

# POTENTIOMETRIC STUDIES ON THE DISSOCIATION OF GALLIC ACID

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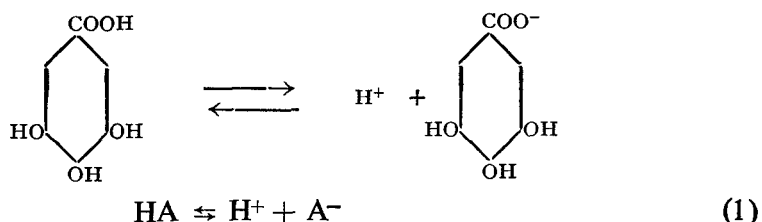
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## 1. INTRODUCTION

GALLIC acid is one of the important constituents which offer colour to sugar-cane juices; and in part contributes to the acid character of the juices. Further gallic acid is employed as an analytical reagent. Thus Neish<sup>1</sup> used gallic acid for precipitation of thorium; Charlot<sup>2</sup> employed the same as a reagent for the ions of the aluminium group; and Datta<sup>3</sup> studied the action of gallic acid on a number of inorganic ions like  $\text{Cu}^{+2}$ ,  $\text{Hg}^{+2}$ ,  $\text{Al}^{+3}$ . To understand the role of gallic acid in the above process, especially the interaction of the anion of gallic acid and the metallic cations, the knowledge of the dissociation constant  $k$  of an apparently primary reaction



is of importance. The data on the subject are scanty in the literature. Using conductometric method Ostwald<sup>4</sup> (1889) obtained a value of  $3.8 \times 10^{-5}$  for the dissociation constant  $k$ , while Magnaini<sup>5</sup> (1891) reported that  $k = 3.4 \times 10^{-5}$ ; both these results refer to a temperature of 25° C. No data exist in the literature for higher temperatures, which appeared desirable in view of the fact that cane juices are operated in sugar factories at temperatures ranging from 60–80° C. The present communication reports the determination, employing potentiometric method, of the dissociation constants of gallic acid in the range 30–80° C.; these have been employed for calculating the thermodynamic functions such as changes in free energy, entropy, etc., associated with the dissociation of gallic acid.

## 2. EXPERIMENTAL

Commercial sample (B.D.H.) of gallic acid was purified by recrystallisation in water. Needle-shaped crystals obtained on slow cooling of the saturated solution of the acid were washed with ice-cooled distilled water; this enabled us to get the purest sample with considerable ease. The crystals were later dried at 160° C. The procedure was repeated till the final product gave a constant melting-point (252° C.).

Merck sodium hydroxide was used; no attempt was made to purify this sample. Its solution was standardised in the usual manner by titrating against a solution of known strength of oxalic acid. This last was of Merck "Extra Pure" quality.

It is known that gallic acid gets readily oxidised in presence of alkalis; the titrations had, therefore, to be carried out in an inert atmosphere. For this purpose the solution in the titration flask was deoxygenated at every stage of titration by bubbling purified nitrogen.

The titration was carried out in a vessel immersed in a paraffin oil thermostat maintained at any desired temperature; the constancy of the thermostat was  $\pm 0.1^\circ$  C.

The hydrogen-ion concentration of the system at every stage of titration was measured by H<sub>2</sub> type pH meter.

## 3. RESULTS

Figure 1 gives a typical series of results selected out of four sets of data obtained during titration of 60 c.c. of gallic acid solution of known strength against 0.094 N NaOH solution. It was interesting to note that as in other cases employing monocarboxylic acids, a remarkably sharp inflexion could be noticed at the end points over the entire range of temperatures investigated. Prolonged titrations for the apparently possible observation of further one or more inflexions due to interactions with NaOH of the phenolic groups of gallic acid could not be carried out on account of the limitations of our apparatus especially the pH measurements therewith.

