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A New Acidity Function, T_0, in Acid-catalyzed Reactions

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In acid-catalyzed reaction systems a new acidity function, T_0, which is related to the first-order rate constant, k_1, by the equation $\log k_1 = C - T_0$ was defined by $T_0 = -\log (a_{\mathrm{H}^+}/a_w{}^{h_5-h_1} f^{\ddagger})$ and was theoretically calculated in much the same manner as in Glueckauf's treatments on a salt solution but with the additional assumption that the character of a hydrated univalent activated complex is represented by that of a hydrated alkali metal cation. The calculated results show that T_0 in hydrochloric acid can be represented by:

$$T_0 = 2.4(3.9 - h_1 + h_5) \log a_w - \log m_a.$$

This equation shows that if the hydration number (the water molecules bound with an activated complex) of an activated complex, h_1, increases by one, the corresponding increment of T_0 becomes $-2.4 \log a_w$. It was also shown that the value of $f_{\mathrm{AH}^+} f_{\mathrm{B}}/f_{\mathrm{A}} f_{\mathrm{BH}^+}$ is not always constant, but depends on the hydration numbers of the AH^+ and BH^+ species as well as on the acid concentrations. The factors affecting the acidity function, T_0, were compared with those affecting the activity of water. The applicability of the T_0 was examined by means of the observed $\log k_1$ value reported by Bunnett.

The following mechanisms of acid-catalyzed[1] reactions in moderately concentrated acid solutions have been proposed by Bunnett,[2–5]

$$\mathrm{S(H_2O)}h_5 + \mathrm{H^+(H_2O)}h_2 \rightleftharpoons \mathrm{SH^+(H_2O)}h_6 + (h_2 + h_5 - h_6)\mathrm{H_2O} \tag{1}$$

$$\mathrm{SH^+(H_2O)}h_6 + (h_1 - h_6)\mathrm{H_2O} \rightleftharpoons [\mathrm{SH^+(H_2O)}h_1]^{\ddagger} \xrightarrow{\mathrm{A}} \mathrm{P} \tag{2}$$

Adding Eq. (1) to Eq. (2) we obtain

$$\mathrm{S(H_2O)}h_5 + \mathrm{H^+(H_2O)}h_2 + (h_1 - h_2 - h_5)\mathrm{H_2O} \overset{K_1}{\rightleftharpoons} [\mathrm{SH^+(H_2O)}h_1]^{\ddagger} \tag{3}$$

$$[\mathrm{SH^+(H_2O)}h_1]^{\ddagger} \xrightarrow{\mathrm{A}} \mathrm{P} \tag{4}$$

The reaction rate, v, can be expressed by Eq.(5):

$$v = km^{\ddagger} = \frac{kK_1 a_{\mathrm{H}^+} f_{\mathrm{S}}}{k_2 a_w{}^{h_5-h_1} f^{\ddagger}} m_5 \tag{5}$$

where K_1, the equilibrium constant of Eq.(3), and K_2, the dissociation constant of protonated water, are given by Eq.(6) and Eq.(7) respectively:

$$K_1 = \frac{f^{\ddagger} m^{\ddagger}}{f_{\mathrm{S}} m_5 a_{\mathrm{H^+(H_2O)}h_2} a_w{}^{h_1-h_2-h_5}} \tag{6}$$

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1) In this paper only strong univalent acids are considered as catalysts.

2) J. F. Bunnett, *J. Am. Chem. Soc.*, **83**, 4956 (1961).

3) J. F. Bunnett, *ibid.*, **83**, 4968 (1961).

4) J. F. Bunnett, *ibid.*, **83**, 4973 (1961).

5) J. F. Bunnett, *ibid.*, **83**, 4978 (1961).

$$K_2 = \frac{a_{\mathrm{H}^+}}{a_{\mathrm{H}^+(\mathrm{H_2O})h_2}a_w{}^{-h_2}} = 1 \qquad (7)^{[6]}$$

Equations (5), (6) and (7) can also be summarized by Eq.(8):

$$\log k_1 = C - T_0 \qquad (8)$$

where: $k_1 = v/m_5$,[7] (9)

$$C = \log(kK_1/K_2) \qquad (10)$$

and $$T_0 = -\log(a_{\mathrm{H}^+} f_{\mathrm{S}}/a_w{}^{h_5-h_1} f^{\ddagger}) \qquad (11)$$

we can introduce T_0 as a new acidity function, while C is constant, independent of the concentration of acid.

Hammett and Deyrup defined the acidity function, H_0, as is shown in Eq. (12):

$$H_0 = -\log \frac{a_{\mathrm{H}^+} f_{\mathrm{A}}}{f_{\mathrm{AH}^+}} \qquad (12)$$

Its value was obtained by observing m_{AH^+} and m_{A}:

$$\log \frac{m_{\mathrm{AH}^+}}{m_{\mathrm{A}}} = C - \mathrm{H}_0, \qquad (13)$$

where they assumed $h_2 = 1$ and $h_5 = 0$. Furthermore they mainly determined the $f_{\mathrm{A}} f_{\mathrm{BH}^+}/f_{\mathrm{AH}^+} f_{\mathrm{B}}$ values of aromatic amines in acid solutions and found that these values were constant, independent of the A and B species as well as of the concentration and the sort of acid. Zucker and Hammett[9,10] have proposed a hypothesis which is useful in distinguishing A-1 mechanisms from A-2 mechanisms. If the reaction proceeds according to an A-1 mechanism, h_1 is zero and Eq. (14) can be derived from Eq. (8):

$$\log k_1 = C + \log \frac{a_{\mathrm{H}^+} f_{\mathrm{S}}}{f_{\mathrm{SH}^{\ddagger}}}$$

$$= C + \log \frac{a_{\mathrm{H}^+} f_{\mathrm{A}}}{f_{\mathrm{AH}^+}} + \log \frac{f_{\mathrm{S}} f_{\mathrm{AH}^+}}{f_{\mathrm{SH}^{\ddagger}} f_{\mathrm{A}}} \qquad (14)$$

