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Thermodynamic Properties of Rare Earth Complexes

II. Free Energy, Enthalpy and Entropy Changes for the Formation of Rare Earth Diglycolate and Dipicolinate Complexes at 25.00°C

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The changes in free energy, enthalpy and entropy for the formation of rare earth diglycolate and dipicolinate complexes have been determined. All data for the diglycolate systems refer to a medium of the ionic strength $I = 1.00$ M and a temperature of 25.00°C. The data for the dipicolinate system refer to a medium of the ionic strength $I = 0.50$ M and a temperature of 25.00°C. The changes in free energy were computed from previously determined stability constants. The corresponding enthalpy changes were obtained from a direct calorimetric determination using the calorimeter and the titration procedure developed by Gerding *et al.* The various entropy changes were computed by the use of the relation:

$$\Delta G_j^\circ = \Delta H_j^\circ - T \cdot \Delta S_j^\circ$$

Very few investigations of the thermodynamic properties (enthalpy and entropy data) of rare earth complexes have been published so far.[1-8] In most of these studies the change in enthalpy has been determined from the variation of the various stability constants with the temperature.[1,2,4-6] In this method the changes in enthalpy and entropy are impaired by large experimental errors. The best method of obtaining accurate thermodynamic functions is a potentiometric determination of the various stability constants followed by a direct calorimetric determination of the corresponding enthalpy change. This method has been used in this series of investigations.

In part I of this series the stability constants for the rare earth diglycolate complexes were reported.[9] The stability constants for the dipicolinate complexes have also been published earlier.[10] The change in free energy for the various complex formation reactions has been computed from these constants. The calorimetric determination of the various heats of reaction were made by using a titration procedure previously described by Gerding *et al.*[11] The reaction calorimeter was the same as that described by these authors. The enthalpy titrations were performed at a temperature of 25.00°C. The ionic strength of the diglycolate solutions was equal to 1.00 M and for the dipicolinate solutions equal to 0.50 M.

In order to obtain the various enthalpy changes from the titration data three different methods were tried, one graphical, one numerical (solution of equation systems) and one least-square method using a high speed digital computer. The graphical and numerical methods were both time-consuming (approx. 5 h for each system). The least-square method had the advantage of giving a better statistical interpretation of the experimental data, and by the use of a high speed computer the computing time was less than 1 min for each system. The final values of the enthalpy changes for the various complex formation reactions were computed (using the IBM 7090 computer) using the least-square program "Letagrop Kalle" developed by Sillén *et al.*[12] This is a program in the "Letagrop" series, specially designed for calorimetric titration data.

CALCULATION OF THE ENTHALPY CHANGE FROM CALORIMETRIC DATA

The notation is the same as in Part I of this series.[9] The following new quantities have to be introduced:

R = the resistance in ohms of the thermistor
ΔR = the change in resistance after addition of titrant
Q = the corresponding heat change in calories
Q_{corr} = the above heat change corrected for heats of dilution
v = the volume in ml of titrant added to the calorimeter
V = $100.0 + v$ = the total volume in ml of the solution in the calorimeter vessel
ε_V = the heat equivalent in calories · ohm^{-1} of the calorimeter system when the total volume is V ml
Δh_v = $\frac{1000}{C_M \cdot V} \cdot \sum_v Q_{\text{corr}}$; the total molar heat change in calories in a titration where v ml of titrant have been added
ΔG_j° = the j:th stepwise free energy change in the standard state
ΔH_j° = the j:th stepwise enthalpy change in the standard state
ΔS_j° = the j:th stepwise entropy change in the standard state
$\Delta \mathcal{G}_j^\circ$ = the j:th overall free energy change in the standard state
$\Delta \mathcal{H}_j^\circ$ = the j:th overall enthalpy change in the standard state
$\Delta \mathcal{S}_j^\circ$ = the j:th overall entropy change in the standard state
α_j = $[\mathrm{MA}_j]/C_M$; degree of formation for the j:th complex

$$\Delta h_v = \sum_{1}^{N} \Delta \mathcal{H}_j^\circ \cdot \alpha_j \tag{1}$$

$$\gamma_1 = \frac{\Delta h_v \cdot \mathrm{X}([\mathrm{A}])}{[\mathrm{A}]} \tag{2}$$

$$\gamma_n = \frac{\gamma_{n-1} - (\gamma_{n-1})_{[\mathrm{A}]=0}}{[\mathrm{A}]} = \sum_{j=n}^{N} \Delta \mathcal{H}_j^\circ \cdot \beta_j [\mathrm{A}]^{j-n} \tag{3}$$

Usually eighteen to twenty corresponding values of Q and v were determined for each of the investigated systems. From the known composition of the liquid phase in each of these determinations a number of equations of type (1) were obtained. This equation system was solved for the unknown values of $\Delta \mathcal{H}_j^\circ$. The method should only be used for values of $N \leq 3$ and in cases where the various complexes are well separated from one another. The graphical method for the determination of $\Delta \mathcal{H}_j^\circ$-values is very similar to the graphical method of obtaining β_j-values.[13] From the known composition of the solution the functions γ_n are computed and plotted *versus* [A] to give the various $\Delta \mathcal{H}_j^\circ$-values.

