Thermodynamic Study of Eu^{3+}/Eu^{2+} Redox Reaction in Aqueous Solutions at Elevated Temperatures and Pressures by Means of Cyclic Voltammetry

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The redox potential of the couple Eu^{3+}/Eu^{2+} in aqueous NaCl, $NaClO_4$ and Na_2SO_4 solutions of different ionic strength and various pH values has been determined by means of cyclic voltammetry up to 458 K and 1 kbar. In all cases reversible voltammograms were obtained. Compared to the redox potential in ClO_4^- solutions of pH 2, no significant shift was observed in Cl-solutions of the same pH, whereas a drastic shift to more negative potentials in solutions of SO_4^{2-} and in Cl^- solutions of higher pH (pH 3–5) was obtained. This indicates a negligible complexation of Eu^{3+} by means of Cl^- but a strong one by means of OH^- and SO_4^{2-}. An isothermal pressure increase up to 1 kbar led to a shift of only few mV more negative, indicating a small pressure dependence of the change of the partial molar volume (ΔV_{el}) accompanying the redox reaction, which results in this case only due to the different degrees of electrostriction. A more drastic shift of the redox potential (in the positive direction) results with increasing temperature. The isobaric temperature dependence of the redox potential is described by a two parameter equation which remains valid up to the saturation pressure at 458 K, due to the small pressure effect. ΔS and ΔH of the redox reaction has been determined.

Key words: Redox potential of Eu^{3+}/Eu^{2+} in aqueous solutions under high p, T conditions; High p, T thermodynamic of redox equilibria; High p, T cyclic voltammetry.

1. Introduction

The knowledge of the redox potential of different ions in aqueous solutions at high temperatures and pressures is of great significance for the study of technical as well as geochemical hydrothermal systems. In particular, the redox potential of the couples Eu^{3+}/Eu^{2+} and Ce^{4+}/Ce^{3+} in hydrothermal solutions determines the anomaly of these two elements within the partition pattern of the lanthanides in the minerals formed from these fluids. Such anomaly indicates the change of the redox potential of the mineral-bearing solution and is, therefore, essential for the interpretation of many geochemical processes.

Sverjensky [1] carried out computer calculations of the redox equilibria of Eu^{3+}/Eu^{2+} in aqueous solutions at elevated temperatures and pressures as functions of the oxygen fugacity and pH. He used the equation of state and the predictive methods for the thermodynamic properties of aqueous species developed by Helgeson et al. [2–5] to estimate the change of the free energy of Eu^{3+} and Eu^{2+} from 25 °C and

1 bar to higher temperature and pressure. The computed apparent standard partial molal Gibbs free energies of formation of Eu species were used to evaluate the equilibrium.

$$Eu_{(aq)}^{2+} + H_{(aq)}^+ + 1/4\,O_{2\,(g)} \overset{K}{\Leftrightarrow} Eu_{(aq)}^{3+} + 1/2\,H_2O_{(l)}, \quad (1)$$
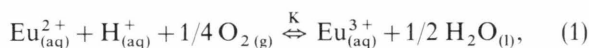
$$\log f_{O_2} = 4\,pH - 4\log K$$
$$+ 4\log(a_{Eu^{3+}}/a_{Eu^{2+}}) + 2\log a_{H_2O}. \quad (1a)$$

Sverjensky discussed the uncertainties in the thermodynamic properties and estimated equation of state coefficients of Eu^{3+} and Eu^{2+}, which are difficult to assess due to the laking data of Eu^{2+}. However, he supposed that these uncertainties would contribute a deviation of about 1000 cal mol^{-1} in ΔG of reaction (1) at 300 °C, which does not significantly affect his calculations.

In this work, the redox potential of the couple Eu^{3+}/Eu^{2+} has been determined by means of cyclic voltammetry at T up to 458 K and p up to 1 kbar. The measurements were carried out in perchlorate, chloride and sulfate media of different concentrations and various initial pH to investigate the thermodynamics of the redox reaction in absence and in presence of complexing agents. Taking the corresponding values

of the redox potential of the reaction

$$4\,H^+_{(aq)} + O_{2\,(g)} + 4\,e^- \Leftrightarrow 2\,H_2O \qquad (2)$$
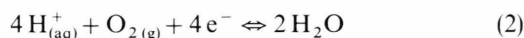
determined previously [6] into account, the results confirm fairly well the calculation of Sverjensky in the investigated p, T region.

2. Experimental

Apparatus

Cyclic voltammetry was performed in a specially constructed autoclave described previously by Becker and Bilal [7]. The same assembly was used to lead the third electrode. Cu and Pt wires were used as working and counter electrode, respectively. (Ag/AgCl)$_{NaCl = 0.1\,m}$ was used for the reference electrode. A glas vessel containing the Eu^{3+} solution was situated inside the inner teflon vessel of the autoclave, and the space between (1.5 cm between the bottoms and 1 cm between the walls) was filled with the same solution as used as background electrolyte. This solution was stirred magnetically in order to obtain the same temperature at every contact point with the glas vessel and so to prevent, as far as possible, thermal convection in the investigated solution.
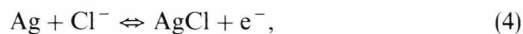
Due to the use of Cu wire as indicator electrode, a hydrogen overvoltage of about $-500\,mV$ could be obtained, so that it was possible to measure the redox potential ($E^0 = -360\,mV$ at $25\,°C$ and atmospheric pressure) before a decomposition of water occured. The electrode surface was first pretreated by immersion in 5 M HNO_3 (1 min.) and subsequently in distilled water to remove all adhered acid.

