

## Thermodynamic Properties of Rare Earth Complexes

### XI. Stability Constants and Free Energy Changes for the Formation of Rare Earth Diglycolate Complexes at 5, 20, 35, and 50°C

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The stability constants for the diglycolato complexes of four trivalent rare earths have been determined at 5, 20, 35, and 50°C. The rare earths selected for the investigation were Pr(III), Sm(III), Dy(III), and Yb(III). The stability constants were obtained by a potentiometric standard method and all data refer to an aqueous sodium perchlorate medium of a total sodium ion concentration of 1.00 M. The changes in free energy were calculated from the stability constants and the temperature dependence was then compared with the results obtained from a calorimetric investigation.

Investigations of complex formation in solution between trivalent lanthanoids and different ligands have shown that thermodynamic quantities such as  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  seldom vary monotonously through the rare earth series.<sup>1-3</sup> The variations are approximately the same for a number of ligands, a fact which might indicate<sup>2,4</sup> that a large part of the observed changes can be ascribed to some property of the central ion; a property, which might be its state of hydration. The observed variations need not necessarily be caused by a change in the number of coordinated water molecules, but rather by a slight change in geometry, brought about by the changing ionic radius. Such a change in geometry in the first hydration shell will also influence, *via* hydrogen bonding, a region of solvent surrounding the hydrated metal ion.<sup>2</sup>

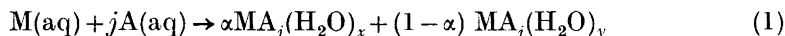
An alternative description has been given, *e.g.*, by Hoard *et al.*,<sup>5</sup> Geier *et al.*,<sup>6,7</sup> and Anderegg and Wenk.<sup>8</sup> According to them, the observed variations of the thermodynamic quantities may be caused by changes in the hydration of the various rare earth complexes.

These two views illustrate well the general difficulty to decide whether an observed change in a thermodynamic function (a “ $\Delta$ ”-quantity) is due to one or several of the species participating in the reaction. The difficulty may, in some cases, be circumvented by studying systems, where the central ion and

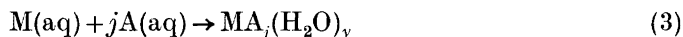
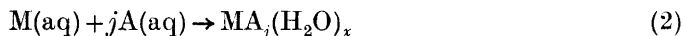
the ligands are systematically varied, a method used previously in this series of investigations. One may ask whether it is possible to decide which of the previous descriptions that is the most probable one.

Geier *et al.*<sup>6</sup> and Anderegg and Wenk<sup>8</sup> have shown that the spectra of some rare earth complexes of EDTA and trimethylenediamine-*N,N,N',N'*-tetraacetate (TMTA) exhibit a strong temperature dependence, *viz.* in those regions of the lanthanoid series where the changes in  $\Delta H^\circ$  and  $\Delta S^\circ$  from one element to the next one are large. This observation was interpreted as due to a change in the coordination number in the complexes, or more explicit, as a change in the number of coordinated water molecules. Spectroscopic studies<sup>9</sup> of rare earth complexes with other ligands, such as diglycolate, dipicolinate and iminodiacetate have shown that the various *f-f* absorption bands change very little with temperature in the range 2–65°C. This might indicate that equilibria of the type discussed by Geier and Anderegg are not present in these systems, or, that the spectroscopic method is not sensitive enough to detect possible differences in the coordination shells.

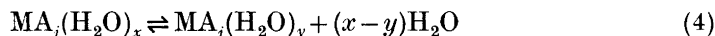
Let us instead investigate the thermodynamic consequences of a possible equilibrium between complexes of two different hydration numbers. Only the changes in  $\Delta G^\circ$  and  $\Delta H^\circ$  for the following over-all reaction are available experimentally.



$\alpha$  and  $1 - \alpha$  are the mol fractions of the two differently hydrated complexes. It is possible to change the relative amounts of  $\text{MA}_j(\text{H}_2\text{O})_x$  and  $\text{MA}_j(\text{H}_2\text{O})_y$  by a change of temperature if the enthalpy changes of the two processes



are different. The change in the relative amounts of the two complexes will give rise to a significant contribution to the temperature dependence of  $\Delta H^\circ$  in a temperature range, where the equilibrium constant  $K$  for the process



is not too large or too small. The contribution will be largest when  $K$  is near unity and is negligible when the equilibrium (4) is strongly displaced either to the right or to the left, *i.e.* when  $K \gg 1$  or  $K \ll 1$ . The possibility of changing  $K$  by a change of the temperature will thus result in a contribution to  $\Delta C_p^\circ$  of (1) which increases from zero up to a maximum and then decreases to zero again as the equilibrium (4) is shifted from the left to the right or *vice versa*. Whether a maximum is obtained within a given temperature range depends, of course, on the magnitude of  $K$ . In the lanthanoid series, a variation of  $K$  with the atomic number  $Z$  will, for a given temperature change, also give rise to varying contributions to  $\Delta C_p^\circ$  in the different reactions (1). This contribution is largest for the element, where  $K$  is closest to unity. If, in a given temperature range, the process (2) is dominating in one end of the lanthanoid series and (3) in the other, then there must exist a range in between, where both reactions are of equal importance.

