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EFFECTS OF CORRECTIONS FOR LIQUID - JUNCTION POTENTIALS OF SATURATED CALOMEL ELECTRODES ON DISSOCIATION CONSTANTS OBTAINED BY ELEC- TROMETRIC TITRATION

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ABSTRACT

Determinations were made of the errors in pH, dissociation constants, "salting-out" coefficients, ionic strength, ionic concentrations, and hydrogen-ion activity coefficients arising from neglect or of partial corrections for the potential of the liquid junction between saturated potassium chloride (4.1 *N* KCl-HgCl electrode) and sodium malonate buffer solutions. The experimental data were obtained in the electrometric titration of 0.1 *M* malonic acid with 0.1007 *N* sodium hydroxide. It was shown that partial corrections produce a larger error in these quantities than no corrections. An error as small as 0.3 percent in pH may produce a change as large as 23 percent in dissociation constants.

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I. INTRODUCTION

Three types¹ of calomel electrodes are in accepted use as reference electrodes for the pH determination of unknown solutions. The remarks of this report will be confined to the saturated type. In its application, two sources of error in potential arise. The first is a liquid-junction potential produced by the contact of the KCl solution (contained in the calomel electrode) and the unknown solution; and the second is a liquid-junction potential introduced by the contact between the KCl solution and some solution of known pH, which has been employed in the calomel electrode calibration. These two potentials are usually of the same sign relative to the calomel electrode and may or may not be of the same numerical value. If the solution

¹ Saturated type (4.81 molal or 4.13 normal with respect to KCl). Normal type (mole KCl per liter of solution). Decinormal type (decimole KCl per 1,000 g of H₂O).

employed for calibration has nearly the same equivalent conductance (equal average ionic mobilities) at the same titratable concentration as the unknowns, these two sources of error are approximately equal. This condition is commonly assumed in routine pH measurements. When this assumption is made, the value 0.2458 v listed by Clark [1]², or the more precise value 0.2454 v obtained by Scatchard [2] with activity corrections, is employed at 25° C for the potential of the saturated type of calomel electrode on the hydrogen scale. However, when this assumption cannot be justified or when pH values of an accuracy of 0.1 percent or better are desired, the errors from these two sources must be eliminated. These two sources of error are also present for the other two types of calomel electrodes, and a study of the liquid-junction potentials involved in their calibration and application is now being made.

II. METHODS USED IN MAKING CORRECTIONS FOR LIQUID-JUNCTION POTENTIALS

Various methods have been proposed for elimination of errors due to liquid-junction potentials. Corrections for one or the other source of error have been made, but rarely for both. Walpole [3] measured the 4.1 *N*, the 3.5 *N*, and the 1.75 *N* calomel electrode against acetic acid-sodium acetate buffer solutions and corrected for the liquid-junction potentials by the Bjerrum [4] extrapolation method. This leads to a value of 0.2507 v for the saturated calomel type at 18° C, or 0.2455 v at 25° C, if the temperature coefficient given by Clark [1] is employed. This value is in error owing, first, to the use of Bjerrum's extrapolation method for liquid-junction correction which has been shown to be open to criticism by Kline, Meacham, and Acree [5] whose work was recently confirmed by McBain and Betz [6]; second, to the use of 1.883×10^{-5} for the ionization constant of acetic acid at 18° C, whereas Harned and Ehlers [7] obtained 1.750×10^{-5} from extensive measurements of galvanic cells free of liquid-junction potentials; and, third, to the employment of Kohlrausch's [8] conductivity data for KCl and acetic acid data which have been more accurately determined by MacInnes and coworkers [9]. The extensively employed values of Britton, 0.2518 v [10]; Glasstone, 0.2426 v [11]; and Ingold and coworkers, 0.2449 v [12]; have been either partially corrected or left uncorrected for liquid-junction potentials. Moreover, the values of Britton and Ingold and coworkers, which are a function of ionization constants of weak electrolytes employed in the calomel electrode calibration, are also in error because these ionization constants have been determined by methods which are also subject to corrections for liquid-junction potentials. Glasstone's potential and ours (p. 607) agree fairly closely; a small part of the difference is due to the numerical values of the activity coefficient of the Cl⁻ ion and the normal potential of the silver-silver chloride electrode employed in the two treatments, and a larger part to Glasstone's neglect of interionic effects (E_r , defined in a following section).

