

# pH of Solutions of Potassium Hydrogen *d*-Tartrate from 0° to 60°C

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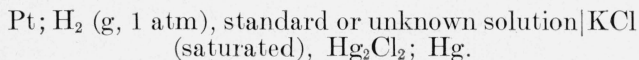
Although it is impossible to establish a thermodynamic scale of hydrogen-ion activity,  $a_{\text{H}}$ , the NBS pH standards are assigned pH values that approach as closely as possible  $-\log a_{\text{H}}$  in dilute buffer solutions. In order to avoid the uncertainties of the liquid junction, electromotive-force measurements of hydrogen-silver chloride cells without liquid junction were used to obtain the standard pH. To assign pH values to four standard tartrate buffer solutions in the temperature range 0° to 60° C, electromotive-force data were obtained for 30 aqueous mixtures of potassium hydrogen tartrate and sodium chloride. One of the proposed standards is a saturated solution of potassium hydrogen tartrate at 25° (pH 3.56), and the others are 0.03-, 0.02-, and 0.01-molar with respect to this salt.

Directions for the preparation and preservation of tartrate buffer standards are given.

## 1. Introduction

For several years the National Bureau of Standards has advocated the universal adoption of a standard scale of pH based upon certain standard reference buffer solutions. The materials from which three of these standards are prepared have been issued as certified pH Standard Samples for more than 6 years. These standards are aqueous solutions of potassium acid phthalate, borax (sodium tetraborate decahydrate), and aqueous mixtures of potassium dihydrogen phosphate and disodium hydrogen phosphate. The pH values assigned to them define fixed points on a modified activity scale. They correspond as closely as possible to the negative of the common logarithm of the activity of hydrogen (hydronium) ion,  $-\log a_{\text{H}}$ , in the respective solutions. It is well recognized, however, that it is impossible to achieve a thermodynamic scale of hydrogen-ion activity [1 to 5].<sup>1</sup>

The practical electrometric determination of pH usually rests on two measurements of the electromotive force of a galvanic cell that may be schematically represented by



The vertical line indicates a liquid junction between the standard (or unknown) and the potassium chloride of the "bridge" solution that forms a part of the calomel electrode. In the most common forms of pH meter, a glass electrode with inner reference replaces the hydrogen electrode at the left of the above scheme. The electromotive force is first obtained with the standard solution in the cell and, secondly, with the unknown solution whose pH it is desired to obtain. These two emf values are designated  $E_s$  and  $E$ , respectively. If the pH of the standard is called  $\text{pH}_s$ , we have

$$\text{pH} = \text{pH}_s + (E - E_s)F / (2.3026RT), \quad (1)$$

<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

where  $F$  is the faraday,  $R$  is the gas constant, and  $T$  is the absolute temperature.<sup>2</sup>

Equation 1 is a definition of the practical pH value and of the practical scale of pH. Evidently the function of the galvanic cell outlined above is simply to compare the pH of the two different solutions, to yield a *difference* of pH. If it were not for defects in the method of comparison, the practical pH would lie on the standard pH scale. However, these defects, chief among which is the variable potential at the liquid junction, have an appreciable effect in highly acid and highly alkaline solutions [7]. In order that the practical pH values shall represent  $-\log a_{\text{H}}$  as nearly as possible, standards with pH close to that of the highly acidic and highly alkaline unknowns are desired. The standards presently available serve successfully to calibrate pH equipment for use in the intermediate range of the pH scale, but others of high and low pH are being sought.

Potassium hydrogen tartrate is only moderately soluble in water, and its saturated solution (about 0.034 molar at 25° C) is a convenient standard with pH near 3.6 [8]. The dissociation constants of tartaric acid do not differ greatly, and accordingly solutions of the primary salt have adequate buffer capacity without the addition of tartaric acid or the secondary salt. For these reasons, potassium hydrogen tartrate was selected as the fourth independent standard of pH, although it offers only a slight extension of the range of the present standards. The assignment of standard pH values to four solutions of potassium hydrogen tartrate is described in the following sections.