Consequently, the contribution to the over-all value of  $\Delta C_p^\circ$  for reaction (1) must pass through a maximum in this range of the series. Provided that this contribution is not too small in comparison with the over-all value of  $\Delta C_p^\circ$  for (1), this maximum should be open to experimental verifications.

*Conclusion.* If the large variations in  $\Delta H^\circ$  and  $\Delta S^\circ$  through the rare earth series are accompanied by changes in  $\Delta C_p^\circ$ , which have maximum in the region, where the changes in  $\Delta H^\circ$  and  $\Delta S^\circ$  are largest, then the presence of an equilibrium of the type (4) is strongly indicated.

The same argument is valid if the coordination number is changed by a difference in the number of coordinated groups in a polydentate ligand. Changes of this type are on the other hand not very probable for the terdentate ligands studied here (or for the EDTA and TMTA complexes for that matter).

In order to study hydration equilibria in the manner discussed above, we have started a series of investigations of the changes of  $\Delta G_j^\circ$  and  $\Delta H_j^\circ$  for the formation of rare earth diglycolate complexes in the temperature range 5–50°C. Other aims of the investigation have been:

(a) to make a comparison between the  $\Delta G_j^\circ(T)$ -data, obtained by direct potentiometric methods with those computed from  $\Delta H_j^\circ(T)$ -data, determined from calorimetric measurements;

(b) to make a determination of the partial molal heat capacities for the various rare earth perchlorates. These data in combination with  $\Delta C_{p_j}^\circ$  values for the various complex formation reactions will make it possible to determine the variations of the partial molal heat capacities for the complexes through the rare earth series. This is one way of getting a direct information of the relative contribution of the various species to a "A"-quantity.

In the present work, four model systems have been chosen in order to study the formation of rare earth diglycolate complexes at various temperatures. These systems have been fully investigated, *i.e.* both the changes of free energy and enthalpy have been determined. For five other systems, only the enthalpy changes have been measured, while the stability constants and the free energy have been calculated on the basis of these measurements<sup>9</sup> and the known stability constants at 20°C.<sup>1</sup> The temperature dependence of the enthalpy changes were determined at 5, 20, 35, and 50°C by using the titration calorimeter, described in a previous publication.<sup>10</sup>

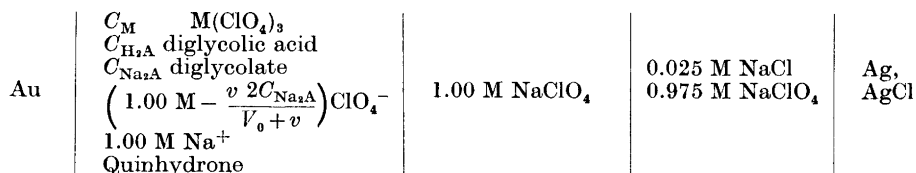
The central ions in the four model systems were Pr(III), Sm(III), Dy(III), and Yb(III). The stability constants of the various complexes, formed between these ions and the diglycolate ion at the above temperatures are reported in this communication. The measurements were made by a potentiometric standard method<sup>1</sup> and the stability constants were computed by a least-squares program, developed by Ingri and Sillén.<sup>11</sup> The constants refer to an aqueous sodium perchlorate medium with 1.00 M total sodium ion concentration. All concentrations given in this paper are in mol l<sup>-1</sup> at 25°C. The notation used is the same as before.<sup>1,2</sup>

## EXPERIMENTAL

*Chemicals.* The various rare earth oxides were obtained from the American Potash & Chemical Corp. Stock solutions of the rare earth perchlorates were prepared and analyzed as described before.<sup>1</sup> The diglycolic acid was obtained from Fluka and was recrystallized

from ethyl acetate. The equivalent weight of the acid was determined to  $67.0 \pm 0.1$  (calc. 67.0). The diglycolate buffers used in the potentiometric titrations were prepared by partial neutralization of the acid with sodium hydroxide. The sodium perchlorate was prepared from perchloric acid (Baker's analyzed) and sodium carbonate (Merck *p.a.*) according to a method described earlier.<sup>12</sup>

*Potentiometric titrations.* The stability constants for the systems investigated were determined by measuring the emf of galvanic cells of the following composition:



The temperature of the right half-cell was kept constant at 25.00°C. The titrations were performed in the left half-cell at 5.00, 20.00, 35.00, and 50.00°C. In order to obtain better thermal stability and to avoid condensation on the walls at the higher temperatures, a special titration vessel with a thermostated top lid was used.