The $-\log(a_{\mathrm{H}^+} f_{\mathrm{A}}/f_{\mathrm{AH}^+})$ term is Hammett's acidity function, and $\log(f_{\mathrm{S}} f_{\mathrm{AH}^+}/f_{\mathrm{SH}^{\ddagger}} f_{\mathrm{A}})$ is constant;[11,12] hence, Eq. (14) can also be expressed by Eq. (15):

$$\log k_1 = C - H_0 \qquad (15)$$

If the reaction proceeds according to an A-2 mechanism, h_1 is one; they postulated empirically that $\log k_1$ is given by Eq. (16):

$$\log k_1 = C + \log m_a \qquad (16)$$

while the Zucker-Hammett hypothesis described above, though it would be useful in distinguishing A-1 from A-2 mechanisms, has been sharply criticized by several authors[2,13,14] and has not been accepted as reasonable.

The Bunnett equation (Eq. (17))[3] can also be derived from Eq. (8); Eq. (18) is thus obtained:

$$\log k_1 = C - H_0 - w \log a_w, \qquad (17)$$

$$\log k_1 = C + \log \frac{a_{\mathrm{H}^+} f_{\mathrm{A}}}{f_{\mathrm{AH}^+}} + (h_5 - h_1) \log a_w$$

$$+ \log \frac{f_{\mathrm{S}} f_{\mathrm{AH}^+}}{f_{\mathrm{SH}^{\ddagger}} f_{\mathrm{A}}} \qquad (18)$$

If the term of $f_{\mathrm{S}} f_{\mathrm{AH}^+}/f_{\mathrm{SH}^{\ddagger}} f_{\mathrm{A}}$ is constant, the last one in Eq. (18) becomes zero; Eq. (18), therefore, becomes equivalent to Eq. (17) when we replace w and H_0 with $(h_1 - h_5)$ and $-\log(a_{\mathrm{H}^+} f_{\mathrm{A}}/f_{\mathrm{AH}^+})$ respectively. Bunnett discussed the reaction mechanism in terms of the value of w. Its value, however, can not be considered to be the hydration number contained in an activated complex, because such large values as 7 and 8 have been obtained. Hence, the value of w must be used only as an fitting parameter for experimental data.

The main features of this study are that an activated complex is considered to be a univalent cation and that the acidity function, T_0, is theoretically derived by applying the treatment described by

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6) K_2 in Eq. (7) is put to be equal to 1. This was done in view of the following facts: in Hammett's treatment of a dilute acid solution, $H_0 = -\log m_a = \mathrm{pH}$ is defined. This automatically involves the $m_a = a_{\mathrm{H}^+}$ relation: in other words, the acid concentration, m_a, is equal to the activity of the non-hydrated proton, a_{H^+}. Also, $a_{\mathrm{H}^+(\mathrm{H_2O})h_2}$ and a_w can, as usual, be defined as being equal to m_a and 1 respectively.

However, in a dilute acid solution, the species related to m_a is not H^+ but $\mathrm{H}^+(\mathrm{H_2O})_{h_2}$. Therefore, as a means to definition $m_a = a_{\mathrm{H}^+}$ seems less reasonable than $m_a = a_{\mathrm{H}^+(\mathrm{H_2O})h_2}$. The more reasonable definitions of T_0 and H_0 both of which are equal to $-\log m_a$ in dilute acid solutions, are given by Eq. (11a) and Eq. (12a) respectively:

$$T_0 = -\log(a_{\mathrm{H}^+(\mathrm{H_2O})h_2} f_{\mathrm{S}}/a_w{}^{h_2+h_5-h_1} f^{\ddagger}) \qquad (11a)$$

$$H_0 = -\log(a_{\mathrm{H}^+(\mathrm{H_2O})} f_{\mathrm{A}}/a_w f_{\mathrm{AH}^+}) \qquad (12a)$$

Here, if $K_2 = 1$, Eq. (11a) and Eq. (12a) are equal to Eq. (11) and Eq. (12) respectively.

7) In the above calculation, the first-order rate constant, k_1, was defined as the v/m_5 quantity. This is an approximation of the correct expression, $k_1 = v/(m_1 + m_5 + m_6)$. However, in the relations now under consideration, and in ordinary acid-catalyzed reactions as well, both m_1 and m_6 are negligibly small as compared with m_5; hence, this approximation is reasonable.

8) L. P. Hammett and A. J. Deyrup, *J. Am. Chem. Soc.*, **54**, 2721 (1932).

9) F. A. Long and M. A. Paul, *Chem. Revs.*, **57**, 935 (1957).

10) L. Zucker and L. P. Hammett, *J. Am. Chem. Soc.*, **61**, 2791 (1939).

11) The value of $f_{\mathrm{SH}^{\ddagger}}$ is assumed to very in essentially the same way as f_{SH^+} in both Hammett's and this paper.

12) It is doubtful whether we can extend the relation in which the $\log(f_{\mathrm{AH}^+} f_{\mathrm{B}}/f_{\mathrm{A}} f_{\mathrm{BH}^+})$ of Hammett base is constant to the S substrate, for S is not a Hammett base.