Reference Electrode

The potential between the working electrode and the Ag/AgCl reference electrode is determined by the emf E_3 of the reaction

$$Eu^{3+} + Ag + Cl^- \Leftrightarrow Eu^{2+}\,AgCl, \qquad (3)$$
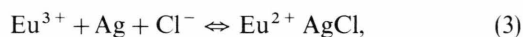
which is the sum of the two reactions,

$$Ag + Cl^- \Leftrightarrow AgCl + e^-, \qquad (4)$$

$$E_4 = E^0_4 + (R\,T/F) \ln(m_{Cl^-}\,\gamma_{Cl^-}) \qquad (4a)$$

and

$$Eu^3 + e^- \Leftrightarrow Eu^{2+}, \qquad (5)$$
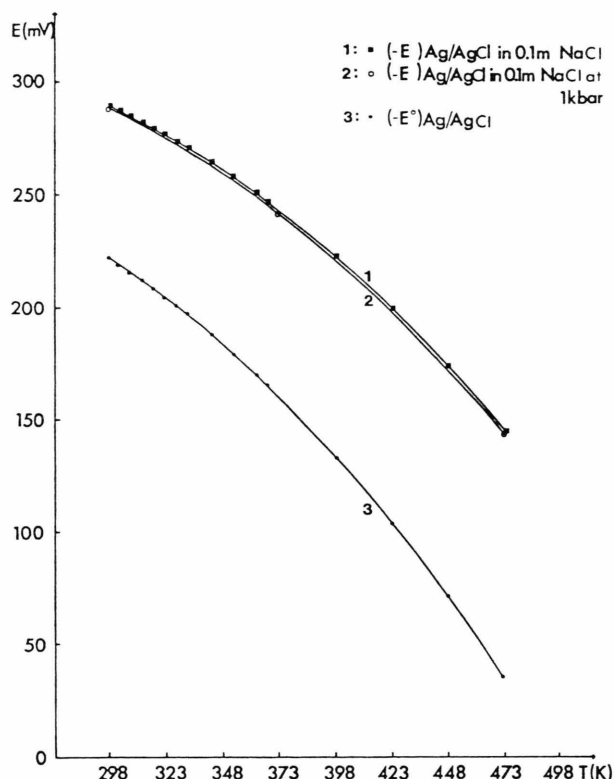
$$E_5 = E^0_5 - (R\,T/F) \ln(a_{Eu^{3+}}/a_{Eu^{2+}}) \qquad (5a)$$

Fig. 1. Potential of the Ag/AgCl electrode vs. T. 1, 3: saturation pressure, 2: 1 kbar.

with

$$E_3 = E_4 + E_5. \qquad (6)$$

Equation (7) is obtained for the redox potential E^0_5 at equal activities of Eu^{3+} and Eu^{2+}.

$$E^0_5 = E_3 - E_4, \qquad (7)$$

where γ_{Cl^-} in (4a) refers to the activity coefficient of the chloride in the 0.1 m NaCl solution of the reference electrode $= (\gamma_\pm)_{NaCl}$.

$E^0_4 (= -E^0_8)$ has been determined previously by different authors [8–10] who measured the emf E_8 of the reaction

$$1/2\,H_2 + AgCl \Leftrightarrow Ag + H^+ + Cl^- \qquad (8)$$

in the cell

$$Pt - H_2\,(p)/HCl\,(m)/AgCl - Ag \qquad (8a)$$
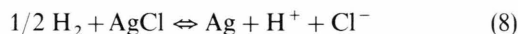
at various temperatures along with the corresponding saturation pressure ($p_{H_2} = p_{tot.} - p_{vapour}$). The standard potential E^0_8 was calculated according to

$$E^0_8 = E_8 + (R\,T/F) \ln(m_{H^+}\,\gamma_{H^+} \cdot m_{Cl^-}\,\gamma_{Cl^-})$$

$$= E_8 + (2\,R\,T/F) \ln(m_{HCl} \cdot \gamma_{\pm\,HCl}), \qquad (8b)$$

where the E_8 values were corrected to 1 atmosphere hydrogen pressure (see curve 3, Figure 1).

