

LABORATORY OF PHYSICAL CHEMISTRY
UNIVERSITY OF CAMBRIDGE
CAMBRIDGE, ENGLAND
R. J. W. NORRISH

RECEIVED APRIL 20, 1938

EFFECT OF X-RAYS ON SURFACE POTENTIALS OF MULTILAYERS

Sir:

Porter and Wyman [THIS JOURNAL, **60**, 1083 (1938)] have reported that stearate X- or Y-films on grounded metal plates acquire negative potentials when exposed to x-rays.

We have produced charges on both X- and Y-multilayers in many different ways, measuring the potentials by the vibrating-plate method and with a polonium–air electrode. This work suggests that the ionized air and the electric field near the x-ray tube are responsible for the charge on the film.

We confirm Porter and Wyman's observation that a self-rectifying x-ray tube in air, operating on 60 kv., a. c., charges the films a few volts negatively even when either tube terminal is grounded. However, if an oil-immersed shockproof x-ray tube is used or if the metal plate is enclosed in a thin aluminum box, a 10-minute exposure, with the same x-ray dosage (28 roentgens), has no effect on the film potential.

Multilayer films exposed to x-rays from a tube in air, operated on 60 kv., d. c., acquire large potentials (10 volts on only 21 layers). The film becomes positively charged if it is at cathode potential and negatively charged if at anode potential, regardless of which terminal is grounded.

When there are high voltage terminals in air, the ionization of the air by x-rays permits a current to flow which can charge the film. We have found that with 60 kv., a. c., applied to a tube in air with its cathode cold so that no x-rays are generated, the films do not become charged. If, however, a pointed wire is attached to the anode terminal so that a corona discharge occurs, the plate becomes negatively charged although there are no x-rays.

A charged film on a grounded plate can be discharged in a few minutes if a grounded polonium electrode is brought close to its surface. Undoubtedly x-rays would discharge a charged film in an aluminum box if x-ray dosages of more than 100 roentgen units were used.

RESEARCH LABORATORY
GENERAL ELECTRIC CO.
SCHENECTADY, NEW YORK
F. J. NORTON
I. LANGMUIR

RECEIVED MAY 24, 1938

THE RELATION BETWEEN RATES OF GENERAL BASIC CATALYSIS IN DIFFERENT REACTIONS

Sir:

It is a well-known characteristic of reactions which are susceptible to general catalysis by bases in the Brönsted sense that the logarithmic plot of catalytic constants k_B against corresponding basic association constants K_B yields several straight lines corresponding to the various charge types, rather than one single straight line.[1] Furthermore, certain substitutions on or near the re-

---

[1] Kilpatrick and Kilpatrick, *Chem. Rev.*, **10**, 213 (1932); Pedersen, *J. Phys. Chem.*, **38**, 581 (1934).

acting center of the base also cause deviations even within a series of the same charge type.[3]

In view of these facts, extreme interest attaches to the accompanying figure, in which catalytic constants[4,7] for the mutarotation of glucose at 18° are plotted logarithmically against the corresponding catalytic constants[2,3,5,6] for the decomposition of nitramide at 15°, both in aqueous solution. The figure includes all the bases whose behavior in both reactions has been studied. No statistical corrections are made. The straight line has a slope of 2.00.

