layer were *Y* layers, as so often happens. It has also been noted repeatedly in forming *X* films that the contact angle while the slide is being withdrawn from the solution shows an alternation of values over a series of dips, *e. g.*, <90°, 90°, <90°, 90° .... This effect, like the stepwise increase of potential, is only marked during the early stages of building *X* films. Later, apparently, the process becomes irregular.

Summary

Contact potentials of stearate *X* films increase with the number of layers and may attain values of many volts. Contact potentials of stearate *Y* films remain constant at a few hundred millivolts and are independent of the number of layers. Sudden very large jumps of potential can be produced by alternating the deposition of *X* and *Y* layers, one or two *X* layers producing large increases in *Y* film potentials and one or two *Y* layers large decreases in *X* film potentials. Such alternations of potential by alternations of *X* and *Y* layers can be continued indefinitely.

Control experiments are presented on the effect of dipping pure *X* and *Y* films and mixed *X* and *Y* films in the various substrates from which these films are deposited and in no case was it found that the substrates produced effects comparable with those of *X* or *Y* layers.

The stabilities of *X* and *Y* films are reported. At room temperature high *X* film potentials persist for many days. On the other hand, when barium–copper stearate *Y* films are heated between 74–85° the potentials decrease by about 200 mv. At about 85° the films begin to turn white and their optical thickness decreases. *Y* films containing only calcium stearate do not become white on heating but otherwise behave the same as those containing barium and copper. *X* films heated above 115° increase in optical thickness and gradually become opaque. The potentials drop to near zero. When heated at lower temperatures the potentials persist at high values.

The effect of X-rays on *X* and *Y* films is to produce large negative potentials, presumably due to the accumulation of charge on or in the film, the magnitude of which depends on the number of layers. *Y* films can be discharged very easily by dipping the slides in water or by heating to a temperature below that which changes the optical thickness. *X* films on the other hand cannot be readily discharged by dipping or by heating to temperatures which discharge *Y* films. Therefore, it is concluded that *X* and *Y* films are not made alike by X-ray treatment.

Very much the same results are obtained when *X* or *Y* films are made one pole in a glow discharge. In this case, however, it is possible to produce either positive or negative potentials according to the direction of the discharge. These *Y* film potentials are more readily reduced by dipping than are the *X* film potentials.

These results are discussed in relation to theories of film structure.

Cambridge, Mass. Received January 22, 1938

[Contribution from the Laboratories of the Rockefeller Institute for Medical Research]

The Meaning and Standardization of the *p*H Scale

By D. A. MacInnes, Donald Belcher and Theodore Shedlovsky

According to almost universal practice *p*H values are computed using the formula

$$pH = \frac{E - E_0}{2.3026RT/F} \qquad (1)$$

in which *R*, *T* and *F* have their usual significance, *E* is the potential of a galvanic cell of the type

$$\text{(Pt)}, H_2;\ \text{solution X} \underset{a}{:} \text{KCl (satd.)} : \text{reference electrode} \qquad \text{(A)}$$

and E_0 is a constant at a given temperature, which depends upon the nature of the reference electrode, and on other considerations which will be discussed in this paper.[1] In cell (A) "solution X" is the fluid the *p*H of which is desired. Although Sørensen[2] originally considered *p*H, as defined by equation (1), to be $-\log C_{H^+}$, in which C_{H^+} is the hydrogen ion concentration, that relation is no longer considered to be valid. It is, however, the basis for the E_0 values mostly used today. More

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[1] The early work on the standardization of the *p*H scale cannot be summarized briefly. It is discussed by W. Mansfield Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, Md., 1928, 3d edition.