Bates and Bower [8] carried out their measurement at T up to 368 K and atmospheric pressure. Greeley, Smith, Stoughton and Lietzke [9] extended the investigation to $T = 548$ K along with the saturation pressure. Measurement of the cell (8 a) at $m_{HCl} = 0.1$ m has been carried out also by the author up to 473 K [10]. The obtained values (corrected to 1 atmosphere hydrogen pressure) are in quite good agreement with those reported in [8] and [9]. Taking the $(\gamma_\pm)_{HCl}$ values given by Greeley et al. [11] into account, the calculated standard potential deviates by only 0.05% in the temperature region up to 373 K and by $(0.07-0.1)\%$ between 373 and 473 K. E_4 was then calculated using the values of the mean activity coefficient of 0.1 m NaCl, determined previously by Liu and Lindsay [12] at T up to 573 K. The values, not given there, were interpolated from a plott $(\gamma_\pm)_{NaCl} = f(T)$. Curve 1 in Fig. 1 shows the $-E_4$ values up to 473 K at the corresponding saturation pressure. At higher pressure up to 1 kbar, E_4 was calculated using the values of $(\gamma_\pm)_{NaCl, I=0.1 m}$, predicted by Helgeson et al. [5]. The potential values at 1 kbar (curve 2, Fig. 1) are (in absolute volt) slightly lower than those at saturation pressure. Such a small pressure effect is due to the small change of the partial molar volume of the reaction (4).

$$\Delta V^0 = V^0_{AgCl} + V^0_{e^-} - V^0_{Cl^-} - V^0_{Ag}. \qquad (9)$$

With the standard partial molar volume ($cm^3 mol^{-1}$) of the components at 298 K and 1 bar, $V^0_{AgCl} = 25.73$, $V^0_{Cl^-} = 17.9$, $V^0_{Ag} = 10.27$ and $V^0_{e^-} = 3.4$ (partial molar volume of the electron in silver (see Heusler and Gaiser [13]) a $\Delta V^0_{298 K, 1 bar}$ of about 0.95 $cm^3 mol^{-1}$ results, which leads according to (20) to a difference $[(E_4)_{298 K, 1 bar} - (E_4)_{298 K, 1 kbar})]$ of about 1 mV.

Procedure

Table 1 lists the systems studied (concentration and ionic strength I are in units mol kg^{-1} (m)). The values of pH and of I are the initial ones at 298 K. I is corrected in the sulfate systems to account for the formation of HSO_4^- and $NaSO_4^-$.

The actual pH values at the different temperatures were measured in separate experiments using the high temperature – high pressure potentiometric cell described in [7]. These are shown in Figure 2. The corresponding values of I and of the free $[SO_4^{2-}]$ were calculated using the association constants of HSO_4^- and
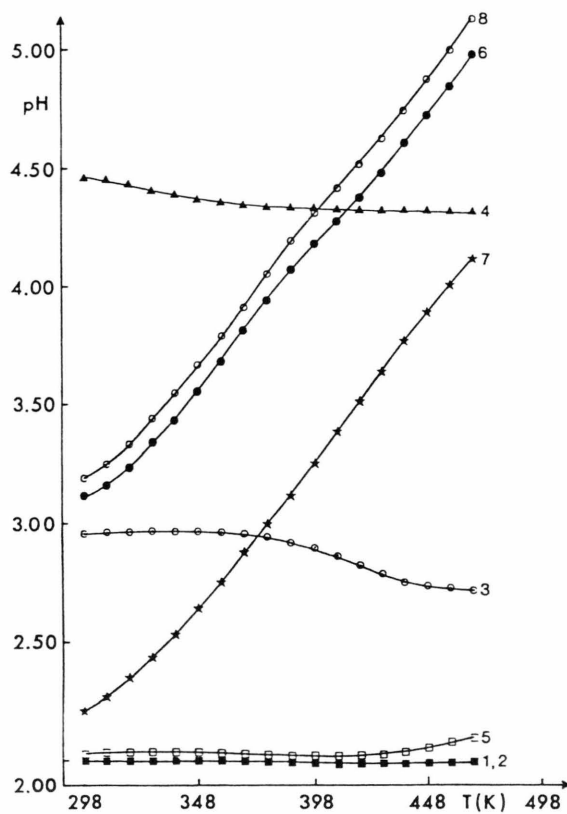

Fig. 2. pH of the systems 1–8 vs. T at the corresponding saturation pressure.

Table 1. The systems studied by means of cyclic voltammetry.

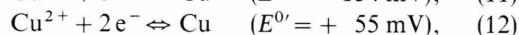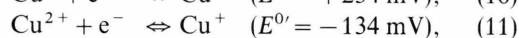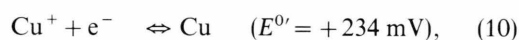| 1	10^{-3} m $Eu(ClO_4)_3$,	10^{-2} m $HClO_4$,	0.984 m $NaClO_4$, (pH = 2, $I = 1.0$ m)
2	10^{-3} m $EuCl_3$,	10^{-2} m HCl,	0.984 m NaCl, (pH = 2, $I = 1.0$ m)
3	10^{-3} m $EuCl_3$,	10^{-3} m HCl,	0.994 m NaCl, (pH = 2.96, $I = 1.0$ m)
4	10^{-5} m $EuCl_3$,	10^{-5} m HCl,	1.0 m NaCl, (pH = 4.44, $I \approx 1.0$ m)
5	5×10^{-3} m $Eu(ClO_4)_3$,	7.5×10^{-3} m H_2SO_4,	(pH = 2.03, $I = 0.045$ m)
6	10^{-3} m $Eu(ClO_4)_3$,	0.0019 m $HClO_4$,	0.05 m Na_2SO_4, (pH = 3.12, $I = 0.192$ m)
7	10^{-3} m $Eu(ClO_4)_3$,	0.0225 m $HClO_4$,	0.1 m Na_2SO_4, (pH = 2.22, $I = 0.247$ m)
8	10^{-3} m $Eu(ClO_4)_3$,	0.0025 m $HClO_4$,	0.1 m Na_2SO_4, (pH = 3.20, $I = 0.256$ m)

$NaSO_4^-$ reported by Marshall and Jones [14], and by Oscarson et al. [15], respectively. The calculation of the activity coefficients was carried out using the approximation given by Davies [16].

