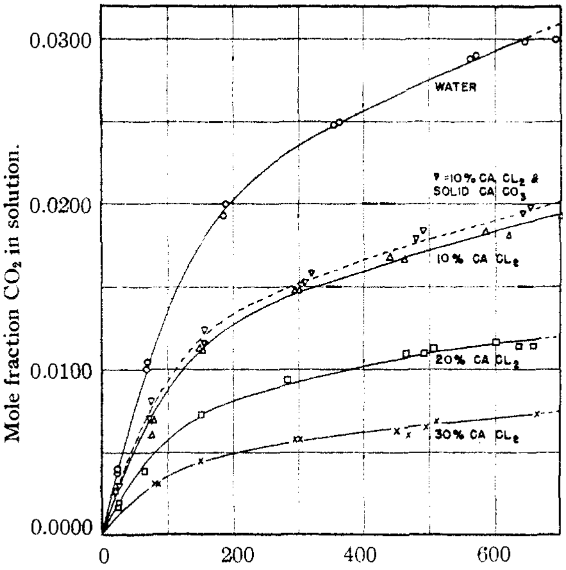

Fig. 4.—Solubility of CO_2 in calcium chloride–water solutions at 120°.

chloric acid and its action on calcium carbonate would result in the formation of a solution containing about 25% calcium chloride. The excess carbon dioxide from such a reaction solution would appear as gas bubbles to loosen drilling mud sheaths, and the reaction should go substantially to completion.

TABLE II

MOLES OF CARBON DIOXIDE IN SOLUTION PER MOLE OF CALCIUM CHLORIDE IN THE ORIGINAL SOLUTION AT 75°

Pressure, atm.	10% $CaCl_2$ solution	20% $CaCl_2$ solution	30% $CaCl_2$ solution
700	1.10	0.32	0.110
400	0.91	.27	.100
300	.84	.25	.092
200	.76	.23	.083
150	.70	.21	.077
100	.59	.17	.065
75	.50	.15	.055
50	.37	.11	.040
25	.21	.06	.021

Summary

The solubility of carbon dioxide in 10, 20, and 30% calcium chloride–water solutions has been determined in a static system for temperatures of 75, 100, and 120°, and pressures up to 700 atm. There was a wide deviation from Henry's law above 100 atm., and this deviation increased with salt concentration.

The low solubility of the carbon dioxide in calcium chloride–water solutions even at high pressures indicates that the action of hydrochloric acid on calcium carbonate formations during the acid treatment of oil wells results in carbon dioxide being evolved during the reaction to provide some mechanical agitation for the dispersion of acid insoluble materials.

CLEVELAND, OHIO RECEIVED MAY 17, 1945

[CONTRIBUTION FROM THE MOORE LABORATORY OF CHEMISTRY, AMHERST COLLEGE]

The Determination of Small Surface Areas by Krypton Adsorption at Low Temperatures

BY RALPH A. BEEBE, JOHN B. BECKWITH AND JURGEN M. HONIG

Extensive use has been made of the method of Brunauer, Emmett and Teller[1] (B.E.T.) for the determination of surface areas of solids. This method consists in determining the volume (v_m) of a gas, usually nitrogen at liquid nitrogen temperature, necessary to complete an adsorbed monolayer. Making use of v_m and of σ_{N_2}, the estimated area occupied by each nitrogen molecule in the monolayer, it is possible to calculate the area of the solid under investigation.

The recent publications of Harkins and Jura[2] present a different approach to the problem. These authors have determined the area of a sample of crystalline, non-porous anatase (TiO_2) powder by an "absolute" calorimetric method, the results of which confirm the validity of the B.E.T. technique. They have also developed a "relative" method which does not require the use of an estimated value of σ_{N_2}.