[2] Sørensen, *Compt. rend. trav. Lab. Carlsberg*, **8**, 1 (1909).

recently it has been customary to interpret pH according to the relation

$$pH = -\log a_{H^+} \qquad (2)$$

in which a_{H^+} is the hydrogen ion activity. The support for this assumption lies in the belief that the liquid junction potential at the boundary a in cell (A) is very small or constant, so that a change in the value of E when solution X is varied can be due only to a change of hydrogen ion activity. There are at least two difficulties with the assumption involved in equation (2). In the first place the Planck and Henderson equations do not, with commonly used solutions as "solution X," indicate that the liquid junction at a is negligible or constant. These equations lead to increasing values of the liquid junction potential as solution X is diluted. The computed liquid junction potentials, and their change with concentration, are also considerably increased over earlier estimates if recently determined values of the transference numbers of potassium chloride are accepted.[3] In addition, equation (2) involves a single ion activity, a_{H^+}, a quantity which cannot be determined thermodynamically.[4]

Since pH measurements are frequently used in investigations of chemical equilibria in which the hydrogen ion constituent is involved, it seems quite desirable that the pH scale should be adjusted to conform as nearly as possible with thermodynamically measurable quantities. To this end Bjerrum and Unmack[5] and Guggenheim and Schindler[6] make use of the equation

$$pH = \frac{E - E_0 - E_L}{2.3026RT/F} \qquad (3)$$

and compute the liquid junction potential E_L from the, admittedly inexact, Henderson equation. Although this procedure can be justified, it seems very improbable that it will be adopted generally, since it involves the computation of a liquid junction potential in connection with every pH determination. This is inconvenient even when the composition of the solution is known, and is otherwise impossible.

It has seemed to the authors that it is better to conform to current usage and compute pH values by means of the unmodified equation (1), but to adjust to thermodynamic quantities as closely as possible by means of a shift of E_0 from the value commonly used. For this purpose measurements of the pH of buffer solutions consisting of mixtures of a weak acid and its salt were utilized. These solutions were placed as "solution X" in cells of type (A). From the potentials, E, of such cells, and by assuming an E_0 value in equation (1), values of the quantity

$$pK'' = pH - \log \frac{C_{A^-}}{C_{HA}} \qquad (4)$$

in which C_{HA} is the concentration of the acid and C_{A^-} that of its negative ion constituent, were obtained. From these figures it was found empirically that, up to a value of the ionic strength μ of about 0.01 mole per liter

$$pK'' = pK_0 - B\sqrt{\mu} \qquad (5)$$

in which pK_0 and B are constants. In computing pK'' it is necessary, with dilute solutions, to correct, as will be described below, the stoichiometric values of C_{HA} and C_{A^-} for changes in the equilibrium

$$HA \rightleftarrows H^+ + A^-$$

We also have the equation

$$K = \frac{a_{H^+}a_{A^-}}{a_{HA}} = \frac{C_{H^+}C_{A^-}}{C_{HA}}\frac{f^2_\pm}{f_u} \qquad (6)$$

in which K is the ionization constant of the acid, the a values are the activities of the components represented by the subscripts, and $f_\pm$ and f_u are, respectively, the mean ion activity coefficient and the activity coefficient of the undissociated acid. Equation (6) can be rearranged to

$$[-\log C_{H^+}f_\pm - \log (C_{A^-}/C_{HA})] = pK + \log (f_\pm/f_u) \qquad (7)$$

in which $pK = -\log K$. It will be observed, by comparing equations (5) and (7), that the quantity on the left-hand side of the latter equation corresponds to pK'' in the former and, also, that the term $B\sqrt{\mu}$ in equation (5) is in the form of the Debye–Hückel limiting law for the term $-\log (f_\pm/f_u)$ of equation (7), since f_u is nearly

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(3) MacInnes and Dole, THIS JOURNAL, **53**, 1357 (1931); MacInnes and Longsworth, *Chem. Rev.*, **11**, 171 (1932).

(4) If a valid correction for the liquid junction potential at a could be made the change of the activity of the hydrogen ion constituent due to a variation of the composition of solution X could be obtained by observing the change, ΔE, in the potential of cell (A). However, the liquid junction potential, E_L, between solutions I and II is obtained from the equation

$$-E_L = \frac{RT}{F}\int_{I}^{II}\sum_n \frac{t_i}{z_i}\,d\log a_i$$

in which t_i, z_i and a_i are, respectively, the transference number, the valence and the activity of the ion constituent i, the summation being over all the n types of ion present. One of the ion constituents present in the liquid junction is the hydrogen ion, the activity of which is the object of the computation. This dilemma is one from which there is apparently no escape. See Guggenheim, *J. Phys. Chem.*, **33**, 842 (1929); MacInnes and Longsworth, *Cold Spring Harbor Symposia on Quantitative Biology*, **4**, 18 (1936).

