The curve for hydrochloric acid is undoubtedly linear in solutions of as low concentrations as the hydrogen-ion concentration of the weaker acids. The curve, however, deviates from linearity at much lower concentrations than is the case with metals. This must be due to a change in the ratio δ_2/δ_1 of equation (4) with hydrochloric acid concentration, or a change in the character of the carbonic acid diffusion layer which gives a similar effect.

Summary

The rate of solution of marble cylinders rotating in dilute solutions of a number of acids and acid mixtures has been measured. Concentration–initial rate curves have been plotted, the effects of rate of rotation and temperature coefficients measured, the effect of inert salt on weak and strong acids and buffer salts on weak acids determined; mixtures of weak and strong acids and solutions of ferric and chromic salts were used.

It has been shown that the rate follows the usual criteria of the diffusion rate theory, but that the original theory must be modified because of the facts that (1) carbonic acid is in no case negligibly weak, (2) freshly liberated carbonic acid is a much stronger acid than the usual equilibrium mixture of carbonic acid and carbon dioxide and (3) the dehydration of carbonic acid is slow enough to influence the rate tremendously.

The rates are not unimolecular and it has been shown that the reason lies in the above facts. A number of similarities and differences between the behavior of metals and marble have been pointed out and discussed.

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Purification and Ultraviolet Transmission of Ethyl Alcohol

BY LOUIS HARRIS

Ninety-five per cent. grain alcohol is the customary source for pure absolute ethyl alcohol. In a recent publication, Leighton, Crary and Schipp[1] called attention to the precautions necessary and have shown by measurements of the ultraviolet absorption how the various treatments in the purification affect the transmission. Our experience with 95% alcohol confirms, in general, the finding of these authors. It seems, however, that the effect of these treatments would depend in some measure on the source of the alcohol.

We have found that commercial absolute alcohol[2] showed a fair transmission in the ultraviolet (a two-centimeter layer transmitted 50% at 2500 Å.) which improved after one distillation. Commercial absolute

(1) Leighton, Crary and Schipp, THIS JOURNAL, **53**, 3017 (1931).

(2) U. S. Industrial Alcohol Sales Co., Baltimore, Maryland.

alcohol treated as recommended by Castille and Henri[3] gives a product of high ultraviolet transmission and low water content. This simple method of purification requires a good grade of zinc. Zinc powders as suggested by Castille and Henri[3] are, in general, not reliable. We have used zinc wool (Kahlbaum) and obtained satisfactory and reproducible results. The distillations were carried out in a specially constructed vacuum jacketed Vigreux column with controlled reflux. The heat for distillation was supplied from an electrically heated air-bath. The temperature remained constant to about 0.05° during distillation. The rate of the final distillation was 100 cubic centimeters per hour.

The light absorption was determined by the method of photographic spectrophotometry using a Hilger E 315 Spectrograph and calibrated screens. The absorption cells were of fused quartz with plane polished windows. The transmission of light through the cells filled with alcohol was compared to the transmission through screens plus the cells filled with conductivity water. (The conductivity water was freshly prepared and had a specific conductivity of less than 1×10^{-6} ohm^{-1} cm.$^{-1}$ before and after use.) Correction for the transmission of the water was made using the values of Kreusler.[4]

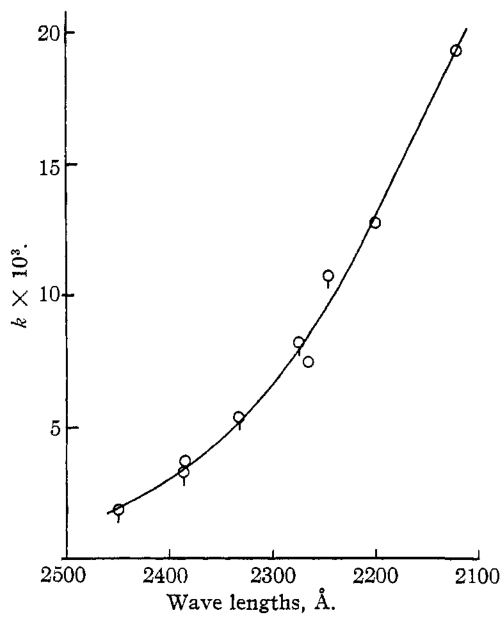

Fig. 1.—Absorption coefficients of ethyl alcohol: O, 2-cm. cell; ♀, 5-cm. cell.

The alcohol was poured from storage bottles into the absorption cells without any special precautions.

The accompanying plot gives the average values of the molal absorption coefficient, k,[5] at different wave lengths.

No correction for reflection at the cell faces has been made. If other values for the transmission of water are found, the final alcohol values will have to be recalculated. The water used here was certainly as pure as that used by Kreusler.

(3) Castille and Henri, *Bull. soc. chim. biol.*, **6**, 299 (1924).

(4) Kreusler, *Ann. Physik*, **6**, 421 (1901).

(5) The molal absorption coefficient, k, is calculated from the equation: $I/I_0 = 10^{-kcd}$; I/I_0 = fraction of light transmitted by alcohol; c = concentration in moles per liter (in this case 17.15); d is the length of path in alcohol in centimeters.

The measurements at the longer wave length barely overlap those reported by Leighton, Crary and Schipp[1] and check them fairly well there. In a private communication Dr. Leighton has reported to us a molar absorption coefficient, k, of 2.85×10^{-3} at 2430 Å. Our value is 2.2×10^{-3} at this wave length. At the shorter wave lengths our alcohol transmits much better than that reported by Bielecki and Henri.[6] (At 2338 Å. the absorption coefficient of their alcohol was about five times that found here.)

The ultraviolet absorption should be one of the best methods of determining small amounts of benzene. The absence of any selective absorption at the benzene absorption maxima (2430, 2480, 2547, and 2611 Å.) indicates quite conclusively that the alcohol contained no appreciable amount of benzene. (Note the comparison above, at 2430 Å., for the alcohol purified by two different methods.) A study with tubes up to 12 centimeters long indicates that if there is any benzene at all, it must certainly be less than 0.001% by weight.

Other physical and chemical properties of this alcohol were determined by Dr. A. A. Ashdown to whom I am indebted also for many helpful suggestions. He found the boiling point to be 78.37° at 760 millimeters compared to 78.32° reported by Brunel, Crenshaw and Tobin.[7] The index of refraction, n_D^{25} was 1.3597 ± 2 compared with 1.3595.[7] The density, d_4^{25} was 0.78527 ± 2, compared with 0.78505.[6] This density corresponds to about 0.05% of water in the alcohol. After being exposed to aluminum amalgam for twelve hours and then distilled, the purified alcohol had a density of 0.78511. After a forty-six hour exposure to amalgam and distillation, the density was 0.78507. Fuchsin–aldehyde reagent showed no aldehyde content—although the reagent was sensitive to 0.02% of aldehyde.

Summary

Ethyl alcohol purified from commercial absolute alcohol yields a product of high purity. The values of the ultraviolet absorption from 2450 to 2120 Å. for purified alcohol are given.

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(6) Bielecki and Henri, *Ber.*, **45**, 2819 (1912).

(7) Brunel, Crenshaw and Tobin, THIS JOURNAL, **43**, 561 (1921).