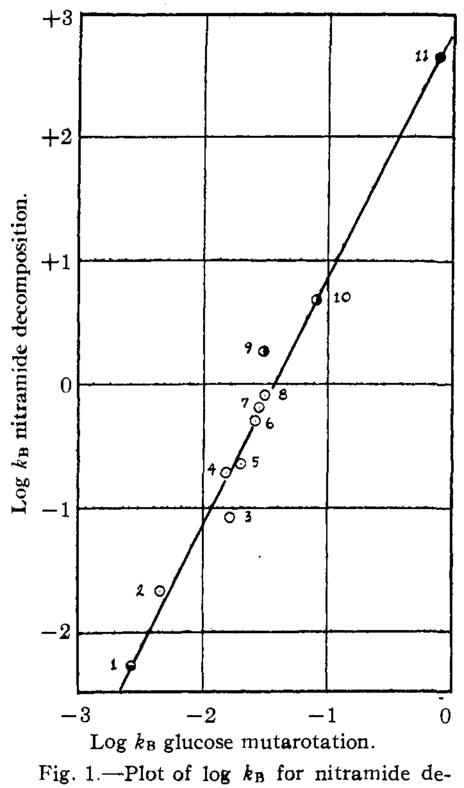

Fig. 1.—Plot of log k_B for nitramide decomposition against log k_B for glucose mutarotation: 1, betaine[2,7]; 2, salicylate[6,4]; 3, formate[3,4]; 4, benzoate[3,4]; 5, phenylacetate[3,4]; 6, acetate[3,4]; 7, propionate[3,4]; 8, trimethylacetate[6,4]; 9, quinoline[2,7]; 10, pyridine[2,4]; 11, Co$(NH_3)_5$-OH^{++}[5,4].

It is immediately apparent that all the points fall reasonably well on the same straight line and that betaine, pyridine, quinoline and even Co$(NH_3)_5OH^{++}$ follow the same relationship which holds for the negative bases such as acetate ion. This is particularly startling in the case of Co$(NH_3)_5OH^{++}$, which in the familiar k_B *vs.* K_B plot deviates from the carboxylate ion curve by as much as two logarithmic units.

It is therefore highly desirable that knowledge of these and other reactions susceptible to general base catalysis be extended to include more bases in common. If the uniqueness of Fig. 1 is upheld by further extension of the data, it implies that the relationship between two series of rate constants for association by bases of protons from two different substrates is more fundamental than the relationship of either series of rate constants to corresponding equilibrium constants. It follows further that deviations which occur in the k_B *vs.* K_B relationships must originate in deviations in the relationships between the rate constants for association and dissociation; this also can be submitted to experimental study.

In its amenability to experimental attack, such an empirical approach differs from the theoretical approach embodied in the transition-state method which assumes the fundamental relationship to be between equilibrium constants and then attempts to derive the connection between rate and equilibrium constants by postulating an equilibrium between initial and transition states, the constant for which can unfortunately not be measured.[8]

---

(2) Work to be published by the writer.

(3) Brönsted and Pedersen, *Z. physik. Chem.*, **108**, 185 (1924).

(4) Brönsted and Guggenheim, THIS JOURNAL, **49**, 2554 (1927).

(5) Brönsted and Volqvartz, *Z. physik. Chem.*, **A155**, 211 (1931).

(6) Baughan and Bell, *Proc. Roy. Soc.* (London), **158A**, 464 (1937).

(7) Westheimer, *J. Org. Chem.*, **2**, 431 (1937).

(8) See symposium in *Trans. Faraday Soc.*, **34**, 29ff. (1938).

SLATERSVILLE, R. I. HELMUTH L. PFLUGER

RECEIVED APRIL 25, 1938

INFLUENCE OF NICOTINIC ACID ON THE FERMENTATION METHOD FOR VITAMIN B_1 DETERMINATION

Sir:

Lohmann and Schuster[1] have shown that a vitamin B_1 pyrophosphate is identical with cocarboxylase. This coenzyme plays an essential part in the series of reactions which produce alcoholic fermentation and, in all probability, was present in the original Harden and Young extracts of cozymase. With regard to our fermentation method for vitamin B_1 determination,[2] it has been our working hypothesis that vitamin B_1, or the aminopyrimidine, is taken inside the

---

(1) K. Lohmann and Ph. Schuster, *Biochem. Z.*, **294**, 188 (1937).

(2) A. S. Schultz, L. Atkin and C. N. Frey, THIS JOURNAL, **59**, (a) 948, (b) 2457 (1937).

living cell and there transformed to cocarboxylase or its equivalent. We have considered the possibility that other substances might, on diffusion into the cell, be likewise converted into one of the elements of cozymase, *i. e.*, codehydrase, cophosphorylase or cocarboxylase. Adenylic acid, which is considered to be equivalent to cophosphorylase and which is contained in codehydrase, has been tested and found to be without action. Nicotinic acid which is present in the codehydrase molecule as the amide shows a certain stimulation.