To obtain these corrections, it is more satisfactory to employ some electrolyte which is completely dissociated, and whose stoichiometrical activity coefficient and pH value are known, in the calibration of the

² The numbers in brackets here and throughout the text refer to the numbered references at the end of this paper.

calomel electrode. HCl(0.1 *N*), which satisfies these three conditions, was used to great advantage by Scatchard [2]. From measurements and calculations of various galvanic cells, both with and without liquid junction, he obtained 0.2454 v at 25° C for the potential of the saturated calomel electrode on the hydrogen scale. However, this potential value contains the liquid-junction potential due to KCl (sat.) | 0.1 *N* HCl junction, the value of which at 25° C may be obtained from

$$E_D = -0.05915 \int t_i d \ln c_i \\ = -0.05915 \frac{C_1(U_1 - V_1) - C_2(U_2 - V_2)}{C_1(U_1 + V_1) - C_2(U_2 + V_2)} \log \frac{C_1(U_1 + V_1)}{C_2(U_2 + V_2)}, \quad (1)$$

where the limits 1 and 2 refer to solution KCl (sat.) and HCl(0.1 *N*) respectively, and t_i and c_i represent, respectively, the ionic transference number and ionic concentration. For the second equality in equation 1 C , U , and V refer, respectively, to concentration in moles per liter, cationic mobility, and anionic mobility of electrolytes referred to in the limits. Upon substitution of the numerical values $C_1 = 4.13$ *N*; $C_2 = 0.1$ *N*; $V_1 = V_2 = 76.32$ [9]; $U_1 = 73.50$ [9]; and $U_2 = 349.72$ [9] in this equation, the value 0.00465 v is obtained for E_D . Scatchard [2] obtained 0.0047 v by his treatment. The above equation is that given by Henderson [13] for a "continuous mixture" solution junction and is based upon classical laws. However, the total potential at the solution junction is given by the integral

$$E_j = -0.05915 \int_1^2 t_i d \ln a_i = -0.05915 \int_1^2 t_i d \ln c_i - 0.05915 \int_1^2 t_i d \ln f_i \quad (2)$$

or

$$E_j = -E_D - 0.05915 \int_1^2 t_i d \ln f_i = -E_D - E_j' \quad (3)$$

where the limits are the same as given in equation 1, a_i is the activity of the individual ions; c_i the ionic concentration; f_i the practical individual ionic activity coefficient; t_i the ionic transference number; and E_j' , the second integral, corrects E_D for its deviation from classical dilution laws due to interionic effects. The numerical value of E_j' may be evaluated by the graphical method of Harned [14] for each ion involved at the boundary KCl (sat.) | HCl (0.1 *N*). This method gives -0.00074 v for H^+ , -0.00245 v for Cl^- , and $+0.00177$ v for K^+ , or a total value for E_j' equal to -0.00142 v. Therefore, the value of the emf of the calomel electrode (sat. type) on the hydrogen scale becomes equal to $(-E_0 - E_D - E_j')$ or numerically to 0.2422 v at 25° C.

