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67. Dielectric Shielding of Ionic Charges in Aqueous Solutions of Different Ionic Strength

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Summary. The thermodynamic functions of the proton transfer $H_2tn^{2+} + tn \rightarrow 2\ Htn^+$ (tn = 1,3-diaminopropane) have been determined in aqueous solutions containing different amounts of KCl ($0.05 \leqslant \mu \leqslant 3.01$). The free energy ($-\Delta G$) of the process decreases, whereas the enthalpy ($-\Delta H$) increases with μ. There is reason to believe that the reaction is entirely controlled by the *Coulomb* forces between the two protonic charges. The electrostatic energy involved can be described in terms of a model incorporating an effective dielectric constant ε_e, such that $\delta\varepsilon_e/\delta\mu$ and $\delta^2\varepsilon_e/\delta\mu\delta T$ are both positive. The polarisation of pure water is produced by orientation of hydrogen-bonded dipole molecules H_2O, whereas the electrolyte solution is polarised in addition by dislocation of the ions K^+ and Cl^-. Our results demonstrate that the former type of polarisation is much more temperature dependent than the latter.

For the interpretation of the thermodynamic functions of reactions taking place between ions in solution it is useful to separate the simple, long-range coulombic interactions from others, such as covalency, ligand field stabilisation, steric effects *etc.* The energies involved will be designated by A_{el} and E_n respectively, both being taken positive in case of attraction and negative in case of repulsion.

Because of the temperature dependence of the effective dielectric constant ε_e, the energy A_{el} is also temperature dependent:

$$A_{el} = \frac{1}{\varepsilon_e} \cdot \text{const} \tag{1}$$

$$\frac{\delta A_{el}}{\delta T} = -\frac{A_{el}}{\varepsilon_e} \cdot \frac{\delta \varepsilon_e}{\delta T} \tag{2}$$

If it is assumed that E_n does not depend on temperature ($\delta E_n/\delta T = 0$), the following expressions for the thermodynamic functions are obtained:

$$\Delta G = -T \cdot (\Delta S_t + \Delta S_r + \Delta S_c + \Delta S_v + R \cdot \ln W) - A_{el} - E_n \tag{3}$$

$$\Delta S = \Delta S_t + \Delta S_r + \Delta S_c + \Delta S_v + R \cdot \ln W - A_{el} \cdot \left(\frac{1}{\varepsilon_e} \cdot \frac{\delta \varepsilon_e}{\delta T}\right) \tag{4}$$

$$\Delta H = -A_{el}\left(1 + \frac{T}{\varepsilon_e} \cdot \frac{\delta \varepsilon_e}{\delta T}\right) - E_n \tag{5}$$

These equations contain many parameters which are difficult to assess. However, we can choose a process in which the number of solute particles does not change (therefore no change of the translational entropy term: $\Delta S_t = 0$) and in which the change in rotational, conformational and vibrational entropy is negligible: $((\Delta S_r + \Delta S_c + \Delta S_v) = 0)$. Furthermore, if the bonds broken and formed during the reaction are alike, E_n can also be neglected. A proton transfer between two bases that differ from one another solely by the presence or absence of an electric charge, is such a process:

$$H{-}\overset{\oplus}{N}H_2{-}X{-}H_2\overset{\oplus}{N}{-}H + NH_2{-}X{-}H_2N \longrightarrow 2\,H{-}\overset{\oplus}{N}H_2{-}X{-}H_2N \tag{6}$$

From reactions of this type we can obtain information about the magnitude of A_{el} and its temperature coefficient.

The second protonation step of a symmetrical diamine $X(NH_2)_2$ differs from the first only by the energy needed to bring up the second proton against electrostatic repulsion of the first proton, provided that the microbasicity of the second basic site does not change on protonation of the first site. The simple statistical term $R \cdot \ln W$ in (3) and (4) is easy to evaluate ($W = 4$). The differences $(\Delta G_1 - \Delta G_2)$, $(\Delta S_1 - \Delta S_2)$ and $(\Delta H_1 - \Delta H_2)$ for the first and second protonation steps furnish the thermodynamic functions of the proton transfer (6):

$$\Delta G = (\Delta G_1 - \Delta G_2) = -2.303\, R \cdot T \cdot \Delta pK = -R \cdot T \cdot \ln 4 - A_{el} \tag{7}$$

$$\Delta S = (\Delta S_1 - \Delta S_2) = R \cdot \ln 4 - A_{el} \frac{1}{\varepsilon_e} \cdot \frac{\delta \varepsilon_e}{\delta T} \tag{8}$$

$$\Delta H = (\Delta H_1 - \Delta H_2) = -A_{el} \cdot \left(1 + \frac{T}{\varepsilon_e} \cdot \frac{\delta \varepsilon_e}{\delta T}\right) \tag{9}$$