Because of these developments it is possible to estimate with considerable confidence the areas of solids of moderately high specific surface area, let us say greater than one sq. m./g. of solid. However, in the case less porous or more coarsely crystalline solids of lower adsorptive capacity, none of the above methods using nitrogen as adsorbate is sufficiently sensitive. An important factor limiting the usefulness of the B.E.T. method and the Harkins and Jura "relative" method, both of which make use of the nitrogen adsorption isotherms up to fairly high relative pressures, is the large correction for unadsorbed nitrogen gas. This results from its high saturation pressure, which is approximately one atmosphere at liquid nitrogen temperature. This correction can be greatly reduced by carrying out the adsorption at temperatures well below the boiling

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[1] Brunauer and Emmett, THIS JOURNAL, **59**, 2682 (1937); Brunauer, Emmett and Teller, *ibid.*, **60**, 309 (1938).

[2] Harkins and Jura, *ibid.*, **66**, 1362 (1944); **66**, 1366 (1944).

point of the vapor which is being adsorbed, with the result that the saturation pressure is low. Livingston[3] has suggested the use of such vapors as water, propyl alcohol and heptane at room temperature, obtaining the isothermal data with the McBain–Bakr balance. Wooten and Brown[4] using ethylene at −195° and butane at −116°, have shown that the B.E.T. equation holds in the region of 0.05 to 0.30 relative pressure. In the work of Wooten and Brown, because of the extremely low saturation pressures of the vapors at the temperatures of adsorption, the correction for unadsorbed vapor was very small indeed, enabling the investigators to estimate surfaces as small as 10 sq. cm. total area.

It occurred to us that the adsorption of krypton vapor, with a saturation pressure of about 2 mm. at the temperature of a commercial liquid nitrogen bath, might be well suited for the measurement by the B.E.T. method of surface areas considerably smaller than could be measured by the method suggested by Livingston, but not so small as to necessitate the application of the exacting technique of Wooten and Brown. Krypton has the advantage in common with nitrogen that it is easy to handle at room temperature without condensation.

Our hopes that the B.E.T. method could be applied with success to the adsorption of krypton appear to be justified by the results of our experiments which have been carried out on a considerable number of solids ranging in specific surface area from 0.02 to 120 sq. m./g.

Experimental

Materials.—The pure krypton gas, as well as the nitrogen and helium, was obtained from the Air Reduction Sales Company, sealed in Pyrex glass.

The anatase powder was supplied through the courtesy of Professor Harkins and Dr. Jura. The zirconium silicate also came from the University of Chicago Laboratory The crushed porous glass was kindly provided by Dr. P. H. Emmett from the same batch used by Emmett and DeWitt.[5] The whitings and quartz spheres were provided through the kindness of Dr. W. R. Smith of Godfrey L. Cabot, Inc.

Apparatus and Procedure.—In all the measurements made with krytpon gas at liquid nitrogen temperature, the apparatus used was essentially the same as the one described previously.[6] The pressure was measured by a McLeod gage of rather low sensitivity. In a few measurements using krypton at −183°[7] and in all the measurements with nitrogen the apparatus was similar to that described by Pease,[8] employing an ordinary manometer and a gas buret of 25-cc. capacity. The volume of the free space in the apparatus was determined by admitting helium to the evacuated system since this gas is not measurably adsorbed at liquid nitrogen temperature. Suitable correction was made for deviation from the gas laws in the nitrogen experiments.[9] This correction was practically negligible in the work with krypton because of the relatively small volume of unadsorbed gas. The saturation pressure was observed in each experiment either by condensing the krypton to the solid state in a small empty glass tube connected to the pressure gage and placed beside the adsorption tube in the bath, or by putting a large excess of krypton in the adsorption tube itself and observing the limiting pressure. Experience showed that the same result was obtained by both methods. Having found the saturation pressure for solid krypton, it was possible to estimate the temperature by making use of the data of Keesom, Mazur and Meihuizen.[10] From these estimated temperatures it was necessary to obtain the extrapolated vapor pressure of *liquid* krypton[11] in the region of −195° to be used as the p_0 value; these extrapolated values were calculated from the empirical equation of Meihuizen and Crommelin.[12] Because of variations in the composition of the commercial liquid nitrogen, the values of the saturation pressure of the solid krypton ranged from 1.80 to 2.62 mm., indicating a temperature variation over the range −195.5 to −193.9°, and a variation in the extrapolated value for p_0 for liquid krypton from 2.63 to 3.72 mm. In the experiments with nitrogen as the adsorbate, p_0 varied from 873 to 892 mm. in different experiments.

