

Ionization and Some Thermodynamic Properties of Germanic Acid in Aqueous Solutions

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The first concentration ionization constant of germanic acid was determined potentiometrically in aqueous potassium chloride solutions at various temperatures. The corresponding thermodynamic constant ($pK_1 = 8.730$) and the parameters of the Debye-Hückel equation were also determined. It was found that temperature has an unexpectedly great effect on the ionization of germanic acid. When the temperature rises from 10° to 45° C, the first thermodynamic ionization constant of the acid increases almost twenty fold. Utilizing values of the thermodynamic ionization constant obtained at various temperatures, the thermodynamic quantities ΔH , ΔS° and ΔG° were computed as functions of temperature. The entropy change appears to increase strongly with temperature while ΔG° seems to remain constant (at 11.65 kcal/mole).

According to present views an aqueous solution of germanium dioxide contains only monomeric germanic acid H_2GeO_3 and its anion¹⁻³. However, when a solution of germanic acid is neutralized, the pentagermanic acid $H_2Ge_5O_{11}$ seems to be formed near the equivalence point⁴⁻⁸. Hence, acid solutions of germanic acid do not contain any polyacids and consequently can be considered aqueous solutions of the monomeric acid.

The ionization constant of germanic acid has been previously determined by several investigators, but their results as can be seen from Table 1, are widely divergent. The influence of temperature on the ionization of germanic acid has not, however, been investigated earlier. The object of this investigation was to determine the first thermodynamic ionization constant of germanic acid at various temperatures and to use these values in the calculation of the values of the thermodynamic functions.

Table 1. Ionization constants of germanic acid according to previous authors

pK_1	pK_2	Method	t°C	Authors
6.921		conductometric	18	Roth and Schwartz ²
8.585	12.722	potentiometric	20	Pugh ⁹
7.301		conductometric	20	Schwarz and Huf ⁴
8.5—9.0		conductometric	25	Gulezian and Müller ¹⁰
8.097	12.699	potentiometric	12	Carpéni ⁵
9.070		potentiometric	?	Lourijzen-Teysse ⁶

EXPERIMENTAL

The measurements were performed by the differential potentiometric method¹¹. A Vernier potentiometer and quinhydrone electrodes were mainly used in the titrations, but some measurements were also performed with a Radiometer PHM 3 tube potentiometer and a Beckman glass electrode No. 4990—83. A saturated calomel electrode was used as reference electrode. The temperature of the thermostat was adjusted in the usual manner with an accuracy of 0.05° C in the temperature range 10—45° C.

In order to remove carbon dioxide from the test solutions, pure nitrogen was conducted through the titration vessels for about 12 hours before the titrations. This was indispensable especially when working in ranges where the buffer capacities were small. In such cases even small quantities of carbonic acid may influence the results (cf. ref. 12, p. 37). A slow continuous flow of nitrogen was maintained also during the whole titration.

The additions of hydroxide solution during the titrations were made from a micro-syringe designed by Ellilä¹³. With this syringe it is possible to obtain an accuracy for small additions of hydroxide that completely corresponds to the accuracy in reading the potentiometer. The volumes of hydroxide solution added were usually 0.005—0.01 ml. When a 0.0944 N solution of sodium hydroxide was used and the concentration of germanic acid was 0.03—0.04 molar, the maximum potential jump was usually 8—12 mV.

The stock solution of germanic acid in water was prepared from Merck's germanium dioxide. The concentration of the solution was checked by titration with sodium hydroxide after adding an excess of mannitol¹⁴⁻¹⁵.

RESULTS AND DISCUSSION

Ionization of germanic acid in aqueous potassium chloride solutions of varying ionic strength at 25° C. The first and second ionization constants of germanic acid are of the order of 10⁻⁹ and 10⁻¹³, respectively. Consequently, the second ionization constant of germanic acid can be disregarded in the calculations as it does not affect the values of the first ionization constant. As, furthermore, the acid in question is exceedingly weak, the ionization constants of the acid can be calculated from the first approximation of the equation proposed by Kilpi¹¹:

$$(1) \quad K_1 = \frac{1}{C_{\text{H}_2\text{GeO}_3}} \cdot \left(\frac{P_m}{4.606} \right)^2,$$

where K_1 is the first concentration ionization constant of germanic acid, $C_{\text{H}_2\text{GeO}_3}$ the stoichiometric concentration of this acid at the inflexion point at the beginning of the titration curve, and P_m the minimum value of the corresponding buffer capacity. Even in this case there is no reason to use the equivalence point of the titration for the determination of P_m as the polymerization of germanic acid in the neighborhood of the equivalence point would then affect the results (cf. refs. 4—8 and ref. 16, p. 22).

The values obtained for the first ionization constant of germanic acid in potassium chloride solutions are presented in Table 2 and Fig. 1 as functions

Table 2. Ionization of germanic acid in aqueous potassium chloride solutions at 25° C.