The basicity difference ΔpK (7) provides an estimate of the electrostatic energy to be gained when the two protonic charges are removed from one another in the course of reaction (6). We can re-write (1) as:

$$A_{el} = N \cdot \frac{e^2}{a \cdot \varepsilon_e}, \tag{10}$$

where 'a' is the mean distance between the two charges in $X(NH_3)^{2+}$, N is *Avogadro*'s number and 'e' the protonic charge. From (10) we obtain an experimental value for the effective dielectric constant ε_e. Furthermore, we can obtain the temperature coefficient of ε_e from the enthalpy change associated with reaction (6).

The effective dielectric constant ε_e is found to be much smaller than the dielectric constant ε_0 of the bulk solvent and it is also less temperature dependent:

$$\varepsilon_e < \varepsilon_0; \quad (-\delta\varepsilon_e/\delta T) < (-\delta\varepsilon_0/\delta T) \qquad (11)$$

As expected, ε_e and its temperature coefficient diminish as the distance 'a' approaches zero. Both quantities diminish also with increasing bulkiness of the hydrocarbon skeleton X carrying the two basic sites.

The experimental data also indicate that the numerical value of the negative quantity $[\delta \ln \varepsilon_e/\delta \ln T]$ becomes smaller with decrease in 'a' and increasing bulkiness of X. Therefore, according to equation (9), the proton transfer (6) becomes more exothermic the less the two interacting charges are dielectrically shielded from one another.

We have now examined the effect of ionic strength of the medium, in which process (6) occurs. The free energies and enthalpies of the two protonation steps of 1,3-diaminopropane were therefore determined at various KCl concentrations.

$H_2N{-}CH_2{-}CH_2{-}CH_2{-}NH_2$: 'tn'

The choice of 1,3-diaminopropane as carrier molecule represents a compromise between several conflicting factors. On the one hand, the part of the field of force going through the carrier molecule with its low effective dielectric constant (~2) should be as small as possible. This calls for a long chain of CH_2-groups between the two basic sites. But when the chain length is increased, the values of the thermodynamic functions for the first and the second protonation step become more equal, so that it becomes increasingly difficult to obtain their differences with sufficient accuracy. A chain length of three CH_2 seems to be a good compromise. Furthermore, such a chain is sufficiently long to justify the assumption that the microbasicity of the second NH_2 does not change on protonation of the first amino group. In any case, such a change should be invariant with ionic strength.

The cation H_2tn^{2+} can be treated as an extended zigzag-chain because of the repulsion of the two charges, so that the distance between the two acidic protons is easy to evaluate. We have used a = 6,6 Å for equation (10).

Table 1. *Concentration constants for the protonation of diaminopropane 'tn'*

$$pK_1 = \log \frac{[Htn^+]}{[H^+]\cdot[tn]}; \quad pK_2 = \log \frac{[H_2tn^{++}]}{[H^+]\cdot[Htn^+]}; \quad pK_w = -\log[H^+]\cdot[OH^-]$$

The ionic strength has been adjusted with KCl. Temperature: 20°

μ (KCl) mol/l^{-1}	pK_1	pK_2	pK_w
0.05	10.625 ± 0.01	8.843 ± 0.01	14.002
0.11	10.715 ± 0.01	8.907 ± 0.01	13.959
0.21	10.733 ± 0.01	8.967 ± 0.01	13.924
0.51	10.805 ± 0.01	9.091 ± 0.01	13.895
1.01	10.929 ± 0.01	9.256 ± 0.01	13.941
1.51	11.029 ± 0.01	9.351 ± 0.01	13.997
2.01	11.126 ± 0.01	9.462 ± 0.01	14.067
2.51	11.196 ± 0.01	9.547 ± 0.01	14.136
3.01	11.294 ± 0.01	9.634 ± 0.01	14.198

Table 2. *Thermodynamic functions for the protonation of diaminopropane (tn) and of OH^- in solvents of different ionic strength,* valid for 20° (kcal per mol and cal · mol^{-1} · $°K^{-1}$ respectively).

