COMMUNICATIONS TO THE EDITOR

TWO NEW METHODS FOR THE DIRECT MEASUREMENT OF THE ABSOLUTE AMOUNT OF ADSORPTION IN LIQUID SURFACES

Sir:

Since sorption on moving surfaces has been found in this Laboratory to bear no relation to the Gibbs theorem, or to the requirements for monomolecular films, but to be wholly dependent upon the conditions of the experiment, no adequate determinations have been made of the amount of adsorption of really soluble substances except with the elaborate and extremely exacting microtome method of McBain and Humphreys,[1] [*J. Phys. Chem.*, **36**, 300 (1032)], which has been continually under test during the past five years. We have therefore developed two simple alternative methods which can be very inexpensively constructed, but which depend upon the availability of a Hilger Raleigh Interferometer, preferably with one meter path as used for gases. We have made the cells with ordinary plate glass and paraffin, but metal is preferable for cleaning purposes.

Both methods depend upon the destruction of a known area of previously motionless surface by means of a moving barrier, and the measurement of the concentration of the resulting liquid, which was formerly partly bulk and partly surface, by means of the interferometer. Both methods are applicable to any solutions whatsoever and may be adapted to liquid–liquid interfaces. In the first ("compressed surface"), the liquid is spread out thin (0.5 mm. deep), after repeated cleaning by sweeping in an enclosed cell. It is then pushed together by the movable barrier which is provided with leak proof end connections as in a Pockels–Langmuir–Adam trough. In the second ("submerged surface"), the liquid is pushed into a rectangular well, past baffles which allow the previous contents of the well to flow up behind the barrier. We have combined both methods in one cell, obtaining three sets of interference bands above each other which may be photographed for record or measurement. Use of a cell 40 to 100 cm. in length (10 cm. broad) instead of the usual 1-cm. path of light increases the accuracy of the analysis in direct proportion, making it of the order of 1 part in 10^7 or even 10^8. With a solution containing 1.5 of β-phenylpropionic acid in one liter, the first method gives 5.6 $\times 10^{-8}$ g. per square cm., the second 5.3 as compared with the microtome 5.1 $\times 10^{-8}$, and Gibbs' calculated value 5.2 $\times 10^{-8}$. The progress of the adsorption with time is readily followed, and the adsorbed material accumulates in the surface until the surface is many (twelve) hours old. Yet another successful method of less generality, needing no interferometer, will shortly be communicated in detail.

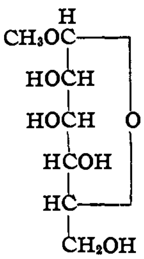
DEPARTMENT OF CHEMISTRY
STANFORD UNIV., CALIF.
T. F. FORD
J. W. MCBAIN

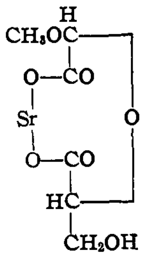
RECEIVED DECEMBER 18, 1935

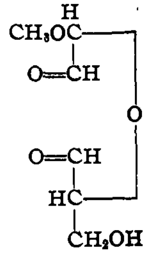
THE OXIDATION OF ALPHA-METHYL *d*-MANNOPYRANOSIDE[1]

Sir:

By the oxidation of alpha-methyl *d*-mannopyranoside in aqueous solution with barium hypobromite a dibasic acid has been produced, the neutral strontium salt of which has been isolated in pure crystalline condition ($[\alpha]^{20}_{D}$ −53.0° in water) in a yield of about 20%. Analyses for strontium, carbon, hydrogen and methoxyl show the empirical formula to be $C_6H_8O_7Sr$. Exact removal of the strontium by sulfuric acid yields an aqueous solution of the organic acid, which does not reduce Fehling's solution. When an aqueous solution of the acid is heated it becomes reducing through hydrolysis. Oxidation of the hydrolyzed acid with bromine water gives good yields of oxalic and *d*-glyceric acids (the latter identified as calcium *d*-glycerate). The structure and configuration of the strontium salt are evi-


(I)


(II)


(III)

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[1] Publication authorized by the Surgeon General, U. S. Public Health Service.

dently limited to formula (II); the oxidation of alpha-methyl *d*-mannopyranoside (I) by hypobromite removes carbon atom 3 and oxidizes carbons 2 and 4 to carboxyl groups.

