

THE APPLICATION OF COLORIMETRY IN THE ULTRAVIOLET TO THE DETERMINATION OF THE STRENGTH OF ACIDS AND BASES

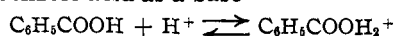
Sir:

The important problem of determining the base strengths of very weak bases (*e. g.*, most organic acids, esters, ketones, aldehydes, ethers, amines, and amides) has been solved by the methods of visual colorimetry for the limited group of bases whose ionization is accompanied by a change in color. Because of the great desirability of obtaining similar quantitative information for uncolored bases, we have investigated the validity of what may be called colorimetry in the ultraviolet as a method of measuring ionization and base strength. For this purpose the ultraviolet absorption spectra of a carboxylic acid (benzoic acid), of a phenolic acid (2,4-dinitrophenol), and of a singly charged acid (anilinium ion, which is the conjugate acid to the simple base aniline) have been measured under the following conditions: (1) in an acid solution in which the ionization of the acid is negligible; (2) in a basic solution in which the acid is completely ionized; (3) in a buffer solution of known acidity in which ionization is approximately half complete. In every case ionization was accompanied by a marked change in the absorption spectrum from which calculation of the extent of ionization was easily possible. The values of acid strength obtained are listed herewith, together with the values (derived from conductivity or hydrolysis measurements) given in the Landolt-Börnstein "Tabellen."

	pK (absorption spectra)	pK (L.-B.)
Benzoic acid	4.16 ± 0.11	4.18
Dinitrophenol	$4.09 \pm .04$	4.10
Anilinium ion	$4.62 \pm .05$	4.62

The deviations represent variations in the pK obtained from different regions of the spectrum.

Having thus demonstrated the validity of the method, we have further investigated the ionization of benzoic acid as a base



by determining its absorption spectrum in a series of increasingly acid sulfuric acid-water mixtures. A large change took place between concentrations of 70 and 95% sulfuric acid, and very little change in any other range of acidity. From these spectra and the visual colorimetric values of the acidity function H_0 for the sulfuric acid solutions, we obtain the following value for the base strength of benzoic acid

$$pK' \equiv -\log a_{\text{B}^+} / a_{\text{BH}^+} = -7.25 \pm 0.25$$

The method will be applied to the determination of the base strengths of other colorless organic compounds.

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RECEIVED AUGUST 3, 1934

IRRADIATION OF YEAST ORYZANIN

Sir:

We have found that a one-hour irradiation of a solution containing 24.4 mg. per liter of yeast oryzanin kindly furnished by S. Ohdake and U. Suzuki, at a distance of 4.3 cm. from a Victor quartz lamp, destroyed its ability to alleviate the neurological symptoms of rats maintained on a vitamin B₁ deficient diet in doses as large as 12 γ . The original solution was active in doses of less than 3 γ . The two-peaked absorption of the compound, which resembles that of cytosine [THIS JOURNAL 56, 1728 (1934)] is rapidly destroyed by the irradiation. On the other hand, irradiation with ultraviolet from which most of the radiations of wave lengths less than 2960 Å. have been filtered

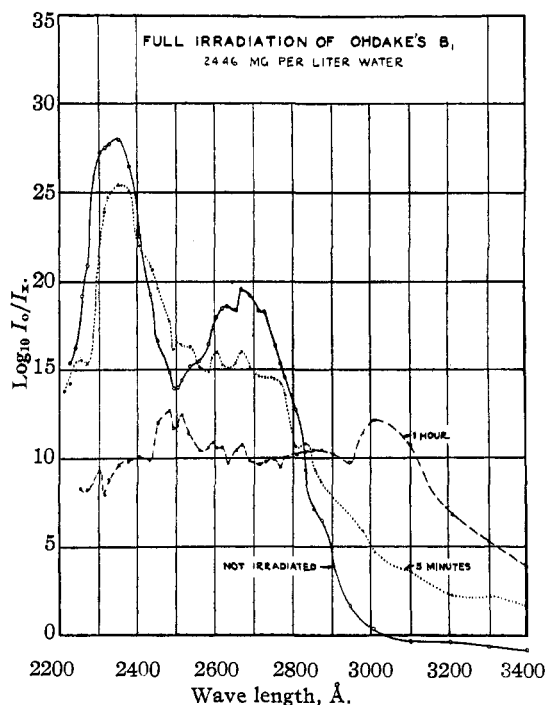


Fig. 1

out, for a period of thirty minutes produces a transient increase in the characteristic absorption, and even after four hours leaves the absorption bands still present, while the biological potency is

only slightly, if at all, diminished. Similar results have been obtained with preparations from other sources.