In the least-square method the error square sum U, where:

$$U = \sum_i w_i(Q_{i\ \mathrm{corr}} - Q_{i\ \mathrm{corr\ calc}})^2$$

was minimized. The weight of each value of $Q_{i\ \mathrm{corr}}$ was equal to unity. The input data were the corresponding values of Q_{corr} and v, the stability constants β_j and values of C_{M} and C_{A}. Values of $\Delta \mathcal{H}_j^\circ$ must also be given but, as the system is linear, any guess will do. The program is designed to give values of $\Delta \mathcal{H}_j^\circ$ with their corresponding standard deviations. The standard deviation in Q_{corr} is also given. Details of this special program will be published later.[12] The "Letagrop" approach for the interpretation of experimental data is outlined in Ref.[14]

All stability constants were determined at 20.0°C, while the calorimetric part of the measurements was made at 25.00°C. In order to get the composition of the solution at 25°C, an iterative procedure had to be performed. All $\Delta \mathcal{H}_j^\circ$-values were first computed using the 20°C stability constants. By using these approximate $\Delta \mathcal{H}_j^\circ$-values the stability constants at 25°C were computed. New enthalpy values were obtained using these constants and so on. Only one iteration had to be made as the difference between the $\Delta \mathcal{H}_j^\circ$-values, obtained from the 20°C, and the 25°C stability constants was in all cases less than one standard deviation.

EXPERIMENTAL

Chemicals used. Stock solutions of the various rare earth perchlorates were prepared and standardized as described before.[9] All rare earths (Lindsay Chemical Co) had a purity > 99.9 %. Stock solutions of the disodium salts of diglycolic (Fluka, purum) and dipicolinic acid (Fluka, purum) were prepared by neutralizing the acids with sodium hydroxide. Sodium perchlorate was prepared as described earlier.[9]

The calorimeter. The constant temperature environment reaction calorimeter described by Gerding *et al.*[11] was used. The calorimeter is equipped with a device for the successive addition of known, varying amounts of a titrant. After each addition the calorimeter can be brought back to the standard reference temperature by the use of built-in cooling or heating devices. The temperature is measured by the use of a thermistor. The temperature sensitivity is $\pm 1 \times 10^{-4}$ degrees corresponding to an accuracy of $\pm$ 0.02 cal. The system is electrically calibrated. The time for equilibrium of the system is less than 3 min. For further details see Ref.[11]

Procedure. The experimental procedure has been described in detail by Gerding *et al.* The calorimeter was filled with 100.0 ml of a solution S and was assembled. A known amount of a solution T was introduced from a syringe into the pipette (in the lower position). The system was equilibrated during an initial period. After equilibrium had been attained, the pipette, now in the upper position, was emptied (the reaction period). The system was then equilibrated during a final period. During the initial and final periods corresponding values of temperature and time were obtained by measuring the time for a 0.2 Ω change in resistance of the thermistor. A plot of resistance *versus* time showed a linear dependence and for small temperature differences the slopes were approximately the same for the initial and final periods. It was not possible to obtain any temperature readings during the reaction period. The change in resistance (*i.e.* the change in temperature) ΔR for the various reactions was obtained in the following way: The resistance versus time lines for the initial and final periods were extrapolated and ΔR taken as the difference in the values of R at a time t_m, where $t_m = t + 15$ sec. t is the time when the pipette is half-emptied. For further details the reader is referred to Gerding *et al.*[11]

The temperature changes were so small that no significant error was introduced by putting the temperature inversely proportional to the resistance of the thermistor. In order to obtain the heat equivalent of the various systems a series of electrical calibrations, usually 3 for each system, were performed. The calibrations were made by using different values of V. The average values established a linear relation between the heat equivalent of the systems and the total amount of T-solution added.