## 2. Method

In order to escape the uncertainties inherent in the reduction or estimation of the liquid-junction potential, the assignment of pH values to standard buffer solutions is based on measurements of the electromotive force of galvanic cells without liquid

<sup>2</sup> Values of  $2.3026RT/F$  in absolute volts are to be found in [6].

junction. The cell with hydrogen and silver-silver-chloride electrodes has been chosen as most suitable for this purpose:

Pt; H<sub>2</sub>(g, 1 atm), buffer solution, Cl<sup>-</sup>, AgCl; Ag.

The electromotive force,  $E$ , of this cell is directly related to the standard potential,  $E^\circ$ , and the activities of the hydrogen and chloride ions in the solution.<sup>3</sup> If the activity of each of these ions is replaced by its equivalent,  $mf$ , where  $m$  is molality and  $f$  the molal activity coefficient, we obtain an expression for the acidity function  $-\log(f_{\text{H}}f_{\text{Cl}}m_{\text{H}})$ , for convenience termed  $\text{pwH}$ :

$$\text{pwH} \equiv -\log(f_{\text{H}}f_{\text{Cl}}m_{\text{H}}) = \frac{(E - E^\circ)F}{(2.3026 RT)} + \log m_{\text{Cl}} \quad (2)$$

A soluble chloride must be added to the buffer solution in order that the silver-silver-chloride electrode can be used successfully, yet the pH of the chloride-free buffer solution is desired. Accordingly,  $\text{pwH}$  was measured for three low chloride concentrations, namely 0.015  $m$ , 0.01  $m$ , and 0.005  $m$ , and the limit,  $\text{pwH}^\circ$ , for vanishingly small chloride concentrations obtained by extrapolation.

The standard pH, that is  $\text{pH}_s$ , is formally defined as  $-\log f_{\text{H}}m_{\text{H}}$  and is related to  $\text{pwH}^\circ$  by the following equation:

$$\text{pH}_s = \text{pwH}^\circ + \log f_{\text{Cl}}^\circ \quad (3)$$

where  $f_{\text{Cl}}^\circ$  is the limit approached by the activity coefficient of chloride ion as the concentration of chloride in the buffer solution approaches zero. Unlike  $\text{pwH}$ , the individual ionic activity coefficient,  $f_{\text{Cl}}^\circ$ , cannot be evaluated without an assumption, and consequently  $\text{pH}_s$  must be defined in an arbitrary manner. The more reasonable and accurate is the estimate of  $f_{\text{Cl}}^\circ$ , the closer the standard pH will approach the desired  $-\log f_{\text{H}}m_{\text{H}}$ .

Various assumptions have been used to compute  $f_{\text{Cl}}^\circ$  for the assignment of  $\text{pH}_s$  values to the standard phthalate [11], phosphate [12], and borax [13] buffer solutions. These and other different approaches yield slightly different  $\text{pH}_s$  values for solutions of ionic strengths greater than about 0.01, but all are reasonable and furnish identical pH values at high dilutions [4, 14]. The calculated activity coefficients are all consistent with the Debye-Hückel equation [15].<sup>4</sup>

$$-\log f_{\text{Cl}}^\circ = A\sqrt{\mu}/(1 + Ba_i\sqrt{\mu}), \quad (4)$$

where  $\mu$  is the ionic strength of the buffer solution. The several approaches differ essentially only in the means by which the value of  $a_i$ , the ion-size parameter, is estimated. There is little basis for choice

<sup>3</sup> The numerical values of the activity depend upon the standard state and the scale of concentration chosen. The NBS standard pH scale is based upon molal activities, and all activity coefficients and pH values in this paper will be referred to the molal basis. The standard potential,  $E^\circ$ , is derived from the measurements of Harned and Ehlers [9] as recalculated by Hamer, Burton, and Acree [10]. Its value from 0° to 60° C in absolute volts is found in [6].