The solution in the left half-cell were prepared by adding an increasing volume,  $v$ , of a solution T to a known volume (25.00 ml =  $V_0$ ) of a solution S. The additions were made by calibrated piston burettes at 25°C. The solutions S and T had the following compositions:



The sodium ion concentration was equal to 1.00 M in all the measurements; *i.e.* the perchlorate concentration varied slightly through the titration. This change did not influence the experimental results as indicated by the fact that measurements performed with a constant sodium perchlorate concentration equal to 1.00 M gave an experimental  $\bar{n}$ -curve coinciding with the one obtained from measurements where the sodium ion concentration was kept constant. This check was made only for the samarium system at 20°C.

The measurements have been carried out at two different buffer compositions. In each series the values of  $C_A$  and  $C_M$  were kept constant. The measured electromotive forces,  $E$ , of the cells used have been corrected for the liquid junction potentials. The corrections have been made according to a method described by Ahrlund,<sup>13</sup> assuming that the junction potential depends only on the hydrogen ion concentration.

The reliability of the quinhydrone electrode was checked against the glass electrode at 5 and 50°C. The difference between the two electrodes never exceeded 0.2 mV.

One remark may be made on the experimental arrangement in the emf measurements. The presence of a temperature gradient in the bridge between the two half-cells will give rise to a potential difference, which might affect the accuracy of the measurements. This potential difference can be eliminated by measuring the emf ( $E^\circ$ ) when the left half-cell above is replaced by a solution of known hydrogen ion concentration. A necessary condition is of course that the temperature gradient can be reproduced. However, the good reproducibility of the measurements indicate that this condition is met.

At all temperatures the additions, volumes and concentrations refer to 25°C. The constants,  $\beta_{j(t)}^{25}$ , calculated from this type of data are related to the true stability constants,  $\beta_{j(t)}$ , on the molar scale according to the equation:

$$\beta_{j(t)} = \beta_{j(t)}^{25} \left[ \frac{\rho_{25}}{\rho_t} \right]^j \quad (5)$$

where  $\beta_{j(t)}^{25}$  and  $\beta_{j(t)}$  are the  $j$ th over-all stability constants at the temperature  $t$  with the concentrations given at the temperature 25°C and  $t$ , respectively.  $\rho_{25}$  and  $\rho_t$  are the densities of the solution at the corresponding temperatures.

If the solution can be regarded as dilute, the weight of the solute can be neglected and the densities of the solution can be replaced by the densities of the solvent. From eqn. (2) we then get:

$$\beta_{j(t)} \rho_t^j = \beta_{j(t)}^{25} \rho_{25}^j = \beta_{j(t)}^{(m)} \quad (6)$$

where  $\beta_{j(t)}^{(m)}$  is given on the molality scale. Under these conditions the relationship between the stability constants given on different concentration scales and the reaction enthalpies can be described according to the equations:

$$\frac{\delta \ln \beta_j^{(c)}}{\delta T} = \frac{\Delta H_j^\circ}{RT^2} - j \frac{\delta \ln \rho}{\delta T} \quad (7)$$

$$\frac{\delta \ln \beta_j^{(m)}}{\delta T} = \frac{\Delta H_j^\circ}{RT^2} \quad (8)$$

where  $\beta_j^{(c)}$  and  $\beta_j^{(m)}$  are the over-all stability constants expressed on the molar and molal scales, respectively, and  $\rho$  is the density of the solvent. It is thus convenient in the calculations to use either  $\beta_j^{(m)}$  or  $\beta_j^{(c)}$ , provided that the density derivative is zero.

In this investigation we have consistently expressed all stability constants as  $\beta_{j(t)}^{25}$ , *i.e.* quantities proportional to the corresponding constants on the molality scale. These stability constants can thus directly be used in eqn. (7) to compute  $\Delta H_j^\circ$ , which may then be compared with the results from the calorimetric investigations.