J. Hine, "Physical Organic Chemistry," Second Ed., McGraw-Hill, Kogakusha, New York, San Francisco, Toronto, London, Tokyo (1956), p. 55.

13) R. W. Taft, Jr., N. C. Deno and P. S. Skell, *Ann. Rev. Phys. Chem.*, **9**, 306 (1958).

14) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y. (1959).

Glueckauf[15] and by Moriyama[16] who showed that an a thermal mixing assumed for the salt solutions led to a reasonable representation of the observed activity coefficients of salt and acids.[17] One of the features which distinguishes our treatment from Hammett's is the difference in the hydration number[18] of the proton: in Hammett's treatment, the value of the hydration number, h_2, must be 1, whereas the h_2 taken in our treatment is 3.9, a value which is widely accepted.[19] The calculated acidity function, T_0, has been represented as a function of the hydration number of an activated complex, the activity of water, and the concentration of the acid. From the calculated results it has been verified that the value of $f_A f_{BH^+}/f_{AH^+} f_B$ depends on the hydration numbers of AH^+ and BH^+ as well as on the concentrations of the acids. Our results, therefore, differ from Bunnett's because his results were obtained by assuming that the value of $f_A f_{BH^+}/f_{AH^+} f_B$ is constant, independent of the A and B species as well as of the concentration and the sort of acid.

Symbols Used

The following list gives the symbols used in this study.

h_1, h_2, h_3, h_5, h_6: hydration numbers of activated complex, proton, univalent anion, substrate, and protonated substrate respectively

$h=h_2+h_3$: hydration number of acid

a_{H^+}, $a_{H^+(H_2O)h_2}$, $a_w=a_4$: activities of proton, hydrated proton, and water respectively

k, $k_1=v/m_5$: rate constant and the first-order rate constant respectively

n_1, n_2, $n_3=n_a=n_1+n_2$, n_4, $n_5=n_S$: numbers of molecules in hydrated activated complex, hydrated proton, hydrated univalent anion, free water, and hydrated substrate respectively

$m_1=m^{\ddagger}$, m_2, m_3, m_5, m_6: molalities of activated complex, proton, anion, substrate, and protonated substrate respectively

$m_a=m_3$: molality of acid

$n_w=n_1h_1+n_2h_2+n_3h_3+n_4+n_5h_5$: total number of water molecules

$n_R=n_1+n_5$: total number of substrates

$\bar{v}_1$, $\bar{v}_2$, $\bar{v}_3$, $\bar{v}_5$, $\bar{v}_4$: partial molar volumes of hydrated activated complex, hydrated proton, hydrated univalent anion, and hydrated substrate respectively, and that of free water. These values were treated as constant in this study.

$V=n_1\bar{v}_1+n_2\bar{v}_2+n_3\bar{v}_3+n_4\bar{v}_4+n_5\bar{v}_5$: total volume of the solution

μ_1, μ_2, μ_3, μ_5, μ_4: chemical potentials of hydrated activated complex, hydrated proton, hydrated anion, and hydrated substrate respectively, and that of free water

$\mu_i{}^{\circ}$: chemical potential in the standard state of *i*th species

$f_{SH^{\ddagger}}=f^{\ddagger}$, f_{SH^+}, f_S, f_A, f_B, f_{AH^+}, f_{BH^+}: activity coefficients of hydrated activated complex, hydrated protonated substrate, hydrated substrate, hydrated substrate A, hydrated substrate B, hydrated protonated substrate AH^+, and hydrated protonated substrate BH^+ respectively

S, A, B: substrates

SH^+, AH^+, BH^+: protonated substrates

$\boldsymbol{k}$: Boltzmann's constant

T: absolute temperature

Theoretical

Model of the Reaction System. The acid-catalyzed reaction system consists of the following five kinds of species: hydrated activated complexes, hydrated protons, hydrated univalent anions, free water, and hydrated substrates. The Gibbs free energy of this system may be calculated in much the same manner as in Glueckauf's treatment of a salt solution, with additional assumptions. Since the structure of an activated complex is too complicated for its exact contribution to the Gibbs free energy to be evaluated, it is assumed that the character of a hydrated univalent activated complex is represented by that of a hydrated alkali metal cation. It is furthermore assumed that a substrate is neutral and that its volume[20] is that of alkali metal in solution. On the other hand, for a substrate the salting-out effect must be considered. Conway[21] theoretically calculated this effect by considering two phenomena: the hydration of ions and the change in the dielectric constant of water due to the solute present in the solution. The former is automatically taken into account in this study, because ions are always treated as

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[15] E. Glueckauf, *Trans. Farad. Soc.*, **51**, 1235 (1955).

[16] M. Moriyama and T. Sugita, *Denki Kagaku (J. Electrochem. Soc. Japan)*, **25**, 617 (1957).

[17] Bascombe theoretically derived the acidity function, H_0, by the application of Glueckauf's treatment of a salt solution, though the details of the theoretical derivation were not described.
K. N. Bascombe and R. P. Bell, *Discussions Faraday Soc.*, **24**, 158 (1957).

[18] In this study the Gibbs free energy has been obtained by calculating the entropy; thus, the water molecules in hydration should be tightly bound with the ion.

[19] 3.9 was taken from Ref. 12. Wicke, Eigen and Ackermann, *Z. Phys. Chem.*, **1**, 340 (1954). Th. Ackermann, *Discussion Faraday Soc.*, **24**, 180 (1957). M. Eigen and L. De Maeyer, "Article in the Structure of Electrolyte Solution," Ed. by W. J. Hamer, John Wiley and Sons, New York, N. Y. (1959).