<sup>4</sup> Values of the constants  $A$  and  $B$  are tabulated in [16].

among them. When the mean activity coefficients of strong electrolytes and the activity-coefficient terms in buffer-chloride mixtures are fitted to the Debye-Hückel equation, the value of the ion-size parameter is often found to lie between 3 and 6.<sup>5</sup> Hence, a choice of 4 for the calculation of  $\log f_{\text{Cl}}^\circ$  and  $\text{pH}_s$  is justifiable, provided the uncertainty is recognized to be at least as large as the difference between the  $\text{pH}_s$  furnished by  $a_i$  values of 4 and 6. The complete equation for  $\text{pH}_s$  thus becomes

$$\text{pH}_s = \text{pwH}^\circ - A\sqrt{\mu}/(1 + Ba_i\sqrt{\mu}), \quad (5)$$

by combination of eq 3 and 4.

### 3. Experimental Procedures and Results

The potassium hydrogen *d*-tartrate was a composite sample of a lot of 250 lb obtained for issuance as NBS Standard Sample 188. The salt was in the form of a powder. Its aqueous solutions were strongly dextrorotatory. The assay was found to be 99.95 percent by titration with a carbonate-free sodium hydroxide solution to the endpoint of phenolphthalein. The results of other standard tests were as follows:

- Chloride: No turbidity with silver nitrate after the solution had been acidified with nitric acid.
- Calcium: No turbidity with ammonium oxalate in ammoniacal solution.
- Insoluble in NH<sub>4</sub>OH: None perceptible.
- Ammonia: 0.0002 percent.
- Phosphate: Less than 0.002 percent PO<sub>4</sub>.<sup>6</sup>
- Iron: Less than 0.001 percent Fe.<sup>6</sup>
- Sulfur compounds: 0.006 percent SO<sub>4</sub>.<sup>6</sup>
- Heavy metals: 0.001 to 0.002 percent Pb.<sup>6</sup>

The sodium chloride was a recrystallized sample free of bromide. Both the chloride and the tartrate were ordinarily dried at 100° C before use. A good grade of distilled water was used. For the preparation of the saturated tartrate solutions, an excess of the tartrate (usually undried) was added to the solution of sodium chloride. The flask was immersed in the bath at 25° for about 2 hours and shaken occasionally. The excess salt was then removed by filtration through sintered glass. Dissolved oxygen and carbon dioxide were removed by passage of nitrogen through the solutions before the cells were filled. The apparatus, electrodes, and techniques have been fully described in earlier publications [7, 18].

The electromotive-force data were corrected in the usual way to 1-atm partial pressure of hydrogen. The corrected values are summarized in table 1. Each entry in the table represents the average potential difference for two pairs of electrodes in the same cell. In view of the decreased solubility of the tartrate at low temperatures, only the 0.01- $m$  solution was studied between 0° and 10° and only this and the 0.02- $m$  solution between 10° and 25°.

<sup>5</sup> A value of 5.5 was found to give the best fit of the activity-coefficient term in mixtures of sodium hydrogen tartrate, sodium tartrate, and sodium chloride [17].

<sup>6</sup> Analysis performed by the Inorganic Chemistry Section of the Bureau.

TABLE 1. *Electromotive-force data for hydrogen-silver-chloride cells containing aqueous mixtures of potassium hydrogen tartrate and sodium chloride*