To permit calculations of the true stability constants,  $\beta_{j(t)}$ , we have measured the density at different temperature of a 1.05 mol kg<sup>-1</sup> (1.00 M at 25°C) sodium perchlorate solution which may be regarded as the solvent in this particular case. The following densities were obtained:

<i>t</i> /°C	<i>ρ</i> /g cm <sup>-3</sup>
5	1.08281
20	1.07739
25	1.07556
35	1.07074
50	1.05888

The correction is largest for  $\beta_3$  at 5 and 50°C where it amounts to about 5 %.

## RESULTS

*The proton diglycolate system.* The formation constants,  $\delta_j$ , of the proton diglycolate complexes were determined at 5, 20, 35, 50, and 65°C. The measurements were made at  $C_M = 0$  in the same type of galvanic cells as described before. Two different total concentrations of ligand were used ( $C_A = 25$  mM

Table 1. The over-all formation constants  $\delta_{j(t)}^{25}$  for the proton diglycolate system with their estimated errors and the stepwise free energy changes  $\Delta G_j^\circ$  at 5, 20, 35, 50, and 65°C.

<i>t</i> /°C	$\delta_1 \times 10^{-3}/M^{-1}$	$\delta_2 \times 10^{-6}/M^{-2}$	$\frac{-\Delta G_1^\circ}{\text{kcal mol}^{-1}}$	$\frac{-\Delta G_2^\circ}{\text{kcal mol}^{-1}}$
5.00	5.37 ± 0.05	3.61 ± 0.04	4.75 ± 0.01	3.60 ± 0.01
20.00	5.65 ± 0.05	3.76 ± 0.04	5.03 ± 0.01	3.78 ± 0.01
35.00	6.05 ± 0.05	3.90 ± 0.04	5.33 ± 0.01	3.96 ± 0.01
50.00	6.72 ± 0.05	4.35 ± 0.04	5.66 ± 0.01	4.15 ± 0.01
65.00	7.80 ± 0.05	5.47 ± 0.04	6.02 ± 0.01	4.40 ± 0.01

and  $C_A = 50$  mM). The corrections for the liquid junction potential did not exceed 0.4 mV.

The formation constants with their estimated errors are given in Table 1 and the stepwise free energy changes with their corresponding errors (see below) are shown in the same table.

*The rare earth diglycolate systems.* All the measurements have been made with two different T-solutions with the buffer ratios  $C_{H_2A}/C_{Na_2A}$  equal to 0.52 and 1.00, respectively. The corrections for the liquid junction potential were all in the range from 0 to 1.1 mV.

The stability constants with their corresponding errors are given in Table 2. The errors given in the over-all constants are equal to three standard deviations. The deviations in the stepwise stability constants have been calculated by addition of relative errors, *e.g.*

$$\frac{\Delta K_2}{K_2} = \frac{\Delta \beta_2}{\beta_2} + \frac{\Delta \beta_1}{\beta_1} \quad (9)$$

Table 2. The over-all stability constants  $\beta_{i(t)}$ <sup>25</sup> for the praseodymium, samarium, dysprosium and ytterbium diglycolate systems with their corresponding standard deviations at 5, 20, 35, and 50°C.

Stability constants	$\beta_1/M^{-1}$	$\beta_2/M^{-2}$	$\beta_3/M^{-3}$
Metal ion	5°C		
Pr	$(2.66 \pm 0.09)10^5$	$(2.53 \pm 0.09)10^9$	$(9.84 \pm 0.36)10^{11}$
Sm	$(4.17 \pm 0.21)10^5$	$(1.15 \pm 0.06)10^{10}$	$(1.24 \pm 0.06)10^{13}$
Dy	$(2.67 \pm 0.12)10^5$	$(1.44 \pm 0.06)10^{10}$	$(4.70 \pm 0.21)10^{13}$
Yb	$(5.85 \pm 0.27)10^5$	$(3.77 \pm 0.15)10^{10}$	$(4.02 \pm 0.21)10^{13}$
	20°C		
Pr	$(2.25 \pm 0.09)10^5$	$(1.88 \pm 0.09)10^9$	$(6.54 \pm 0.33)10^{11}$
Sm	$(4.19 \pm 0.18)10^5$	$(1.02 \pm 0.03)10^{10}$	$(1.07 \pm 0.06)10^{13}$
Dy	$(2.61 \pm 0.12)10^5$	$(1.23 \pm 0.03)10^{10}$	$(3.25 \pm 0.15)10^{13}$
Yb	$(5.03 \pm 0.30)10^5$	$(3.48 \pm 0.15)10^{10}$	$(2.53 \pm 0.15)10^{13}$
	35°C		
Pr	$(2.41 \pm 0.09)10^5$	$(1.98 \pm 0.09)10^9$	$(6.69 \pm 0.30)10^{11}$
Sm	$(4.03 \pm 0.15)10^5$	$(8.33 \pm 0.39)10^9$	$(7.46 \pm 0.42)10^{12}$
Dy	$(3.13 \pm 0.12)10^5$	$(1.20 \pm 0.03)10^{10}$	$(2.29 \pm 0.12)10^{13}$
Yb	$(6.32 \pm 0.33)10^5$	$(3.70 \pm 0.18)10^{10}$	$(1.53 \pm 0.09)10^{13}$
	50°C		
Pr	$(2.39 \pm 0.12)10^5$	$(1.82 \pm 0.09)10^9$	$(5.12 \pm 0.33)10^{11}$
Sm	$(3.33 \pm 0.18)10^5$	$(6.12 \pm 0.33)10^9$	$(4.27 \pm 0.30)10^{12}$
Dy	$(3.12 \pm 0.18)10^5$	$(1.11 \pm 0.06)10^{10}$	$(1.55 \pm 0.12)10^{13}$
Yb	$(6.78 \pm 0.36)10^5$	$(4.11 \pm 0.21)10^{10}$	$(1.15 \pm 0.09)10^{13}$