## 4. COMPUTATION OF CLASSICAL DISSOCIATION CONSTANT *k*

From the data in Fig. 1, the equilibrium concentrations of undissociated acid (HA) and that of anion (A) were computed for different volumes of the titrant added. It follows from the equation

$$k = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad (2)$$

that value of *k* could be obtained by plotting corresponding values of pH against log [HA]/[A<sup>-</sup>]: the value of pH at log [HA]/[A<sup>-</sup>] = 0 gives *p**k*.

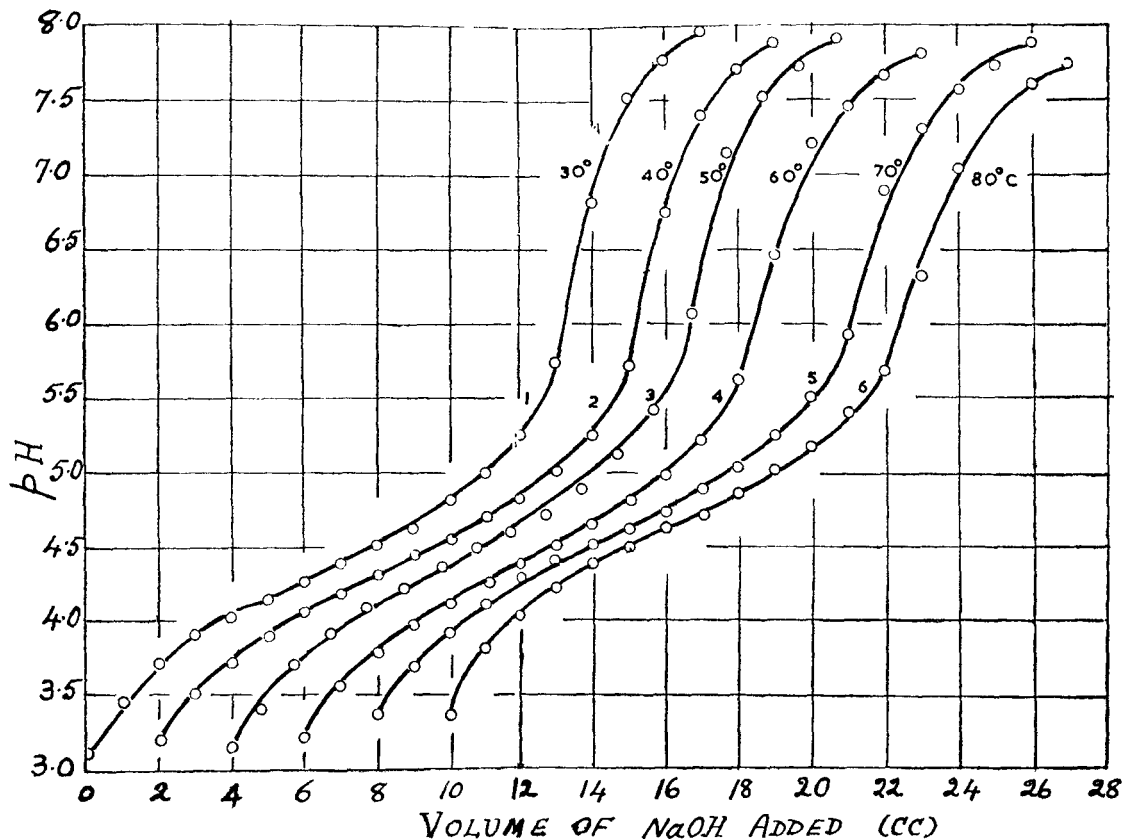


FIG. 1. Curves representing the variation of pH during titration of gallic acid against standard NaOH. The scale on the abscissa is for curve 1; the other curves have been shifted progressively to the right by 2 c.c.