Results and Discussion

Application of the Method of Brunauer, Emmett and Teller.—In applying the B.E.T. method to the calculation of surface areas from the adsorption data with krypton, it is necessary to decide what value is to be used for σ_{Kr}, the area occupied by the krypton atom in the adsorbed monolayer. In the initial experiments with nitrogen, Brunauer and Emmett were forced to estimate σ_{N_2} on the assumption that the adsorbed monolayer was either a close-packed solid or liquid, with the areas per molecule of 13.8 and 16.2 sq. Å., respectively; and of these two, they adopted 16.2 sq. Å. in their future calculations. A similar estimate for krypton yields 14.0 sq. Å. for a close-packed solid monolayer using the crystal data of Ruhemann and Simon,[13] and 15.2 sq. Å. for the closest packing in a liquid monolayer at the temperature of liquid nitrogen.[14] Fortunately, however, we are now in a position to *measure* the value of σ_{Kr} in the case of one solid, hav-

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(3) Livingston, THIS JOURNAL, **66**, 569 (1944).

(4) Wooten and Brown, *ibid.*, **65**, 113 (1943).

(5) Emmett and DeWitt, *ibid.*, **65**, 1253 (1943).

(6) Beebe and Dowden, *ibid.*, **60**, 2912 (1938).

(7) A few isotherms were obtained with krypton in a liquid oxygen bath. In this case the saturation pressure of the krypton was approximately 20 mm. and the method appeared to be applicable at this temperature.

(8) Pease, THIS JOURNAL, **45**, 1198 (1923).

(9) Emmett and Brunauer, *ibid.*, **59**, 1553 (1937).

(10) Keesom, Mazur and Meihuizen, *Physica*, **II**, 669 (1935).

(11) The supercooled liquid vapor pressure has been used at the suggestion of Dr. P. H. Emmett (private communication), because the isotherms for krypton at −195° appear to behave as though they were governed by the vapor pressure of the supercooled liquid, rather than the vapor pressure of the solid. In this respect, the isotherms for krypton resemble those of Brunauer and Emmett[1] for carbon dioxide at −78° and those of Wooten and Brown[4] for ethylene at −195°.

(12) Meihuizen and Crommelin, *Physica*, **IV**, 1 (1937).

(13) The data used were those of Ruhemann and Simon [*Z. physik. Chem.*, **B15**, 389 (1932)]. From their determinations of the lattice constants of solid krypton at −181, −184, and −191°, these authors have calculated the densities 2.986, 2.994 and 3.004 g./cc., respectively, for the solid krypton. In our calculations, the value 3.01 g./cc. has been used.

(14) In making this calculation, we have used the data of Mathias, Crommelin, and Meihuizen, *Physica* **IV**, 1200 (1937). These authors give their experimental values for the density of liquid krypton in the temperature range from −65 to −147°. From these data, the extrapolated values for the density of liquid krypton, in the region of liquid air temperatures, are 2.59 and 2.65 g./cc. at −183 and −195.8°, respectively.

ing at our disposal a sample of anatase of known area. The value of Σ, the specific surface area, for this material had already been determined by Harkins and Jura[2] both by their "absolute" method and by the B.E.T. method using σ_{N_2} = 16.2 sq. Å. The values of Σ determined by these two methods were, respectively, 13.8 sq. m./g. and 13.92 ± 0.06 sq. m./g.

The results of our measurements on a 4.0-g. sample of anatase both with nitrogen and with krypton, are shown in Fig. 1 in which the relative pressure p/p_0 is plotted against $p/v(p_0 - p)$.