Table 3. The stepwise free energy changes  $\Delta G_i^\circ$  of the complex formation of the praseodymium, samarium, dysprosium and ytterbium diglycolate systems at 5, 20, 35, and 50°C.

Metal ion	$-\Delta G_1^\circ$	$-\Delta G_2^\circ$	$-\Delta G_3^\circ$
	kcal mol <sup>-1</sup>	kcal mol <sup>-1</sup>	kcal mol <sup>-1</sup>
5°C			
Pr	6.90 ± 0.02	5.06 ± 0.04	3.29 ± 0.04
Sm	7.15 ± 0.03	5.64 ± 0.06	3.86 ± 0.06
Dy	6.90 ± 0.03	6.02 ± 0.05	4.47 ± 0.05
Yb	7.33 ± 0.02	6.11 ± 0.04	3.85 ± 0.05
20°C			
Pr	7.18 ± 0.02	5.26 ± 0.05	3.41 ± 0.06
Sm	7.54 ± 0.03	5.88 ± 0.04	4.05 ± 0.05
Dy	7.26 ± 0.03	6.27 ± 0.05	4.59 ± 0.05
Yb	7.64 ± 0.03	6.49 ± 0.06	3.84 ± 0.06
35°C			
Pr	7.59 ± 0.02	5.52 ± 0.05	3.57 ± 0.05
Sm	7.90 ± 0.02	6.09 ± 0.05	4.16 ± 0.06
Dy	7.75 ± 0.02	6.46 ± 0.04	4.63 ± 0.05
Yb	8.18 ± 0.03	6.72 ± 0.06	3.69 ± 0.06
50°C			
Pr	7.96 ± 0.03	5.75 ± 0.06	3.63 ± 0.07
Sm	8.17 ± 0.03	6.31 ± 0.07	4.21 ± 0.07
Dy	8.13 ± 0.04	6.74 ± 0.07	4.65 ± 0.08
Yb	8.63 ± 0.03	7.08 ± 0.07	3.63 ± 0.08

The stepwise free energy changes with their corresponding errors are shown in Table 3.

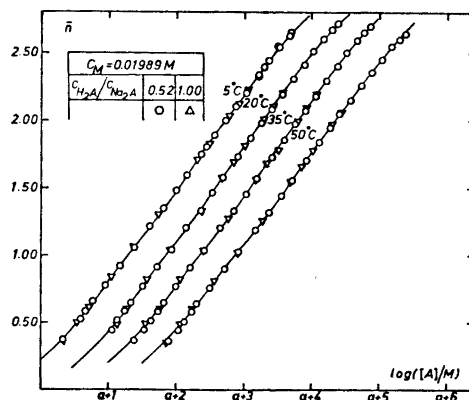


Fig. 1. The plots of  $\bar{n}$  versus  $\log [A]$  for the praseodymium diglycolate system at 5, 20, 35, and 50°C. The values of  $a$  are for the various temperatures beginning at 5°C: -6.00, -6.50, -7.00, and -7.50.

The experimental data for the praseodymium diglycolate system are also given in Fig. 1 as plots of  $\bar{n}$  versus  $\log [A]$  at four temperatures. The fulldrawn curves were computed from the constants in Table 2. The plots show that the stability constants used are in good agreement with the experimental data. This is also true for the other systems investigated.