These data are returned in Table I. The data in column 3, Table I, refer to the values of the dissociation constant computed from half neutralisation points on the curves in Fig. 1. It is seen that the values of  $k$  obtained by the two methods agree fairly closely. The data in column 2, *i.e.*, the values of  $k$  obtained from plots pH vs.  $\log [HA]/[A^-]$  were, however, employed for further considerations reported hereinafter.

##### 5. CALCULATION OF THERMODYNAMIC DISSOCIATION CONSTANT $K$

Applying the concept of activity coefficients, we get that the thermodynamic dissociation constant  $K$  of the acid is given by

$$K = \frac{f_{H^+} \cdot f_{A^-}}{f_{HA}} \cdot \frac{[H^+][A^-]}{[HA]} \quad (3)$$

TABLE I  
*Classical dissociation constant of gallic acid*

Temperature ° C.	pK (From Fig. 1)	pK (From Fig. 2)
30	4.38	4.38
40	4.40	4.42
50	4.45	4.45
60	4.46	4.47
70	4.48	4.50
80	4.65	4.68

where  $f$  represents the activity coefficients of the constituents. The following modified Debye and Huckel equation<sup>6</sup> can be employed for the computation of the value of  $f$ :

$$-\log f_{\pm} = \frac{AZ_i^2 \sqrt{\mu}}{1 + \sqrt{\mu}} \quad (4)$$

where  $\mu$  is the ionic strength of the solution. The values of the Debye-Huckel constant  $A$  employed in the present calculations were due to Bates and co-workers.<sup>7</sup> It is assumed that the activity coefficient of the undissociated molecule is unity. The ionic strengths of the system at different stages of titration were calculated for evaluation of  $K$ . The values of  $K$  were obtained from the plots pH vs. the ratio of the activities of HA and A<sup>-</sup> (see Fig. 3). These are given in Table II.

#### 6. THERMODYNAMIC DISSOCIATION CONSTANT OF GALLIC ACID FROM ADDITIVITY PRINCIPLE

Dippy and Williams<sup>8</sup> determined the values of thermodynamic dissociation constants of substituted benzoic acids. The values of  $K$  for *o*-, *m*- and *p*-hydroxy benzoic acids are given in Table III.<sup>9</sup> It is seen that introduction of a hydroxyl group into the nucleus of the benzoic acid alters the dissociation constant  $K$  of the acid by a known magnitude depending upon the position of substitution. This is elucidated as follows from the standpoint of the electronic theory of valency.<sup>10, 11</sup> The carboxyl group attached to an aromatic ring is a powerful electron attracting group; it tends to draw

towards itself electrons from *ortho*- and *para*-positions. Consequently the carboxyl group becomes a centre of negative charge while the hydroxyl group acquires an induced positive charge. The dissociation of the proton from the carboxyl group is, therefore, opposed. A hydroxyl group in the *ortho*-position to the carboxyl group, however, tends to form a hydrogen bond with the latter resulting in apparent neutralisation of the induced negative charge on the electronegative group. This renders the proton of the hydroxyl group more tightly bound. The overall effects of the above factors can be summarised as follows<sup>11</sup>:

TABLE II  
Thermodynamic dissociation constant of gallic acid

Temperature °C.	<i>pK</i> (From Fig. 3)	<i>pK</i> (From Eq. 6)
30	4.46	4.43
40	4.49	4.49
50	4.53	4.54
60	4.56	4.60
70	4.64	4.66
80	4.77	4.72

1. *Hydroxyl group in ortho-position.*—Dissociation of COOH group is aided and the dissociation of hydroxyl group is suppressed.
2. *Hydroxyl group in meta-position.*—No marked influence is observed.
3. *Hydroxyl group in para-position.*—The carboxyl group is rendered less ionisable while the OH group becomes more acidic in character.

Ingold<sup>12</sup> discussed the influence of the substituted hydroxyl group on the dissociation of the carboxyl group of benzoic acid. It is known that it follows a simple additivity principle in case of *ortho*- and *para*-substituents. Thus the effect of introduction of a hydroxyl group in *ortho*-position to COOH group is to lower the *pK* value by 1.17 units, while the addition of OH in the *para*-position increases *pK* by 0.37 units.