(5) Bjerrum and Unmack, *K. Danske Videnskab. Selskab., Math.-fys. Medd.*, **9**, 1 (1929).

(6) Guggenheim and Schindler, *J. Phys. Chem.*, **38**, 533 (1934).

unity, at least for dilute solutions. Furthermore, it will be shown below that the experimental values of B in equation (5) are not far from that of A in the limiting Debye–Hückel expression $-\log f_{\pm} = A\sqrt{\mu}$. The method for selecting E_0 is, therefore, to adjust it until pH values computed with the aid of equation (1), and used in equations (4) and (5), will yield a value of pK_0 equal to the thermodynamic constant pK. It is important in this connection to realize that pK_0 is an empirical constant which is valid for the ionic strengths and the solvent medium investigated. Since the theories of liquid junction potentials indicate that the potential at the surface a in cell (A) would continue to vary as "solution X" is diluted, pK_0 is not necessarily the limit in pK'' that would be obtained if the ionic strength were given extremely low values. The method outlined above for obtaining E_0 yields pH values which are not equal to $-\log C_{H^+}f_{\pm}$ but are probably as close as they can be adjusted to such equality using the unmodified equation (1). The method is essentially that suggested by Cohn, Heyroth and Menkin.[7]

Experimental

The experimental work consisted in the measurement of the potentials of cells of the form

(Pt) H_2; HAc(C_1), NaAc (C_2): KCl (satd.) :
KCl(C_3), HgCl; Hg

in which HAc and NaAc represent acetic acid and its sodium salt, at the temperatures 12.0, 25.0 and 38.0°. Measurements at 25°, using chloroacetic acid and its sodium salt, were also made.

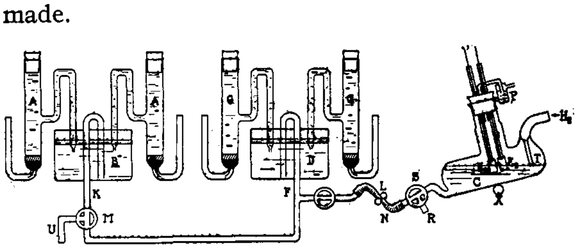

Fig. 1.

The apparatus used in the determination of the potentials of the cells of type (A) is shown in Fig. 1. The hydrogen electrodes E_1 and E_2 are shown in position in vessel C, which contained the buffer mixtures. The vessel was mounted so as to rock gently about the axis X. Hydrogen gas entered C through the tube H_2, bubbled under the surface of the solution through the tube T, and made its exit through the trap P. The hydrogen used, which contained less than 0.001% of oxygen, was obtained by passing tank hydrogen over reduced copper in a quartz tube at 600°. A liquid junction of the solution in vessel C with saturated potassium chloride was made with the aid of the three-way stopcock S. The solution and the saturated potassium chloride were, in turn, passed through the stopcock and out of the reject tube R. The two solutions were then connected through the barrel of the stopcock and the liquid junction drawn into the left hand tube by loosening the pinchcock L on the rubber tube N. Two groups of calomel electrodes, one containing 0.1 N, and the other saturated potassium chloride, were used as references. The saturated electrodes G, G, of which six were actually used, are shown in the figure grouped around the reservoir D of saturated potassium chloride, over which a layer of oil was flowed to prevent evaporation. At 12 and 25° both the 0.1 N and saturated electrodes showed average deviations of 0.05 mv. or less. At 38° the deviation was of the order of 0.1 mv. Electrical connection was made through the tube F. Six 0.1 N calomel electrodes, A, A, in the figure, dipped into the reservoir B of 0.1 N potassium chloride. A liquid junction between the two potassium chloride solutions was conveniently made by opening the stopcock M to the position shown. With a rough adjustment of the levels of the solutions in the reservoirs B and D both solutions flowed out of the tube U. The potential obtained was the same whether the solutions were flowing or not. The arrangement also afforded a comparison of the saturated and 0.1 N calomel electrodes.