In applications, it is a rather simple matter to employ the Henderson equation to calculate E_D , but the calculation of E_j' by the above defined method is obviously complex. In addition, the latter modification is based upon several assumptions, namely, (1) calculation of ionic activity coefficients by the MacInnes [15] postulation of equality of activity coefficients of K^+ and Cl^- in KCl solutions; (2) uniform ionic diffusion at the boundary junction; and (3) accuracy of the graphical relation between the ionic activity coefficients and ionic transference numbers. In view of these assumptions and the complexity of the mathematical treatment, it is much more convenient

to disregard E_f . This disregard is not as serious as it might at first appear, since an E_f value must also be calculated for the junction $\text{KCl (sat.)} | \text{unknown}$ and this value will oppose the value of -0.00142 v obtained above in the calibration. For example, in the titration of 0.1 M malonic acid by 0.1007 N sodium hydroxide, Burton, Hamer, and Acree [16] obtained -0.00203 v for E_f at the point where 1 ml of alkali had been added to 25 ml of acid. Therefore, for this point on the titration curve of malonic acid, the disregard of E_f produces an error of -0.00061 v. It must be emphasized at this point that this error is strictly relative, as one quantity, f_{H} (the practical activity coefficient of the hydrogen ion), depends upon the value assigned to E_f , and E_f depends upon a value assigned to f_{H} , which, in turn, depends upon the assumption that the emf corrected for E_0 and E_D gives the hydrogen-ion concentration; the magnitude of the error may be somewhat smaller than that calculated above depending upon the value initially assigned to one of these quantities. The important point is that these two E_f values are of the same sign and consequently to some extent counteract each other. The same general conclusions persist throughout the titration. Furthermore, the semithermodynamic equation for the emf at 25°C obtained in the measurement of the pH of an unknown is

$$E = E_0 + E_D + E_f - 0.05915 \log c_{\text{H}} f_{\text{H}}, \quad (4)$$

where E is the measured emf, E_0 is the potential of the saturated calomel electrode on the hydrogen scale, E_D and E_f as previously defined are in this case values for the liquid junction $\text{KCl (sat.)} | \text{unknown}$, c_{H} is the hydrogen-ion concentration, in moles per liter, and f_{H} is the practical activity coefficient of the hydrogen ion. Inspection of this equation shows that an additional factor, namely, $-0.05915 \log f_{\text{H}}$ must be considered. In the calibration, this was done by Scatchard [2], but for the unknown this correction opposes the negative difference (-0.00061 v) obtained by disregarding E_f ; it is positive owing to the fact that the activity coefficients of most if not all electrolytes in dilute solutions are less than unity, with the resultant positive value for $-0.05915 \log f_{\text{H}}$, and the subsequent reduction in error produced by a disregard of E_f . The correction due to $-0.05915 \log f_{\text{H}}$ is a variable depending upon the concentration and is introduced into the calculations of the dissociation constants at each point on the titration curve.

In conclusion, therefore, pending additional study of the effects due to E_f , the value 0.2407 v is more useful and adaptable than 0.2422 v for the calomel electrode (sat. type) potential, providing the Henderson equation is employed for calculating the liquid-junction potential between the saturated KCl and the known buffers. If the latter equation is not employed, 0.2454 v is recommended for this potential.

III. APPLICATIONS OF CORRECTIONS

1. pH VALUES

When the saturated calomel electrode is employed for pH determinations, two distinct treatments are in common practise, namely, (1) no corrections for liquid-junction potentials are made and (2) liquid-junction potential corrections are made for the junction $\text{KCl (sat.)} | \text{unknown}$, in both of which 0.2454 v is employed at 25°C as

the normal electrode potential [16]. A third treatment, and one less subject to error and criticism, is one in which account is taken of all potentials due to solution contacts, including corrections upon the calomel half-cell, with use of 0.2407 v as its electropotential on the hydrogen scale. These three treatments may be illustrated by the data on malonic acid previously reported [16].

