

ortho, para ratio in the halogenation of aromatic compounds.

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#### OPTICAL MEASUREMENT OF THE THICKNESS OF A FILM ADSORBED FROM A SOLUTION

Sir:

A single layer of molecules deposited from a water surface on a built-up film produces [I. Langmuir, V. J. Schaefer and D. Wrinch, *Science*, **85**, 76-80 (1937); K. B. Blodgett and I. Langmuir, *Phys. Rev.*, **51**, 964 (1937)] a perceptible change in the color given by interference of light from the top and bottom of the film.

We can condition the surface of the built-up film to enable it to adsorb organic or inorganic substances from solution, and determine the dimensions of adsorbed molecules by the change in color.

Dipping the film into a solution containing a second substance reactive to the first, a second adsorbed film can be formed. Sometimes successive alternating layers can be built.

One method of conditioning a plate is to deposit upon it an A-layer of stearic acid from a water surface and to bring it into an aluminum chloride solution ( $10^{-3}$  molar). After washing, it is ready to adsorb many organic substances which contain polar groups.

For example a drop of a 1% solution of egg albumin is applied to the wet plate which is then washed and dried. The apparent increase in thickness is equivalent to 2 barium stearate layers (50 Å.). With Stanley's tobacco virus protein we obtain a maximum thickness of 12 stearate layers equivalent to 300 Å.

A surface conditioned by a monolayer of egg albumin deposited from a water surface takes up an adsorbed film of tobacco protein having a maximum thickness of only 5 stearate layers. This may be the thickness of molecules lying flat on the surface. Adsorbed films of other proteins on aluminized surfaces give films of from 2 to 8 stearate layers. As these are not always proportional to the cube root of the molecular weight, some protein molecules seem to be non-spherical.

It facilitates the formation of a complete layer to apply the protein in successive stages, washing

and drying the plate after each addition of the protein, probably because of consolidation by surface tension.

The molecular dimension (normal to the surface) of adsorbed molecules in a film which is only 70% complete may be determined by filling the interstices between molecules with hexadecane after covering with 4 barium stearate layers to render the surface non-wettable by oil.

Coöperating with Dr. Harry Sobotka we have conditioned a surface by deposition of a monolayer of cholesterol (18 Å.). This surface takes digitonin from aqueous solution giving an adsorbed film of 36 Å. Another layer of cholesterol can be deposited and a second adsorbed film of digitonin, etc. These multilayers give accurate measurement of molecular dimensions.

With Dr. E. F. Porter, we have adsorbed diphtheria toxin on a plate conditioned by aluminum chloride obtaining a monofilm of 36 Å. On dipping the plate into diphtheria antitoxin, there was an increase in thickness of 75 Å. Successive alternating layers of toxin-antitoxin can be built up indefinitely.

Not only the thickness but many other properties of adsorbed films can be measured such as contact angles with various liquids, solubilities, adsorbing power for substances in solution, refractive index, etc.

We believe the methods outlined are useful for detecting and identifying minute amounts of substances of biological interest and for studying the structure, reactivities and other properties of these substances.

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IRVING LANGMUIR  
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#### PHENOXYPYRIDINE

Sir:

Thanks to Professor Chichibabin, my attention has been called to some inaccuracies in a recent article by Renshaw and Conn [THIS JOURNAL, **59**, 297 (1937)], where the statement is made: "A number of 2-pyridyl ethers were prepared by heating 2-bromopyridine with the alkali salts of alcohols and phenols . . ." and farther on: "This is a more satisfactory method than that reported by Chichibabin [*J. Russ. Phys.-Chem. Soc.*, **50**, 502 (1918)] for the preparation of 2-phenoxy pyridine, the only alpha-substituted pyridine reported in the literature."

It now appears that Professor Chichibabin did not as a matter of fact report the diazotate reaction as a method for the preparation of alpha-phenoxy pyridine, its isolation being merely incidental in the reaction which he was investigating. Unfortunately, we had only abstracts of the Russian article at our disposal.