The data on acetate buffers at 25° are given in Table I, together with a summary of typical computations. The first two columns of the table give the stoichiometric concentrations of acid and salt in the buffer, the third column gives the potential corrected to 1 atm. of hydrogen of cell (A), using the 0.1 N calomel electrodes as reference. In the fourth column is given the pH obtained with the final value of E determined as described above. The ionic strength, μ, given in the next column is

$$\mu = C_{\text{NaAc}} + C_{\text{H}^+} = C_{\text{NaAc}} + [\text{antilog}(-p\text{H})]/f$$

the activity coefficient, f, being computed from the Debye–Hückel limiting law, which is sufficiently accurate. Values of C_{H^+}, in this connection, are important only in the more dilute solu-

Table I

The Determination of E_0 for the pH Scale at 25° with Sodium Acetate–Acetic Acid Buffers

Concentrations, mole per liter		E. m. f., 1 atm. H_2	pH	Ionic strength, μ	pK''	
CH_3-COOH	CH_3-COONa				Obsd.	Calcd.
0.009000	0.001000	0.5636	3.851	0.001147	4.739	4.737
.008000	.002000	.5811	4.147	.002075	4.729	4.730
.01800	.002000	.5614	3.814	.002163	4.730	4.729
.01600	.004000	.5799	4.127	.004081	4.718	4.719
.01160	.004717	.5921	4.333	.004767	4.717	4.716
.01115	.006181	.5994	4.456	.006219	4.708	4.710
.01055	.007594	.6056	4.561	.007625	4.701	4.706
.01008	.009134	.6113	4.658	.009159	4.699	4.710
.01000	.01000	.6140	4.703	.01002	4.701	4.699
.01015	.01278	.6195	4.796	.01280	4.694	4.691

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[7] Cohn, Heyroth and Menkin, This Journal, 50, 2068 (1928).

tions. The pK'' (observed) values in the sixth column have been obtained from equation (4), the concentrations in the last term having been obtained by subtraction and addition of the hydrogen ion concentration (obtained as given above) from the stoichiometric concentrations.

The pK'' values in Table I can be expressed accurately by equation (5) in the form

$$pK'' = 4.756 - 0.5774\sqrt{\mu}$$

as is shown by comparison of the computed values of pK'' in the last column of the table with those found from the measurements.

The value of pK ($= pK_0$) of acetic acid has been obtained from the closely agreeing determinations by MacInnes and Shedlovsky[8] and by Harned and Ehlers[9] who obtained, respectively, 1.753×10^{-5} ($pK = 4.7562$) and 1.749×10^{-5} ($pK = 4.7572$) for the thermodynamic ionization constant of acetic acid. The E_0 value at 25° resulting from these computations is 0.3358 at 25° when a tenth normal calomel electrode is used as the reference electrode.

The series of measurements involving chloroacetic acid and its sodium salt at 25° given in Table II yielded the pK'' values given in the last column of the table. These may be expressed by the equation

$$pK'' = 2.853 - 0.642\sqrt{\mu}$$

in which the first constant on the right-hand side is the negative logarithm of the ionization constant $K = 1.396 \times 10^{-3}$ of chloroacetic acid at 25° obtained by Shedlovsky, Brown and MacInnes.[10] This series of measurements yielded a value of E_0 0.3357 ± 0.0001 at 25°, in close but not exact agreement with that obtained from the acetic acid buffers. We will, however, adopt the value obtained from the acetate buffers as the computations involving the shift of the ionization equilibrium are less certain with the data on the stronger acid.