[20] In view of the co-volume effects of ions, Glueckauf obtained the activity of ions. On the other hand, the molar volume of a neutral substrate determines the dependency of its activity coefficient on the acid concentration.[24] Hence, among various physical properties belonging to a neutral substrate, the molar volume is the most predominant in the calculation of the activity.

[21] B. E. Conway, J. E. Desnoyers and A. C. Smith, *Phil. Trans. Roy. Soc. London*, **256**, 389 (1964).

hydrated in the calculation of the Gibbs free energy. Therefore, only the contribution from the latter is formally introduced as $G^{s.o.}$ in the equation.

Taking the five species (four hydrated species and free water mentioned above) as the standard state in the calculation of the Gibbs free energy of the system, and subjecting them to athermal mixing, the Gibbs free energy of mixing, $\Delta G'^{mix.}$, is given by Eq. (19):

$$\Delta G'^{mix.} = \boldsymbol{k}T \sum_{i=1}^{5} n_i \ln \frac{n_i \bar{v}_i}{V}. \tag{19}$$

The fundamental equation of the total free energy of the mixing of the system can, therefore, be obtained by adding the electrostatic effect, $G^{el.}$,[22] caused by the interaction between ions, and $G^{s.o.}$ to Eq. (19):

$$\begin{aligned}\Delta G^{mix.} &= \sum_{i=1}^{5} n_1\mu_i - \sum_{i=1}^{5} n_i\mu_i^0 \\ &= \boldsymbol{k}T \sum_{i=1}^{5} n_i \ln \frac{n_i\bar{v}_i}{V} + G^{el.} + G^{s.o.}\end{aligned} \tag{20}$$

The Acidity Function, T_0. To find the equation of the acidity function, T_0, the variation in the free energy in the process of the formation of the activated complex must be evaluated. As is shown by Eq. (3), a hydrated activated complex molecule is formed by the consumption of one hydrated proton molecule and one hydrated substrate molecule, leaving free water molecules $(h_2+h_5-h_1)$. This process corresponds to the partial differentiation of the total free energy with respect to n_1 at constant n_w, n_3 and n_R values, as is shown by Eq. (21):

$$\begin{aligned}\left(\frac{\partial \Delta G^{mix.}}{\partial n_1}\right)_{n_w,\, n_3,\, n_R} &= (\mu_1-\mu_1^0) - (\mu_2-\mu_2^0) \\ &\quad + (h_2+h_5-h_1)(\mu_4-\mu_4^0) - (\mu_5-\mu_5^0) \\ &= \boldsymbol{k}T\,[\ln n_1 - \ln n_2 - \ln n_5 + (h_2+h_5-h_1) \ln \frac{n_4\bar{v}_4}{V} \\ &\quad + \ln \frac{V}{\bar{v}_4} - (\sum_{i=1}^{5} n_i) \frac{(\bar{v}_1-h_1\bar{v}_4-\bar{v}_2+h_2\bar{v}_4-\bar{v}_5+h_5\bar{v}_4)}{V} \\ &\quad + \ln \frac{\bar{v}_1\bar{v}_4}{\bar{v}_2\bar{v}_5} + (h_2+h_5-h_1) - 1] + \left(\frac{\partial G^{el.}}{\partial n_1}\right) \\ &\quad + \left(\frac{\partial G^{s.o.}}{\partial n_1}\right)\end{aligned} \tag{21}$$

From Eq. (21) the acidity function, T_0, can be derived:

$$\begin{aligned}T_0 &= -\log \frac{a_{\mathrm{H}^+} f_{\mathrm{S}}}{a_w{}^{h_5-h_1} f^{\neq}} \\ &= -\log m_a + (h_2+h_5-h_1) \log \frac{(1-0.018\, hm_a)}{(1+0.018\, rm_a)} \\ &\quad + \log (1+0.018\, \mathrm{r}m_a) \\ &\quad + \frac{0.434\times 0.018 m_a(r+h-2)\Delta h}{1+0.018\, rm_a} \\ &\quad + \frac{0.434}{\boldsymbol{k}T} \left\{\left(\frac{\partial G^{el.}}{\partial n_1}\right) + \left(\frac{\partial G^{s.o.}}{\partial n_1}\right)\right\}\end{aligned} \tag{22}$$

where the term of $\ln(\bar{v}_1\bar{v}_4/\bar{v}_2\bar{v}_5)+(h_2+h_5-h_1)-\ln 0.018-\Delta h$ is omitted because this term is independent of the concentration of acid. The following six relationships were used for the sake of simplicity:

$$n_i = 0.018\, m_i n_w \tag{23}$$

$$h = h_2 + h_3 \tag{24}$$

$$r\bar{v}_4 = (\bar{v}_2+\bar{v}_3) - (h_2+h_3)\bar{v}_4 \tag{25}$$

$$\Delta h\bar{v}_4 = (\bar{v}_1-h_1\bar{v}_4) - (\bar{v}_2-h_2\bar{v}_4) - (\bar{v}_5-h_5\bar{v}_4) \tag{26}$$

$$\mu_i - \mu_i^0 = \boldsymbol{k}T \ln a_i = \boldsymbol{k}T \ln f_i m_i \tag{27}$$

$$m_1,\ m_5 \ll m_2 \tag{28}$$

$(0.434/\boldsymbol{k}T)(\partial G^{el.}/\partial n_1)$ in Eq. (22) corresponds to the difference in electrostatic contribution between a hydrated proton and a hydrated activated complex to the Gibbs free energy in an acid. This difference may be small because of the small difference in radius between a hydrated proton and a hydrated alkali metal cation.[23] Its approximate value can be calculated from the difference in the logarithms of the mean activity coefficients, $f_\pm{}^{el.}$, due to only the electrostatic effect between a hydrated proton in acid and a hydrated alkali metal cation in salt present in the solution. The value of $\log f_\pm{}^{el.}$ is represented as:

$$\log f_\pm^{el.} = -\frac{0.509\sqrt{I}}{1+0.329\times 10^8 a\sqrt{I}}$$

where I is the ionic strength and where "a" is the arbitrary parameter, which can be interpreted as the shortest distance from the center of a cation to that of an anion. We then obtain:

$$\begin{aligned}\frac{0.434}{\boldsymbol{k}T}\left(\frac{\partial G^{el.}}{\partial n_1}\right) &= -\frac{0.509\sqrt{I}}{1+0.329\times 10^8 a_1\sqrt{I}} \\ &\quad + \frac{0.509\sqrt{I}}{1+0.329\times 10^8 a_2\sqrt{I}}\end{aligned} \tag{29}$$

where a_1 and a_2 are arbitrary parameters of a salt and an acid respectively.

The $(0.434/\boldsymbol{k}T)(\partial G^{s.o.}/\partial n_1)$ term in Eq. (22) is neglected, for the molar volume of a neutral substrate (that of alkali metal in our model) is small.[24] Conway[21] also showed that this term was small for a small neutral substrate.

Results

Results of Calculation. For the calculation of the hydration terms in Eq. (22), the hydration numbers of Li^+, Na^+, K^+, and Rb^+ were taken from the results tabulated by Glueckauf.[15] The values of $\bar{v}_1$, $\bar{v}_2$, $\bar{v}_3$, and $\bar{v}_5$[19] were taken from the results computed by Noyes[25] and were treated as

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[22] The value of $G^{el.}$ takes account of the electrostatic interaction among ions in the aqueous solution when there is no neutral substrate in it.

[23] R. H. Stokes and R. A. Robinson, *J. Am. Chem. Soc.*, **70**, 1870 (1948).

[24] F. A. Long and W. F. McDevit, *Chem. Revs.*, **51**, 119 (1952).

[25] R. M. Noyes, *J. Am. Chem. Soc.*, **86**, 971 (1964).

Table 1. T_0 calculated by Eq. (22) in the case of Li^+ in hydrochloric acid at 25°C

Molality	0.1	0.5	1.0	2.0	3.0
I	1.000	0.301	0.000	−0.301	−0.477
II	−0.002	−0.011	−0.023	−0.048	−0.075
III	0.001	0.004	0.008	0.016	0.023
IV	0.000	−0.002	−0.005	−0.009	−0.013
V	−0.001	−0.001	−0.002	−0.004	−0.004
T_0	0.998	0.291	−0.022	−0.346	−0.546

$h_1=3.4$, $\Delta h=-0.50$, $\bar{v}_5=6.9\,\mathrm{m}l$, $r=1.00$, $h=4.8$, $h_5=0$

I, $-\log m_a$

II, $(h_2+h_5-h_1)\log(1-0.018\,hm_a)/(1+0.018\,rm_a)$

III, $\log(1+0.018\,rm_a)$

IV, $0.434\times0.018\,m_a(r+h-2)\Delta h/(1+0.018\,rm_a)$

V, $(0.434/\boldsymbol{k}T)(\partial G^{el\cdot}/\partial n_1)$

Table 2. T_0 calculated by Eq. (22) in the case of Na^+ in hydrochloric acid at 25°C

Molality	0.1	0.5	1.0	2.0	3.0
I	1.000	0.301	0.000	−0.301	−0.477
II	−0.008	−0.042	−0.087	−0.182	−0.285
III	0.001	0.004	0.008	0.016	0.023
IV	−0.001	−0.006	−0.012	−0.023	−0.033
V	−0.001	−0.003	−0.006	−0.012	−0.018
T_0	0.991	0.254	−0.097	−0.502	−0.790

$h_1=2.0$, $\Delta h=-0.41$, $\bar{v}_5=11.8\,\mathrm{m}l$, $h_5=0$

Table 3. T_0 calculated by Eq. (22) in the case of K^+ in hydrochloric acid at 25°C

Molality	0.1	0.5	1.0	2.0	3.0
I	1.000	0.301	0.000	−0.301	−0.477
II	−0.013	−0.073	−0.152	−0.317	−0.495
III	0.001	0.004	0.008	0.016	0.023
IV	−0.001	−0.003	−0.007	−0.013	−0.020
V	−0.001	−0.007	−0.013	−0.026	−0.039
T_0	0.986	0.222	−0.164	−0.641	−1.008

$h_1=0.6$, $\Delta h=-0.24$, $\bar{v}_5=13.2\,\mathrm{m}l$, $h_5=0$

Table 4. T_0 calculated by Eq. (22) in the case of Rb^+ in hydrochloric acid at 25°C

Molality	0.1	0.5	1.0	2.0	3.0
I	1.000	0.301	0.000	−0.301	−0.477
II	−0.015	−0.086	−0.180	−0.375	−0.588
III	0.001	0.004	0.008	0.016	0.023
IV	0.000	−0.003	−0.005	−0.011	−0.016
V	−0.002	−0.009	−0.017	−0.034	−0.051
T_0	0.984	0.207	−0.194	−0.705	−1.106

$h_1=0$, $\Delta h=-0.19$, $\bar{v}_5=17.1\,\mathrm{m}l$, $h_5=0$

constants.