The results shown in the present and in the following communications<sup>9</sup> are abstracted from the Ph. D. dissertation by Heikki Ots, University of Lund, 1970. The complete experimental data can be obtained either from the University Library of Lund or directly from the authors.

### DISCUSSION

Several investigations have been published, where enthalpy changes and, in some cases, even heat capacity changes have been computed from the temperature dependence of the corresponding free energy changes. The  $\Delta H^\circ$  and  $\Delta C_p^\circ$  data obtained in this way are usually fairly uncertain due to propagation of errors when first and second temperature derivatives are calculated from experimental free energy data, determined at various temperatures. It is generally agreed that direct calorimetric measurements give more accurate values of  $\Delta H^\circ$  and  $\Delta C_p^\circ$ . It is possible to make a direct comparison of the two methods by using the data in this and in the following communication.<sup>9</sup>

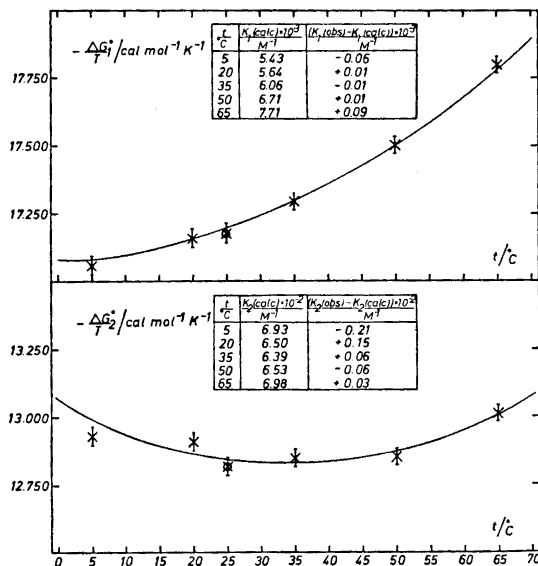


Fig. 2. The stepwise values of  $\Delta G_1^\circ/T$  and  $\Delta G_2^\circ/T$  for the formation of diglycolic acid as functions of temperature. The values ( $\oplus$ ) at 25°C are taken from the work of Grenthe and Hansson.<sup>16</sup> The fulldrawn curves in this figure and in Figs. 3 and 4 are calculated from the calorimetric data using four parameters. The constant  $A$  has been chosen so as to give the best fit to the free energy data.



In Fig. 2, the stepwise functions,  $\Delta G_1^\circ/T$  and  $\Delta G_2^\circ/T$ , for the protonation of diglycolate, have been plotted as functions of temperature. The curvature of the fulldrawn lines have been calculated from  $\Delta H_j^\circ(T)$ -data<sup>9</sup> and then the resulting curve has been moved to give the best fit to the free energy data. The agreement between the two sets of measurements is satisfactory, as seen from the differences between the observed and calculated protonation constants given in the tables of Fig. 2. The differences are also in accordance with the estimated errors in the potentiometric values. It can be concluded that no systematic errors have been introduced in the determinations of  $\Delta G_j^\circ$  as a function of temperature. The calculated constants have been obtained from the free energy functions given in Table 4.

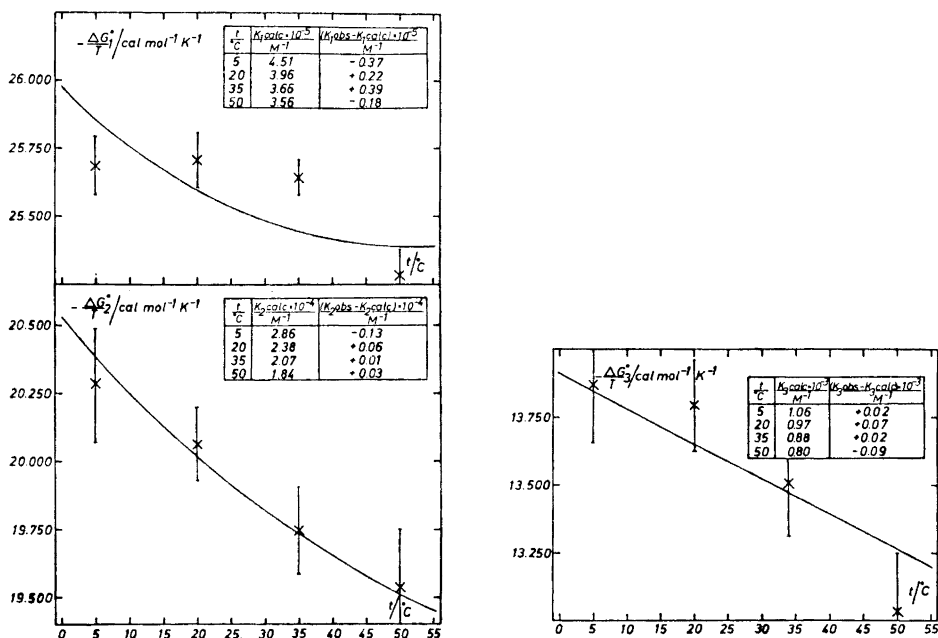
Table 4. The stepwise free energy functions  $\Delta G_j^\circ/T = A + (B/T) + C \ln(T/K) + DT + ET^2$  for the samarium diglycolato complexes and for diglycolic acid. The number of figures in the constants  $A - E$  allows a calculation of  $\Delta G_j^\circ$  which describes the experimental data within 1 cal in the given temperature range.