It is of interest to examine the applicability of this additivity principle to compute the thermodynamic dissociation constant *K* of gallic acid, a

molecule of which contains three hydroxy groups, 2 in *meta*-position and 1 in *para*-position, to —COOH group. This leads to a value of 4.44 for  $pK$  for gallic acid, in good agreement with observed value of 4.46 at 30° C. (see Table III).

#### 7. EFFECT OF TEMPERATURE ON THERMODYNAMIC DISSOCIATION CONSTANT $K$

The values of  $K$  obtained at different temperatures in the range 300–360 Å are given in Table III (Fig. 2). It is of interest to note that  $K$  decreases progressively with rise in temperature. Essentially similar results were

TABLE III  
*Dissociation constants of substituted benzoic acids*

Acid	$pK$	Contribution of the substituted groups
1. Benzoic acid	.. 4.17	..
2. O-hydroxy benzoic acid	.. 3.30	—1.17
3. <i>m</i> -hydroxy benzoic acid	.. 4.12	—0.05
4. <i>p</i> -hydroxy benzoic acid	.. 4.54	+0.37
5. Gallic acid	.. 4.44 (4.46)	+0.27

obtained for other carboxylic acids like acetic acid.<sup>13</sup> Detailed examination of the data in Table III shows that the variation of  $K$  with temperature can be represented by the following equation.<sup>14</sup>

$$- \ln K = \frac{A}{T} + B + CT. \quad (6)$$

The constants  $A$ ,  $B$  and  $C$  of equation (6) were computed from the data in Table III employing the method of least squares. These are as follows:

$$A = 84.11$$

$$B = 5.59$$

$$C = 14.29 \times 10^{-3}.$$

It may be noted that equation (6) governs well the variation of  $K$  with temperature as evidenced by the fact that the values of  $K$  calculated from

equation (6), agreed closely with those obtained from the experimental data (cf. columns 2 and 3, Table II; also Fig. 2).

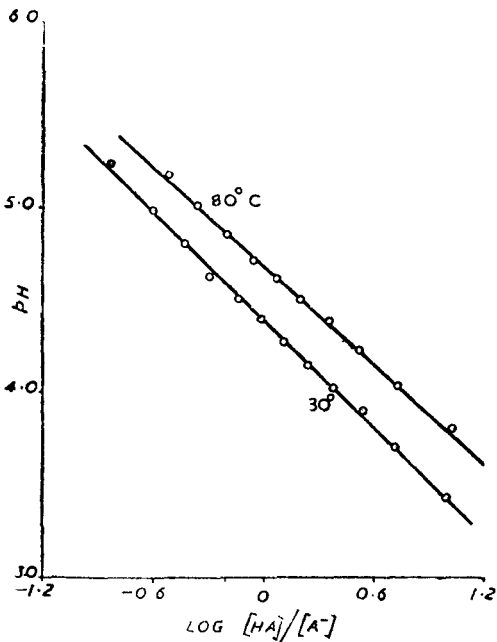


FIG. 2. Computation of classical dissociation constant of gallic acid.

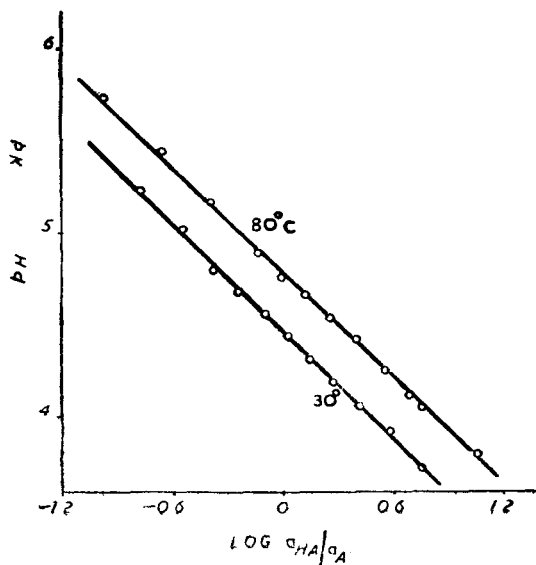


FIG. 3. Computation of thermodynamic dissociation constant of gallic acid.