The composition of the liquid phase could be calculated after each addition from the known values of the stability constants, the concentrations and the amounts of the solutions S and T. The enthalpy change could thus be referred to defined initial and final states. The solutions S and T had for the diglycolate systems the following composition:

$$\text{S}\begin{cases} C_\text{M} & (\sim 20\ \text{mM}) \\ C_{\text{HClO}_4} & (\sim 0.2\ \text{mM}) \\ I = 1.00\ (\text{M}) \end{cases} \qquad \text{T}\begin{cases} C_{\text{Na}_2\text{A}} & (323.1\ \text{mM}) \\ I = 1.00\ (\text{M}) \end{cases}$$

and for the dipicolinate systems the composition:

$$\text{S}\begin{cases} C_\text{M} & (\sim 10\ \text{mM}) \\ C_{\text{HClO}_4} & (\sim 0.1\ \text{mM}) \\ I = 0.50\ (\text{M}) \end{cases} \qquad \text{T}\begin{cases} C_{\text{Na}_2\text{A}} & (169.4\ \text{mM}) \\ I = 0.50\ (\text{M}) \end{cases}$$

The heats of dilution of the ligands were also determined and the results are given in Table 1. The heats of dilution of $Nd(ClO_4)_3$ and $Yb(ClO_4)_3$ were supposed to be representative for the heats of dilution of all other rare earths. The molar heat of dilution from $C_M = 20$ mM to $C_M = 0.4$ mM was zero for both these metal ions. It was assumed that the heat of dilution of the various complexes was zero. This assumption was supported by the fact the $\Delta\mathcal{H}_j°$-values did not vary with C_M.

Reduction of measured thermodynamic properties to corresponding standard states. After each addition of titrant T to the solution S, the following reactions will occur:

$$\text{M (aq, } m_\text{M}) + j\text{A (aq, m}_\text{A}) \rightarrow \text{MA}_j\ (\text{aq, m}_j);\ j = 1-N \tag{4}$$

where m_M, m_A and m_j denote the molar concentrations of the species M, A and MA_j. The thermodynamic standard state is the solution of the ionic strength I M infinite

Table 1. Molar heats of dilution of Na_2diglyc. and Na_2dipic. The initial concentrations are 323.1 mM and 169.4 mM, respectively, and the final concentrations after dilution C_A (mM).

Na_2diglyc $I = 1.00$ (M)		Na_2dipic $I = 0.50$ (M)	
C_A (mM)	$Q_{Dil.}$ (cal)	C_A (mM)	$Q_{Dil.}$ (cal)
3.20	330	3.32	375
9.41	354	6.51	320
15.4	347	9.59	297
21.1	350	12.5	323
32.0	310	15.4	285
51.6	310		

dilute in regard to the species M, A and MA_j. The activity coefficients of the species are by definition equal to unity. The reduction to the standard state is performed by the use of the measured heats of dilution of the species M, A and MA_j. By the use of eqns. (5)–(7):

$$\Delta G^\circ = \Delta G_0{}^\circ + RT\ \Sigma\ \nu_i \ln\gamma_i \tag{5}$$

$$\Delta H^\circ = \Delta H_0{}^\circ - RT^2\ \Sigma\ \nu_i \partial(\ln\gamma_i)/\partial T \tag{6}$$

$$\Delta S^\circ = \Delta S_0{}^\circ - R[T\ \Sigma\ \nu_i \partial(\ln\gamma_i)/\partial T - \Sigma\ \nu_i \ln\gamma_i] \tag{7}$$

the above standard state is related to the usual thermodynamic standard state in pure solvent. ν_i is the number of moles of the species i with the activity coefficient γ_i. The activity coefficients in eqns. (5)–(7) are referred to the pure solvent standard state. The changes in the thermodynamic functions in this state is denoted by zero as subscript and superscript ($\Delta G_0{}^0$ etc).

By the use of a medium with a high concentration of neutral salt the activity coefficients of solute and solvent will be constant for small variations in the composition of the solution. Spedding *et al*[15] have shown that for a given ionic strength the activity coefficients of the different lanthanides differ by less than 5 %. It is reasonable to assume that the variations of the activity coefficients of the various complexes through the lanthanide series are of the same order of magnitude. The activity dependent terms in eqns. (5)–(7) are thus approximately constant for each of the reactions (4) through the lanthanide series and the variations of the values of $\Delta G_j{}^\circ$, $\Delta H_j{}^\circ$, and $\Delta S_j{}^\circ$ through the series are the same as the variations in the activity independent values of $\Delta G_{j0}{}^0$, $\Delta H_{j0}{}^0$ and $\Delta S_{j0}{}^0$. However, the variations of the values of $\Delta G_j{}^\circ$, $\Delta H_j{}^\circ$ and $\Delta S_j{}^\circ$ for the stepwise reactions (j = 1, 2, 3) are not the same as the corresponding variations in $\Delta G_{j0}{}^0$, $\Delta H_{j0}{}^0$ and $\Delta S_{j0}{}^0$ because of the unknown activity coefficients.