	Constants →	$A$ kcal mol <sup>-1</sup> K <sup>-1</sup>	$-B$ kcal mol <sup>-1</sup>	$-C$ kcal mol <sup>-1</sup> K <sup>-1</sup>	$D \times 10^3$ kcal mol <sup>-1</sup> K <sup>-2</sup>	$-E \times 10^6$ kcal mol <sup>-1</sup> K <sup>-3</sup>
Sm- diglyc.	$\Delta G_1^\circ/T$	5.952181	119.900	1.142185	3.759520	2.123457
	$\Delta G_2^\circ/T$	7.881845	159.179	1.505553	4.839253	2.617284
	$\Delta G_3^\circ/T$	9.254303	180.570	1.775654	5.821404	3.160494
Diglyc. acid	$\Delta G_1^\circ/T$	11.345559	221.569	2.178046	7.203716	4.024692
	$\Delta G_2^\circ/T$	15.671473	307.695	3.002863	9.867164	5.456790

An error in the protonation constants affects the values of the corresponding enthalpy and heat capacity changes. By using expressions derived by King<sup>14</sup> and Please<sup>15</sup> and the estimated errors of the stepwise constants, it is found that the uncertainties in  $\Delta H_1^\circ$  and  $\Delta H_2^\circ$  at 25°C are  $\pm 120$  cal mol<sup>-1</sup> and  $\pm 250$  cal mol<sup>-1</sup>, respectively. Comparison of these uncertainties with the results obtained by direct calorimetric investigations (*cf.* Table 5 of Ref. 9) shows that it is possible to estimate the magnitude of the enthalpy changes from  $\Delta G_j^\circ(T)$ -data. However, a calculation of the corresponding stepwise heat capacity changes from the above free energy data turns out to be meaningless. In order to obtain accurate data of this kind, the accuracy of the protonation constants has to be improved at least by a factor ten.

The corresponding values of  $\Delta G_1^\circ/T$ ,  $\Delta G_2^\circ/T$  and  $\Delta G_3^\circ/T$  vs.  $T$  for the samarium diglycolate systems are shown in Figs. 3 and 4. The fulldrawn curves have been obtained from enthalpy data as described before. The equations for the curves are given in Table 4.

It is obvious from these graphs that the differences between the observed and calculated stability constants are much larger for the samarium diglycolate



Figs. 3 and 4. The stepwise free energy changes  $\Delta G_1^\circ/T$ ,  $\Delta G_2^\circ/T$ , and  $\Delta G_3^\circ/T$  for the samarium diglycolate system as functions of temperature.

than for the proton diglycolate system. The  $\Delta G_2^\circ/T$  and  $\Delta G_3^\circ/T$  plots in Figs. 3 and 4 show, however, that these differences are in most instances within the error limits given.

An exception is the  $\Delta G_1^\circ/T$  plot, where the error limits given are too low. More realistic errors are obtained if the deviations in  $\beta_1$  (Table 2) are multiplied by a factor between one and two.

We do not think that this is a result of a systematic error in the titration procedure; *cf.* the protonation constant data. It is more probable, in our opinion, that the standard deviations in the least-squares refinement of the stability constants do not always represent realistic error estimates. It is well known, that the standard deviations are strongly dependent on the weighting scheme used. Our choice of giving a unit weight to all experimental quantities might thus not be the best one.