The calculated values of T_0 at various concentrations of the hydrochloric acid solution for the formation of the activated complex ions are shown in Tables 1—4, where the activated complex ions are represented by Li^+, Na^+, K^+, and Rb^+. These tables show that the contribution from the hydration to T_0 is predominant, whereas that from the electrostatic is small. In Fig. 1 $-T_0$, $-H_0$, and $\log m_a$ are plotted against the acid concentration, m_a. In the case of Rb^+, the hydration number of which is zero, $-T_0$ is largest and the deviation of the T_0 from $\log m_a$ is nearly equal to H_0. On the contrary, in the case of Li^+, the hydration number of which is 3.4, $-T_0$ is small and nearly equal to $\log m_a$. In order to determine the correlation of $-T_0$ with the hydration number of the activated complex, the $-T_0$ values in a hydrochloric acid solution at a molality of 3 are plotted *versus* the hydration number in Fig. 2. Figure 2 shows that $-T_0$ increases linearly with the hydration number. Therefore, the T_0 can be represented as in Eq. (30):

$$T_0 = -0.161(3.9-h_1+h_5) - \log m_a, \tag{30}$$

where h_2 is 3.9. Since the value of $\log a_w$ is -0.068 at the molality of hydrochloric acid of 3, Eq. (30) can be rewritten as:

$$T_0 = 2.4(3.9-h_1+h_5)\log a_w - \log m_a \tag{31}$$

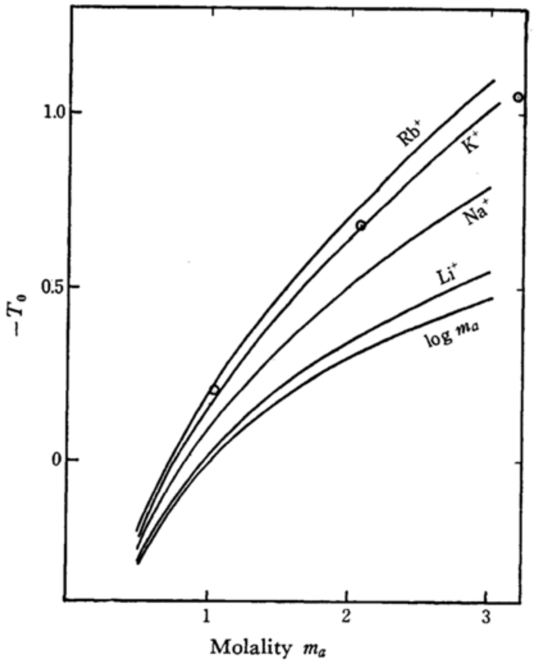

Fig. 1. $-T_0$, $-H_0$* and $\log m_a$ *versus* the molality of hydrochloric acid, m_a, at 25°C. Hydration number of Rb^+, K^+, Na^+, and Li^+ are 0, 0.6, 2.0, and 3.4 respectively.

○ observed $-H_0$

* M. A. Paul and F. A. Long, *Chem. Revs.*, **57**, 1 (1957).

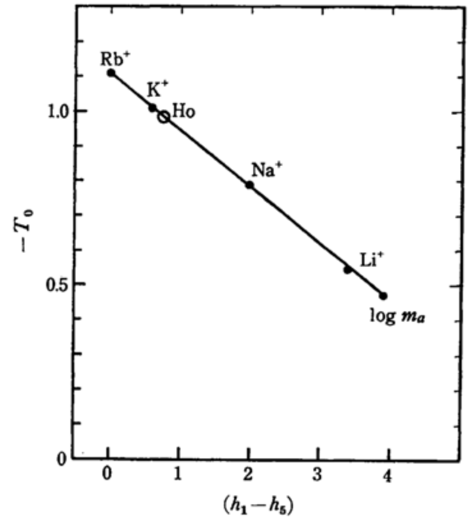

Fig. 2. $-T_0$ *versus* (h_1-h_5) at the molality of hydrochloric acid of 3 at 25°C. Since h_5, the hydration number of a substrate, can be assumed to be 0, (h_1-h_5) becomes equal to h_1, which is the number of water molecules contained in an activated complex. The hydration number of aromatic amines, which was used to determine H_0, becomes apparently 0.7 from this figure.

TABLE 5. T_0 CALCULATED BY EQ. (22) IN THE CASE OF Rb$^+$ IN NITRIC ACID AT 25°C

Molality	0.1	0.5	1.0	2.0	3.0
I	1.000	0.301	0.000	−0.301	−0.477
II	−0.019	−0.090	−0.179	−0.359	−0.550
III	0.002	0.008	0.014	0.026	0.038
IV	0.000	−0.003	−0.005	−0.011	−0.016
V	−0.002	−0.009	−0.017	−0.034	−0.051
T_0	0.981	0.225	−0.187	−0.679	−1.056

$r=1.68$, $h=3.9$

TABLE 6. T_0 CALCULATED BY EQ. (22) IN THE CASE OF Rb$^+$ IN PERCHLORIC ACID AT 25°C

Molality	0.1	0.5	1.0	2.0	3.0
I	1.000	0.301	0.000	−0.301	−0.477
II	−0.031	−0.113	−0.222	−0.425	−0.655
III	0.004	0.012	0.023	0.038	0.056
IV	−0.001	−0.003	−0.007	−0.013	−0.018
V	−0.002	−0.009	−0.017	−0.034	−0.051
T_0	0.970	0.188	−0.223	−0.735	−1.145