	$tn + H^+ \rightleftharpoons Htn^+$			$Htn^+ + H^+ \rightleftharpoons H_2tn^{2+}$			$H^+ + OH^- \rightleftharpoons H_2O$		
μ	$-\Delta G_1$	$-\Delta H_1$	ΔS_1	$-\Delta G_2$	$-\Delta H_2$	ΔS_2	$-\Delta G$	$-\Delta H$	ΔS
0.11	14.37 ± 0.01			11.95 ± 0.01	12.03 ± 0.1	−0.3 ± 0.3	18.73	13.66	17.3
0.21	14.40 ± 0.01	12.71 ± 0.02	5.8 ± 0.2	12.03 ± 0.01	12.11 ± 0.25	−0.2 ± 0.8	18.68	13.70	17.0
0.51	14.49 ± 0.01	12.93 ± 0.07	5.3 ± 0.3	12.20 ± 0.01	12.20 ± 0.15	0 ± 0.5	18.64	13.80	16.5
1.01	14.66 ± 0.01	13.20 ± 0.02	5.0 ± 0.2	12.42 ± 0.01	12.32 ± 0.04	0.3 ± 0.2	18.70	13.92	16.3
2.01	14.92 ± 0.01	13.59 ± 0.09	4.5 ± 0.3	12.69 ± 0.01	12.57 ± 0.09	0.4 ± 0.3	18.87	14.08	16.3
2.51	15.02 ± 0.01	13.83 ± 0.06	4.1 ± 0.2	12.81 ± 0.01	12.61 ± 0.05	0.7 ± 0.2	18.96	14.15	16.4
3.01	15.15 ± 0.01	13.96 ± 0.05	4.1 ± 0.2	12.92 ± 0.01	12.76 ± 0.09	0.5 ± 0.3	19.05	14.20	16.5

Basicity constants of proton acceptors can be determined with great accuracy. The results obtained with diaminopropane have been collected in Table 1 together with the ionic product of water K_w, which is needed for the evaluation of the pH-measurements and has been taken from the work of *Harned & Hamer* [2].

It is much more difficult to obtain the heat of reaction with high accuracy. Many calorimetric measurements had to be carried out at the same ionic strength in order to get a reliable average. However, we restricted ourselves to a somewhat smaller number of solvents which seemed permissible because of the almost linear dependence of ΔH on $\sqrt{\mu}$. The results are collected in Table 2. The values ΔG have been calculated from the equilibrium constants in Table 1 and ΔS was obtained from ΔG and ΔH according to the ***Gibbs-Helmholtz equation***. The enthalpies of neutralisation of H^+ and OH^- have been taken from *Harned & Hamer* [3] and were checked by a few determinations of our own.

In spite of the care with which the quantities in Table 2 have been determined, the differences needed for equations (7) and (9) show considerable scatter. The experimental values ΔG and ΔH were therefore plotted as functions of $\sqrt{\mu}$. Such plots should be almost linear because of the well known dependence of the ionic activity coefficients on ionic strength (*Debye-Hückel*). Smooth curves were drawn through the experimental points (Fig. 1 and 2), and the differences $(\Delta G_1 - \Delta G_2)$ and $(\Delta H_1 - \Delta H_2)$ were finally obtained graphically. The results are collected in Table 3 together with the quantities A_{el} (from equation 7), ε_e (from equation 10) and $\delta_e/\delta T$ (from equation 9).