KH tartrate molality	NaCl molality	Electromotive force at— (° C)													
		0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°	55°	60°	
Saturated at 25° C	0.015	-----	-----	-----	-----	-----	0.54487	0.54669	0.54846	0.55029	0.55217	0.55398	0.55582	0.55760	
		-----	-----	-----	-----	-----	.54488	.54670	.54851	.55035	.55221	.55406	.55588	.55769	
		-----	-----	-----	-----	-----	.54476	.54662	.54830	.55012	.55199	.55382	.55554	.55736	
	.010	-----	-----	-----	-----	-----	.54468	.54641	.54825	.55008	.55191	.55371	.55554	.55736	
		-----	-----	-----	-----	-----	.55533	.55731	.55931	.56131	.56333	.56529	.56720	.56911	
		-----	-----	-----	-----	-----	.55532	.55737	.55936	.56136	.56340	.56545	.56748	.56950	
	.005	-----	-----	-----	-----	-----	.55537	.55730	.55928	.56123	.56326	.56532	.56729	.56923	
		-----	-----	-----	-----	-----	.55520	.55724	.55920	.56103	.56298	.56506	.56695	.56912	
		-----	-----	-----	-----	-----	.57340	.57562	.57788	.58081	.58243	.58466	.58708	.58951	
	0.03	.015	-----	-----	-----	-----	-----	.57343	.57571	.57789	.58013	.58241	.58469	.58716	.58926
			-----	-----	-----	-----	-----	.57347	.57566	.57795	.58018	.58248	.58470	.58694	.58923
			-----	-----	-----	-----	-----	.57346	.57561	.57812	.58032	.58257	.58503	.58721	.58962
.010		-----	-----	-----	-----	-----	.54503	.54695	.54877	.55059	.55245	.55427	.55610	.55800	
		-----	-----	-----	-----	-----	.54502	.54689	.54871	.55055	.55239	.55422	.55595	.55765	
		-----	-----	-----	-----	-----	.55570	.55768	.55960	.56167	.56374	.56573	.56790	.56987	
.005		-----	-----	-----	-----	-----	.55558	.55752	.55955	.56153	.56345	-----	-----	-----	
		-----	-----	-----	-----	-----	.57372	.57615	-----	-----	-----	-----	-----	-----	
		-----	-----	-----	-----	-----	.57373	.57609	.57835	.58071	.58293	.58518	.58750	.58949	
0.02		.015	-----	-----	0.54035	0.54230	0.54410	.57370	.57601	.57825	.58057	.58287	-----	-----	-----
			-----	-----	.54031	.54214	.54401	.54590	.54786	.54965	.55153	.55340	.55536	.55720	.55902
			-----	-----	.55052	.55260	.55455	.55664	.55854	.56051	.56258	.56455	.56665	.56859	.57059
	.010	-----	-----	.56763	.57001	.57226	.57449	.57694	.57928	.58160	.58393	.58641	.58873	.59115	
		-----	-----	.56758	.56986	.57221	.57460	.57689	.57925	.58134	.58385	.58624	.58853	.59076	
		-----	-----	.54185	.54375	.54567	.54752	.54939	.55119	.55309	.55508	.55700	.55873	.56049	
	.005	-----	-----	-----	-----	-----	.54757	.54948	.55127	.55317	.55502	.55698	.55883	.56083	
		-----	-----	-----	-----	-----	.55799	.56032	.56244	.56455	.56671	.56883	.57086	.57297	
		-----	-----	-----	-----	-----	.55824	.56028	.56224	.56430	.56630	.56836	.57028	.57225	
	0.01	.010	-----	-----	-----	-----	-----	.57633	.57872	.58104	.58346	.58585	.58822	.59045	.59282
			-----	-----	-----	-----	-----	.57632	.57873	.58096	.58335	.58571	.58829	.59065	.59303
			-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
.005		-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	
		-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	
		-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	

#### 4. Calculation of $pH_s$

The  $pW$  was obtained from each emf value by eq 2. These values at each temperature were plotted as a function of the chloride molality, as shown in figure 1, and  $pW^0$  obtained by a straight-line extrapolation to zero concentration of chloride. The values of  $pW^0$  for the four solutions are summarized in table 2. The accuracy of  $pW^0$  is judged to be about  $\pm 0.002$  unit at 25° and  $\pm 0.003$  unit at the other temperatures.