This weighting scheme must especially be questioned for low values of  $\bar{n}$ . Because of the very unfavourable ratios between  $\beta_1$  and the protonation constants  $\delta_1$  and  $\delta_2/\delta_1$ , it is not possible to determine  $[A]$  accurately in this  $\bar{n}$ -region. This has in our case partly been circumvented by choice of the lower integration limit in a region where accurate  $\bar{n}$ - $[A]$  values can be determined. The choice is, however, subjective and a different weighting scheme for the lower  $\bar{n}$ -values would perhaps have given more realistic errors in  $\beta_1$ .

The three other rare earth diglycolate systems investigated show the same behaviour as the samarium system.

The larger errors in the stability constants for the samarium system, in comparison with the proton diglycolate system, results in larger uncertainties in the calculated enthalpy changes. Using the same expressions as before, we get for samarium the following standard errors in the stepwise enthalpy changes: for  $\Delta H_1^\circ \pm 970$  cal mol<sup>-1</sup>, for  $\Delta H_2^\circ \pm 360$  cal mol<sup>-1</sup>, and for  $\Delta H_3^\circ \pm 600$  cal mol<sup>-1</sup>. These errors are of the same order of magnitude as the total enthalpy changes (cf. Table 5 in Ref. 9). The errors in the stability constants are approximately the same for all rare earth systems investigated here, and the same is then also true for the absolute errors in the  $\Delta H_i^\circ$ -values.

The percental errors depend, on the other hand, on the magnitudes of  $\Delta H$ ; e.g., for the ytterbium system the enthalpy changes for the third reaction step at 20°C are around  $-4.5 \pm 0.8$  kcal mol<sup>-1</sup> ( $\pm 18$  %), while the corresponding change for samarium is  $-1.1 \pm 0.6$  kcal mol<sup>-1</sup> ( $\pm 55$  %).

It can thus be concluded that, despite of relatively larger errors in the stability constants for the rare earth diglycolates, compared with the proton diglycolate system, fair estimations of the enthalpy changes can be made from the free energy data and that these estimations become more favourable, the larger the enthalpy changes are. However, it is quite clear that the method cannot be used to determine accurate enthalpy changes and far less to determine heat capacity changes.

The stability constants at 20°C obtained in this study are slightly different from those obtained earlier.<sup>1</sup> The reason for this is to be found in an erroneous correction for the liquid junction potential in the earlier work. This error is only made in the determinations of the  $\delta_j$ -values. A recalculation of the data from the praseodymium diglycolate system in the previous investigation using the correct  $\delta_j$ -values gives an  $\bar{n}$ -curve, which almost coincides with the one obtained in the present investigation.

A discussion of the observed dependence of the various thermodynamic functions on temperature will be given in the following communication.<sup>9</sup>

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#### REFERENCES

1. Grenthe, I. and Tobiasson, I. *Acta Chem. Scand.* **17** (1963) 2101.
2. Grenthe, I. *Acta Chem. Scand.* **18** (1964) 293.
3. Moeller, T., Birnbaum, E. R., Forsby, J. H. and Gayhart, R. B. In Eyring, L., Ed., *Progress in the Science and Technology of the Rare Earths*, Pergamon, Glasgow 1968, Vol. 3, Chap. 3.
4. Spedding, F. H. and Atkinson, G. In Hamer, J. W., Ed., *The Structure of Electrolytic Solutions*, Wiley, New York 1959, Chap. 22.
5. Hoard, J. L., Byunkook, L. and Lind, M. D. *J. Am. Chem. Soc.* **87** (1965) 1612.
6. Geier, G., Karlén, U. and v. Zelewsky, A. *Helv. Chim. Acta* **52** (1969) 1967.
7. Geier, G. and Karlén, U. *Helv. Chim. Acta* **54** (1971) 135.
8. Anderegg, G. and Wenk, F. *Helv. Chim. Acta* **54** (1971) 216.
9. Grenthe, I. and Ots, H. *Acta Chem. Scand.* **26** (1972) 1229.
10. Grenthe, I. and Ots, H. *Acta Chem. Scand.* **24** (1970) 1067.

11. Ingri, N. and Sillén, L. G. *Arkiv Kemi* **23** (1965) 97.
12. Grenthe, I. and Williams, D. R. *Acta Chem. Scand.* **21** (1967) 341.
13. Åhrland, S. *Acta Chem. Scand.* **3** (1949) 783.
14. King, E. J. *Acid-Base Equilibria*, The International Encyclopedia of Physical Chemistry and Chemical Physics, Pergamon, Oxford 1965, p. 194.
15. Please, N. W. *Biochem. J.* **56** (1964) 196.
16. Grenthe, I. and Hansson, E. *Acta Chem. Scand.* **23** (1969) 611.

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