Table 3. *The changes of free energy and enthalpy for the proton transfer (6): $H_2tn^{2+} + tn \rightleftharpoons 2\,Htn^+$ and the quantities A_{el}* (in kcal per mol), *ε_e and $\delta\varepsilon_e/\delta T$ calculated with the equations (7), (10) and (9)*

μ	$-\Delta G$	$-\Delta H$	A_{el}	ε_e	$\delta\varepsilon_e/\delta T$	$\bar{d}_K$ (Å)
0.05	2.47	–	1.66	30	–	32.14
0.11	2.41	0.55	1.60	31	−0.070	24.71
0.21	2.37	0.62	1.56	32	−0.066	19.92
0.51	2.30	0.74	1.49	34	−0.059	14.82
1.01	2.25	0.88	1.44	35	−0.046	11.80
1.51	2.22	0.97	1.41	36	−0.038	10.32
2.01	2.21	1.05	1.40	36	−0.031	9.38
2.51	2.22	1.14	1.41	36	−0.023	8.71
3.01	2.23	1.26	1.42	36	−0.015	8.20

In Fig. 4 the effective dielectric constant and its temperature coefficient, which have been empirically determined as outlined, are plotted as a function of the mean distance between the cations of the inert electrolyte $\bar{d}_K$:

Mean distance between K⁺ ions in Å units: $$\bar{d}_K = \left(\frac{10^{27}}{\mu \cdot N}\right)^{1/3} \qquad (12)$$

The course of these functions is at first unexpected. As expressed with (11), the effective dielectric constant ε_e is always smaller than that of the bulk solvent ε_0 and has a smaller temperature coefficient. A reduction of ε_e brought about by decreasing the distance a, by increasing the bulkiness of the charge carrier or by increasing electrostriction (multiple charges on carrier) is regularly accompanied by a decrease of $(-\,\delta\varepsilon_e/\delta T)$ as well as a decrease of $(-\,\delta \ln \varepsilon_e/\delta \ln T)$. As demonstrated by Fig. 4 the effective dielectric constant increases with increasing ionic strength, but it becomes less temperature dependent.

These trends can be interpreted by considering two different types of polarisation of the medium between the interacting charges. In pure water, the polarisation is mainly due to an orientation of the dipole molecules H_2O. If an electrolyte solution (KCl) is used as medium however, polarisation can be achieved in addition by altering the positions of the ions K^+ and Cl^-. Our results show that the first type of polarisation is much more temperature dependent than the second type. The electric field at the site of the second basic group is lowered, in the case of dipolar molecules by favorable position and orientation, which are disturbed by increasing temperature. The favorable arrangement of spherical ions however, is less temperature dependent. This is demonstrated by the simultaneous rise of ε_e and decrease of $-\delta\varepsilon_e/\delta T$ in increasing the concentration of KCl.

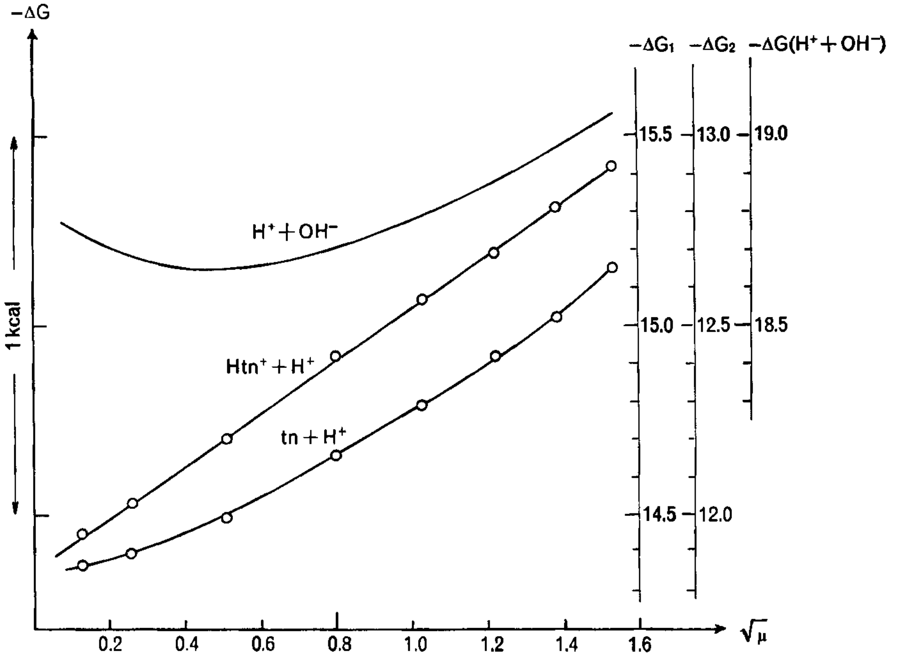

Fig. 1. *Thermodynamic functions ΔG, ΔH, ΔS for the protonation of tn, Htn^+ and OH^- as a function of $\sqrt{\mu}$*