TABLE 2.  $pW^0$  for solutions of potassium hydrogen tartrate

° C	Saturated at 25°	0.03 m	0.02 m	0.01 m
0	-----	-----	-----	3.757
5	-----	-----	-----	3.738
10	-----	-----	3.688	3.719
15	-----	-----	3.674	3.703
20	-----	-----	3.663	3.695
25	3.635	3.641	3.654	3.685
30	3.629	3.636	3.650	3.682
35	3.627	3.632	3.649	3.679
40	3.626	3.632	3.646	3.680
45	3.629	3.637	3.653	3.684
50	3.633	3.641	3.660	3.691
55	3.641	3.649	3.666	3.697
60	3.651	3.656	3.675	3.706

The positions of the straight lines shown in figure 1 were determined by the method of least squares. For the other temperatures, the lines were drawn by inspection. The intercepts obtained by inspection at 25° agreed to 0.001 unit with those obtained by the method of least squares. The concentration of chloride in these mixtures was of the same order of magnitude as that of the tartrate, and the lines might

be expected to display some curvature as the chloride molality decreased. Furthermore, the different solubility of the tartrate in the three chloride solutions

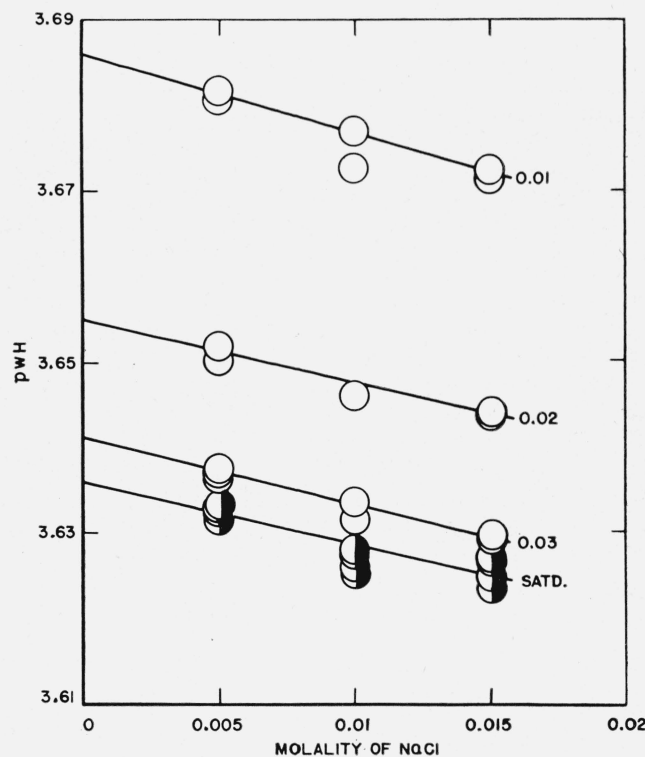


FIGURE 1.  $pW$  of solutions of potassium hydrogen tartrate at 25° plotted as a function of the molality of added sodium chloride.

The molality of potassium hydrogen tartrate appears beside each line. The diameter of each circle corresponds to the estimated experimental uncertainty of 0.1 mV in the emf.

might accentuate the curvature for the saturated solution. Nevertheless, the evidence of curvature was deemed insufficient to justify abandoning the usual linear variation.

The ionic strengths,  $\mu$ , of the tartrate solutions without chloride are required in order to estimate  $\log f_{\text{Cl}^-}$  and to calculate pH from  $\text{pW}^\circ$ . If  $m$  is the molality of potassium hydrogen tartrate (KHTar), the ionic strength is

$$\mu = m - m_{\text{H}_2\text{Tar}} + 2m_{\text{Tar}^-}. \quad (6)$$

The molalities of tartaric acid and tartrate ion can be evaluated with sufficient accuracy in the following manner [20]. From the two overlapping dissociative processes we have

$$m_{\text{Tar}^-} = m_{\text{H}_2\text{Tar}} + m_{\text{H}}. \quad (7)$$

As the sum of the molalities of the three tartrate species is  $m$ ,

$$m_{\text{H}_2\text{Tar}} = 1/2(m - m_{\text{HTar}^-} - m_{\text{H}}), \quad (8)$$

and

$$m_{\text{Tar}^-} = 1/2(m - m_{\text{HTar}^-} + m_{\text{H}}). \quad (9)$$

The equilibrium among the three forms is expressed in terms of the concentration dissociation constants,  $k_1$  and  $k_2$ , of tartaric acid by

$$\frac{k_2}{k_1} = \frac{m_{\text{H}_2\text{Tar}} m_{\text{Tar}^-}}{(m_{\text{HTar}^-})^2}. \quad (10)$$