## 8. THERMODYNAMIC FUNCTION OF THE DISSOCIATION OF GALLIC ACID

The thermodynamic functions associated with the dissociation of gallic acid were calculated from the constants of equation (6) using the following relationships:

$$\Delta F = R(A - BT - CT^2) \quad (7)$$

$$\Delta H = R(A - CT^2) \quad (8)$$

$$\Delta S = R(-B - 2CT) \quad (9)$$

$$\Delta C_p = R(-2CT) \quad (10)$$

The values of these functions at different temperatures are returned in Table IV.

TABLE IV

*Thermodynamic functions of dissociation of gallic acid*

Temperature ° K.	$\Delta F$ I.J./mole	$\Delta H$ I.J./mole	$\Delta S$ I.J./deg./mole	$\Delta C_p$ I.J./deg./mole
303	25689	-10206	-118.5	-71.9
313	26884	-12335	-120.8	-74.2
323	28105	-13091	-123.2	-76.7
333	29348	-13870	-125.6	-79.1
343	30616	-14672	-127.9	-81.5
353	31906	-15499	-130.3	-83.9

Shorter and Stubbs<sup>15</sup> reviewed the work on the ionisation of substituted benzoic acids. These authors showed that the change in free energy of ionisation is altered by each substituent by a characteristic amount. The effect on the free energy of ionisation of two substituents in the same nucleus is roughly the sum of their individual effects. Thus, substitution of a hydroxyl group in the *para*-position was found to change  $\Delta F$  by + 500 cal./mole, while  $\Delta F$  for *meta*-substituted acid differed from that of the benzoic acid by - 120 cal./mole. These considerations suggest that  $\Delta F$  for gallic acid should have a value of 24.93 kilointernational joules/mole at 25° C. in accord with a value of 25.689 kilointernational joules/mole at 30° C, obtained in the present work.



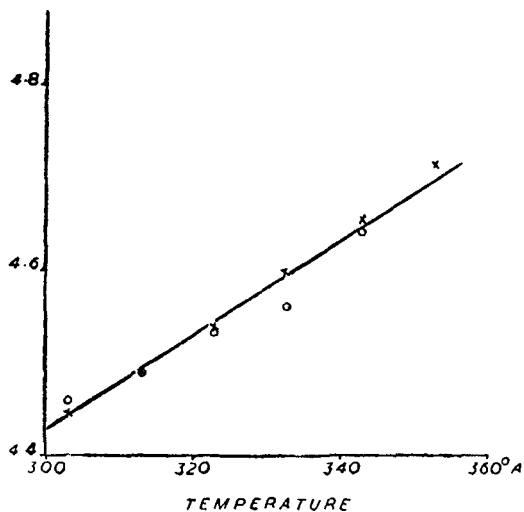


FIG. 4. Variation of  $pK$  with temperature of the system. O, observed; x, calculated.