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RECEIVED AUGUST 2, 1934

THERMAL DIFFUSION OF GASES NEAR A HOT METAL SURFACE

Sir:

In an experimental study of the equilibrium of molten iron and steam [THIS JOURNAL, 55, 3131 (1933)] the only criterion of equilibrium was the fact that the oxygen content of the iron reached a constant and reproducible value at a constant steam-hydrogen ratio. The surprising results of Emmett and Shultz [*ibid.*, 55, 1376 (1933)], in which a thermal separation of steam and hydrogen was observed even in a flowing system, raised the question as to whether such a phenomenon could have occurred in our experiments. This suspicion was heightened by the fact that for a given oxygen content of the liquid iron the observed ratio of steam to hydrogen was consistently a little higher than that calculated from the ratio $\text{CO}_2:\text{CO}$ found by Vacher and Hamilton [*Trans. Am. Inst. Mining Met. Eng.*, 95, 124 (1931)].

It should be possible to diminish the temperature gradient and thereby also the amount of thermal separation by preheating the gas stream as it approaches the hot metal surface. The preheating due to radiation from the liquid iron will be the more efficient the lower the lineal velocity of the gases. In the earlier experiments the gases were introduced through a 3-mm. tube at 250 to 450 cc. per minute, whereas Vacher [*Bur. Standards J. Res.*, 11, 541 (1933)], using a larger tube and lower rate of flow, obtained a lower ratio of steam to hydrogen.

A series of experiments has been conducted in which the steam-hydrogen mixture was admitted through a 7-mm. tube containing an electrically heated spiral of platinum wire. In another series this preheating was supplemented by a cast chromium sleeve which fitted over the top of the crucible containing the melt and which was heated by induction to a temperature approximating that of the liquid iron. The results of these experiments at 1600° and 0.065% oxygen in the liquid iron are given in Table I. The temperature recorded for the platinum coil is its average de-

termined by its resistance. The end nearest the exit was several hundred degrees hotter. The recorded sleeve temperatures are estimates.

TABLE I

THE EQUILIBRIUM: $\text{FeO (IN Fe)} + \text{H}_2 = \text{Fe(l)} + \text{H}_2\text{O AT } 1600^\circ$

Expt.	$\frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2} \times \% \text{O}}$	Flow cc./min.	Coil temp., °C.	Conditions
1-18	4.75	300	..	3-mm. tube
33	4.58	300	..	7-mm. tube
34	4.33	300	1170	No sleeve
35	4.23	300	1320	No sleeve
51	4.20	300	1170	Sleeve about 1500°
52	4.04	300	1170	Sleeve about 1600°
53	3.94	200	1170	Same as 52
55	4.20	450	1050	No sleeve

The results substantiate the hypothesis of partial thermal separation of the cold gases near the hot metal surface, which results in a diffusion of steam away from the surface and a low oxygen content of the liquid iron. In experiments 52 and 53 the preheating is believed to have been sufficient to largely eliminate this source of error. These two experiments are also in very good agreement with calculations from similar data on the system $\text{Fe}:\text{C}:\text{O}$.

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RECEIVED AUGUST 9, 1934

MAGNETIC SUSCEPTIBILITY OF METAL KETYLs

Sir:

We have recently made an investigation on the magnetic susceptibilities of some of the metal ketyls in solution by the Gouy method. The root mean square permanent magnetic moment per molecule was calculated from the molal susceptibility χ_M of the solute by means of the Langevin relation

$$\mu = 2.83 \sqrt{T(\chi_M - N\alpha)}$$

μ being in Bohr magnetons. The values of $N\alpha$ were found by Pascal's rule from values in the "International Critical Tables." The percentage dissociation of the metal ketyls under the conditions given in the table below was calculated from the relation

$$D = 100 (\mu^2/3)$$

which follows from the assumption that the radicals have a magnetic moment of $\sqrt{3}$ Bohr magnetons.