The pH values and hydrogen-ion concentrations at 25° C obtained by these three methods are given by the equations
 $(E - 0.2454)/0.05915 = -\log c_H = \text{pH}$ (without corrections); (5)
 $(E - 0.2454 - E_D)/0.05915 = -\log c_H = \text{pH}$ (with buffer corrections); (6)
 $(E - 0.2407 - E_D)/0.05915 = -\log c_H = \text{pH}$ (with total corrections); (7)
 where E_D is the liquid junction potential between KCl (sat.) and the buffer. Owing to the small magnitude of c_H , the values for E_D are the same in equations 6 and 7 [16]. These values as well as pH values by equation 6 have been reported previously. The pH values calculated by equations 5 and 7 are, respectively, 0.05 and 0.08 unit higher than those obtained with the use of equation 6. The values of c_H obtained from these equations are used to calculate the data in tables 1 to 4 inclusive.

2. DISSOCIATION CONSTANTS FOR ENTIRE pH CURVE

Illustrative values of K_1^c and K_2^c , the dissociation constants without corrections for interionic attraction, obtained by the respective expressions $c_H c_{\text{HAN}}/c_{\text{H}_2\text{AN}}$ and $c_H c_{\text{AN}}/c_{\text{HAN}}$, corresponding to the three treatments, are given in table 1. The corresponding ionic strengths are also listed. The designating numbers refer to the pH equations from which the hydrogen-ion concentration was obtained. The corresponding values of the constants corrected for interionic attraction, K_1^a and K_2^a , as well as the hydrogen-ion activity coefficients, are given in table 2 in columns labeled according to the above method. These latter values were calculated from the equation

$$\log K_1^a = \log K_1^c + \log f_H - A \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} + \beta\mu \quad (8)$$

and

$$\log K_2^a = \log K_2^c + \log f_H - 3A \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} + (\beta' - \beta)\mu, \quad (9)$$

in which the "salting-out" terms β and β' for mono- and dibasic salts are provisionally assumed to be zero.

TABLE 1.—Dissociation constants and ionic strengths for malonic acid at 25° C by the three methods

FIRST EQUIVALENT OF SODIUM HYDROXIDE

0.1007 N NaOH	$K_1^c \times 10^3$ (5)°	$K_1^c \times 10^3$ (6)	$K_1^c \times 10^3$ (7)	μ (5)	μ (6)	μ (7)
ml						
0.00	1.95	2.56	1.75	0.01955	0.02229	0.01858
1.00	2.15	2.74	1.93	.02098	.02329	.02002
5.11	2.27	2.67	2.08	.02598	.02709	.02541
11.08	2.29	2.60	2.10	.03462	.03505	.03435
17.10	2.29	2.57	2.11	.04234	.04250	.04223
22.10	2.44	2.84	2.35	.04768	.04774	.04766
24.25	6.31	7.09	5.77	.04978	.04974	.04977

TABLE 1.—Dissociation constants and ionic strengths for malonic acid at 25° C by the three methods—Continued

SECOND EQUIVALENT OF SODIUM HYDROXIDE						
	$K^{\alpha_2} \times 10^6$ (5)	$K^{\alpha_2} \times 10^6$ (6)	$K^{\alpha_2} \times 10^6$ (7)			
25.36	1.99	2.20	1.82	0.05199	0.05201	0.05197
25.86	3.10	3.40	2.84	.05342	.05344	.05341
27.40	4.79	5.27	4.39	.05771	.05771	.05770
28.35	5.21	5.70	4.78	.06024	.06025	.06024
30.39	5.61	6.15	5.14	.06541	.06542	.06541
33.85	5.73	6.31	5.26	.07339	.07340	.07339
39.85	5.67	6.28	5.21	.08522	.08522	.08522
42.85	5.52	6.10	5.06	.09036	.09036	.09036
44.83	5.35	5.95	4.91	.09351	.09351	.09351

^a The numbers given after the K and μ values refer to the equations and methods employed to calculate pH values.