$r=2.51$, $h=4.2$

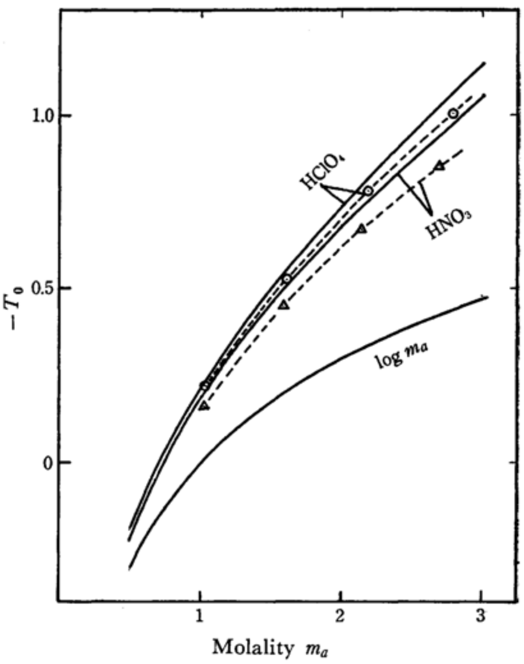

Fig. 3. $-T_0$, $-H_0$,* and $\log m_a$ *versus* the molality of nitric acid and perchloric acid, m_a at 25°C.

—— calculated $-T_0$
······ observed $-H_0$

* M. A. Paul and F. A. Long, *Chem. Revs.*, **57**, 1 (1957).

For nitric acid and perchloric acid, the calculated values of T_0 are shown in Tables 5 and 6 and in Fig. 3. From these results, the respective acidity functions, T_0, for these solutions are given by Eqs. (32) and (33):

in nitric acid solutions:

$$T_0 = -0.148(3.9-h_1+h_5) - \log m_a$$
$$= 2.3(3.9-h_1+h_5)\log a_w - \log m_a \qquad (32)$$

in perchloric acid solutions:

$$T_0 = -0.171(3.9-h_1+h_5) - \log m_a$$
$$= 2.3(3.9-h_1+h_5)\log a_w - \log m_a \qquad (33)$$

The contribution from the electrostatic effect in these acid solutions is assumed to be the same as in hydrochloric acid solutions.

Discussion

Consideration with Respect to T_0. The most important conclusion is that if the h_1 increases by one, the corresponding increment of T_0 is $-2.4\log a_w$. If we considered only the behavior of water, however, the increment would be $-\log a_w$, because the disappearance of one molecule of free water is related to the increase of h_1 by one. In order to investigate this difference, let us compare the factors affecting the activity of water in the reaction system with those affecting the acidity function, T_0.

The activity of water can be determined from the free-energy change due to the introduction of one molecule of water into the acid solution. The equation for this free-energy change can be obtained by differentiating Eq. (20) with respect to n_w at constant n_1, n_2, n_3, and n_5 values. The equation thus obtained is:

$$\left(\frac{\partial \Delta G^{mix.}}{\partial n_w}\right)_{n_1, n_2, n_3, n_5} = \left(\frac{\partial \Delta G^{mix.}}{\partial n_4}\right)_{n_1, n_2, n_3, n_5}$$

$$= \mu_4 - \mu_4{}^0 = \boldsymbol{k}T\left[\ln\frac{n_4\bar{v}_4}{V} + \left(1 - \frac{\sum_{i=1}^{5} n_i}{V}\frac{\partial V}{\partial n_4}\right)\right] \quad (34)$$

The first term of Eq. (34) is the contribution due to the increase in the number of water molecules, while the second is that due to the volume increase of the solution caused by the increase in the number of water molecules. Using the relations represented by Eq. (23)—(28), we can obtain:

$$\log a_w = \log\frac{1-0.018\,hm_a}{1+0.018\,rm_a} + \frac{0.434\times0.018(r+h-2)m_a}{1+0.018\,rm_a} \quad (35)$$

The first and second terms in Eq. (35) correspond to the second and fourth terms in Eq. (22) respectively. As is shown in Table 7, the value of each term in Eq. (35) is comparable in order to the absolute magnitude, while in Eq. (22) (see Table 4) the second term, responsible for the increase in the number of water molecules, contributes to T_0 predominantly, and the contribution of the fourth term, related to the increase in the volume of the system (which was caused by the formation of the activated complex), is small. The large increase in the volume in the calculation of water activity may be attributed to the introduction of a water molecule into the system from outside. While the small volume change in the calculation of T_0 is ascribed to the fact that the system is closed; the total numbers of the water molecule, n_w, the substrate, n_R, and acid, n_a, are constant. Since the number of water molecules freed from a hydrated proton upon the formation of an activated complex is $(h_2+h_5-h_1)$, the contribution of these water molecules to T_0 becomes $(h_2+h_5-h_1)\log a_w$. This means that the increase of h_1 by one contributes $-\log a_w$ to T_0. However, it is not enough to evaluate the small change in volume described above in the calculation of T_0 through only the value of $-\log a_w$.

TABLE 7. $\log a_w$ CALCULATED BY EQ. (35) IN HYDROCHLORIC ACID SOLUTION AT 25°C

Molality	0.1	0.5	1.0	2.0	3.0
I	−0.004	−0.022	−0.046	−0.096	−0.150
II	0.003	0.014	0.028	0.056	0.082
$\log a_w$	−0.001	−0.008	−0.018	−0.040	−0.068

$r=1.00$, $h=4.8$

I, $\log(1-0.018\,hm_a)/(1+0.018\,rm_a)$

II, $0.434\times0.018(r+h-2)m_a/(1+0.018\,rm_a)$

Consideration of the Salting-out Effects. The activity coefficient of a neutral substrate in this study can be obtained by differentiating Eq. (20) with respect to n_5, with no change of n_1, n_2, n_3, and n_4 and with $h_5=0$:

$$\log f_5 = -\log(1+0.018\,rm_a) + \frac{0.434\times0.018(\bar{v}_5/\bar{v}_4)(r+h-2)m_a}{1+0.018\,rm_a} \quad (36)$$

