

LABORATORY PHYSICAL CHEMISTRY

Part One: Reference

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Part Two: Experiments

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10 Ionization Constants by Spectrophotometry

OBJECTIVES. To determine the ionization constants of weak acids and bases by the spectrophotometric method.

CLASSIFICATION. (a) Specific directions. (b) Physical method of observation. (c) Individual or pair experimentation.

GENERAL REFERENCES

S. Glasstone and D. Lewis, *Elements of Physical Chemistry*, pp. 541–555, Princeton, N.J., Van Nostrand, 1960.

Cf. pp. 523 to 540 for general treatment of acid-base equilibria.

L. A. Flexser, L. P. Hammett, and A. Dingwall, *J. Amer. Chem. Soc.*, 57: 2106 (1935).

E. Sawicki and F. E. Ray, *J. Org. Chem.*, 19: 1686 (1954).

EQUIPMENT. A spectrophotometer covering the absorption range of the acid or base system chosen for investigation; suitable matching cells; two or three 100-ml volumetric flasks; bottles for containing prepared solutions.

Discussion

The negative logarithm of the acid ionization constant (pK_a) of a substance is equal to the pH of a solution that contains an equal number of ionized and nonionized molecules. A simple approximate method for its determination is to dissolve a weighed amount of the substance, add exactly one-half the equivalent amount of hydrochloric acid (for bases) or sodium hydroxide (for acids), and determine the pH of the resulting solution. A more elegant method is to titrate the substance with an acid or base and determine the point of inflection of the curve. A preferred method is spectrophotometric; the absorbance of light (visible or ultraviolet) of three very dilute solutions of the compound is determined. One solution is made strongly acidic; the second, strongly basic; and the third, buffered to give an absorbance about midway between those of the acidic and basic solutions.

If, for example, we wish to determine the ionization constant of an organic base, B, we prepare these three dilute (5×10^{-5} M) solutions. In the strongly acidic solution the base will be completely ionized, BH^+ . In the strongly basic solution it will be in the nonionized form, B. By the proper selection of buffer it is possible to obtain approximately equal amounts of the two forms,

or intermediate form m . The exact value of pK_a is then calculated from the equation:

$$pK_a = pH_m + \log \frac{A_B - A_m}{A_m - A_{BH^+}} \quad (1)$$

where pH_m is the pH of the intermediate buffer solution. This is corrected by the logarithm of the fraction, in which A_B is the absorbance of the uncharged molecule A_{BH^+} is that of the completely ionized molecule, and A_m is the absorbance of the intermediate form.

Procedure

Prepare solutions (100 ml each) about 0.2 N of hydrochloric acid, potassium chloride, sodium acetate, acetic acid, borax, boric acid, and sodium hydroxide. Using these solutions, prepare solutions of pH approximately 2, 4, 6, 7, and 8.

pH 2 Mix potassium chloride (25 ml) and hydrochloric acid (6.5 ml).

pH 4 To 25 ml of sodium acetate add acetic acid slowly until the desired pH is obtained.

pH 6, 7, and 8 Mix borax and boric acid in the proper proportions to obtain these buffers. If necessary, sodium hydroxide may be added to borax to obtain pH 8.

Other buffer systems may be used.¹ [See Note (2).] While the solutions do not have to be exactly pH 2, 4, 6, 7, and 8, they should be within 0.3 pH unit, and the pH of each must be accurately determined with a pH meter.

In determining ionization constants, bases should be weighed as their hydrochlorides, and acids as their sodium salts or as the free acids if these are soluble in water. If a substance is insoluble in water, it should be dissolved in ethyl alcohol. When it is later mixed with the buffer, a 50% alcoholic solution is obtained. The values in 50% alcohol are not the same as for water, so the solvent used must be stated in the report. The concentration should be 1×10^{-4} M, and 100 ml of this solution should be made.

For the measurements, mix 10-ml portions of the 1×10^{-4} M solution with 10 ml of each buffer. This gives concentrations of 5×10^{-5} M. In addition, mix 10 ml of the 1×10^{-4} M solution with an equal volume of 0.2 N hydrochloric acid to convert it entirely to the ionic form; and mix a like portion with 10 ml of 0.2 N sodium hydroxide to convert it to the free base. The pH of each solution should be accurately determined just before its absorbance is measured. Each solution should be compared with its matching buffer diluted equally with either water or alcohol, depending on which solvent was used for the compound measured.

¹N. A. Lange, *Handbook of Chemistry*, Handbook Publishers, Sandusky, Ohio.