All eight systems were studied at atmospheric pressure and T up to 368 K. The system 3 was investigated
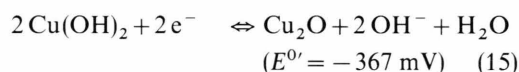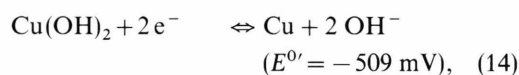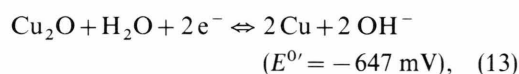
up to 458 K and the system 4 up to 428 K, both along with the corresponding saturation pressure. The experiments at T up to 368 K and p up to 739 bar were carried out using the system 2. The samples were first degassed with argon, which was then pressurized at 298 K to the different initial pressures 1, 162, 362, 447 and 541 bar. The pressure increased at 368 K to 1.25, 209, 493, 604 and 739 bar, respectively. To elucidate the pure pressure effect, the system 2 was scanned at 298 K and increased pressure up to 1 kbar.

3. Results and Discussion

The redox reactions of Cu ions in aqueous solutions occur in acidic region according to

$$Cu^+ + e^- \Leftrightarrow Cu \quad (E^{0'} = +234 \text{ mV}), \quad (10)$$
$$Cu^{2+} + e^- \Leftrightarrow Cu^+ \quad (E^{0'} = -134 \text{ mV}), \quad (11)$$
$$Cu^{2+} + 2e^- \Leftrightarrow Cu \quad (E^{0'} = + 55 \text{ mV}), \quad (12)$$

whereas in alkaline region the reactions

$$Cu_2O + H_2O + 2e^- \Leftrightarrow 2Cu + 2OH^-$$
$$(E^{0'} = -647 \text{ mV}), \quad (13)$$

$$Cu(OH)_2 + 2e^- \Leftrightarrow Cu + 2OH^-$$
$$(E^{0'} = -509 \text{ mV}), \quad (14)$$

$$2Cu(OH)_2 + 2e^- \Leftrightarrow Cu_2O + 2OH^- + H_2O$$
$$(E^{0'} = -367 \text{ mV}) \quad (15)$$

take place ($E^{0'}$ is the redox potential versus the used Ag/AgCl electrode at 298 K and atmospheric pressure).

At pH 5 the potentials of the reactions (13), (14), and (15) are shifted to -115, $+23$, and $+165$ mV, so that no interference occured in the scannig region (-200 to -900 mV).

Figure 3 shows the cyclic voltammogram obtained in system 2. Such simple reversible voltammograms $((E_{pc} - E_{pa}) \approx 65 \text{ mV})$ were observed also in the case of all other systems, even at elevated temperatures and pressures. This indicates a Nernstian behaviour of the electrode. In systems where complex formation of the Eu ions (particularly of Eu^{3+}) with SO_4^{2-} or OH^- (at pH >3) occurs, also no splitting of the peaks was observed, and only simple voltammograms with the expected shift of $E_{1/2}$ were obtained, even at higher scan rate of 100 mV/s. This indicates that Eu^{3+} and Eu^{2+} are the only electroactive species in these systems and that the coupled successive equilibria be-
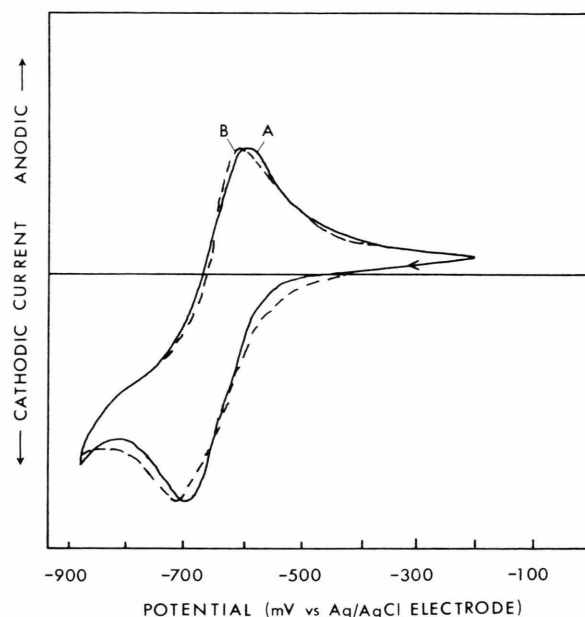

Fig. 3. Cyclic voltammogram of the system 2 at 298 K: Scan rate = 20 mV/s; (A) $p = 1$ bar; (B) $p = 1$ kbar.

tween the Eu ions and their complexed species are instantly established.