TABLE II

THE DETERMINATION OF E_0 WITH CHLOROACETIC ACID–SODIUM CHLOROACETATE BUFFERS AT 25°

Concentrations, mole per liter CH_2ClOOH	$CH_2ClOONa$	E. m. f. 1 atm. H_2	pK''
0.001072	0.001900	0.5176	2.827
.006716	.005108	.4946	2.805
.007840	.007390	.4995	2.795
.008680	.01143	.5075	2.784
.01169	.01647	.5084	2.771
.01443	.01840	.5056	2.766

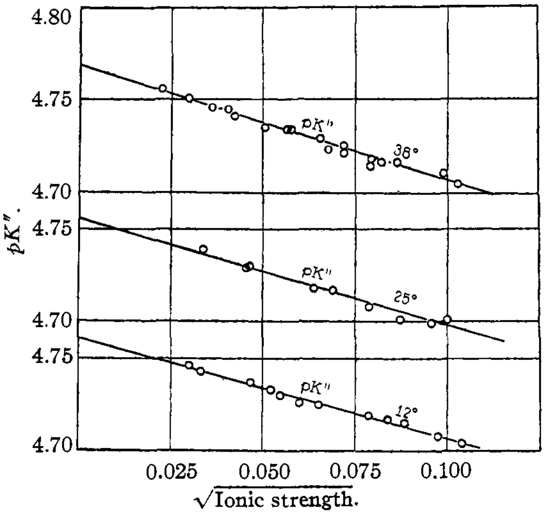

Fig. 2.

The data on the acetate buffers at 12 and 38° are given in Tables III and IV. In Fig. 2 a plot is given of the results of the measurements for these buffers at three temperatures, the pK'' val-

TABLE III

THE DETERMINATION OF E_0 WITH SODIUM ACETATE–ACETIC ACID BUFFERS AT 12°

Concentrations, mole per liter CH_3COOH	CH_3COONa	E. m. f., 1 atm. H_2	pK''
0.001176	0.0008791	0.5989	4.746
.001446	.001081	.5985	4.743
.002879	.002151	.5977	4.737
.003951	.002953	.5972	4.730
.005753	.004299	.5968	4.725
.008206	.006132	.5964	4.719
.01073	.008020	.5960	4.713
.01263	.009435	.5957	4.708

TABLE IV

THE DETERMINATION OF E_0 WITH SODIUM ACETATE–ACETIC ACID BUFFERS AT 38°

Concentrations, mole per liter CH_3COOH	CH_3COONa	E. m. f., 1 atm. H_2	pK''
0.0005684	0.0004896	0.6268	4.756
.0009071	.0008770	.6287	4.751
.001532	.001632	.6304	4.745
.002944	.002536	.6240	4.735
.004445	.004298	.6265	4.729
.005320	.004583	.6230	4.723
.005980	.005216	.6230	4.721
.008666	.007465	.6225	4.716
.01141	.009825	.6221	4.710

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[8] MacInnes and Shedlovsky, THIS JOURNAL, **54**, 1429 (1932).

[9] Harned and Ehlers, *ibid.*, **54**, 1350 (1932). It should be remarked that since the available e. m. f. and conductance measurements are, respectively, on the molar, m, and concentration, C, bases, the ionization constants derived from the two will have slightly different values on that account. The relations between the two constants readily may be shown to be $K_m\rho_0 = K_c$, in which ρ_0 is the density of the solvent. The K_c values are given here and elsewhere in this paper.

[10] Shedlovsky, Brown and MacInnes, *Trans. Electrochem. Soc.*, **66**, 165 (1934).

ues serving as ordinates and the square root of the ionic strength as abscissas. It will be observed that the plots are straight lines for the concentration range involved, that is, up to an ionic strength of about 0.01 mole per liter. At higher ionic strengths the lines tend to curve upward. The values of pK_0 and B of the equation $pK'' = pK_0 - B\sqrt{\mu}$ for the equation for the different series of measurements are collected in columns 3 and 4 of Table V. The pK_0 values given for the acetate buffers at 12° and 38° are the negative logarithms of the ionization constant of acetic acid determined by Harned and Ehlers.[11] Table V also contains a comparison of the experimental value of B of equation (5) with the Debye–Hückel constant A in the equation $\log f = -A\sqrt{\mu}$. It will be seen that the experimental value is in every case larger than the theoretical constant. Also the theory, and recent experimental work,[12] indicate that if the pH were a measure of a mean ion activity, plots such as Fig. 2 would not be linear, but would be curves with tangents approaching the value A in the last column of the table. The most ready explanation of these facts is that the liquid junction at the point *a* in cells of type (A) is not constant, but changes with the concentration of the buffer.