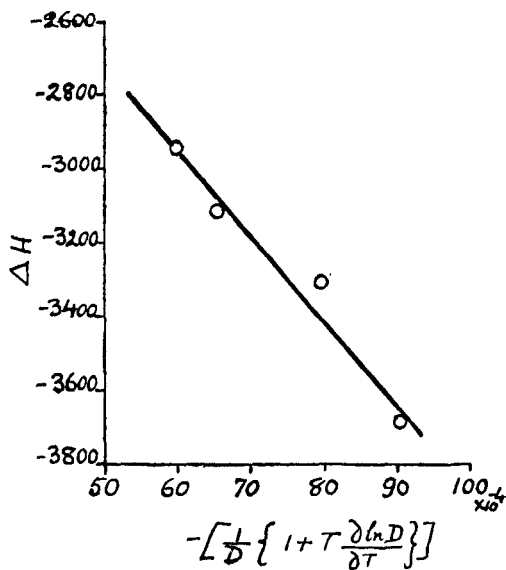


FIG. 5. Linear variation of  $\Delta H$  with  $\frac{1}{D} \left[ 1 + T \frac{\partial \ln D}{\partial T} \right]$

## 9. IONIC RADIUS OF GALLIC ACID ANION

Baughan<sup>16,17</sup> on the basis of the theoretical suggestions made by Gurney derived the equation for  $\Delta H$  in terms of the heat of ionization ( $\Delta H_x$ ), dielectric constant  $D$ , etc.

$$\Delta H = \Delta H_x + C \left[ \frac{1}{D} \left( 1 + T \frac{\partial \ln D}{\partial T} \right) \right]. \quad (11)$$

Here  $\Delta H_x$  may be regarded either as the heat of ionisation in a medium of infinite dielectric constant where no electric work would be involved, or as the heat effect if there were no separation of the electrical charges in the dissociation process.<sup>18</sup> Equation (11) requires that  $\Delta H$  should be linearly variant with

$$\left[ \frac{1}{D} \left( 1 + T \frac{\partial \ln D}{\partial T} \right) \right].$$

For evaluation of this expression, Wyman's<sup>19, 20</sup> data on dielectric constants were employed. It is instructive to note from the data in Fig. 4 that the plot of  $\Delta H$  in cal./mole vs.

$$\left[ \frac{1}{D} \left( 1 + T \frac{\partial \ln D}{\partial T} \right) \right]$$

was sensibly linear in accord with equation (11). The slope of the plot in Fig. 4 gives the value of  $C$  of equation (11). Born<sup>21</sup> observes that  $C$  refers to the work involved in creating the electrical field around the anion and is given by

$$C = \frac{N\epsilon^2}{2} \left( \frac{1}{r^+} + \frac{1}{r^-} \right) \quad (12)$$

where  $\epsilon$  is the elementary charge,  $N$  Avogadro number and  $r^+$  and  $r^-$  are the radii of hydronium ion and the gallic acid anion. Using a value of  $6.02 \times 10^{23}$  for  $N$ ,  $4.8 \times 10^{-10}$  for  $\epsilon$  and  $0.74 \text{ \AA}$  for the *ionic radius* of hydronium ion,<sup>22</sup> we obtain a value of  $0.78 \text{ \AA}$  as the radius of the gallic acid anion. It is instructive to compare this value with the *ionic radii* of the anions of acetic acid and formic acid, which are  $0.77$  and  $0.68 \text{ \AA}$  respectively.<sup>23</sup>

## 9. SUMMARY

Dissociation of gallic acid at different temperatures in the range 300–380  $\text{\AA}$  was investigated using glass and calomel electrodes. Applying modified Debye-Huckel equation the thermodynamic dissociation constant  $K$  was calculated. The variation of  $K$  with temperature  $T$  appeared to follow;—

$$-\ln K = \frac{A}{T} + B + CT$$

where the constants **A**, **B** and **C** for gallic acid were 84·11, 5·59 and 14·29  $\times 10^{-3}$  respectively. From these, the thermodynamic functions  $\Delta F$ ,  $\Delta H$ ,  $\Delta S$  and  $\Delta Cp$  were computed. The effect of substitution of three hydroxyl groups in the nucleus of benzoic acid on  $pK$  and  $\Delta F$  was discussed. The radius of the anion of gallic acid was computed from the calculated values of  $\Delta H$ ; it corresponded to 0·78 Å.

#### 10. ACKNOWLEDGEMENT

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