Pressure effect

The isothermal pressure dependence of the potential is in general given by

$$(\partial E/\partial p)_T = -\Delta V(p)/zF \quad (16)$$

(z = number of the electrons transferred, ΔV = the change of partial molar volume accompanying the electrochemical reaction, F = Faraday constant). In systems containing gas components, ΔV results from the equation

$$p\Delta V = RT(1 + Bp + Cp^2 + \ldots), \quad (17)$$

where B and C are virial coefficients. Substitution of ΔV from (17) in (16) and integration from atmospheric pressure to higher pressure p yields

$$E^p = E^1 - RT/zF [\ln p + B(p-1) + C/2(p^2-1)]. \quad (18)$$

Since no gas components are involved in the redox reaction

$$(Eu^{3+})_{aq, \text{Ligand}} + e^- \Leftrightarrow (Eu^{2+})_{aq, \text{Ligand}}, \quad (19)$$
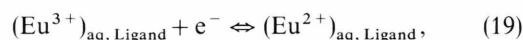
the only volume change which can be regarded in (16) is ΔV_{el}, which is due to the different degree of elec-
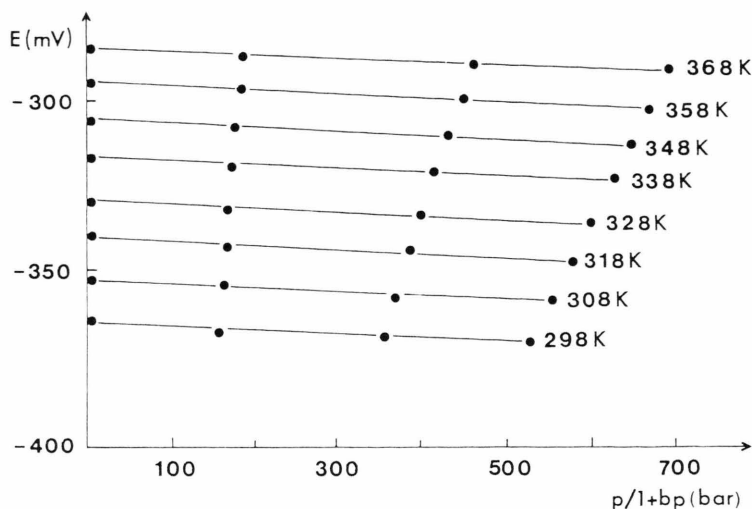
Fig. 4. Redox potential of reaction (19) as a function of $p/(1 + b\,p)$ at different T.

trostriction in the solution accompanying the change of the oxidation state of Eu. Neglecting the complex formation (exchange of one or two of the nine respectively eight coordinated water molecules), mainly the electrostatic interaction between Eu ions and the water dipoles accounts for more electrostriction in case of Eu^{3+} than in case of Eu^{2+}. A pressure increase which favours the volume contraction must, therefore, contradict the reduction which then requires more energy and so occurs at more negative potential. In this case, to integrate (16) from 1 bar to the higher pressure p, an expression of the form

$$E^p = E^1 - (\Delta V_{el}^1/z\,F)\,f(p) \qquad (20)$$

is next used to account for the pressure dependence of ΔV_{el}, where $f(p)$ is a function of pressure which would be equal to p if ΔV_{el} were independent of pressure. Considering only water dipoles in the coordination sphere of Eu ions, $f(p)$ in (20) must account for the change of ΔV_{el} due to the variation of the structure of water arround the central ion caused by the pressure increase (Break of the hydrogen bonds of the more or less ordered tetrahedral structure and transition to the volumen contracting configuration of "close packed spheres" yielding higher electrostatic interaction due to the free orientation of water dipoles). It is, therefore, reasonable to assume that $f(p)$ in (20) is the same one which applies for the pressure dependence of ΔV_{el} accompanying the dissociation of weak acids and bases in water. Owen and Brinkely [17] proposed a logarithmic form for $f(p)$ which works rather good but requires two adjustable parameters in addition to the

ΔV_{el}^1. El'yanov and Gonikberg [18] later found that $f(p)$ is actually a universal function for the ionization of a wide range of weak acids and bases in water which is virtually independent of the temperature and the reaction system. El'yanov and Hamann [19] subsequently showed that it could be expressed analytically by

$$f(p) = p/(1 + b\,p), \qquad (21)$$

where for aqueous solutions b is a constant $= 9.2 \times 10^{-5}\,bar^{-1}$.

To check the validity of this expression for (20), the redox potential E_5^0 in (7), measured at T up to 368 K and p up to 739 bar, was plotted as a function of $p/(1 + b\,p)$. Figure 4 shows that indeed a good linearity was obtained. The volume increase $(cm^3\,mol^{-1})$ due to the reduction of Eu^{3+} to Eu^{2+} at 1 bar is calculated from the slope of the lines to: $\Delta V_{el}^1 = (10.3)_{298\,K}$, $(10.5)_{328\,K}$, $(10.7)_{348\,K}$, and $(11.3)_{368\,K}$.