Table V

Buffer mixture	Temp., °C.	pK_0	Obsd. const., B	Debye-Hückel const., A
CH_3COOH, CH_3COONa	12	4.761	0.533	0.495
CH_3COOH, CH_3COONa	25	4.756	.577	.506
CH_3COOH, CH_3COONa	38	4.769	.628	.519
$CH_2ClCOOH$, $CH_2ClCOONa$	25	2.853	.642	.506

The E_0 values at the different temperatures are gathered in Table VI, which also includes interpolated values at 5° intervals. This interpolation can be carried out accurately since the results follow the equation

$$E_{0_t} = 0.3358 - 4.6 \times 10^{-5}(t - 25°)$$

in which t is the temperature. In the last column of the table the values of the same constant as recommended by Clark[1] are given. These are somewhat higher, *i. e.*, 1.8 mv. (0.03 pH unit) at 25° and 0.9 mv. (0.02 pH unit) at 38°.

Table VI

Values of E_0 for the pH Scale, with the 0.1 N Calomel Electrode at Various Temperatures. Figures in Brackets are Interpolated

Temp., °C.		Clark
12	0.3364	....
15	[.3363]	....
20	[.3360]	0.3379
25	.3358	.3376
30	[.3355]	.3371
35	[.3353]	.3365
38	[.3352]	.3361

As already stated, measurements were made of the cell

Hg; HgCl, KCl (satd.): KCl (0.1 *N*), HgCl; Hg

the results at the three temperatures being 12°, 0.0834 v.; 25°, 0.0912 v.; 38°, 0.0977 v. However, from our experience and from a study of the literature, the saturated calomel electrode does not appear to be as reproducible as the tenth normal electrode, possibly due to the fact that the solution of the saturated electrode must be in equilibrium with two solids, a condition which may give rise to pseudo-equilibria and hysteresis effects.

It has seemed desirable to the authors to make accurate redeterminations on the new basis of the pH values of a number of commonly used buffers in standardizing apparatus for pH measurements. For this purpose cells of type (A) were measured, the reference electrode being saturated calomel. The liquid junction between the buffer solution and the saturated potassium chloride was made with the five-way stopcock arrangement described by MacInnes and Belcher.[13] It was, however, adapted, by means of a mercury seal, to be used in a water thermostat. The measurements were referred to a 0.01 N solution of both acetic acid and sodium acetate, the pH value of which was obtained from the work already described in this article. With this standard, pH measurements were made on buffers made from (*a*) a mixture of 0.1 N acetic acid and 0.1 N sodium acetate, and (*b*) 0.05 N potassium acid phthalate, with the results given in the second column of Table VII. The acid phthalate buffer is particularly convenient for use with glass electrodes. With hydrogen electrodes, however, there is evidence of a slight reduction of the material, indicated by potentials which vary with the time and with the rate of flow of the hydrogen. These fluctuations may, however, be minimized by the use of very thinly

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(11) Harned and Ehlers, This Journal, **55**, 652 (1933), see footnote 9.

(12) Brown and MacInnes, *ibid.*, **57**, 1356 (1935); Shedlovsky and MacInnes, *ibid.*, **59**, 503 (1937).

(13) MacInnes and Belcher, *Ind. Eng. Chem., Anal. Ed.*, **5**, 199 (1933); MacInnes and Longsworth, *Trans. Electrochem. Soc.*, **71**, 73 (1937).

platinized electrodes. The values for the two buffers at 12° are based on hydrogen electrode measurements, but with the type of apparatus illustrated by Fig. 1. At 38° sufficiently accurate measurements on the phthalate buffer cannot be made with the hydrogen electrode so that the comparison of the buffers was made with the precision glass electrode apparatus described elsewhere.[13] In addition many measurements were made with glass electrodes at 25° confirming the values given in Table VII.