Table 2. Corresponding values of Q_{corr} and v for the rare earth diglycolate systems. The Q_{corr}-values are averages of two titrations. C_M is the initial rare earth concentration in the solution S.

v (ml) →		2.01	4.02	6.03	8.04	10.05	12.05	14.06	16.07	18.08	20.09
Metal ion	C_M (mM)	$-Q_{corr}$ (cal)									
La	20.44	0.04	0.08	0.18	0.35	0.40	0.30	0.10	−0.02	−0.03	−0.02
Ce	20.20	0.28	0.30	0.36	0.41	0.50	0.47	0.33	0.23	0.18	0.14
Pr	19.97	0.23	0.44	0.46	0.56	0.62	0.63	0.53	0.37	0.33	0.23
Nd	19.90	0.54	0.58	0.61	0.73	0.74	0.71	0.58	0.48	0.37	0.24
Sm	19.88	0.70	0.75	0.82	1.00	1.10	1.07	0.91	0.79	0.61	0.36
Eu	19.93	0.54	0.65	0.83	1.05	1.21	1.23	1.19	0.95	0.73	0.42
Gd	20.13	0.29	0.45	0.69	0.99	1.24	1.33	1.24	1.11	0.93	0.49
Tb	20.65	−0.33	−0.03	0.35	0.76	1.16	1.44	1.54	1.55	1.37	0.81
Dy	20.00	−0.68	−0.31	0.12	0.59	1.05	1.47	1.76	1.89	1.65	0.80
Ho	20.24	−0.86	−0.52	−0.15	0.30	0.78	1.32	1.88	2.23	2.06	1.07
Er	19.76	−0.92	−0.70	−0.37	0.00	0.48	1.14	2.01	2.50	2.23	1.10
Tm	20.96	−0.95	−0.79	−0.54	−0.28	0.06	0.54	1.56	2.46	2.45	1.72
Yb	20.08	−0.84	−0.70	−0.49	−0.23	0.04	0.55	1.93	2.38	1.92	1.20
Lu	21.28	−0.73	−0.56	−0.44	−0.21	0.01	0.27	1.27	2.19	1.90	1.40
Y	20.48	−1.02	−0.74	−0.38	0.05	0.51	1.07	1.68	2.09	2.04	1.25

Table 3. The overall values of $\Delta\mathcal{H}_j^\circ$, $\Delta\mathcal{G}_j^\circ$ and $\Delta\mathcal{S}_j^\circ$ for the various rare earth diglycolate systems at the ionic strength $I = 1.00$ M. The $\Delta\mathcal{H}_j^\circ$-values are tabulated with their corresponding standard deviations. The standard deviation in the measured Q_{corr} values are also given.

Metal ion	$-\Delta\mathcal{H}_1^\circ \pm \sigma\Delta\mathcal{H}_1^\circ$ (kcal.mole^{-1})	$-\Delta\mathcal{G}_1^\circ$ (kcal.mole^{-1})	$\Delta\mathcal{S}_1^\circ$ (e.u.)	$-\Delta\mathcal{H}_2^\circ \pm \sigma\Delta\mathcal{H}_2^\circ$ (kcal.mole^{-1})	$-\Delta\mathcal{G}_2^\circ$ (kcal.mole^{-1})	$\Delta\mathcal{S}_2^\circ$ (e.u.)	$-\Delta\mathcal{H}_3^\circ \pm \sigma\Delta\mathcal{H}_3^\circ$ (kcal.mole^{-1})	$-\Delta\mathcal{G}_3^\circ$ (kcal.mole^{-1})	$\Delta\mathcal{S}_3^\circ$ (e.u.)	σQ corr (cal)
La	0.070±0.016	6.73	22.3	0.828±0.021	11.46	35.6	0.474±0.040	13.97	45.2	0.022
Ce	0.401±0.017	7.03	22.2	1.270±0.023	12.15	36.5	1.764±0.032	15.29	45.4	0.016
Pr	0.680±0.016	7.27	22.1	1.712±0.021	12.57	36.4	2.500±0.030	15.82	44.7	0.024
Nd	0.848±0.014	7.42	22.1	2.103±0.019	12.93	36.4	3.000±0.024	16.55	45.4	0.020
Sm	1.048±0.018	7.55	21.8	2.878±0.023	13.45	35.5	4.291±0.028	17.39	43.9	0.023
Eu	0.781±0.017	7.53	22.6	2.943±0.021	13.65	35.9	4.507±0.024	17.94	45.0	0.021
Gd	0.360±0.019	7.37	23.5	2.672±0.022	13.50	36.3	4.590±0.027	17.71	44.0	0.023
Tb	−0.765±0.021	7.28	27.0	1.887±0.023	13.58	39.2	4.464±0.026	18.01	45.4	0.023
Dy	−1.323±0.022	7.27	28.8	1.081±0.019	13.60	42.0	4.413±0.022	18.16	46.1	0.024
Ho	−1.591±0.023	7.23	29.6	0.261±0.025	13.56	44.6	4.384±0.029	18.09	46.0	0.025
Er	−1.660±0.072	7.32	30.1	−0.699±0.078	13.69	48.2	4.202±0.093	17.98	46.2	0.080
Tm	−1.574±0.056	7.52	30.5	−1.165±0.061	13.97	50.8	3.819±0.076	18.07	47.8	0.066
Yb	−1.423±0.026	7.60	30.2	−1.046±0.028	14.16	51.0	3.857±0.036	17.91	47.1	0.030
Lu	−1.230±0.021	7.71	30.0	−0.781±0.022	14.41	50.9	3.819±0.030	17.89	47.2	0.025
Y	−1.732±0.031	7.18	30.0	−0.489±0.035	13.33	46.4	3.709±0.040	17.73	47.2	0.035