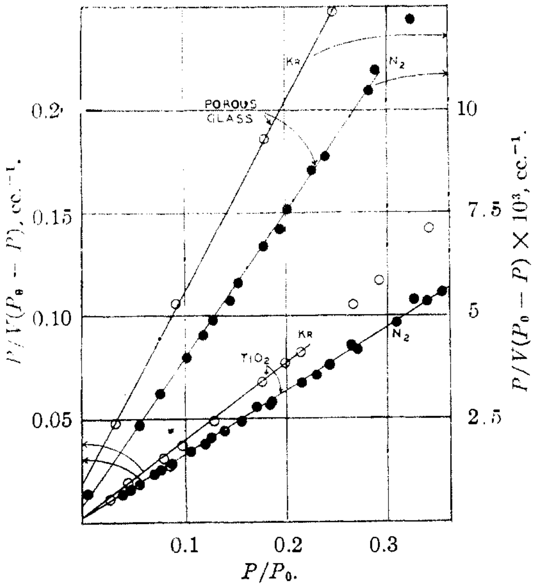

Fig. 1.—B.E.T. plots of adsorption data for krypton and nitrogen at liquid nitrogen temperature. Right hand ordinate refers to porous glass, left-hand ordinate refers to TiO_2.

Our data with nitrogen yield a value of Σ = 13.96 ± 0.25 sq. m./g. using σ_{N_2} = 16.2 sq. Å. Because, in using the "absolute" method, no assumption is necessary concerning the magnitude of σ_{N_2}, we shall use 13.8 sq. m./g. for Σ in our calculations. Confidence in the correctness of this value is of course considerably increased by the agreement with the results obtained by the B.E.T. method both by Harkins and Jura and in this Laboratory.

We may now calculate v_m from the data on krypton given in Fig. 1 and from this we may obtain N, the number of krypton molecules in the monolayer per gram of anatase. It is then a simple matter to obtain σ_{Kr} from the following relationship

$$\sigma_{Kr} = \Sigma/N \qquad (1)$$

From the experimental data we find v_m = 2.64 ± 0.05 cc./g. Hence N is 7.09 ± 0.14 × 10^{19} molecules/g. and σ_{Kr} is 19.5 ± 0.4 sq. Å. per molecule. Because the experimentally determined value of σ_{Kr} on anatase is considerably higher than would be predicted on the assumption that the atoms form a close-packed liquid in the monolayer, it seems evident that the spacing of the adsorbed krypton atoms is not independent of the arrangement of the atomic units in the adsorbing solid surface. If this be true, then there is no reason to assume that the spacing of krypton in the adsorbed monolayer will be exactly the same on different adsorbent surfaces. However, in the absence of experimentally determined values on other solids, the use of the value 19.5 sq. Å. for σ_{Kr}, found on anatase, is provisionally recommended for other adsorbents.

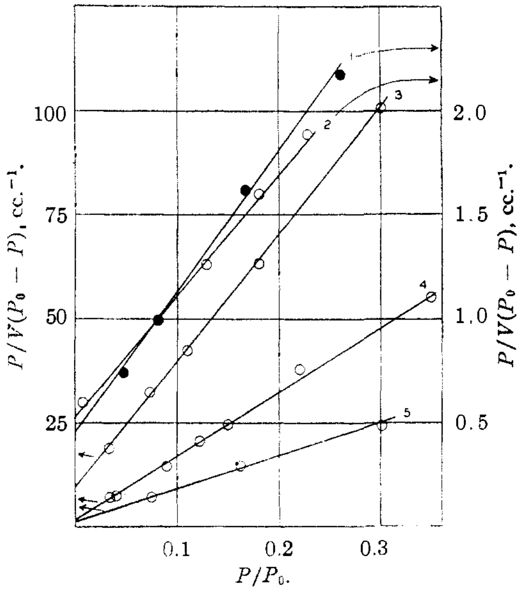

Fig. 2.—B.E.T. plots for krypton adsorption at liquid nitrogen temperature: cork 1, cotton 2, marble 3, quartz spheres 4, glass wool 5.