\sqrt{I}	$C_{\text{H}_2\text{GeO}_3}$	$P_m \cdot 10^5$	pK_1
0.0102	0.03193	3.583	8.722
0.1751	0.03192	3.892	8.632
0.4558	0.03196	4.500	8.526
0.6500	0.03189	4.310	8.563
0.9998	0.03200	4.271	8.571
1.231	0.03193	3.464	8.751

$$pK_{1,0} = 8.730$$

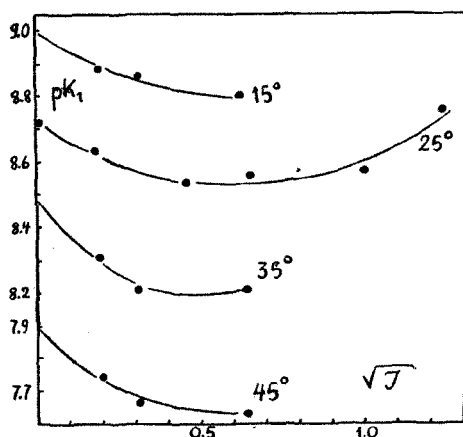


Fig. 1. The first ionization constant of germanic acid in aqueous potassium chloride solutions as a function of $I^{1/2}$ at various temperatures.

of the ionic strength at 25° C. The corresponding parameters of the Debye-Hückel equation and the thermodynamic ionization constant of germanic acid computed from these values were found to be:

$$(2) \quad pK_{1,0} = 8.730, \quad \alpha = 2.180, \quad B = 0.165$$

The obtained value of $pK_{1,0}$ ($K_1 = 1.86 \cdot 10^{-9}$) is in the best agreement with the value in Table 1 which Gulezian and Müller computed from conductivity data. The conductivity measurements of other authors have given much higher values for the ionization constant than this value. The reason for this may be that the germanic acid solutions used in the latter conductivity measurements have contained foreign strong electrolytes. On the other hand, with the differential potentiometric method used in this investigation, small quantities of strong electrolytes do not affect the results. The divergencies noted in Table 1 may also be due to the polymerizing effect of alkali mentioned above. This effect is eliminated when the method used in this investigation is employed.

Effect of temperature on the ionization of germanic acid. In the investigation of the effect of temperature on the first ionization constant of germanic acid, the differential potentiometric titration method and equation (1) pertaining to it were again employed. The results obtained for the temperature range 10—45° C. are presented in Table 3. It is seen that the first ionization constant of germanic acid increases about twenty fold in this range. This effect of temperature is unexpectedly great and it does not conform with the ordinary type of variation observed for weak acids by Harned and Embree¹⁷. According to these authors the ionization constant of a weak acid should first increase with increasing temperature to a maximum and then decrease. As can be seen from Fig. 2, the first ionization constant of germanic acid seems, however, to attain a minimum value at low temperatures and to increase continuously with increasing temperature. This phenomenon may be explained to be due to the polymerization of germanic acid. It is in fact possible that as the temperature increases some polygermanic acid which is stronger than the monomeric germanic acid is formed in the solution. The values of the ionization constants given in Table 3 must con-

Table 3. Effect of the temperature on the ionization of germanic acid in aqueous potassium chloride solutions of varying ionic strength.

$t^{\circ}\text{C}$	\sqrt{I}	$C_{\text{H}_2\text{GeO}_3}$	$F_m \cdot 10^6$	pK_1	$pK_{1,0}$
10	0.6326	0.03200	3.140	8.839	9.045
15	0.1998	0.03199	2.996	8.880	
15	0.3160	0.03200	3.050	8.864	8.980
20	0.6318	0.03190	3.966	8.635	8.920
25	0.6500	0.03189	4.310	8.563	8.730
30	0.6352	0.03192	5.278	8.378	8.615
35	0.1987	0.03198	5.761	8.311	
35	0.3158	0.03192	6.510	8.204	8.450
35	0.6363	0.03187	6.475	8.208	
40	0.6356	0.03185	9.100	7.913	8.175
40	0.6296	0.03178	10.04	7.827	
45	0.1990	0.03186	11.02	7.747	
45	0.6294	0.03175	13.44	7.573	7.900
45	0.6291	0.03173	12.30	7.650	

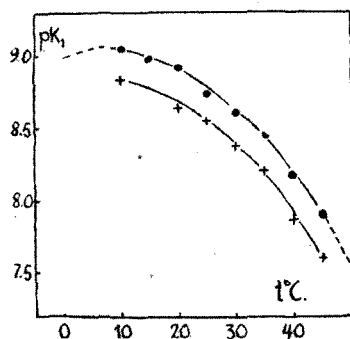


Fig. 2. The influence of the temperature on the ionization of germanic acid in aqueous solutions. ● the first thermodynamic ionization constant calculated using the values in Tables 2—3 and the Debye-Hückel equation. + the first ionization constant measured in about 0.4 molar sodium chloride solutions.

sequently be considered only apparent values. A more detailed study of this polymerization phenomenon will be described elsewhere in the near future.