RESULTS

The M^{3+}-diglycolate systems. The heat of dilution of the ligand is given in Table 1. The heat equivalent was determined for all the investigated systems. The calibrations were made by using three different values of v. The heat equivalent was the same for all rare earths and the values for $v = 0$, 10.05, and 20.09 ml were:

$$\varepsilon_{100} = 2.12 \text{ cal·ohm}^{-1}$$
$$\varepsilon_{110} = 2.33 \text{ cal·ohm}^{-1}$$
$$\varepsilon_{120} = 2.55 \text{ cal·ohm}^{-1}$$

Values of Q_{corr} and v for the systems are given in Table 2. The tabulated values are the averages of two titrations. The computer calculated $\Delta \mathcal{H}_j^\circ$-values with their corresponding standard deviations are given in Table 3. The values of $\Delta \mathcal{G}_j^\circ$, $\Delta \mathcal{S}_j^\circ$ and the standard deviation $\sigma_{Q \text{ corr}}$ are also tabulated in Table 3.

The M^{3+}-dipicolinate systems. The measured heats of dilution of the ligand are tabulated in Table 1. The experimental values of Q_{corr} and v are given in Table 4. Only half the experimental material has been included. The various thermodynamic functions for the rare earth dipicolinate complexes are given in Table 5. The heat equivalent was also in this case the same for all the rare earth systems and the following values were obtained:

$$\varepsilon_{100} = 2.14 \text{ cal·ohm}^{-1}$$
$$\varepsilon_{110} = 2.35 \text{ cal·ohm}^{-1}$$
$$\varepsilon_{120} = 2.57 \text{ cal·ohm}^{-1}$$

Table 4. Corresponding values of Q_{corr} and v for the rare earth dipicolinate systems. Only half the experimental material is given in this table. C_{M} is the initial rare earth concentration in the solution S.

v (ml) →		2.01	4.02	6.03	8.04	10.05	12.05	14.06	16.07	18.08
Metal ion	C_{M} (mM)	$-Q_{\text{corr}}$ (cal)								
La	10.22	1.08	1.05	1.07	1.11	1.07	1.01	0.86	0.76	0.63
Ce	10.10	1.21	1.22	1.23	1.24	1.21	1.19	1.10	1.07	0.90
Pr	10.05	1.39	1.35	1.32	1.32	1.32	1.32	1.23	1.18	1.09
Nd	9.95	1.40	1.38	1.39	1.39	1.39	1.37	1.30	1.27	1.07
Sm	9.94	1.46	1.46	1.51	1.58	1.59	1.56	1.50	1.32	1.15
Eu	9.97	1.41	1.42	1.51	1.65	1.67	1.67	1.61	1.57	1.31
Gd	10.07	1.22	1.27	1.41	1.61	1.71	1.76	1.68	1.69	1.55
Tb	10.33	0.94	1.02	1.21	1.50	1.74	1.81	1.92	1.95	1.95
Dy	10.00	0.75	0.83	1.09	1.39	1.63	1.86	2.10	2.22	1.89
Ho	10.12	0.68	0.75	0.93	1.22	1.44	1.78	2.22	2.42	2.22
Er	9.88	0.65	0.74	0.91	1.10	1.30	1.73	2.39	2.58	2.06
Tm	10.48	0.64	0.72	0.85	1.02	1.17	1.39	2.15	2.53	2.53
Yb	10.04	0.70	0.75	0.93	1.08	1.25	1.51	2.35	2.42	2.02
Lu	10.64	0.74	0.81	0.92	1.06	1.22	1.33	1.96	2.24	2.20
Y	10.24	0.50	0.60	0.77	1.01	1.26	1.58	2.08	2.30	2.31

Table 5. The overall values of $\Delta\mathcal{H}_j^\circ$, $\Delta\mathcal{G}_j^\circ$, and $\Delta\mathcal{S}_j^\circ$ for the various rare earth dipicolinate systems at the ionic strength $I=0.50$ M. The $\Delta\mathcal{H}_j^\circ$-values are tabulated with their corresponding standard deviations. The standard deviation $\sigma_{Q\,\mathrm{corr}}$ in the measured Q_{corr} values are also given.