The experimental results for the different solids studied are given in the form of the $p/v(p_0 - p)$ *vs.* p/p_0 plot in Figs. 1 and 2. From the slopes and intercepts, the values of v_m have been calculated as usual in the B.E.T. method. In the case of each adsorbent, the specific surface area has been calculated from v_m, using σ_{Kr} = 19.5 sq. Å. per molecule; the results are recorded in column 3 of Table I. Column 4 contains the available

Table I

(1) Absorbent	(2) Sample, g.	(3) Σ, sq. m. per g. (σ_{Kr} = 19.5)	(4) Σ, sq. m. per g. (σ_{N_2} = 16.2)	(5) Revised σ_{Kr}, sq. Å.
Marble	34.32	1.69×10^{-2}		
Quartz	11.38	3.70×10^{-2}	(2×10^{-2})	
Glass wool	1.77	5.94×10^{-1}		
Cork	0.854	7.10×10^{-1}		
Cotton	0.805	8.01×10^{-1}		
Whiting 3	2.78	1.62	1.59	19.2
Whiting 6	2.10	3.94	3.55	17.7
Whiting 4	0.859	3.97	3.94	19.5
Anatase	4.00	13.92	13.92	19.5
Porous glass	0.427	110	121	21.5

data for Σ based on nitrogen adsorption experiments using σ_{N_2} = 16.2 sq. Å. The value here given for porous glass was found from our own experiments with nitrogen, shown in Fig. 1. This is in good agreement with the results of Emmett and DeWitt who found Σ = 121 sq. m./g. on another sample from the same batch of material. Σ was determined by nitrogen adsorption in the case of the three whitings by C. B. Wendell of Godfrey L. Cabot, Inc.[15] In our measurements on each of the three whitings, the results recorded in column 3 of Table I were obtained on samples from the same batch studied by Wendell. The area recorded in column 4 for the quartz spheres, also due to Wendell, is obviously only a rough estimate because of the very low specific surface, to which the nitrogen method is not quantitatively applicable.

Except in the case of the anatase we have no "absolute" measurement of Σ. It is of course doubtful whether the assumed value of 16.2 sq. Å. is exactly the true area per nitrogen molecule in each case.[16] But for want of more definite information we have taken the values of Σ in column 4 as true values in calculating the data in column 5. In this column are given the values of σ_{Kr} necessary to make the areas calculated from the krypton adsorption data agree with those given in column 4.

Application of the "Relative" Method of Harkins and Jura.—Harkins and Jura[2] have discussed the validity of the equation

$$\Sigma = ks^{1/2} \qquad (2)$$

where Σ is the specific surface area, k is a constant and s is the slope of the straight line obtained by plotting log p/p_0 against $1/v^2$ in the region where it appears that the adsorbed monolayer is present as a condensed phase. Using the value Σ = 13.8 sq. Å. for anatase, and obtaining the value of s from their data on the adsorption of nitrogen on that adsorbent, these authors have determined k for that gas at $-195.8°$ to be 4.06. Assuming that this value of k can be applied to other adsorbents they have determined Σ for eighty-six different solids by this "relative" method without making any assumptions concerning σ_{N_2}.

Unfortunately, because most of our measurements were made before the description of the above method appeared in the literature, we have an insufficient number of points on most of the krypton isotherms to warrant a quantitative application of this method in most cases. However, we have been able to make use of our data on the three adsorbents: anatase, zirconium silicate and whiting no. 6. The results are shown in Fig. 3. The straight lines obtained from the data of three runs on anatase over the range of relative pressure from 0.001 to 0.40 appear to justify the application of the equation of Harkins and Jura. Using 13.8 sq. m./g. for Σ and taking s from our data in Fig. 3 we have calculated k to be 4.20 for krypton as the average of three runs.[17]