TABLE 2.—Dissociation constants and activity coefficients of the hydrogen ion for malonic acid at 25° C by the three methods

FIRST EQUIVALENT OF SODIUM HYDROXIDE						
0.1007 N NaOH	$K^{\alpha_1} \times 10^3$ (5) ^a	$K^{\alpha_1} \times 10^3$ (6)	$K^{\alpha_1} \times 10^3$ (7)	f_H (5)	f_H (6)	f_H (7)
ml						
0.00	1.52	1.95	1.37	0.895	0.887	0.897
1.00	1.67	2.10	1.51	.901	.893	.903
5.11	1.79	2.08	1.64	.926	.920	.928
11.08	1.81	2.04	1.67	.949	.945	.951
17.10	1.82	2.04	1.67	.949	.945	.951
22.10	1.95	2.26	1.87	.982	.979	.982
24.25	5.04	5.66	4.61	.986	.986	.987
SECOND EQUIVALENT OF SODIUM HYDROXIDE						
	$K^{\alpha_2} \times 10^6$ (5)	$K^{\alpha_2} \times 10^6$ (6)	$K^{\alpha_2} \times 10^6$ (7)			
25.36	1.03	1.14	0.94	.990	.989	.990
25.86	1.59	1.75	1.46	.990	.991	.991
27.40	2.42	2.66	2.22	.993	.993	.994
28.35	2.60	2.85	2.39	.994	.994	.995
30.39	2.74	2.98	2.51	.996	.996	.996
33.85	2.73	2.99	2.51	.998	.998	.998
39.85	2.57	2.85	2.36	.999	1.0	.999
42.85	2.46	2.72	2.23	1.0	1.0	1.0
44.83	2.36	2.62	2.08	1.0	1.0	1.0

^a The numbers given after the K and f_H values have the same significance as in table 1.

TABLE 3.—Concentration of each ion and the unneutralized acid, ionic strengths^a and the primary and secondary dissociation constants of malonic acid at 25° C within the intermediate range

0.1007 N NaOH	C_{Na_2An}	C_{NaHAn}	C_{H_2An}	μ	$K^{\alpha_1} \times 10^3$	$K^{\alpha_2} \times 10^6$
ml						
22.10	0.000868	0.046118	0.000602	0.04886	1.67	2.69
24.25	.001940	.046041	.000268	.05192	1.67	2.66
25.36	.003005	.044394	.000165	.05395	1.67	2.65
25.86	.003601	.044134	.000133	.05497	1.67	2.63
27.40	.005649	.041240	.000074	.05821	1.66	2.60
28.35	.007032	.039213	.000054	.06052	1.66	2.57
30.39	.010087	.034683	.000018	.06495	1.65	2.53

3. DISSOCIATION CONSTANTS FOR INTERMEDIATE RANGE OF pH CURVE

The values of the dissociation constants given in tables 1 and 2 for the first and second equivalent of sodium hydroxide were calculated upon the postulation that any part of the pH titration curve could be treated as though each acid group behaved like a monobasic acid, that is, that the neutralization of the first and second acid groups proceeded separately. That this is not true is evident from the high values obtained for K^c_1 and K^a_1 and the low values obtained for K^c_2 and K^a_2 for the middle portion of the titration curve. More complete data obtained by the method which embodies partial corrections for liquid-junction potentials were reported previously [16]. To obtain the constants for this intermediate range, use may be made of the method given previously [16]. At this point only the treatment which includes total corrections for liquid-junction potentials will be given. The average values of K^c_1 (4.26 to 21.10 ml of added alkali) and K^c_2 (31.85 ml to 44.83 ml of added alkali) were found to be, respectively, 2.10×10^{-3} and 5.16×10^{-6} . These were employed to calculate the concentrations of each ionic species and of the undissociated acid for the intermediate range (22.10 ml to 30.39 ml of added alkali) by the method previously reported [16]. Illustrative values obtained in this manner are given in table 3 in columns labeled according to the above method.