If  $m_{\text{H}}$  is so small compared with  $m_{\text{HTar}^-}$  that its contribution can be neglected, we can combine eq 8 and 9 with eq 10 and solve for  $m_{\text{HTar}^-}$ :

$$m_{\text{HTar}^-} = m / (1 + \sqrt{4k_2/k_1}). \quad (11)$$

Combining eq 8 and 9 with eq 6 and substituting the value of  $m_{\text{HTar}^-}$  from eq 11 gives the approximate expression for the ionic strength [20]:

$$\mu = m(1 + 0.5x) + 1.5m_{\text{H}}, \quad (12)$$

where

$$x \equiv \frac{\sqrt{4k_2/k_1}}{1 + \sqrt{4k_2/k_1}}. \quad (13)$$

The ratio of the concentration constants,  $k_2/k_1$ , was calculated from  $K_2/K_1$ , the ratio of the thermodynamic constants [17] by

$$\log(k_2/k_1) = \log(K_2/K_1) + 2A\sqrt{\mu}/(1 + 4B\sqrt{\mu}), \quad (14)$$

and the hydrogen-ion concentration was obtained with sufficient accuracy from  $\text{pW}^\circ$ :

$$-\log m_{\text{H}} = \text{pW}^\circ - 2A\sqrt{\mu}/(1 + 4B\sqrt{\mu}). \quad (15)$$

In this way, the ionic strengths of the 0.01- $m$ , 0.02- $m$ , and 0.03- $m$  solutions and that saturated at

25° were found to be 0.012, 0.024, 0.035, and 0.040, respectively. The values of  $\mu$  at the other temperatures were not appreciably different from those at 25°.

The  $\text{pH}_s$  at 25° was calculated by eq 5 with three values of  $a_i$ , namely 2, 4, and 6. The results are shown in figure 2. It is evident that the arbitrary choice of  $a_i$  limits the accuracy with which the pH can be assigned to about  $\pm 0.009$  unit for the saturated solution and about  $\pm 0.003$  for the 0.01- $m$  solution. The  $\text{pH}_s$  was calculated at the other temperatures with  $a_i=4$ .

## 5. Tartrate Buffer Standards

It is apparent from figure 2 that the pH of solutions of potassium hydrogen tartrate increases by only 0.09 unit when the saturated solution is diluted to 0.01  $m$ . Furthermore, it is ordinarily convenient to prepare the unsaturated solutions on a volume basis rather than on a weight basis, that is, to a definite molarity instead of a definite molality. It should be emphasized that this change does not involve an alteration of the standard state to which the numerical values of the activity are referred (compare footnote 3). Inasmuch as  $d(\text{pH})/dm$  is known from the slopes of the plots shown in figure 2, only a determination of density is needed to reveal the difference of pH between 0.01-, 0.02-, and 0.03-*molar* solutions and solutions of numerically equal *molarity*. The density of the saturated solution was found with the aid of a pycnometer of 50-ml capacity to be 1.0036 g ml<sup>-1</sup>. Thus the 0.03000-*molar* solution would be about 0.03005 *molal*, and there would be no perceptible difference between the pH of the 0.03-*molar* and the 0.03-*molal* solutions. This conclusion applies as well to the more dilute solutions. Consequently, the  $\text{pH}_s$  values computed by eq 5 with  $a_i=4$  are listed in table 3 for concentrations on the molar ( $M$ ) scale. The combined uncertainties of the pH values are estimated to be  $\pm 0.012$  unit for the saturated solution and  $\pm 0.006$  unit for the 0.01- $M$  solution.