If it is generally true that an increase of ionic strength brings about an increase of ε_e, the electrostatic energy A_{el} will become smaller (equation 1), which reduces the quantity $-\Delta G$ numerically (equation 3) and lowers the association constant. But when this increase of ε_e is accompanied by a decrease of $(-\delta\varepsilon_e/\delta T)$, ΔH will become

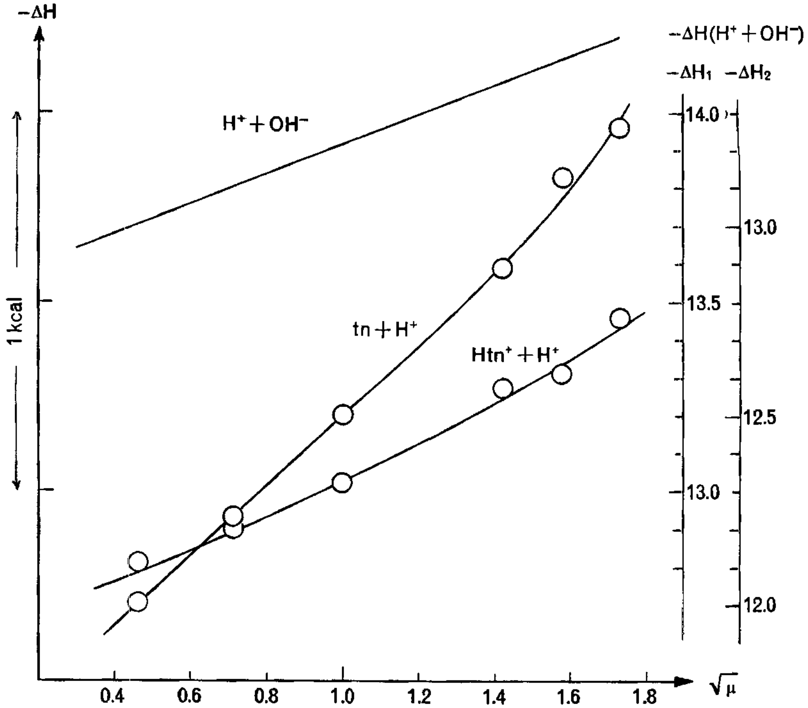

Fig. 2. *Thermodynamic functions ΔG, ΔH, ΔS for the protonation of tn, Htn$^+$ and OH$^-$ as a function of $\sqrt{\mu}$*

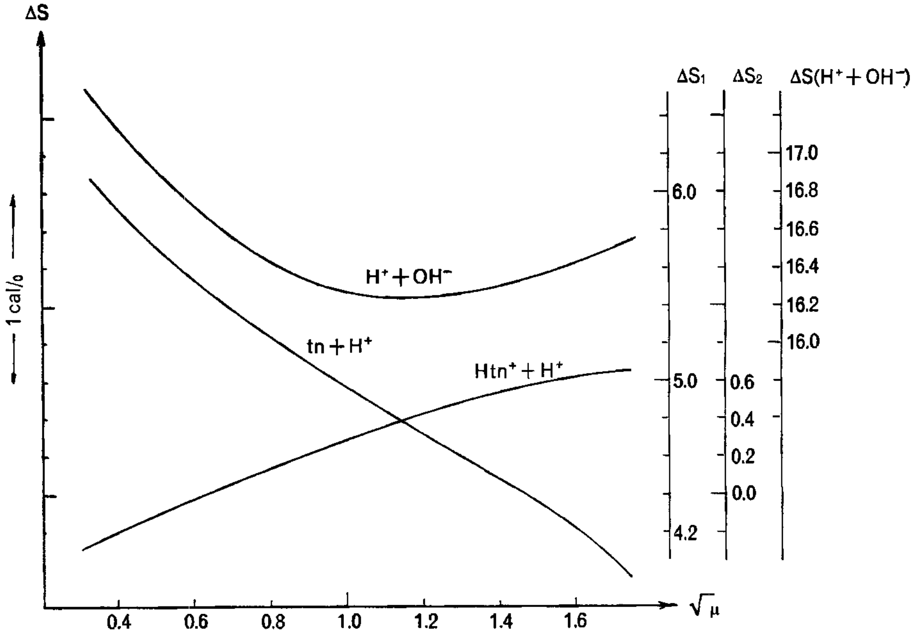

Fig. 3. *Thermodynamic functions ΔG, ΔH, ΔS for the protonation of tn, Htn$^+$ and OH$^-$ as a function of $\sqrt{\mu}$*

