

constant, or (b) a change in the chemical character of the substance, its quantity remaining constant, or, (c) more likely, a change in both the quantity and constitution.

From these data it may be seen that the plant has its least hemolytic activity, *i. e.*, may be assumed to be least toxic, in late summer and fall, increasing to a maximum in early spring. There is also a small drop in the summer about during the periods of June and July. What the significance of this drop is, is not known. It may refer to a fluctuation in the weather which influenced the growth of the plant, moisture conditions or other causes. The increase in the hemolytic activity of the plant, however, coincides with the observed periods of increased toxicity of the plant for sheep during the feeding experiments.

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### $p_{\text{H}}$ DETERMINATIONS IN ALCOHOLIC SOLUTIONS.

BY RALPH B. SMITH.

The effect of changes in the hydrogen-ion concentration of many types of reactions has been widely studied during the past few years and these investigations have covered almost every field of chemistry. In the field of bio-chemistry a vast amount of work has been done and many interesting and valuable results have been obtained.

These  $p_{\text{H}}$  studies in the bio-chemical field have been almost entirely limited to water solutions; there are, however, many cases in which alcoholic extractions of vegetable or animal products must be made. The hydrogen-ion concentration is known to be a factor of great importance in aqueous solutions and must also be an influential factor in alcoholic solutions. These considerations have led to a study in this laboratory of the hydrogen-ion concentration of alcoholic solutions and tinctures.

It is known from the work of Lapworth, *et al.*<sup>1</sup> that stable and reproducible e. m. f. values could be obtained from concentration cells in which absolute to 98% alcohol was used as a solvent. They also used calomel half-cells made up with alcohol instead of water.

Bishop, Kittredge and Hildebrand<sup>2</sup> made a series of electrometric titrations of various acids and bases in alcohol as a solvent. They used *N*/10 NaBr half-cells made up with 95% and absolute alcohol. Smooth titration curves similar to those obtained when water is used as a solvent were obtained with the difference that there was a greater e. m. f. interval between the acid and the basic parts of the curve. This is due to the fact that the dissociation constant of alcohol is smaller than that of water. This difference in the dissociation products gives rise to a new and different system each time the concentration of the alcohol is changed. All these systems must have contact potentials which many investigators have practically ignored. The data accumulated by Lapworth, *et al.*<sup>1</sup> shows that these contact potentials cannot be ignored even over small changes in the water content of the alcohol.

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<sup>1</sup> *Jour. Chem. Soc.*, 99 (1911), 1417; 99 (1911), 2242; 101 (1912), 2249; 105 (1914), 2553 and 107 (1915), 1520.

<sup>2</sup> *Jour. Amer. Chem. Soc.*, 44 (1922), 135.

Any investigation of alcoholic solutions will of necessity involve many different concentrations, and it will generally be undesirable to determine the exact concentration of the solution at hand. The saturated calomel half-cell is very largely used in all types of  $p_H$  work and in this case has a peculiar advantage. Lapworth, *et al.*<sup>1</sup> in the fifth paper of their series have shown by the capillary electrometer method that the absolute potential of mercury in a saturated solution of a salt in any solvent is independent of the nature of the solvent provided that the ions present have all the same affinity for that solvent. They verified this by placing in contact a calomel half-cell made up with a saturated water solution of NaCl and a calomel half-cell made up with a saturated alcoholic solution of NaCl. They found that at the moment of contact there was less than one millivolt difference in potential between the two cells but due to diffusion and precipitation of the NaCl the contact voltage soon rose to between 6 and 15 millivolts. Since the alcoholic solution will be saturated with KCl at the interface it would seem probable that it is only the above contact potential which must be considered where a saturated calomel electrode is used.

This method was carefully checked on a set of 19 pairs of buffer mixtures made up according to the directions given by Clark.<sup>2</sup> One mixture of each pair was made up using water as a solvent and the other was made up so as to contain 50% alcohol by volume. The voltage of each of these buffer mixtures against a saturated calomel half-cell was determined at  $25 \pm 0.05^\circ \text{C}$ . The calomel half-cell and tube for the solution under test were the same as described by Clark and Cohen.<sup>3</sup> This cell is constructed so as to reduce diffusion to a minimum, and the design also allows it and the solution to be immersed in a constant temperature oil-bath. When such a cell is not available the ordinary half-cell and an agar salt bridge may be used with equally good results.