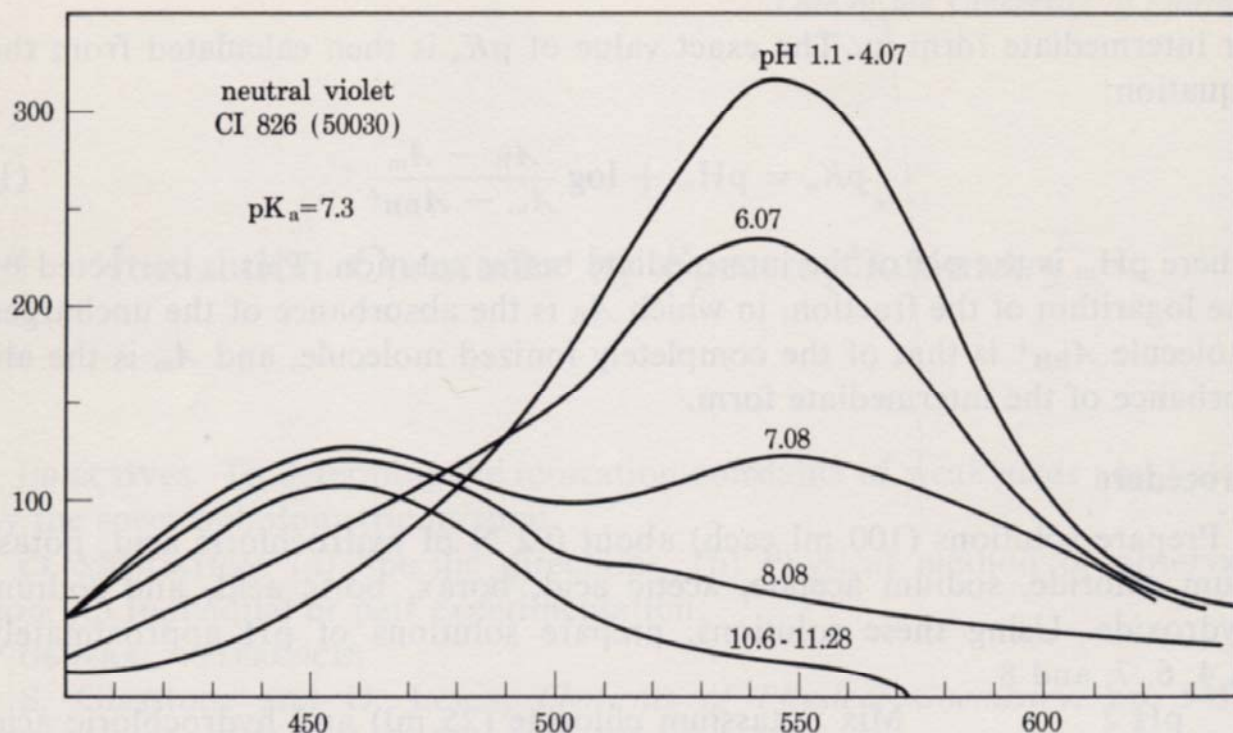


FIG. 1. A typical family of curves.

Measurements should be made every 10 $m\mu$. If a colored substance is used, the range should be about 400 to 700 $m\mu$. At one or more wavelengths all the solutions should have the same absorbance. This is known as the *isosbestic point*. For colorless substances, measurements should be made from 400 $m\mu$ down to the lower limit of the instrument (about 220 $m\mu$).

Calculation of pK_a

The values used always include the hydrochloric acid and the sodium hydroxide solutions. The third value selected is that of the buffer with a pH value about halfway between these. The equation is:

$$pK_a = pH_m + \log \frac{A_B - A_m}{A_m - A_{BH^+}} \quad (1)$$

where A_B is the absorbance of the uncharged molecule (in NaOH). A_{BH^+} is that of the completely charged ion (in HCl.) A_m is the absorbance of a mixture of charged and uncharged molecules (buffer solution). Values should not be used closer than 10 $m\mu$ to the isosbestic point or to the maximum or minimum points. The most reliable values are those obtained about halfway between these points. Record at least six values for the pK_a calculated at different wavelengths and take the average value. Tabulate the results under "wave-length," "absorbance," and " pK_a ." Record the wavelengths of isosbestic points and maximum and minimum points. A graph of the curves should be made.

Notes

1. Simple basic dyes may be used to advantage in this experiment. *o*-toluidine may be diazotized and coupled with dimethylaniline, β -naph-

thylamine, etc. Colorless substances, of course, show the usefulness of the method: benzoic acid, mandelic acid, phenylacetic acid, aniline, toluidine, the naphthylamines and benzylamine are suggested. An amino acid such as glycine or a dibasic substance makes an interesting extension for the better student (succinic acid, phthalic acid, phenylene diamine, etc.). The differences between aliphatic and aromatic acids and bases is graphically illustrated by using benzoic acid and phenylacetic acid; or toluidine and benzyl amine.

(It is assumed that the student has already run a simple curve on the spectrophotometer. If not, a preliminary study of the instrument and its application is suggested.)

2. When working in the UV range, the possibility of light absorption by the buffer system in use should be investigated.

3. A typical family of curves is shown in Fig. 1, from the work of F. E. Ray and co-workers.