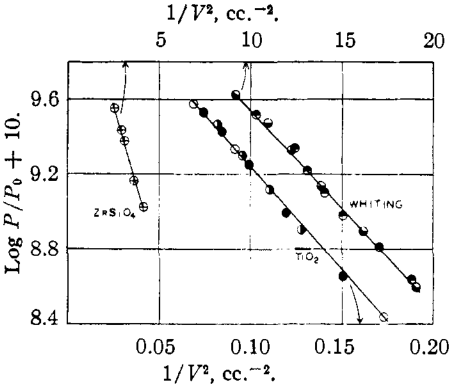

Fig. 3.—Data on krypton at liquid nitrogen temperature plotted according to the method of Harkins and Jura: $ZrSiO_4$ ⊗; TiO_2, Series 1, 2, and 3 ○, ●, ◑; whiting no. 6, Series 1 and 2, ⊖ and ◓.

The data for whiting no. 6 and for zirconium silicate are shown in Fig. 3. Using the value 4.20 for k and taking the values of s as the slopes of the straight lines obtained for these two adsorbents we have calculated the values of Σ to be 4.23 sq. m./g. and 2.34 sq. m./g., respectively. If we assume that these are the true specific areas, we may calculate σ_{Kr} on these two solids from the equation $\sigma_{Kr} = \Sigma/N$. N, the number of molecules in the monolayer, is obtained from the values of v_m obtained by the B.E.T. method. By this method of calculation we find σ_{Kr} to be 21.0 sq. Å. for whiting no. 6 and 20.7 sq. Å. for zirconium silicate.

Because of insufficient experimental data we cannot apply this method quantitatively to the other solids listed in Table I. However, rough estimates of σ_{Kr} made by the Harkins and Jura method for whitings 3 and 4, the glass wool and the quartz spheres give values which are in qualitative agreement with those obtained by the B.E.T. method using σ_{Kr} = 19.5 sq. Å.

In the case of the porous glass no straight line relationship between log p/p_0 and $1/v^2$ was exhibited in the region of low relative pressure. According to the theory of Harkins and Jura, this indicates the absence of a condensed phase for krypton. A similar plot of our data with nitrogen on porous glass did give a straight line, resulting in a calculated value of 124 sq. m./g. in good agreement with the results obtained by the B.E.T. method.

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[15] Wendell reported (private communication) that the apparatus employed was designed for adsorbents of considerably higher specific surface.

[16] The calculations of Harkins and Jura, based on the assumption that k in equation 2 is truly constant on different solids, indicate that σ_N may vary from 13.8 to 16.2 sq. Å. on different surfaces.

[17] Dr. Jura has reported a decrease of approximately one per cent. per degree rise in temperature in the value of k for nitrogen, and a similar variation with temperature might be expected for krypton. Our runs 1, 2 and 3 shown in Fig. 3 were made at -194.5, -194.1 and $-193.7°$, respectively, and not at $-195.8°$, the boiling point of pure nitrogen.

Conclusion.—An appraisal of the krypton adsorption method leads us to conclude that it may be used with a fair degree of accuracy on solids of specific surface area as small as 0.04 sq. m./g. (*e. g.*, quartz spheres). Further work is of course required to establish the limits of variation of σ_{Kr} for various adsorbents. Because in the case of the sample of anatase, the surface had been measured by independent methods including the absolute method of Harkins and Jura, we feel certain that the value 19.5 ± 0.4 sq. Å. for σ_{Kr} determined on anatase may be accepted with considerable confidence.

Summary

1. The method of Brunauer, Emmett and Teller has been applied with success to the measurement of specific surface areas in solids as low as 0.04 sq. m./g. using krypton vapor at liquid nitrogen temperatures.

2. The use of krypton offers the advantage of a low saturation pressure (approximately 2 mm.) at the conveniently obtainable liquid nitrogen temperature.