This unusual type of oxidation is that which has been postulated recently by Hérissey, Fleury and Joly [*J. pharm. chim.* [8] **20,** 149 (1934); *cf.* Malaprade, *Bull. soc. chim.* [4] **43,** 683 (1928); *ibid.* [5] **1,** 833 (1934); Karrer and Pfaehler, *Helv. Chim. Acta,* **17,** 766 (1934)] to account for the analytical data which they obtained in the oxidation of various methyl aldohexosides by periodic acid, with the difference that carbons 2 and 4 are oxidized by this reagent only to the aldehyde group (formula III). To test the matter we have oxidized alpha-methyl *d*-mannopyranoside with periodic acid, followed by an oxidation of the assumed dialdehyde (III) with bromine water in the presence of strontium carbonate; the above mentioned strontium salt (II) was obtained readily in a yield of about 65%. Inspection of the formulas shows that this strontium salt should be expected from all the alpha-methyl *d*-aldohexopyranosides; we have obtained it from alpha-methyl *d*-glucoside by oxidation with periodic acid, followed by bromine water, with the same yield as reported for the mannoside. The work is being extended.[2]

(2) One of us (C. S. H.) has expressed the view [THIS JOURNAL, **52,** 1680 (1930)] that alpha-methyl mannoside ($[\alpha]_D$ +79°) possesses a 1,4-ring. Subsequent criticisms of this view, especially by Haworth, Hirst and their collaborators [Haworth and Hirst, *J. Chem. Soc.,* 2615 (1930), *et seq.*] have shown that it is not tenable and that the 1,5-ring structure pertains to the substance. The properties of the strontium salt herewith reported (particularly the presence of *d*-glyceric acid in its structure) also show that the 1,4-ring cannot be present in the mannoside and limit the ring to position 1,5 or 1,6; well-known evidence, which need not here be discussed, excludes the 1,6 ring.

NATIONAL INSTITUTE OF HEALTH ERNEST L. JACKSON
WASHINGTON, D. C. C. S. HUDSON

RECEIVED JANUARY 20, 1936

A NEW SYNTHESIS OF N-PHENYLPIPERAZINO-N'-BETA-ETHANOL

Sir:

N-Phenylpiperazino-N'-beta-ethanol has been synthesized previously by two methods. Prelog and Blazek [*Coll. Czechoslov. Chem. Comm.,* **6,** 549 (1934)] prepared it by the action of ethylene oxide on N-monophenylpiperazine; while D. E. Adelson and C. B. Pollard [THIS JOURNAL, **57,** 1430 (1935)] prepared it by the reduction of N-phenylpiperazino-N'-ethyl acetate. The former report a melting point of 91°; the latter, 83°.

The writer has now prepared this compound by the condensation of triethanolamine with aniline in the presence of concentrated sulfuric acid as dehydrating agent.

The amines are mixed in molecular proportions and the acid slowly added, the mixture being mechanically stirred and gently heated at the same time. With a charge of 80 g. of triethanolamine, 60 g. of acid was used. After addition of the acid is completed, the mixture is boiled gently under a reflux condenser for six to eight hours. On cooling, the mixture sets to a brown gummy mass. The free base is liberated by means of a concentrated sodium hydroxide solution and the dark brown viscous oil is fractionated under vacuum, b. p. 171–175° (uncorr.) at 1 mm. (uncorr.). The almost colorless oil solidifies to a white crystalline mass in the receiver. Recrystallizations from ethyl ether gave pure white needles, melting sharply at 84° (corr.). Analysis for nitrogen gave: calcd. N, 13.59; found, N, 13.46.

This work is being continued.

DEPARTMENT OF CHEMISTRY CHESTER B. KREMER
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NEW YORK, N. Y.

RECEIVED DECEMBER 27, 1935

REVERSIBLE ADSORPTION IN THE SURFACE OF SOAP SOLUTIONS

Sir:

Many substances greatly lower the surface tension of water in dilute solution but the surface tension then passes through a minimum and rises again with increasing concentration. This appears almost inexplicable from the standpoint of the Gibbs adsorption theorem, $\Gamma = d\sigma/d\mu$ or $-\frac{a}{RT} \times \frac{d\sigma}{da}$ or, approximately, $-\frac{c}{RT} \times \frac{d\sigma}{dc}$, which predicts a large amount of adsorption in the free surface of the dilute solutions, followed by no adsorption at the minimum where the slope is horizontal, followed by negative adsorption for all the higher concentrations. In other words, where the surface tension is most greatly lowered there is no adsorption to cause the lowering, and where the surface tension is still low the surface-active material is supposed to be relatively absent from the surface. True, most authors have plotted surface tension against concentration, instead of using the accurate thermodynamic formula based upon chemical potential or activity. This, however, affords no relief from the dilemma because for any solution capable of stable existence, concentration and activity must be identical in sign. Furthermore, the activity is definitely that pertaining to the bulk of the homogeneous liquid. The presence or absence of colloid likewise makes no difference to the thermodynamic formulation.