Temperature Effect

The temperature dependence of the potential is as expected a more drastic on. At constant pressure it is given theoretically by

$$(\partial E/\partial T)_p = \Delta S(T)/z\,F, \qquad (22)$$

where ΔS denotes the change of the partial molar entropy of the reaction and is itself a function of the temperature according to

$$(\Delta S)_p = \int \Delta C_p\,dT/T \qquad (23)$$

and
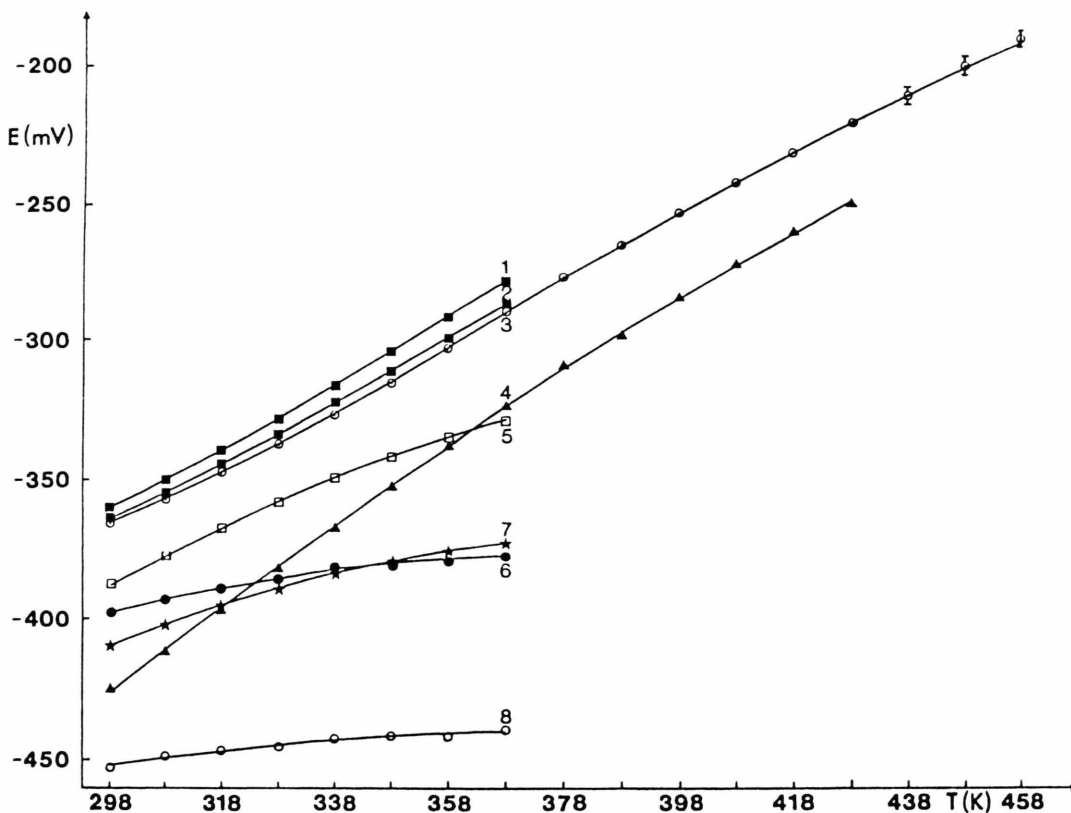
$$\Delta C_p = A + B\,T + C\,T^2 + \dots \qquad (24)$$

Fig. 5. Redox potential of reaction (19) as a function of T at the corresponding saturation pressure.

(ΔC_p = the change of the partial molar heat capacity of the redox reaction at constant pressure, $A = \Delta C_p$ at a reference temperature T_0, B and C are again virial coefficients). The integration of (22) from T^0 to T yields

$$E^T = E_0^T + 1/z\,F\,[A\,\{T(\ln T - 1) - T_0(\ln T_0 - 1)\} \quad (25)$$
$$+ B\,\{T^2/2\,(\ln T - 1/2) - T_0^2/2\,(\ln T_0 - 1/2)\}$$
$$+ C\,\{T^3/3\,(\ln T - 1/3) - T_0^3/3\,(\ln T_0 - 1/3)\}].$$

However, the isobaric temperature dependence of the redox potential (Fig. 5) can be described to a good approximation by the empirical equation

$$E^T = E_0^T + a\,(T - T_0) + b\,(T - T_0)^2, \quad (26)$$

where the coefficients a and b are determined graphically. Equation (26) holds also fairly well at higher temperature up to 458 K along with the saturation pressure, where the pressure effect is still negligible. Table 2 contains the values of a and b for the different systems studied and the temperature region in which

Table 2. The values of a and b and the region of their validity.