It was found that the alcoholic buffer solutions gave stable readings which were reproducible within 1–2 millivolts. The e. m. f. of the alcoholic solutions was in every case higher than that of the corresponding solution made up with water as a solvent. The constant of the hydrogen electrode in alcoholic solution is unknown so that it is impossible to calculate the  $p_H$  from the results obtained. It is not convenient, however, to express the results in terms of e. m. f. and it has therefore become customary in this laboratory to calculate the results to  $p_H$  using the ordinary constants for water. When this is done in the case of the above buffer solutions it is found that the variation of the two members of the pairs is from 0.16 to 1.88  $p_H$  units. The least variation was in the case of KCl-HCl buffer mixtures and greatest in the case of the phthalate-NaOH buffer mixtures. The results of the whole series suggest that the variation is less in the case of strong acids and greater in the case of weak acids, but it would require further investigation of a number of other acids to determine this.

The method used above was extended to a number of alcoholic tinctures. In determining the  $p_H$  of such materials it is very important to use a freshly plated

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<sup>1</sup> *Jour. Chem. Soc.*, 99 (1911), 1417; 99 (1911), 2242; 101 (1912), 2249; 105 (1914), 2553 and 107 (1915), 1520.

<sup>2</sup> "Determinations of Hydrogen Ions," 2nd Edition, page 106.

<sup>3</sup> "Studies on Oxidation—Reduction III," Reprint No. 834, from the *Public Health Reports* (May 4, 1923).

electrode which has been presaturated with hydrogen immediately before it is placed in the sample to be investigated. The voltage of the electrode will usually come to a stable reading in 5-15 minutes and remain there for 15-20 minutes or even longer. After this time the electrode usually starts to poison and the voltage drops off. The  $p_H$  is calculated from the maximum voltage. There is every indication that this maximum point is of real significance since it can usually be checked within 5 millivolts and when it is considered that these solutions are known to slowly poison the electrodes, this would seem to be good agreement. There are occasional samples which poison an electrode so rapidly that no stable reading can be obtained. The reason for this is still unknown for in all such cases the sample had the same history as others which did not poison the electrodes.

The  $p_H$  of tinctures of digitalis, aconite and strophanthus have been determined and found to have the following values.

Tincture of digitalis U. S. P.	5.12-5.77
Tincture of aconite U. S. P.	5.20-5.51
Tincture of strophanthus U. S. P.	5.43
Tincture of ergot (U. S. P. X)	4.97

The  $p_H$  of several tinctures of aconite which were known to have been made with acid menstruums were determined and found to have values between 2.32 and 4.53.

*Conclusions.*—A method has been developed for determining  $p_H$  in alcoholic solutions using only the set-up common to most laboratories making such measurements on aqueous solutions which will give stable and reproducible values. Such a method should find wide use in any investigation of the alcoholic extractions or changes in the stability of the tinctures obtained. Some results obtained with tinctures of digitalis, aconite, strophanthus and ergot are given.

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## THE EFFECT OF VARIOUS COMPOUNDS ON THE RATE OF DEVELOPMENT OF RANCIDITY IN FATS AND OILS.\*

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In a previous article (1) by the present authors it was shown that benzoic and cinnamic acids have no effect on the rate of development of rancidity in lard. This work has been extended to other substances.

### EXPERIMENTAL METHODS.

The Kreis test (2) was used for detecting rancidity, the odor of the test samples serving as a confirmatory test. The tests were carried out as follows:

Five-cc. portions of oil of sweet almonds, with and without added substances, were placed in special 30-cc. Pyrex glass-stoppered test-tubes, with graduations at the 5-, 10- and 15-cc. levels for convenience in adding the reagents in the Kreis test. The tubes were placed in a water-bath at about 60° and held at this temperature for one hour, with occasional gentle agitation. They were then placed in a rack in a north window. After intervals of one week and two weeks the odor was noted and the entire sample then used in making the Kreis test.

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