4. ERRORS INVOLVED

The values for each of the preceding quantities calculated by the third treatment (with total liquid-junction potential corrections) are accurate to within ± 0.10 percent; deviations are due to experimental errors and differences in the two E_f values. The errors produced in these quantities when no corrections are made will be designated ewc (errors without corrections) and the errors produced by partial corrections will be designated ebc (errors due to buffer corrections only). These errors are summarized in table 4.

TABLE 4.—Summary of errors

MINIMUM ERRORS					
Quantity	ewc	ebc	Quantity	ewc	ebc
	Percent	Percent		Percent	Percent
emf	-0.0013	-0.0047	$f_H(K^c_1)^d$	-0.10	-0.10
pH	- .30	- .70	$f_H(K^c_2)^d$	$\pm .00$	$\pm .00$
K^c_1	+9.35	+22.87	$C_{NaHA_n}(IR)^e$		+ .81
K^a_1	+16.67	+38.89	$C_{Na_2A_n}(IR)^e$		- .62
K^c_2	+9.33	+22.78	$C_{H_2A_n}(IR)^e$		- .43
K^a_2	+22.22	+36.60	β^b	(+)	(-)
$\mu(K^c_1)^d$	+ .03	+ .09	$(\beta^a - \beta)^b$	(-)	(-)
$\mu(K^c_2)^d$	$\pm .00$	+ .61	$K^a_1(IR)^e$		+23.95
$\mu(IR)^d$		- .66	$K^a_2(IR)^e$		+10.74

MAXIMUM ERRORS					
Quantity	ewc	ebc	Quantity	ewc	ebc
	Percent	Percent		Percent	Percent
emf	- .0023	- .0047	$f_H(K^c_1)^d$	- .22	- 1.11
pH	- 1.00	- 4.20	$f_H(K^c_2)^d$	- .10	- .20
K^c_1	+11.42	+46.28	$C_{NaHA_n}(IR)^e$		+1.04
K^a_1	+8.29	+20.60	$C_{Na_2A_n}(IR)^e$		- 1.49
K^c_2	+10.95	+42.34	$C_{H_2A_n}(IR)^e$		+6.11
K^a_2	+22.88	+44.44	β^b	(+)	(-)
$\mu(K^c_1)^d$	+5.20	+19.95	$(\beta^a - \beta)^b$	(-)	(-)
$\mu(K^c_2)^d$	+1.96	+1.92	$K^a_1(IR)^e$		+27.27
$\mu(IR)^e$		+ .86	$K^a_2(IR)^e$		+25.30

^a Unit is volt.

^e Not for the product, but for the quantity in parenthesis.

^b Sign only (magnitude can only be estimated).

^d Intermediate range (IR).

It is to be noted that in all cases partial corrections for the liquid-junction potentials produce a larger error than no corrections. This is due to the same sign of the potentials for the junctions KCl (sat.) | HCl (0.1 *M*), and KCl (sat.) | malonate buffers which oppose each other in the setup of galvanic cells for pH measurements. It is also to be noted that the difference in the minimum and maximum error for K^a is less than for K^c , and is due to the negative error in f_H and the positive errors in the β values, which is equivalent to a negative error in the activity coefficients of the malonate ions (Debye-Hückel-Guggenheim calculation [16]). Although the errors in pH are small (0.3 to 4.2%), the errors in the dissociation constants become as much as 46 percent. This emphasizes the fact that although pH values may be in error by a small percentage only, interpretations or values calculated from them may be far from the truth or the correct magnitude.

Another error, although expressed in sign only, leads to a serious misinterpretation. The "salting-out" coefficient, β , for monobasic salts has a positive value when all or no corrections are made, but partial corrections give this coefficient a negative value. For the same coefficient (β') for dibasic salts, the sign (—) remains the same for all three treatments, but ($\beta' - \beta$) is of less magnitude when all corrections are made.