Hence the suggestion has been made that surface tensions recorded in the literature for such materials as soaps and soap-like alkyl sulfuric acids have not referred to reversible surfaces and the observed minima might be explained away as due to partly irreversible adsorption. This we have tested in a new application of the Adam trough, the soap solution being, of course, on both sides of the barrier. With clean water, there is a momentary disturbance of the balance as the surface on one side is greatly enlarged or diminished but the original null point is immediately regained. Potassium laurate solutions of concentrations 6, 8, 10, 15 and 30 g. per liter behave just like water. On the other hand, the dilute solutions before the minimum require longer and longer time before equilibrium is restored, the times ranging from two seconds to forty minutes. Hence all the surfaces are in fact reversible, and some other way out of the difficulty remains to be proposed.

These and cognate studies in which it is shown that very many hours are required to complete the adsorption even of simple substances in the surface of their solutions appear to render suspect nearly all determinations of surface tension recorded in the literature for two reasons: (a) the solutions have not been swept clean from permanent or adventitious contamination, (b) the surfaces have not been maintained at rest free from contamination and evaporation for the necessary time before measurement.

The use of the Langmuir-Adam trough here illustrated affords a general method of sweeping clean at least one side of any solution and then observing the change in surface tension with time.

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY
STANFORD UNIV., CALIF.

J. W. MCBAIN
D. A. WILSON

RECEIVED DECEMBER 18, 1935

NEW BOOKS

Das Buch der Alaune und Salze. (The Book of Alums and Salts.) Translated, edited and annotated by JULIUS RUSKA. Verlag Chemie G. m. b. H., Corneliusstrasse 3, Berlin W 35, Germany, 1935. 127 pp. 16.5 × 25 cm. Price, RM. 15.

"The Book of Alums and Salts," here printed in the original Arabic recently discovered by Professor Ruska and in early Latin and modern German translations, is one of the most important source texts of mediaeval chemistry. Ruska's study of it, and his work on *al-Razi* from whom "The Book of Alums and Salts" is largely derived, constitute a fundamental contribution to our knowledge of the subject. We learn not only where the doctrines and the information come from, but learn the better to apprehend the contents of the treatises and to place them in their proper relationships.

Abu Bakr Muhammad ibn Zakariya al-Razi (Latin *Rhazes*) (860–925), a great physician and chemist, "the greatest clinician of Islam," wrote among many other things a *Kitab Sirr al-Asrar*, or "Book of the Secret of Secrets," a sober work on chemistry containing nothing mysterious and divided into three parts which deal respectively with the materials, the apparatus, and the processes of chemistry. Either directly, or through secondary Arabic works based upon it, this treatise supplied much of the material of the chemistry and alchemy of Latin Europe. Ruska has found an Arabic original of it and an early Latin translation, and other Latin translations which appear to be revisions and amplifications of the original text. He has published elsewhere a translation and compilation of *al-Razi*'s "Secret of Secrets"[1] and a discussion of the relation of *al-Razi* to the history of chemistry.[2] The book at present under review is a report of another portion of his studies on *al-Razi*.

The Book of Alums and Salts was known to Vincent of Beauvais, who ascribed it to *al-Razi* and quoted extensively from a Latin version of it. A Latin translation by Gerard of Cremona has recently been published by Robert Steele.[3] A number of anonymous manuscripts of the treatise are also known. Ruska points out that the Arabic original of the work does not exist among the known authentic writings of *al-Razi*, and that the internal evidence indicates that the treatise is a compilation based upon the writings of *al-Razi* and *Jabir* and upon Alexandrian sources. He has studied carefully and compared the Latin Paris Ms. 6514, which bears the name of *al-Razi*, and the supplement, *De Mineralibus Liber*, of the *Compendium Alchemiae* of John Garland which was printed at Basel in 1560—*Tractatus de Salium Aluminumque varietate, compositione et usu Scriptoris incerti*. Ruska seems to have been the first to note the resemblance of the latter to the Book of

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(1) Ruska, "Uebersetzung und Bearbeitungen von *al-Razi*'s Buch Geheimnis der Geheimnisse," *Quellen zur Geschichte der Naturwissenschaften und der Medizin*, IV, **3**, 1–87 (1935).

(2) Ruska, "Die Alchemie ar-Razi's," *Der Islam*, **22**, 281–319 (1935).

(3) Steele, "Practical Chemistry in the Twelfth Century," *Rasis de Aluminibus et Salibus*," translated by Gerard of Cremona, *Isis*, **12**, 10–46 (1929).