more negative (equation 5), so that the association will be more exothermic. This should be so not only when we approach ions of opposite charge, but also when we remove charges of the same sign from one another as demonstrated by ΔG and ΔH of Table 3. We have to ask now, whether this is a general phenomenon or not.

Unfortunately, there are hardly any data in the literature, which are suitable for such an inspection. Thousands of stability constants have been determined [4] from which ΔG-values can be calculated, but only a small part of these association processes have also been investigated calorimetrically in order to find the enthalpy changes [5]. Not many chemists seem to have gone through the trouble of measuring reliable values for ΔG and ΔH as a function of ionic strength.

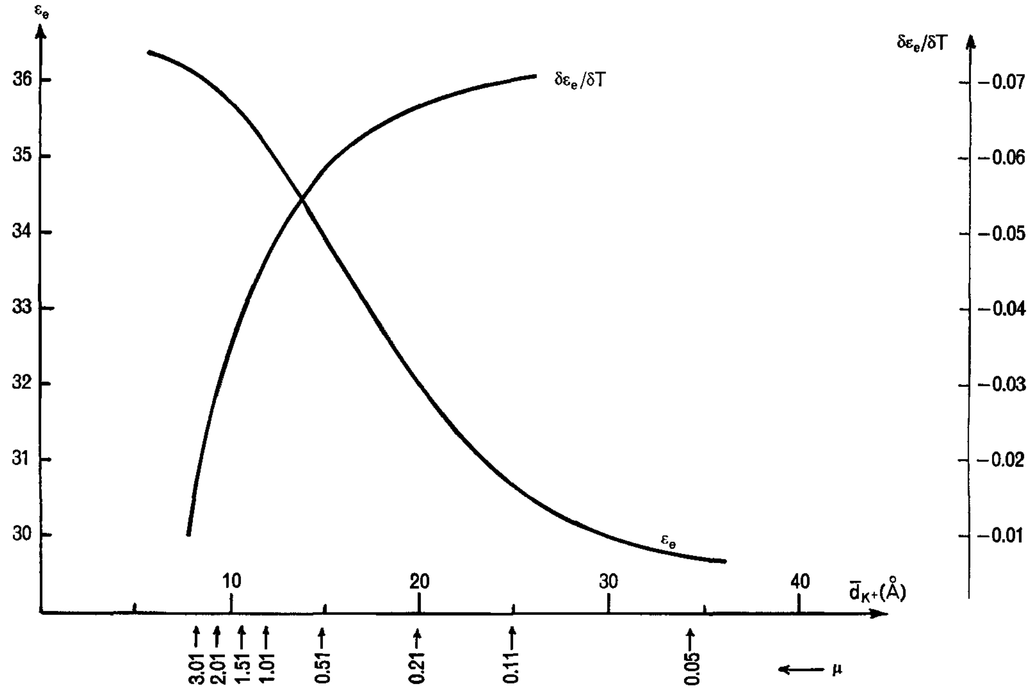

Fig. 4. *The apparent dielectric constant ε_e and its temperature coefficient,* effective for protonic charges on the ends of an organic carrier molecule $\overset{\oplus}{H_3N}-CH_2-CH_2-CH_2-\overset{\oplus}{NH_3}$ to be separated from one another in solutions of different ionic strength μ as a function of the mean distance of the cations K^+ of the inert electrolyte KCl.