Metal ion	$-\Delta\mathcal{H}_1^\circ\pm\sigma\Delta\mathcal{H}_1^\circ$ (kcal.mole^{-1})	$-\Delta\mathcal{G}_1^\circ$ (kcal.mole^{-1})	$\Delta\mathcal{S}_1^\circ$ (e.u.)	$-\Delta\mathcal{H}_2^\circ\pm\sigma\Delta\mathcal{H}_2^\circ$ (kcal.mole^{-1})	$-\Delta\mathcal{G}_2^\circ$ (kcal.mole^{-1})	$\Delta\mathcal{S}_2^\circ$ (e.u.)	$-\Delta\mathcal{H}_3^\circ\pm\sigma\Delta\mathcal{H}_3^\circ$ (kcal.mole^{-1})	$-\Delta\mathcal{G}_3^\circ$ (kcal.mole^{-1})	$\Delta\mathcal{S}_3^\circ$ (e.u.)	σ_Q corr (cal)
La	3.125±0.020	10.83	25.8	6.401±0.028	18.71	41.3	8.631±0.033	24.50	53.2	0.015
Ce	3.547±0.027	11.32	26.1	7.140±0.037	19.55	41.6	10.296±0.043	25.48	50.9	0.020
Pr	3.913±0.026	11.70	26.1	7.869±0.037	20.46	42.3	11.370±0.043	27.00	52.4	0.020
Nd	4.012±0.043	11.91	26.5	8.109±0.059	21.00	43.2	11.883±0.068	27.84	53.5	0.032
Sm	4.283±0.053	12.01	25.9	8.971±0.070	21.51	42.1	13.265±0.081	28.76	52.0	0.038
Eu	4.073±0.035	11.99	26.6	9.123±0.046	21.64	42.0	13.732±0.053	29.08	51.5	0.025
Gd	3.582±0.036	11.87	27.8	8.731±0.046	21.77	43.7	13.619±0.053	29.56	53.5	0.025
Tb	2.689±0.017	11.80	30.5	8.007±0.017	21.85	46.4	13.811±0.019	29.83	53.7	0.016
Dy	2.169±0.031	11.83	32.4	7.158±0.037	21.97	49.7	13.820±0.043	29.98	54.2	0.020
Ho	1.946±0.033	11.85	33.2	6.166±0.033	21.81	52.4	13.557±0.038	29.89	54.8	0.026
Er	1.850±0.035	11.94	33.8	5.752±0.032	22.27	55.4	13.406±0.037	29.97	55.5	0.025
Tm	1.834±0.043	12.03	34.2	5.471±0.050	22.48	57.0	12.870±0.061	29.86	57.0	0.028
Yb	1.925±0.025	12.05	34.0	5.785±0.029	22.57	56.3	12.907±0.035	29.44	55.4	0.016
Lu	2.191±0.033	12.29	33.9	5.995±0.039	22.83	56.4	12.658±0.049	29.11	55.2	0.023
Y	1.438±0.028	11.52	33.8	5.311±0.034	21.37	53.9	12.236±0.040	28.90	55.9	0.019

Table 6. Values of Q_{corr}, $Q_{\text{corr calc}}$ and $(Q_{\text{corr}}-Q_{\text{corr calc}})$ for the Gd^{3+}-diglycolate and dipicolinate systems.

Gd^{3+}-diglyc			Gd^{3+}-dipic		
Q_{corr} (cal)	$Q_{\text{corr calc}}$ (cal)	$Q_{\text{corr}}-Q_{\text{corr calc}}$ (cal)	Q_{corr} (cal)	$Q_{\text{corr calc}}$ (cal)	$Q_{\text{corr}}-Q_{\text{corr calc}}$ (cal)
0.28	0.294	0.014	0.61	0.612	−0.002
0.47	0.461	−0.009	1.25	1.242	0.008
0.70	0.702	0.002	1.31	1.314	−0.004
1.00	0.980	−0.020	1.48	1.481	−0.001
1.22	1.212	−0.008	1.66	1.679	−0.019
1.32	1.323	0.003	1.73	1.717	0.013
1.24	1.274	0.034	1.71	1.701	0.009
1.12	1.138	0.018	1.67	1.674	−0.004
0.93	0.893	−0.037	1.65	1.660	−0.010
0.50	0.479	−0.021			