A mathematical equation can also be derived for the thermodynamic values obtained by extrapolation and given in Table 3. Assuming that the ionization constant varies as a function of temperature which has the form of an ordinary secondpower equation (*cf.* Fig. 2), the constant terms of the equation may be computed by the method of least squares. Thus we obtain the equation

$$(3) \quad pK_{1,0} = pK_{1,0}^0 + at + bt^2,$$

where $a = 1.30 \cdot 10^{-2}$, $b = -8.50 \cdot 10^{-4}$ and $pK_{1,0}^0 = 9.00$. The latter constant is the value of the thermodynamic ionization constant referring to 0°C . It can be noted from Fig. 2 that the curve representing the equation of the form (3) agrees with high accuracy with the curve plotting the experimental values. Employing the obtained equation, it is also found that the curve has a maximum value, $pK_{1,\text{max.}} = 9.06$, when the temperature is 7.5°C .

By the aid of equation (3) it is possible to compute the heat of ionization ΔH for this ionization reaction at different temperatures. This equation combined with van't Hoff's equation yields the following equation:

$$(4) \quad \Delta H = RT^2 (3.91 \cdot 10^{-3}t - 2.99 \cdot 10^{-2}).$$

Further, the thermodynamic functions ΔG° and ΔS° for the reaction in question can be computed by utilizing the equations

$$(5) \quad \Delta G^\circ = \Delta H - T\Delta S^\circ$$

$$\Delta G^\circ = -RT \ln K_{1,0}$$

The thermodynamic values thus obtained are given in Table 4. It should also

Table 4. Thermodynamic constants of the ionization reaction of germanic acid as a function of temperature. The values were calculated using the $pK_{1,0}$ -values in Table 3. (cf. eq. (4))

$t^\circ \text{C}$	ΔH kcal/mole	ΔG° kcal/mole	ΔS° e.u.
0	-4.45	11.20	-57.3
10	1.45	11.65	-36.2
20	8.25	11.90	-12.2
30	15.85	11.90	+13.0
40	25.70	11.70	+44.7
50	34.20	11.45	+70.5

in this connection be noted that these values are only to be considered apparent values, since, as already mentioned, it is probable that the investigated reaction does not involve only an ionization reaction of the germanic acid H_2GeO_3 . It appears from the data in Table 4 and Figs. 3 and 4 that the entropy change increases greatly with increasing temperature and that this increase varies linearly with the corresponding enthalpy change (*i.e.* slope $\Delta H/\Delta S^\circ = 0.3$) in the temperature range studied. It is also interesting to note that ΔG° seems to remain constant with increasing temperature ($\Delta G^\circ = 11.65 \text{ kcal/mole} \pm 1.8\%$).

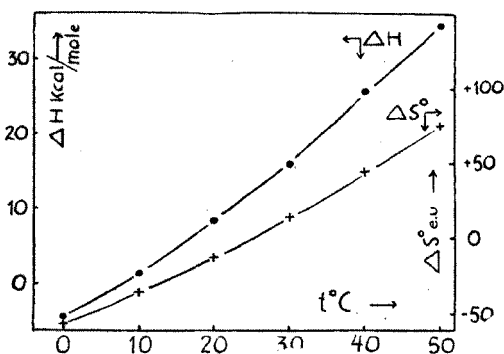


Fig. 3. Variation of ΔH and ΔS° with temperature.

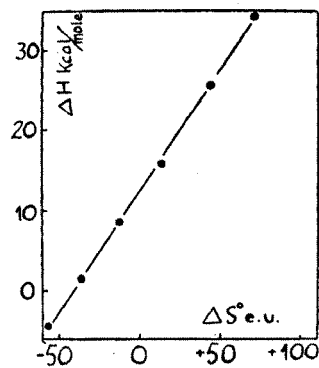


Fig. 4. Variation of ΔH as a function of ΔS° .

The increase noted in ΔS° is quite exceptional, when compared with data for other weak acids. This phenomenon may be explicable in terms of decreasing anionic solvation when anionic polymerization occurs.

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A Method for the Calculation of Stability Constants of Complexes

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A method of computing stability constants of complexes based on the method of least squares is described. The method is suitable for the determination of constants of relatively weak mononuclear complexes when the ligand concentration is large compared to the central ion concentration and can be varied at constant intervals.

In the determination of stability constants of consecutive complexes *e.g.*, from polarographic data, the methods usually employed^{1,2} are based on the general treatments of Bjerrum³ and Leden⁴. In recent years a number of papers have appeared in the literature that deal with various new and modified methods for the calculation and graphical determination of formation constants⁵⁻¹³. The method of least squares has also been used in this connection^{8,10}.

In the present paper a method based on the least squares treatment is proposed for the calculation of stability constants of relatively weak mononuclear complexes. The labor involved in the least square method is greatly reduced if one can vary the independent variable, *i.e.*, the free ligand concentration, at even intervals. When the polarographic method is employed, it is in some cases possible to satisfy this condition almost exactly, in other words, the free ligand concentration will be practically the same as the total or added ligand concentration, which can be varied at even intervals.