TABLE 3. pH of solutions of potassium hydrogen tartrate computed with  $a_i=4$

$t$	Saturated at 25°	0.03 $M$	0.02 $M$	0.01 $M$
°C				
0	-----	-----	-----	3.710
5	-----	-----	-----	3.690
10	-----	-----	3.624	3.671
15	-----	-----	3.610	3.655
20	-----	-----	3.598	3.647
25	3.555	3.564	3.590	3.637
30	3.547	3.558	3.584	3.633
35	3.545	3.554	3.583	3.629
40	3.543	3.553	3.579	3.630
45	3.545	3.557	3.586	3.634
50	3.549	3.561	3.592	3.640
55	3.556	3.568	3.597	3.646
60	3.565	3.574	3.606	3.654

\* Lingane chose  $3.57 \pm 0.02$  as the pH of the saturated standard [8]. For the 0.03- $M$  solution, Hitchcock and Taylor found 3.567 at 25° [21]. These

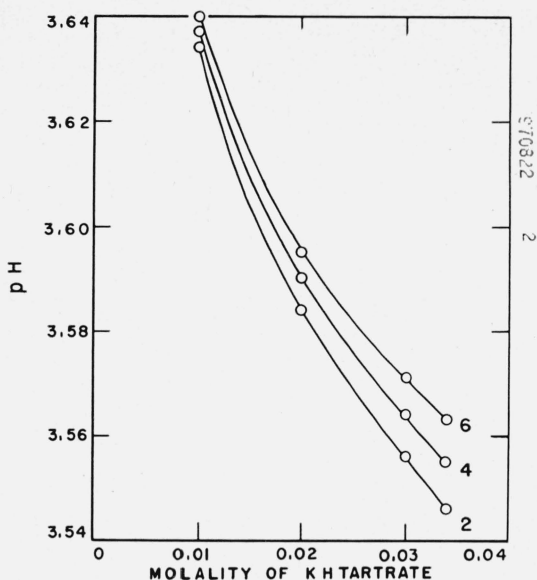


FIGURE 2. pH of solutions of potassium hydrogen tartrate at 25° as a function of molality.

The three curves represent pH obtained by eq 5 with  $\alpha_1$  values of 6, 4, and 2, as marked.

are in good agreement with 3.555 and 3.564, respectively, the values listed in table 3.

It is important to consider the internal consistency of the scale defined by the four pH standards presently available. Ten solutions saturated with potassium hydrogen tartrate were prepared and their pH values measured by a glass-electrode pH meter calibrated with the standard phthalate and phosphate buffer solutions. The pH of each solution at 24° was found to be 3.55 or 3.56. The value obtained in an earlier study by comparison with the phosphate standard in a double hydrogen-electrode cell with liquid junction was 3.561 [7]. The  $\text{pH}_s$  assigned to this saturated standard is  $3.555 \pm 0.012$  at 25° (table 3).

The change of pH suffered by the tartrate standards on alteration of the temperature is primarily determined by the variation of  $-\log K_1K_2$  for tartaric acid. This quantity has been shown to pass through a minimum at a temperature near 35° [17]. Consequently, the change of  $\text{pH}_s$  between 25° and 60° is less than 0.03 unit, as figure 3 demonstrates. The pH of the 0.01-M solution is about 0.08 unit higher at 0° than at 25°.