Accuracy of the results. Values of $Q_{\text{corr, calc}}$ and the difference $(Q_{\text{corr}}-Q_{\text{corr, calc}})$ for the diglycolate and dipicolinate systems are given in Table 6. From the error-distribution it is obvious that no systematic calculation errors are present. The accuracy of the calorimetric part of the investigation will be dependent on the accuracy of the stability constants. In Table 7 values of $\Delta \mathscr{H}_j^\circ$ for a few rare earth diglycolate and dipicolinate systems have been calculated by using different values of β_j. From this table it is obvious that the values of $\Delta \mathscr{H}_j^\circ$ do not vary very much with the value of β_j. The magnitude of the difference $(Q_{\text{corr}}-Q_{\text{corr, calc}})$ is of the magnitude expected from the accuracy of the calorimeter. From the known standard deviations in the free energy and enthalpy terms the standard deviation in the corresponding entropy term has

Table 7. $\Delta \mathscr{H}_j^\circ$-values for various rare earth-diglycolate and dipicolinate systems using different sets of β_j-values.

The diglycolate systems				The dipicolinate systems			
Metal ion	β_j	$-\Delta \mathscr{H}_j^\circ \pm \sigma \Delta \mathscr{H}_j^\circ$ (kcal.mole^{-1})	$\sigma\ Q_{\text{corr}}$ (cal)	Metal ion	β_j	$-\Delta \mathscr{H}_j^\circ \pm \sigma \Delta \mathscr{H}_j^\circ$ (kcal.mole^{-1})	$\sigma\ Q_{\text{corr}}$ (cal)
Ce	1.34×10^{5}	0.435 ± 0.013	0.020	Ce	2.06×10^{8}	3.547 ± 0.027	0.020
	1.12×10^{9}	1.332 ± 0.019			2.00×10^{14}	7.142 ± 0.037	
	2.50×10^{11}	1.770 ± 0.025			4.80×10^{18}	10.284 ± 0.049	
Tm	3.35×10^{5}	-1.551 ± 0.048	0.057	Gd	4.90×10^{8}	3.579 ± 0.036	0.025
	1.69×10^{10}	-1.191 ± 0.053			9.20×10^{15}	8.735 ± 0.046	
	1.83×10^{13}	3.786 ± 0.065			4.40×10^{21}	13.623 ± 0.053	
	3.25×10^{5}	-1.583 ± 0.062	0.073	Yb	6.77×10^{8}	1.938 ± 0.023	0.015
	1.77×10^{10}	-1.148 ± 0.068			3.30×10^{16}	5.785 ± 0.027	
	1.65×10^{13}	3.855 ± 0.085			3.96×10^{21}	12.909 ± 0.032	

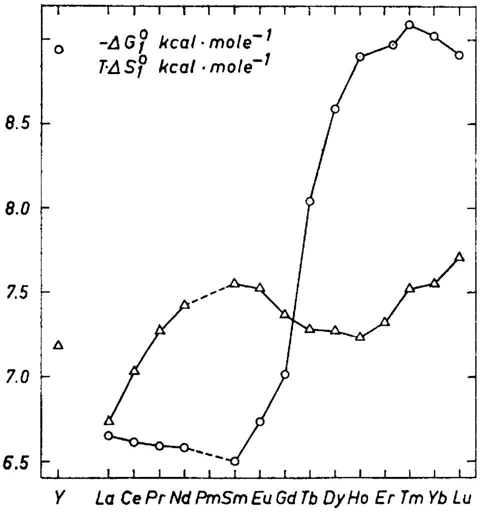

Fig. 1. $-\Delta G_1^\circ$ (△) and $T{\cdot}\Delta S_1^\circ$ (O) for the various rare earth diglycolate systems.

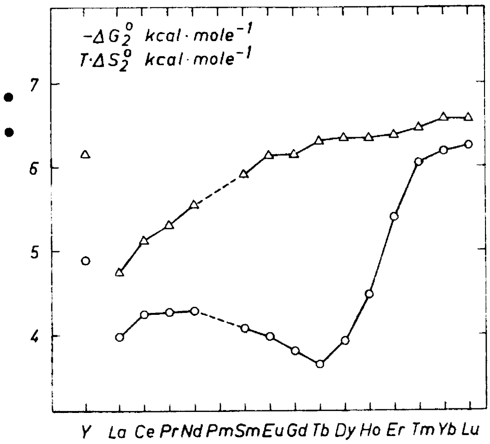

Fig. 2. $-\Delta G_2^\circ$ (△) and $T{\cdot}\Delta S_2^\circ$ (O) for the various rare earth diglycolate systems.