A few data of this type have been determined at the University of Lund [6] and are collected in Table 4. As expected, ΔG becomes always less negative with increasing ionic strength and ΔH indeed becomes in most cases slightly more negative. However, this is so only up to about $\mu = 1$. At higher salt concentrations this trend is apparently overshadowed by other effects, probably by the formation of weak complexes (ion pairs) of the reactants with the ions of the inert electrolyte and by desolvatation of the reactants brought about by the latter. Generally, we can state that an increase of ionic strength influences not only A_{el} and its temperature coefficient,

Table 4. *Thermodynamic functions for the formation of 1:1-complexes of cadmium in solutions of different ionic strength brought about with* $NaClO_4$ (25° kcal per mol). $Cd^{2+} + X^- \rightleftharpoons CdX^+$

Ligand X^-	$\mu = 0.25$			$\mu = 0.50$			$\mu = 1.00$			$\mu = 2.00$			$\mu = 3.00$		
	K	$-\Delta G$	$-\Delta H$	K	$-\Delta G$	$-\Delta H$	K	$-\Delta G$	$-\Delta H$	K	$-\Delta G$	$-\Delta H$	K	$-\Delta G$	$-\Delta H$
Chloride Cl^-	28	1.97	−0.21	23.5	1.87	−0.25	22.3	1.84	−0.13	26.5	1.94	0.00	38.5	2.16	0.10
Iodide J^-	88	2.65	2.32	77	2.57	2.43	75	2.56	2.45	94	2.69	2.32	121	2.84	2.26
Thiocyanate SCN^-	27	1.95	2.24	22.6	1.85	2.24	20.7	1.80	2.29	22.0	1.83	2.22	25.5	1.92	1.94
Acetate AcO^-	18.5	1.73	−1.69	15.5	1.62	−1.76	15.0	1.60	−1.62	17.2	1.69	−1.50	20.0	1.78	−1.46

but also other parameters of the equations (3) to (5). This circumstance makes it especially difficult to interpret the curves of the Fig. 1 to 3. The considerable decrease of ΔG and ΔH of the first as well as the second protonation step of the diamine 'tn' is almost certainly caused by desolvatation of the reactants, especially the hydrogen ion brought about by the increasing concentration of KCl. Only the differences $(\Delta G_1 - \Delta G_2)$ and $(\Delta H_1 - \Delta H_2)$, the thermodynamic quantities of the proton transfer (6), are easy to interpret. There is no free hydrogen ion involved and on both sides of the chemical equation, there are two free amino groups and two protonated amino groups, so that changes of solvatation due to the increasing salt concentration cancel. The only driving force of the proton transfer is the repulsion of the two protonic charges and it seems justified therefore to calculate the energy A_{el} caused by this *Coulomb* force from the thermodynamics of process (6) as we have done.

Experimental Part

A comparatively large quantity of 1,3-diamin propane (*Fluka*) has been distilled in pure nitrogen of atmospheric pressure (720 Torr) after the addition of metallic sodium. The fraction collected between the boiling points 135.0° and 135.5° was used to make up a stock solution of $tn(HCl)_2$ containing a small excess of HCl. After dilution to a total concentration $[tn]_t$ of about 0.002 and adding the appropriate amount of solid KCl, titrations were carried out with 0,1 M of KOH of the same ionic strength. The titrant was prepared from pure KCl-solution and solid Ag_2O. The sum of the concentrations of KCl and HCl (added by preparing the stock-solution) was taken as ionic strength μ. Actually, μ is somewhat larger as long as the doubly charged cation H_2tn^{2+} is present. The glass electrode was standardized before every titration run. This was done by means of a titration of HCl at the same ionic strength. The accuracy of the pH-determinations was better than 0.01 units. The degree of protonation $\bar{p}$ was calculated with (13):

$$\bar{p} = \frac{C_{HCl} - C_{KOH} - [H^+] + [OH^-]}{[tn]_t} \tag{13}$$

The protonation function is given by:

$$\bar{p} + (\bar{p}-1) \cdot [H^+] \cdot 10^{pK_1} + (\bar{p}-2) \cdot [H]^2 \cdot 10^{pK_1+pK_2} = 0 \tag{14}$$