System	Temp.-region (K)	a (mV · K^{-1})	b (mV · K^{-2})
1	298–368	+0.998	+2.48 × 10^{-3}
2	298–368	+0.901	+2.85 × 10^{-3}
3	298–368	+0.796	+3.91 × 10^{-3}
	378–458	+1.298	−2.33 × 10^{-3}
4	298–428	+1.530	−1.22 × 10^{-3}
5	298–368	+1.180	−4.80 × 10^{-3}
6	298–368	+0.640	−4.30 × 10^{-3}
7	298–368	+0.850	−4.50 × 10^{-3}
8	298–368	+0.320	−1.20 × 10^{-3}

they are valid. The differentiation of (26) with respect to the temperature yields ΔS of the redox reaction (19) at constant pressure.

$$\Delta S = (\partial E/\partial T)\,z\,F = \{a + 2\,b\,(T - T_0)\}\,z\,F. \quad (27)$$

ΔH is then calculated from the fundamental equation

$$\Delta H = \Delta G + T\Delta S = [T\,\{a + 2\,b\,(T - T^0)\} - E]\,z\,F. \quad (28)$$
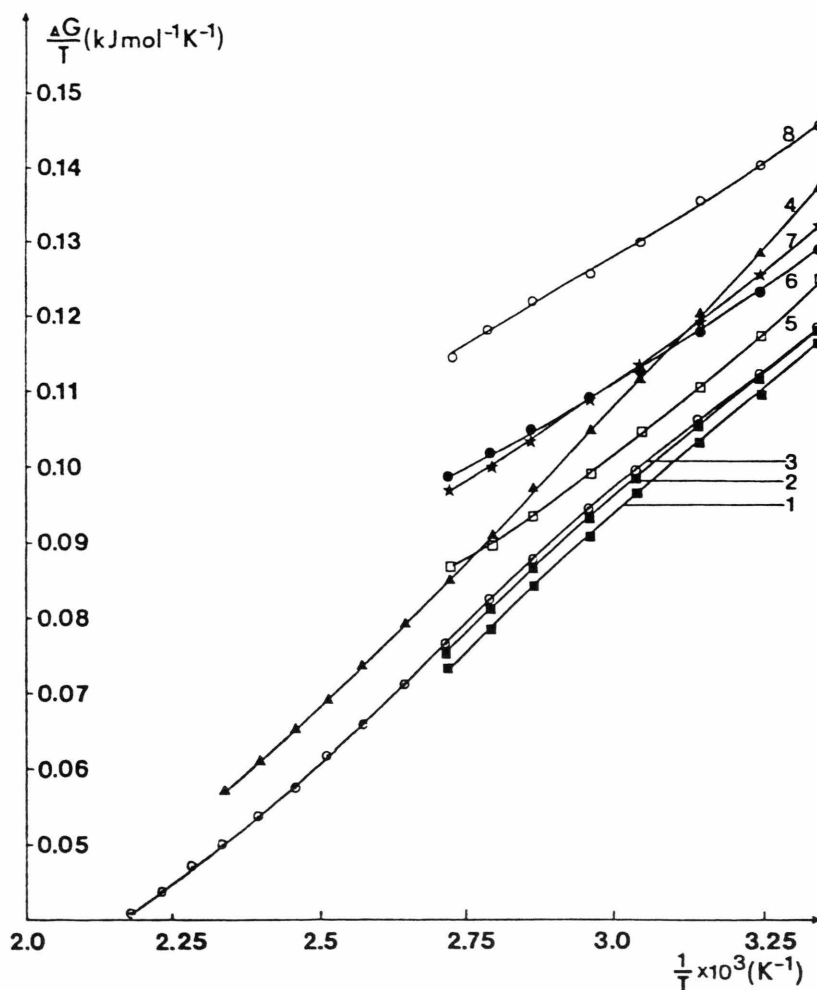
Fig. 6. $\Delta G/T$ of reaction (19) as a function of $1/T$ at the corresponding saturation pressure.

ΔS and ΔH are also determined graphically from the slopes of the plotts E vs. T (Fig. 5) respectively $\Delta G/T$ vs. $1/T$ (Figure 6). The ΔS and ΔH of the reaction (19) are shown in Fig. 7 and Figure 8.

The potential curves of the systems 1 and 2 (Fig. 5), where no significant complexation of Eu^{3+} takes place, have an increasing slope. The curve of system 3 (pH_i 3) is slightly s – shaped and the increasing slope turns to decrease around 348 K. This behaviour indicates the complexation of Eu^{3+} by means of OH^- which is increasingly formed from the dissociation of water. Bilal and Langer [20] have already shown that the formation of such hydrolysed species of the lanthanides occurs in solutions having pH 3.6 at $T >$ 333 K, even if these solutions contain complexing ligands such as F^-. Since the bond between the lanthanides central ion and the coordinating ligands is

mainly an electrostatic one, the stability of the complexes increases in general with increasing temperature due to the decreasing dielectric constant of water. This complexation effect (which leads to the reduction of Eu^{3+} at more negative potential) is enhanced in the system 4 due to the higher OH^- concentration, as well as in all sulfate systems. The higher concentration of the "free" $[SO_4^{2-}]$ on going from the system 5 to the systems 6, 7, and 8 leads to the increasing formation of sulfato complexes, and therefore to the observed flattening of the potential curves, which are progressively shifted to the more negative region.

