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.

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RECEIVED APRIL 20, 1938

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[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

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[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.

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(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