IV. DISCUSSION

The true dissociation constants of malonic acid in the presence of sodium malonate salts when all corrections have been made are $K_1^a = 1.67 \times 10^{-3}$ (NaHAn = 0.016815 to 0.046526 *N*) and $K_2^a = 2.51 \times 10^{-6}$ (Na₂An = 0.010133 to 0.018250 *N* and NaHAn = 0.035002 to 0.022835 *N*).³ These are average values in the middle range of the titration of each acid group. They are equal to the true ionization constants (K_1 and K_2) in pure water only, providing β and ($\beta' - \beta$) have zero value. That this is not the case is evident from the slight decrease in K_1^a values and slight increase in K_2^a values, as the ionic strength decreases. Since β has been found to be positive and ($\beta' - \beta$) negative the true value of K_1 must be smaller than K_1^a and K_2 must be larger than K_2^a , providing the trend found here persists from ionic strengths of 0.02 and 0.05, respectively, to zero ionic strength. The magnitudes of β and ($\beta' - \beta$) can only be estimated from these measurements, since in the titration a variable buffer ratio is present and extrapolations are made over too large a concentration range. The average value of K_1 obtained from conductivity measurements is 1.64×10^{-3} which agrees fairly well with 1.67×10^{-3} obtained here. Vogel and Jeffery's [16] value of 1.397×10^{-3} , obtained by conductivity, may be low owing to their introduced assumption of similarity of conductivity for the carboxyl and carbamyl groups because of the near identity in the parachors of these groups. Gane and Ingold's [12] value of 1.49×10^{-3} may be low because of the method they employed in elimination of liquid junction in their titration determination. The conductivity data for K_2 vary from 1.0 to 2.1×10^{-6} [16] (Wegscheider's [16] value of 10.0×10^{-6} excepted) and the electrometric data from 2.03 to 4.45×10^{-6} [10, 16]. This large discrepancy is due to three facts: (1) neglect of liquid-junction potentials in the

³ These values may still contain a small error due to effects of E_j , and work on a method for measuring the pH of unknowns in which no liquid junction is present is now in progress. Other incidental errors which may influence these results are (1) method of junction formation, Guggenheim, *J. Am. Chem. Soc.* **52**, 1316 (1930), and (2) heats of mixing at the junctions, Hamer, *J. Am. Chem. Soc.* **57**, 662 (1935).

latter values; (2) neglect of interionic attraction effects in both methods; and (3) methods employed for extrapolation to obtain limiting ionic mobilities in the former case.

If the classical treatment corrected for activity as described previously [16] is employed K^a_1 becomes 1.5×10^{-3} and K^a_2 becomes 2.2×10^{-6} . K^a_1 is in poorer agreement with the average conductivity data but K^a_2 is in better agreement. However, this agreement cannot be used as a criterion for preference of this treatment because of reasons given previously [16], because of the quality of the data and because of the assumptions that must be employed in this classical treatment.

V. SUMMARY

The potential of the saturated type of calomel electrode free of liquid-junction potentials was found to be 0.2422 v on the hydrogen scale at 25° C. It was shown that the value 0.2407 v is a more useful and adaptable value for pH determinations of known buffers, providing the Henderson equation is subsequently employed for the evaluation of the liquid-junction potential between KCl (sat.) and the buffer.

Errors in pH, dissociation constants, ionic strength, signs of "salting-out" coefficients, and hydrogen-ion activity, due to neglect of or partial corrections for potentials of the liquid junctions were calculated for malonic acid at 25° C. It was found that partial corrections lead to larger errors than no corrections. It was also found that, although maximum errors in pH may be only 4.2 percent, the maximum errors in derived quantities (dissociation constants) may become as much as 46 percent.

The primary and secondary dissociation constants of malonic acid in sodium malonate buffer solutions at 25° C were found to be, respectively, 1.67×10^{-3} and 2.51×10^{-6} when total liquid-junction potential corrections are made. The relations of these values to those expected in pure water were discussed.

VI. REFERENCES

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