TABLE I

Addition	Ml. gas per 3 hrs. (3 tests)			Av. diff. due to nicotinic acid	Possible error in a vit. B_1 assay
None (standard control mixture)	220	222	220		
1 mg. nicotinic acid	222	224	224	+2	
2 gamma vitamin B_1	296	295	300		
2 gamma vitamin B_1 plus 1 mg. nicotinic acid	306	308	305	+9	15%
4 gamma vitamin B_1	355	353	359		
4 gamma vitamin B_1 plus 1 mg. nicotinic acid	360	368	362	+7	7%

Table I shows how the effect was measured. The absolute values obtained cannot be compared with our previous data[2] but it will be observed that $\Delta_{4\gamma-0\gamma}$ and $\Delta_{4\gamma-2\gamma}$ correspond reasonably well. This is not at all surprising since relatively small variations in the vitamin and moisture content of the compressed yeast used will affect the rate of gas production of the controls. A single pair of measurements, either zero and 4 gamma or 2 and 4 gamma, wlll automatically correct for these variations, and from then on the same pound of yeast may be used until it is exhausted, with no more than a single control (2 or 4 gamma) in each run.

Increasing amounts of nicotinic acid up to 50 mg. did not show an increased effect. The amide of nicotinic acid was tested but did not show any greater activity. The effect of nicotinic acid though small is significant and the resulting possible error in a vitamin assay should be eliminated if possible. This is readily done by including nicotinic acid in all tests. Since large amounts show no further stimulation the addition of 1 mg. of nicotinic acid removes the possible source of error. The negligible effect of added nicotinic acid on the blank determination is interesting and may account for the general failure to observe this effect heretofore. Following our work on vitamin B_1 as a bios factor,[3] we tested nicotinic acid for bios activity but up to the present we have obtained no positive results.

THE FLEISCHMANN LABORATORIES
STANDARD BRANDS INCORPORATED
810 GRAND CONCOURSE
NEW YORK, N. Y.

A. S. SCHULTZ
L. ATKIN
C. N. FREY

RECEIVED APRIL 20, 1938

---

[3] A. S. Schultz, L. Atkin and C. N. Frey, THIS JOURNAL, **60**, 490 (1938).

RESTRICTED INTERNAL ROTATION IN HYDROCARBONS

Sir:

In the short time since we presented the first definite conclusion[1] in favor of the existence of a high potential restricting the internal rotation in ethane, considerable discussion and additional evidence[2] have appeared in the literature. Most recently Kistiakowsky and Wilson[2g] have satisfactorily summarized the general situation; however, certain of their statements appear to be misleading, particularly in view of new evidence obtained in this Laboratory.

A general though approximate method for conveniently relating thermodynamic functions and potential barriers for various molecules has been given.[2b] It of course should be realized that restricting potentials calculated by this method have exact meaning only in connection with the assumed shape of potential barrier. This, however, detracts little from their usefulness in correlating a large amount of thermodynamic data because the same assumed shape of potential barrier will have been used throughout. Indeed, such a correlation of the various thermodynamic data as yet available was made, which showed the general applicability and correctness of accurate entropies obtained through the third law of thermodynamics. Kistiakowsky and Wilson, however, assert that the selection of the magnitude of some of the potentials was "arbitrary" and that "without the knowledge of the laws of force responsible for the hindrance of internal rotation" calculations such as these are "rather meaningless. . . ." It is of course true that in a few cases potential barriers were estimated; however, the only assumption made was the almost axiomatic one that the restriction of rotation about a given C—C bond is related to the position and character of the groups

---

[1] Kemp and Pitzer, *J. Chem. Physics*, **4**, 749 (1936); THIS JOURNAL, **59**, 276 (1937).

[2] (a) Howard, *Phys. Rev.*, **51**, 53 (1937); *J. Chem. Physics*, **5**, 442, 451 (1937); (b) Pitzer, *ibid.*, **5**, 469, 473 (1937); (c) Bartholome and Karwill, *Naturwiss.*, **25**, 476 (1937); (d) Aston, Siller and Messerly, THIS JOURNAL, **59**, 1743 (1937); (e) Kassel, *ibid.*, **59**, 2745 (1937); (f) Kistiakowsky and Nazmi, *J. Chem. Physics*, **6**, 18 (1938); (g) Kistiakowsky and Wilson, THIS JOURNAL, **60**, 494 (1938).

attached to these carbon atoms. A recent "third law" investigation of the entropy of propane[3] has demonstrated the reliability of the potential estimated for this molecule. The value of the entropy at the boiling point calculated using the estimated barrier agrees with the observed value within 0.2 cal. per deg. per mole. It might also be pointed out that the evidence cited by Kistiakowsky and Wilson showing a lower potential barrier for the 2-butenes than for ethane really supports the calculations in question since the barriers used are quite in accord with these data.