TABLE VII

THE *p*H VALUES OF SOME BUFFERS AT DIFFERENT TEMPERATURES

Buffer	12°	25°	38°
CH_3COOH (0.01 *N*) CH_3COONa (0.01 *N*)	4.710 ± 0.005	4.700 ± 0.005	4.710 ± 0.005
CH_3COOH (0.1 *N*) CH_3COONa (0.1 *N*)	4.650 ± .005	4.640 ± .005	4.635 ± .005
Potassium acid phthalate (0.05 *M*)	4.000 ± .005	4.000 ± .005	4.015 ± .005

Summary

Measurement of the potentials, E, of cells of the type (Pt), H_2; buffer solution: KCl (satd.): KCl (0.1 *N*), HgCl; Hg were made at 12, 25 and 38°. The results were interpreted with the purpose of obtaining values of E_0 in the equation $pH = (E - E_0)/(2.3026RT/F)$ which will yield values of *p*H which are as useful as appears to be possible in the determination of ionization and other equilibrium constants. The *p*H values of commonly used acetate and phthalate buffers have been redetermined at the temperatures given and expressed on the basis just described.

NEW YORK, N. Y. RECEIVED JANUARY 6, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

Ternary Systems. XXIII. Solid Solution among the Picromerite Double Salts at 25°. The Zinc, Copper and Nickel Ammonium Sulfates

BY ARTHUR E. HILL AND WILLIAM J. TAYLOR, JR.[1]

The picromerite series of double salts, so named from the naturally occurring mineral picromerite,[2] $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$ (also known as schönite), includes a large number of compounds formed from sulfates of the divalent metals Mg, Zn, Cu, Ni, Co, Fe (ferrous), Mn or Cd (in general, the vitriol formers) with the alkali metals K, Rb, Cs, NH_4 and Tl. These crystallize from water as hexahydrates, in the monoclinic system, and show close resemblances in many properties; the existence of solid solutions of several pairs of these salts, at temperatures of 12–13°, was demonstrated by Fock,[3] and they have in general been regarded as an isomorphous series. This paper reports a study of three pairs of salts of this series, under conditions of crystallization from aqueous solution so chosen as to ensure attainment of equilibrium. The method used already has been reported on for several of the alums;[4] it consists simply in preparing duplicate samples for each ratio of salts to be studied, with a difference in order of addition. In one sample, one of the two salts is dissolved completely in the water and the second then added in solid form; in the second the order of addition is reversed, with the result that the equilibrium condition in the solid solution will be approached from the two compositions of the two pure salts. Analysis of the liquid solutions gives identical results when the two samples have reached equilibrium, which may be checked by analysis of the solid phases or by the common methods of determining composition indirectly in three-component systems by extrapolation. By following this simple procedure we are relieved from any uncertainty as to attainment of equilibrium—an uncertainty which has been attached to the majority of investigations of this class and because of which the greater part of the data available are not suitable for quantitative use.

The double salts studied are three in number, $(NH_4)_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$, $(NH_4)_2SO_4 \cdot NiSO_4 \cdot 6H_2O$ and $(NH_4)_2SO_4 \cdot CuSO_4 \cdot 6H_2O$, giving three pairs of isomorphous compounds. We have also repeated work on the formation of two of these compounds from their components.

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(1) The material of this paper is an abbreviation of the thesis presented by Mr. Taylor in partial fulfilment of the requirements for the degree of Ph.D. at New York University, June, 1937.

(2) Winchell, "Microscopic Characters of Artificial Minerals," John Wiley and Sons, Inc., New York, N. Y., 1931, p. 240; Dana, "Textbook of Mineralogy," John Wiley and Sons, Inc., 1932, p. 763.

(3) Fock, *Z. Krist.*, **28**, 337 (1897).

(4) Hill and Kaplan, THIS JOURNAL, **60**, 550 (1938).