The growth of molds in solutions of potassium hydrogen tartrate, particularly in the saturated solution, sometimes causes appreciable changes of pH within a few days after the solution is prepared [22]. It is easy to replace the saturated solution as frequently as necessary, but the solutions of lower concentration, though less susceptible to molding, are not as easily prepared. Hence, some experiments were performed to ascertain the usefulness of thymol in retarding the growth of molds. A saturated solution of potassium hydrogen tartrate to which a large crystal of thymol had been added was found to be free of mold 2 months after preparation, whereas two

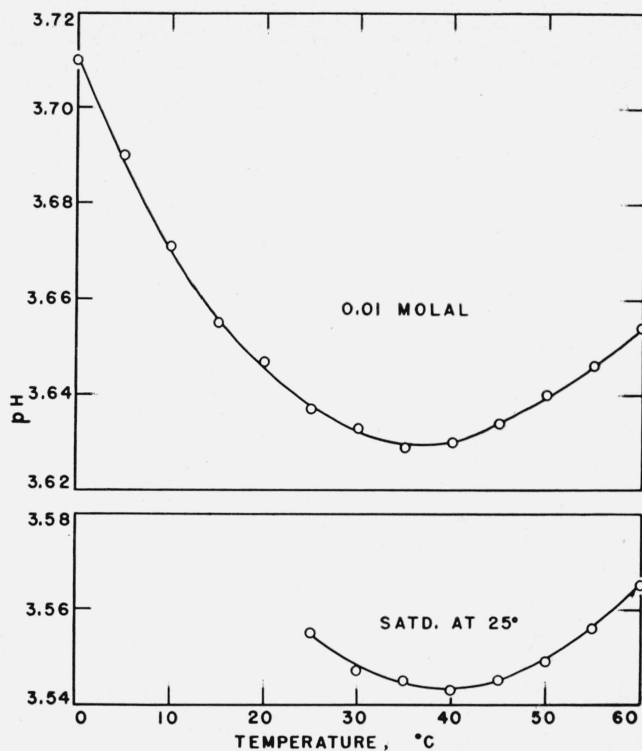


FIGURE 3. pH of the 0.01-M and saturated solutions of potassium hydrogen tartrate as a function of temperature.

others without preservative molded in about 14 days. Two 0.01-M solutions of the tartrate salt, to one of which thymol had been added, were both free of molds 6 weeks after preparation. Thymol is only slightly soluble in aqueous solutions (about 0.006 mole dissolves in a liter of water at room temperature), and pH measurements with the glass-electrode pH meter indicated that its presence did not alter the pH of either the 0.01-M or the saturated buffer solution by more than 0.01 unit. Experiments with the hydrogen electrode were unsuccessful; it appeared that dissolved thymol was catalytically reduced by hydrogen at the platinum surface. Nevertheless, the usefulness of thymol in delaying the molding of tartrate solutions has been affirmed. It is suggested that a crystal of thymol, 8 to 10 mm in diameter, be added to each bottle of standard tartrate buffer.

Potassium hydrogen tartrate is not appreciably hygroscopic, and it is difficult to imagine that the salt could absorb enough moisture to alter significantly the pH of standard tartrate solutions without becoming noticeably wet. A 10-percent error in the concentration of the 0.02-M solution changes the pH by only 0.01 unit. Hence, it is usually unnecessary to dry the salt before it is used.

A good grade of distilled water should be used for the preparation of tartrate standards, but dissolved carbon dioxide need not be removed. The conductance of the water should not exceed  $2 \times 10^{-6}$  ohm<sup>-1</sup> cm<sup>-1</sup> at 25°. Higher conductances may indicate the presence of small amounts of acidic or basic impurities that have a relatively large effect on the pH.

The solubility of potassium hydrogen tartrate is about 0.028 *M* at 20°, 0.034 *M* at 25°, and 0.040 *M* at 30° [19]. By reference to figure 2, it can be seen that the pH at 25° of the solution saturated at 20° does not differ by more than 0.01 unit from the pH of that saturated at 25°. The pH at 30° of the solution saturated at 30° also differs by about 0.01 unit from the pH at 30° of the solution saturated at 25°. Accordingly, the temperature at which the saturated standard is prepared need not be carefully controlled. It is suggested that the excess of the powdered salt be removed by filtration or decantation after the solution has been prepared and the solid allowed to settle. Although a crystal of thymol may successfully retard the growth of molds, these and other pH standards should probably not be considered reliable for more than 2 months after preparation.

## 6. References

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