The determination of most of these potential barriers was not "arbitrary" but based upon experimental thermodynamic data in conjunction with the method of calculation mentioned above. As a result the uncertainties in using this method of calculation depend not on a detailed understanding of "the laws of force responsible for the hindrance of internal rotation" but rather upon the accuracy of the thermodynamic and molecular structure data employed.

CHEMICAL LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA
KENNETH S. PITZER
J. D. KEMP

RECEIVED FEBRUARY 21, 1938

---

[3] Kemp and Egan, to be published.

NEW BOOKS

Calculations in Quantitative Chemical Analysis. Second edition. By JOHN A. WILKINSON, Ph.D., Professor of Analytical and Inorganic Chemistry at Iowa State College. McGraw-Hill Book Company, Inc., 330 West 42d St., New York, N. Y., 1938. x + 154 pp. 14.5 × 21 cm. Price, $1.75.

Weakness in the calculations of arithmetic and algebra afflicts a large proportion of any elementary chemistry class, and is far from rare among those who reach Quantitative Analysis. This solid little book should be of great assistance to such troubled students. Its twenty-three chapters furnish clear and logical discussions of principles, well-chosen and worked out illustrative examples, and numerous problems of varied types: on chemical formulas and equations, factors, indirect analysis, percentages of constituents sought, analytical errors in gravimetric analysis, as well as on volumetric calibrations, standardizations of solutions, acidimetry, precipitation titrations, differential and oxidation–reduction titrations, and the calculation of volumetric results.

As stated in the Preface, changes from the first edition appear chiefly in the chapter on "Calculations from Equations," in the revision and rewording of many of the problems, the use of ml. instead of the older cc., and the recalculations necessitated by the atomic weight changes of the last ten years.

ALLEN D. BLISS

The Retardation of Chemical Reactions. By KENNETH C. BAILEY, Sc.D., Litt.D., F.I.C., Professor of Physical Chemistry in the University of Dublin. Edward Arnold and Co.: Longmans, Green and Company, 114 Fifth Avenue, New York, N. Y., 1937. viii + 479 pp. 15.5 × 23.5 cm. Price, $8.00.

A feature of this book is the eighty-seven page bibliography, with cross references to related investigations and to the discussions in the text. It is evident from the titles of the articles that this compilation could not be made by an investigator merely by consulting such headings as retardation or negative catalysis in abstract journals.

The author states in the preface: "The order of the chapters has been decided by types of reaction. An arrangement according to mechanisms of retardation would be more logical, but is scarcely possible in the present state of our knowledge." In the book many instances are noted in which the experimental results are incomplete or even contradictory.

Two-thirds of the text is devoted to reactions of oxygen with various substances, and the discussion is not restricted to retardations. The types of oxygen reactions are as follows: reactions with phosphorus and hydrogen Chapters 3, 4 and 6; with hydrocarbons or other substances in the gaseous phase, two chapters; with solutions or liquids, six chapters; and with solids, one chapter. Anti-knock compounds, the protection of rubber, and the prevention of metallic corrosion are discussed in the next three chapters. In some of the remaining chapters, which deal with other types of reaction, oxygen appears in the role of an inhibitor, *e. g.*, in the reaction of hydrogen with chlorine or bromine.

The development of the idea of chain reactions is traced in Chapter 5, and in the later discussions many of the reactions involving oxygen are cited as examples.

The interruption of reaction chains is, of course, not a universal explanation for all retardations. Some of the other theories discussed and illustrated by the author are: destruction or activation of positive catalysts, action at solid surfaces, action at liquid surfaces, the conduction away of heat, and the absorption of light or radiation.

Each topic is treated historically. In discussions of negative catalysis considerable space is given to early theories which assumed the regeneration of the inhibitor in a homogeneous medium. The author rejects this type of