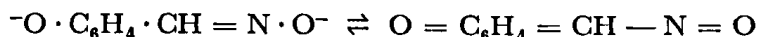


absorption of salicylaldehyde in the wavelength ranges 200—270 m $\mu$  and 290—360 m $\mu$ <sup>8</sup>, it seems possible to make some assignments of absorption bands to the oxime and phenolic hydroxyl groups. By comparing the spectra of the RH<sub>3</sub><sup>+</sup> and RH<sub>2</sub> forms, it is seen that the loss of the extra proton from the oxime nitrogen does not have any appreciable effect on the heights of the different absorption maxima, only the position of the maximum at 325 m $\mu$  being shifted to a shorter wavelength 303 m $\mu$ . At the same time the absorption is reinforced slightly, obviously owing to the stronger resonance within the molecule. Already from this displacement of the maximum we can conclude that the changes in the absorption maximum in the 300—360 m $\mu$  range must be largely determined by the state of ionization of the oxime group.

When, further, the phenolic hydroxyl group is ionized, we observe a strong change in the absorption spectrum ( $\epsilon_{RH^-}$ ). The spectrum is displaced as a whole to longer wavelengths and the absorption maximum in the shortest wavelength range appears at 225 m $\mu$ . The strong absorption maximum at 257 m $\mu$  in the spectra of the RH<sub>3</sub><sup>+</sup> and RH<sub>2</sub> forms is seen only as a broad shoulder in the spectrum of the RH<sup>-</sup> form. Therefore the absorption maximum (at 257 m $\mu$ ) is evidently due to the intramolecular hydrogen bonding of the phenolic hydroxyl group and the oxime nitrogen<sup>9</sup>. Simultaneously the absorption at the shortest wavelengths is weakened and that at the longer wavelengths strengthened. Finally the band in the 330—360 m $\mu$  range is reinforced by the ionization of the oxime hydroxyl group and displaced a little to shorter wavelengths. The band at 225 m $\mu$  is weakened and a peak appears at 266 m $\mu$ . This may be due to the possible carbonyl group resonance:



The conclusions made are strengthened when the presented spectral data are compared with the spectral data given in the literature for benzene, benzaldehyde, phenol<sup>8</sup> and hydroxylamine<sup>10</sup>.

The present data explain and support the conclusions made in the literature about the structures of the metal chelates of salicylaldehyde<sup>8,9,11</sup>.

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## The Thermodynamics of the Ionization of Telluric Acid in Aqueous Solutions

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The first ionization constant of telluric acid has been determined potentiometrically in aqueous potassium chloride solutions at various temperatures. The corresponding thermodynamic constants were also determined. It appears that the first thermodynamic ionization constant increases about ten fold when the temperature rises from 0° to 50° C. Using values of the thermodynamic ionization constants obtained at various temperatures, the thermodynamic quantities  $\Delta H$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  were calculated as functions of temperature. The entropy change for the ionization reaction studied seems to be negative at temperatures from 0° to 40° C and appears to increase with increase of temperature. These results may be explained to be due to the polymerization of telluric acid with increasing in the temperature.

The ionization constant of telluric acid has been determined previously by several investigators<sup>1-4</sup>, but their results are widely divergent. According to some earlier investigations<sup>2-9</sup> increasing in the concentration of telluric acid and in the temperature of the solution favour the formation of a number of strong polytelluric acids. It is also apparent that the influence of added alkali has the same polymerization effect. Thus the above-mentioned deviations in the ionization constants of telluric acid can be due to all these factors. In an earlier investigation, the present author<sup>4</sup> has determined the first ionization constant of telluric acid using a method, where the above-mentioned effects are neglected. The object of the present investigation was to determine the first thermodynamic ionization constant of telluric acid at various temperatures using the same potentiometric method and to use the values obtained in calculating the values of some thermodynamic functions for the ionization reaction of telluric acid.

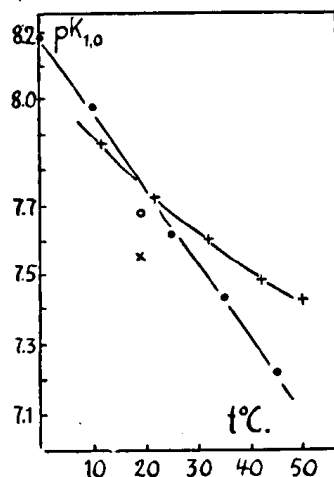


Fig. 1. The influence of the temperature on the ionization of telluric acid in aqueous solutions. The first thermodynamic ionization constant obtained 1) by the present author ● (cf. Table 1.), 2) by Fouasson<sup>2</sup> + (measurements of conductivity) and × using pH measurements) 3) by Britton and Robinson<sup>1</sup> ○.