The designation of 2-phenoxy pyridine as the only alpha-substituted pyridine reported in the literature (page 297) is a very patent error, since a large number of alpha-substituted pyridines have been known for many years and the writer had dealt with derivatives of such compounds in two earlier publications, as well as in the paper under discussion. (Note reference to Grave's article page 298.) On examination it was found that this error was due to the accidental omission of *aryloxy-* after *alpha-* in the term "alpha-substituted pyridine," in the final typing of the manuscript.

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R. R. RENSHAW

RECEIVED MARCH 31, 1937

#### FLUOROCARBONS

Sir:

From a reaction mixture of carbon and fluorine the following fluorocarbons have been isolated and identified by their molecular weights: profluorane,  $C_3F_8$ ; bufluorane,  $C_4F_{10}$ ; pentafluorane,  $C_5F_{12}$ ; and hexfluorane,  $C_6F_{14}$ . The well-known compounds methfluorane,  $CF_4$ , and ethfluorane,  $C_2F_6$ , were also formed in the reaction. The separation was made by distillation and the molecular weights were determined with an all-glass density balance. Seven to fifteen grams of each compound was obtained. The boiling and freezing points have been determined approximately and are: profluorane f. p.  $-183^\circ$ , b. p.  $-36^\circ$ ; bufluorane f. p.  $-84.5^\circ$ , b. p.  $+4^\circ$ ; pentafluorane f. p.  $-10^\circ$ , b. p.  $+30^\circ$ ; and hexfluorane f. p.  $-4^\circ$ , b. p.  $+60^\circ$ .

The distillation was performed in a low temperature column packed with glass helices. It was carried out at 200 mm. and the temperature remained constant within  $1^\circ$  during the collection of each fraction. The molecular weights as obtained from the density balance and determined at short intervals during the distillation remained constant so long as the temperature remained constant. Each fraction was redistilled and the same molecular weights obtained:  $C_3F_8$  184,

188;  $C_4F_{10}$  234, 238;  $C_5F_{12}$  277, 288; and  $C_6F_{14}$  328, 338. The precision of the density balance decreased as the molecular weight increased, and the increased adsorption of the higher boiling substances resulted in low values. The balance was calibrated with oxygen and carbon dioxide and was checked with  $CF_4$  and  $C_2F_6$ , which gave the theoretical values of 88 and 138. The redistilled fractions had relatively sharp melting points when observed visually.

The existence of these compounds has been previously postulated from the properties of small quantities of mixtures of fluorocarbons [Ruff and Keim, *Z. anorg. allgem. Chem.*, **192**, 249 (1930); Ruff and Bretschneider, *ibid.*, **210**, 173 (1933); **217**, 1 (1934); **217**, 19 (1934)]. Their separation and individual identification however, has not been reported previously. A greater quantity will be made and the chemical and physical properties determined.

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#### A CONCENTRATION OF $N^{15}$ BY A CHEMICAL EXCHANGE REACTION

Sir:

Using the exchange reaction between ammonia gas and ammonium sulfate solution suggested by Urey and Greiff [THIS JOURNAL **57**, 321 (1935)] and investigated by Aten and Urey [*Phys. Rev.*, **50**, 575 (1936)] and using the apparatus devised by Huffman and Urey [*Ind. Eng. Chem.*, **29**, 531 (1937)] we have attempted to concentrate the heavy isotope of nitrogen for use in biochemical and chemical investigations. The method consists of pumping a 30% solution of ammonium sulfate at a constant rate of 15 cc. per minute into the top of the fractionation column under low pressure, liberating the ammonia from the salt in solution at the bottom by the addition of sodium hydroxide and stripping the ammonia from the solution by a packed stripping column. This ammonia was fed back to the bottom of the column and escaped from the top. As the result of a thirteen-day run of this kind we have produced nitrogen containing 2.54% of  $N^{15}$ , a  $6\frac{1}{2}$  fold increase in concentration.

The transport of heavy ammonia is equal to the total flow multiplied by the difference in concentration of heavy ammonia in the solution and gas