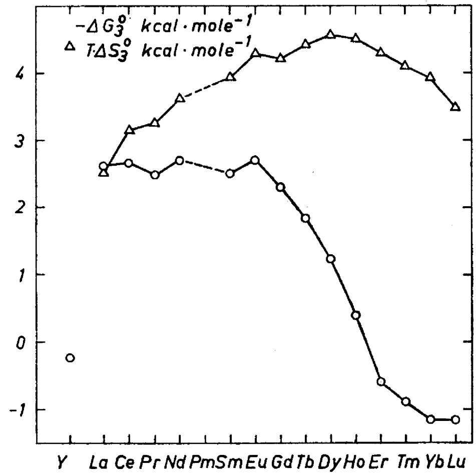

Fig. 3. $-\Delta G_3^\circ$ (△) and $T{\cdot}\Delta S_3^\circ$ (O) for the various rare earth diglycolate systems.

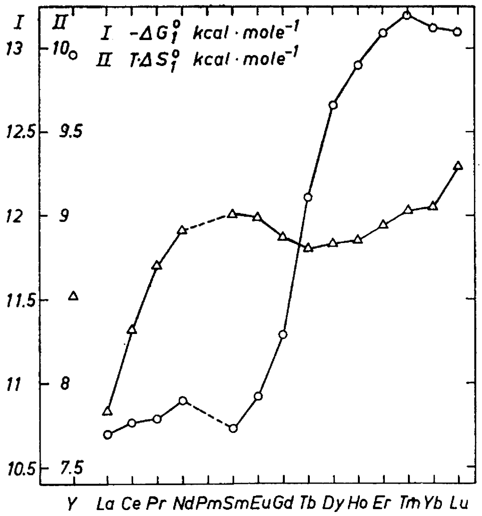

Fig. 4. $-\Delta G_1^\circ$ (△) and $T{\cdot}\Delta S_1^\circ$ (O) for the rare earth dipicolinate systems.

been estimated. For the rare earth diglycolate systems $\sigma\Delta\mathcal{S}_j^\circ$ are approximately 0.2, 0.3, and 0.4 e.u. for $j = 1, 2, 3$ and for the dipicolinate systems the corresponding figures are 0.3, 0.3 and 0.4 e.u.

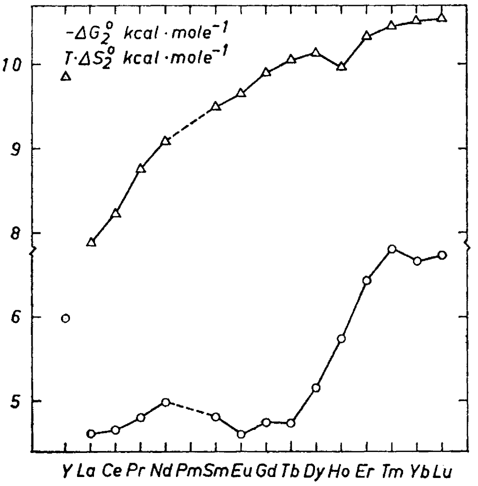

Fig. 5. $-\Delta G_2°$ (△) and $T{\cdot}\Delta S_2°$ (○) for the rare earth dipicolinate systems.

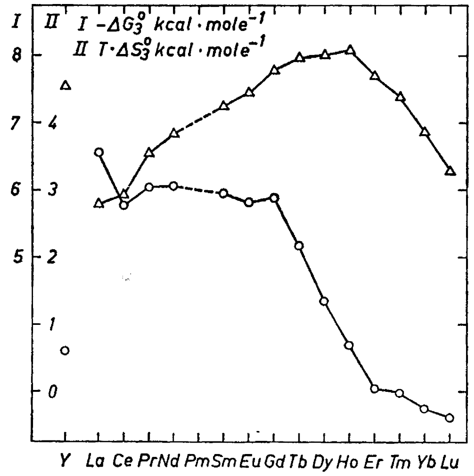

Fig. 6. $-\Delta G_3°$ (△) and $T{\cdot}\Delta S_3°$ (○) for the rare earth dipicolinate systems.

DISCUSSION

The stepwise values of $-\Delta G_j°$ and $T \cdot \Delta S_j°$ for the rare earth diglycolate systems are plotted in Figs. 1—3 and the corresponding values for the dipicolinate systems in Figs. 4—6. From these figures it is obvious that the variations in free energy, enthalpy and entropy are not simple monotonic functions of the ionic radius. The effect of decreasing ionic radius is complicated by solvation and coordination effects.

In part I of this series [9] the similarities in the variations of the β_j-values for the rare earth diglycolate and dipicolinate complexes were pointed out. These similarities are even more pronounced when we consider the variations of the $\Delta H_j°$ and $\Delta S_j°$ values through the lanthanide series.

In part III of this series the thermodynamic properties of certain rare earth acetate, glycolate and thioglycolate complexes will be described. A discussion of the properties of the rare earth carboxylate complexes will be postponed until then.

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