3. Making use of an anatase (TiO_2) sample the surface of which had been measured by the absolute method of Harkins and Jura, we have determined the value of σ_{Kr}, the area occupied by the krypton atom in the monolayer. This value is 19.5 ± 0.4 sq. Å. which is considerably higher than would be predicted on the assumption that the krypton atoms in the monolayer form a close-packed liquid monolayer.

4. To evaluate k for krypton in the equation of Harkins and Jura: $\Sigma = ks^{1/2}$, s has been determined from our adsorption data on anatase. Using the previously determined value of Σ, k is found to be 4.20 at the temperature of liquid nitrogen.

AMHERST, MASS. RECEIVED JUNE 2, 1945

[CONTRIBUTION FROM THE VENABLE LABORATORIES OF THE UNIVERSITY OF NORTH CAROLINA]

Indicator Constants in Solutions Containing Organic Solvents[1]

BY JOSEPH F. MASI AND SAMUEL B. KNIGHT

Numerous investigations have been concerned with the so-called "solvent effect" in the colorimetric determination of *p*H but, as yet, not enough data have been reported to draw theoretical conclusions as to the exact nature of the solvent error. Michaelis and Mizutani[2] have measured pK_{I} for a number of indicators in different alcohol concentrations, and Kolthoff[3,4] and co-workers have done work on the dissociation constants of indicators in alcohol and methanol.

The purpose of this paper is to show the effect of certain organic solvents on the constant of thymol blue (acid range) and brom thymol blue. To accomplish this purpose, hydrogen-ion activities have been determined in hydrochloric acid solutions in which the solvent is water, or water–ethanol, or water–ethylene glycol. Hydrogen-ion activities were also determined in citrate and phosphate buffers in the same solvents. These hydrogen-ion activity values were used along with spectrophotometric data to calculate the apparent indicator constants in each of the solvents.

Theoretical

In a solution containing a weak indicator acid, the constant of the indicator is related to the hydrogen-ion activity of the solution and the ratio of indicator in the "acid" and "basic" forms by the well-known indicator equation

$$pK_{\mathrm{I}} = pa_{\mathrm{H}^+} - \log \frac{x}{1-x} \tag{1}$$

where pK_{I} is the negative log of the apparent indicator constant, and x is the fraction of indicator transformed into the basic form.

The fraction, x, of equation (1) is determined most accurately from spectrophotometric data. Therefore, by combining spectrophotometric data with precise hydrogen-ion activity measurements, pK_{I} may be calculated directly.

From electromotive force measurements on the silver–silver chloride electrode combined with the hydrogen electrode, hydrogen-ion activities may be calculated at 25° by the equation

$$-\log a_{\mathrm{H}^+} = \frac{E - E^0}{0.05915} + \log C_{\mathrm{Cl}^-} - \frac{A\sqrt{\mu}}{1 + aB\sqrt{\mu}} + C'\mu + \log \frac{d_0}{d + 0.001\,(M_1 - M_2)C} \tag{2}$$

where C_{Cl^-} is the molarity of the chloride ion, A and B are Debye–Hückel constants, a is the ion-size parameter, μ is the ionic strength, C' is the "salting-out" constant, d_0 and d are densities of the solvent and the solution, M_2 is the molecular weight of the chloride ion, and M_1 the mean molecular weight of the solvent.

The last term of equation (2) is added so that activities shall be expressed in moles per liter, and, since the electromotive force of the hydrogen–silver–silver chloride cell in its standard state depends on the units in which the activities are expressed, the proper value of E^0 must be used. At 25°, $E^0_{\mathrm{c}} = E^0_{\mathrm{m}} + 0.1183 \log d_0$, where d_0 is the density of the solvent. E^0 must be deter-

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[1] Original manuscript received December 16, 1944.

[2] L. Michaelis and M. Mizutani, *Biochem. Z.*, **174**, 7 (1924).

[3] I. M. Kolthoff, *J. Phys. Chem.*, **35**, 2732–2748 (1931).

[4] I. M. Kolthoff and L. S. Guss, THIS JOURNAL, **60**, 2516 (1938); **61**, 16 (1939).