NOTES

The Formal Identity of Langmuir's Adsorption Equation with the Law of Mass Action.—In his work on the adsorption of gases on the surfaces of solids, Langmuir[1] deduced, on the basis of his theory, a number of equations relating the amount of gas adsorbed to the pressure at equilibrium. The simplest of these equations is

$$q = abp/(1 + ap) \qquad (1)$$

where q is the amount adsorbed, p the pressure at equilibrium and a and b are constants. In connection with certain experiments[2] that were found to be fitted by such an equation, the writer noticed that an equation of exactly similar form could be derived from the law of mass action. Consider a reversible reaction between two substances A and B to form a compound AB. From the mass law,

$$\frac{(A)\,(B)}{(AB)} = k;\ \frac{(A)}{(AB)} = \frac{k}{(B)};\ \frac{(A) + (AB)}{(AB)} = \frac{k + (B)}{(B)};\ (AB) = \frac{\dfrac{(A) + (AB)}{k}\,(B)}{1 + \dfrac{(B)}{k}}. \qquad (2)$$

For an experiment in which the total A (that is, the sum of the concentrations of A and AB) is kept constant, Equation 2 is of the same form as Equation 1. The variables AB and B correspond to q and p, while the constant $1/k$ corresponds to a and the constant A + AB to b. Hence it must be concluded that the agreement of experimental data with an equation of this type is not decisive in determining whether the reaction in question is one of adsorption or chemical combination.

This fact seems to have been overlooked by H. Rinde,[3] who found that certain data of Jacques Loeb[4] on the equilibrium between gelatin solutions and hydrochloric acid could be fitted by such an equation. Rinde concluded that "it is therefore very likely that the 'reaction' between gelatin and HCl is not a chemical reaction in the sense assumed by Loeb, but an adsorption process.." Obviously Rinde's calculation adds nothing to the decision of this question. Other data bearing on the case of gelatin and hydrochloric acid have been presented by Jacques Loeb[5] and by the writer.[6]

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[1] Langmuir, THIS JOURNAL, **40**, 1384 (1918).

[2] Hitchcock, *J. Gen. Physiol.*, **8**, 61 (1925–1926).

[3] Rinde, *Phil. Mag.*, [7] **1**, 46 (1926).

[4] Loeb, "Proteins and the Theory of Colloidal Behavior," McGraw-Hill Book Co., New York and London, 2nd ed., **1924**, p. 183.

[5] Ref. 4, Chapters 2 and 4.

[6] Hitchcock, *J. Gen. Physiol.*, **6**, 95, 201 (1922–23).

The Serial Solubility of Some Rare Earth Bromates.—Bromates of dysprosium with holmium, containing some yttrium, erbium and terbium, were crystallized with bromates of lanthanum, praseodymium and neodymium, and fractionated for about three months. Such fractions as had the same appearance were united. Each fraction was then separated into the elements of the yttrium group and into those of the cerium group by the sodium sulfate method. In the least soluble fraction the separation was carried out by crystallizing the double magnesium nitrates together with bismuth magnesium nitrate. The absorption spectra of the fractions, 26 in all, were examined; the elements were arranged in the following order: (most soluble) erbium, lanthanum, yttrium, holmium, praseodymium, dysprosium, neodymium, terbium, (gadolinium), (least sol.). In crystallizing the bromates, the fractions were cooled to room temperature (20–25°); it is probable that by allowing them to crystallize at a lower temperature, the elements might show another order. Especially neodymium, which was found only slightly more soluble than terbium, might then come between terbium and gadolinium.

These results are confirmed by direct determinations of solubilities carried out in this Laboratory; this work will be published in the near future.

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A NEW COLOR REACTION FOR PROCAINE AND SOME OTHER LOCAL ANESTHETICS, AND ITS APPLICATION TO THE DETERMINATION OF PROCAINE

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Introduction

When to a solution containing approximately 1 mg. of procaine hydrochloride per cubic centimeter, a few drops of hydrochloric acid, of a solution of sodium nitrite, and of concd. aqueous ammonia are added, in the order named, an intense yellow color develops. Several other local anesthetics respond to this test, while others do not, as recorded in Part I of this paper, which part also includes the results of the test on a number of additional substances.

On suitable dilution, the yellow solution obtained with procaine may be made the basis of a colorimetric method for its determination. The procedure and necessary cautions are detailed in Part II.