Table 5. *Calorimetric measurements*

	before the mixing			after the mixing				
μ	HCl (mm)	tn (mm)	V (ml)	HCl (mm)	tn (mm)	V (ml)	Q (cal)	Result (kcal, mol^{-1})
0.11	0	0.3735	101.20	0.3395	0.3735	102.40	4.407	
	0.3395	0.3735	102.40	0.6790	0.3735	103.60	4.127	$\Delta H_1 = 12.78 \pm 0.06$
	0	0.3816	94.68	0.3395	0.3816	95.88	4.430	$\Delta H_{1-2} = 24.81 \pm 0.06$
	0.3395	0.3816	95.88	0.6790	0.3816	97.08	4.156	
0.21	0.3395	0.3726	102.32	0.6790	0.3726	103.52	4.178	
	0.3395	0.3702	101.97	0.6790	0.3702	103.17	4.130	$\Delta H_1 = 12.71 \pm 0.13$
	0	0.3731	90.83	0.3395	0.3731	92.03	4.412	$\Delta H_{1-2} = 24.83 \pm 0.12$
	0.3395	0.3731	92.09	0.6790	0.3731	93.23	4.144	
0.51	0	0.5596	99.65	0.3395	0.5596	100.85	4.514	
	0.3395	0.5596	100.85	0.6790	0.5596	102.05	4.340	$\Delta H_1 = 12.94 \pm 0.07$
	0.6790	0.5596	102.05	1.0184	0.5596	103.25	4.157	$\Delta H_{1-2} = 25.14 \pm 0.08$
	0	0.5593	96.67	0.3395	0.5593	97.97	4.475	

Table 5. (Continued)

1.01	0	0.5601	95.61	0.3395	0.5601	96.81	4.575	
	0.3395	0.5601	96.81	0.6790	0.5601	98.01	4.394	$\Delta H_1 = 13.20 \pm 0.02$
	0	0.5601	97.26	0.3395	0.5601	98.46	4.567	$\Delta H_{1-2} = 25.52 \pm 0.02$
	0.3395	0.5601	98.46	0.6790	0.5601	99.66	4.399	
2.02	0	0.5600	92.91	0.3395	0.5600	94.11	4.700	
	0.3395	0.5600	95.11	0.6790	0.5600	95.31	4.491	$\Delta H_1 = 13.59 \pm 0.09$
	0.6790	0.5600	95.31	1.0184	0.5600	97.51	4.304	$\Delta H_{1-2} = 26.16 \pm 0.10$
	0	0.3680	94.44	0.3395	0.3680	95.64	4.627	
2.51	0	0.3728	91.18	0.3395	0.3728	92.38	4.620	
	0.3395	0.3728	92.38	0.6790	0.3728	93.58	4.355	$\Delta H_1 = 13.35 \pm 0.04$
	0	0.3731	91.55	0.3395	0.3731	92.75	6.611	$\Delta H_{1-2} = 25.96 \pm 0.04$
	0.3395	0.3731	92.75	0.6790	0.3731	93.95	4.339	
3.01	0.5375	0.5599	93.28	1.0467	0.5599	96.08	6.600	
	0	0.5612	91.91	0.5092	0.5612	93.71	7.110	$\Delta H_1 = 13.96 \pm 0.05$
	0.5092	0.5612	93.71	1.0184	0.5612	95.51	6.646	$\Delta H_{1-2} = 26.73 \pm 0.04$
	0	0.5602	89.45	0.5092	0.5602	91.25	7.086	
	0.5092	0.5602	91.25	1.0184	0.5602	93.05	6.605	

For the calculation of pK_1 and pK_2 20–25 pairs $\bar{p}$, pH were used. For the computer program see *Anderegg* [7]. The standard deviations for individual protonation curves were between 0.001 and 0.003. The results from different curves agreed not so well. The data in Table 1 are the mean values from 3 to 4 curves.

The details of the calorimetric measurements carried out in Florence with a LKB-8700 instrument are given in Table 5. In the columns 'HCl', 'tn' the number of millimoles of hydrochloric acid and diamine are given, which are present in the volume V together with KCl to produce the ionic strength given in the first column before and after the operation of mixing, which produces the heat Q. The concentrations of tn, Htn^+, H_2tn^{2+} and OH^- before and after mixing are calculated with the data of Table 1 and finish the molar quantities with which the reactions $OH^- \rightarrow H_2O$, $tn \rightarrow Htn^+$, $Htn^+ \rightarrow H_2tn^{2+}$ have taken place in the production of Q calories. From these data the reaction enthalpies for the single (ΔH_1) and double protonation (ΔH_{1-2}) are obtained with the standard deviations given in the Table.

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