The calculated values of $\log f_5$ in the case of Rb have been tabulated in Table 8. The values are small, increase linearly with the concentration of acid, and are almost independent of the sort of acids. In Table 9 the observed values of $\log f$ of hydrogen are tabulated at the molality of 1.[24] It has been known that the salting-out effects increase almost linearly with the molar volume of a substrate.[24] The value of $\log f$ of Rb represented in Table 9 were, therefore, obtained by multiplying the $\log f$ of hydrogen by 0.65, the ratio of the molar volume of Rb to that of hydrogen. Good agreements between the calculated values of Tables 8 and 9 are observed in hydrochloric acid and in nitric acid, though there is a large discrepancy in perchloric acid. This discrepancy probably results from neglecting the $(0.434/\boldsymbol{k}T)(\partial G^{s.o.}/\partial n_1)$ term. If this term could be exactly estimated, the discrepancy might be adjustable.[26]

TABLE 8. $\log f_5$ OF Rb CALCULATED BY EQ. (36) IN ACID SOLUTIONS AT 25°C

Molality	0.1	0.5	1.0	2.0	3.0
in HCl	0.002	0.009	0.019	0.037	0.055
in HNO_3	0.001	0.006	0.013	0.024	0.035
in $HClO_4$	0.001	0.007	0.014	0.026	0.037

$\bar{v}_5=17.1\,ml$

TABLE 9. $\log f$ OF HYDROGEN OBSERVED AT A MOLALITY OF 1 AND VALUES OF $\log f_5$ OF Rb CALCULATED BY MULTIPLYING THE $\log f$ OF HYDROGEN BY 0.64

	Hydrogen[24]	Rb
HCl	0.036	0.020
HNO_3	0.022	0.014
$HClO_4$	−0.030*1	−0.019

$\bar{v}_5$ of hydrogen is 26 ml.

*1 Calculated from the value of benzene.

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[26] Conway[21] calculated the salting-out effect in view of the two phenomena mentioned above; however, further phenomena such as the structure-making influence of non-polar solutes[21] must be taken into account in calculating the exact value of the salting-out effect.

The Value of ($f_A f_{BH^+}/f_{AH^+} f_B$). As was described in the first paragraph, Hammett and Deyrup found that the value of $(f_A f_{BH^+}/f_{AH^+} f_B)$ determined with aromatic amines was constant, independent of the species, A or B, as well as of the concentrations and of the sort of acids. However, it can be shown by the following procedure that this value is not always constant. The value of the acidity function, T_0, of the "0" system is compared with that of the "1" system at the same concentration of hydrochloric acid, where the "0" system and the "1" system are defined as the systems of $(h_1-h_5)=0$ and 1 respectively. From Eq. (31) we can obtain:

$$\Delta T_0 = T_{00} - T_{01} = 2.4 \log a_w \tag{37}$$

where the $_0$ and $_1$ subscripts represent the "0" system and the "1" system respectively. From the definition of T_0, in Eq. (11):

$$\begin{aligned} \Delta T_0 &= -\log \frac{a_{H^+} f_{S_0}}{f_0{}^{\ne}} + \log \frac{a_{H^+} f_{S_1}}{a_w{}^{-1} f_1{}^{\ne}} \\ &= -\log \frac{f_{S_0} f_1{}^{\ne}}{f_0{}^{\ne} f_{S_1}} + \log a_w \end{aligned} \tag{38}$$

From Eqs. (37) and (38), Eq. (39) can then be derived:

$$-\log \frac{f_{S_0} f_1{}^{\ne}}{f_0{}^{\ne} f_{S_1}} = 1.4 \log a_w \tag{39}$$

Eq. (39) shows that the values of $(f_A f_{BH^+}/f_{AH^+} f_B)$ is not always constant,[12] but depends on the hydration number of the AH^+ and BH^+ species as well as on the acid concentration.

Bunnett's equation (17) was derived by considering the relation $(f_A f_{BH^+}/f_{AH^+} f_B)$ to be constant. If the w or (h_1-h_5) is increased by one, the increment of $\log k_1$ is $\log a_w$ in his treatment, but 2.4 $\log a_w$ in our treatment.

Comparison between the Observed log k_1 and the T_0. Using Eq. (8), Eq. (31), and the dependence of $\log k_1$ upon the concentration of acid, we can obtain the hydration number of an activated complex or the number of water molecules contained in an activated complex.[18] The applicability of T_0 can be examined by comparing the T_0 and the observed $\log k_1$. Bunnett reported that, for many reactions, the values of w were fairly evenly distributed from -2 to $+8$.[2] If the hydration number of an activated complex increases from 0 to 3.9 in hydrochloric acid at the molality of 3, T_0 varies from -1.106 to -0.477; also, this variation in T_0 corresponds to that in w from -1.8 to 9.2. The fact that the ranges of the distribution of w observed for many reactions agree with those of the variation in T_0 indicates that the dependence of $\log k_1$ on the concentration of acid is effected mainly through the hydration number of an activated complex, because, as is shown in Tables 1—6, the variation in T_0 can be explained mainly by the hydration effect. Also, this fact would allow us to obtain the approximate number of water molecules contained in an activated complex by the application of T_0 to $\log k_1$. The more accurate numbers must be obtained by estimating the value of the salting-out effect exactly.

The relation between H_0 and T_0 is much the same as that between T_0 and $\log k_1$. The hydration number of aromatic amines, which was used to determine H_0, apparently becomes 0.7 when we apply T_0 to H_0, as is shown in Fig. 2.