Table 1. The values of the first ionization constant of telluric acid obtained at various temperatures and ionic strengths (KCl).

t° C.	$\sqrt{I}$	$C_{H_6TeO_6}$	$P_m \times 10^4$	$pK_1$	$pK_{1,0}$
0	0.316	0.009965	0.9260	7.899	8.187
	0.631	0.009975	0.6400	7.714	
	1.266	0.009980	0.6482	7.704	
10	0.316	0.009977	0.6380	7.717	7.975
	0.632	0.009962	0.7511	7.576	
	1.258	0.009972	0.8372	7.741	
25	—	—	—	—	7.611 <sup>1)</sup>
35	0.316	0.009998	1.145	7.209	7.427
	0.632	0.009990	1.340	7.072	
	1.260	0.009975	1.391	7.040	
45	0.315	0.009942	1.572	6.990	7.120
	0.631	0.009950	1.680	6.876	
	1.260	0.009975	1.551	6.946	

1) cf. ref. 4.

The values of the first ionization constant of telluric acid obtained at various temperatures and ionic strengths are given in Table 1. For the calculations of the thermodynamic ionization constants an equation of Debye-Hückel's type has been used. It appears that the effect of temperature on the ionization of telluric acid is unexpectedly large and it seems to be conform with the following equation at temperatures from 0° to 50° C.

$$(1) \quad pK_{1,0} = 8.180 - 2.36 \times 10^{-2} \times t$$

It is obvious that the wide variation of the  $pK_{1,0}$  values with temperature is due to the polymerization of telluric acid mentioned above<sup>5-7</sup> (cf. germanic acid<sup>10</sup> and an equation of Harned and Embree<sup>11</sup>).

With the aid of eqn. (1) it is possible to calculate the heat of ionization  $\Delta H$  for the ionization reaction in question at different temperatures. This equation combined with van't Hoff's equation yields the following equation:

$$(2) \quad \Delta H = 5.44 \cdot 10^{-2} RT^2$$

Further, the thermodynamic functions  $\Delta G^\circ$  and  $\Delta S^\circ$  for the reaction in question can be calculated utilizing equations:

$$(3) \quad \begin{aligned} \Delta G^\circ &= \Delta H - T\Delta S^\circ \\ \Delta G^\circ &= 2.303 RT pK_{1,0} \end{aligned}$$

The results of these calculations are given in Table 2. It should in this connection

Table 2. Thermodynamic quantities of the ionization reaction of germanic acid as a function of temperature. The values were calculated using the  $pK_{1,0}$  values in Table 1.

t° C.	$\Delta H$ kcal	$\Delta G^\circ$ kcal	$-\Delta S^\circ$ E.U.
0	8.05	10.45	8.8
10	8.65	10.50	6.6
20	9.25	10.60	4.7
30	9.90	10.70	2.6
40	10.60	10.70	0.4
50	11.25	10.75	-1.6

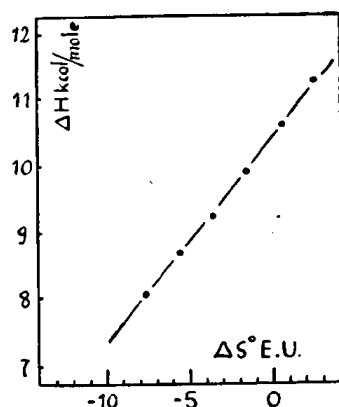
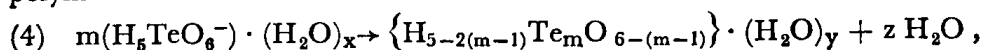


Fig. 2. Variation of  $\Delta H$  as a function of  $\Delta S^\circ$ .

be noted that these values are only be considered a p p a r e n t values because it is obvious that the corresponding reaction does not only be an ionization reaction as mentioned above. This appears also from the results in Table 2. The entropy change seems to be increase with increasing temperature. This phenomenon may be explicable in terms of following anionic solvation and polymerization reaction:



where the number of the particles should be increased with increasing temperature. It is interesting to note that the increase of the entropy change varies linearly with the corresponding enthalpy change, the slope  $\Delta H/\Delta S^\circ = 0.31$  being almost equal with that for the ionization reaction of germanic acid<sup>10</sup> (cf. Fig. 2.).

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