Figure 9 shows log f_{O_2} of reaction (1) as a function of temperature at different pH and sulfate concentrations, where equal activities of Eu^{3+} and Eu^{2+} and unit activity of water are assumed. The stars (*) are the points given by Sverjensky for 298, 373 and 523 K
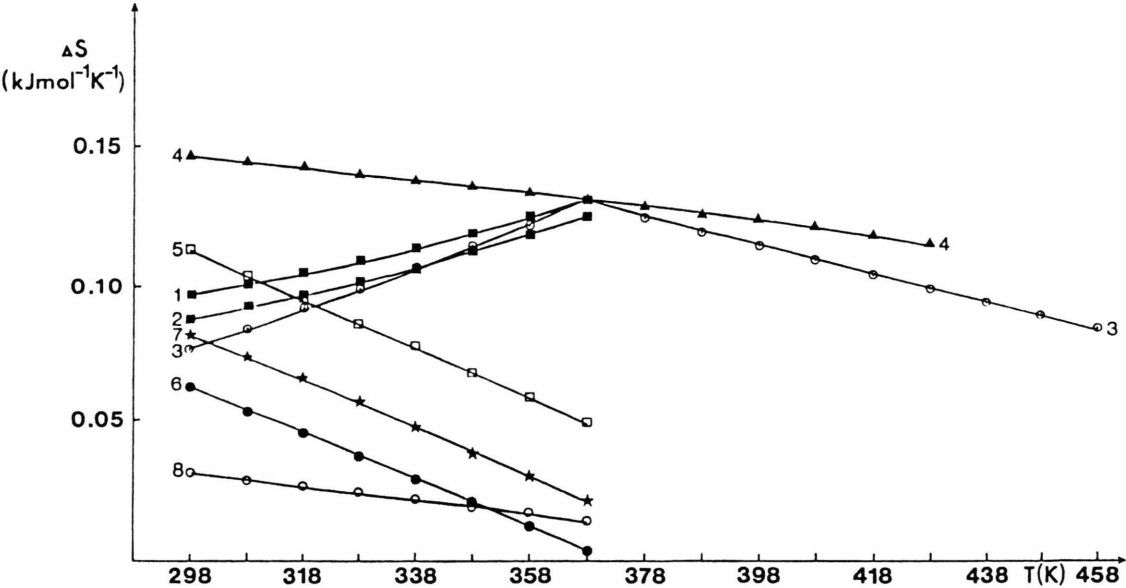
Fig. 7. ΔS of reaction (19) as function of T at the corresponding saturation pressure.
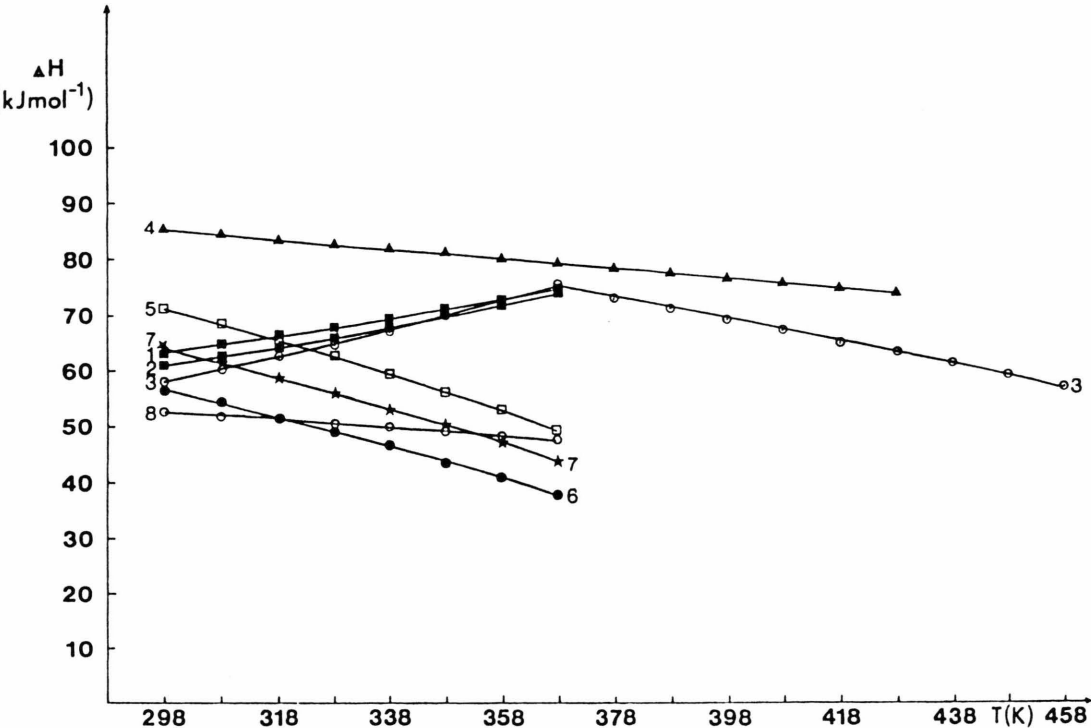

Fig. 8. ΔH of reaction (19) as function of T at the corresponding saturation pressure.
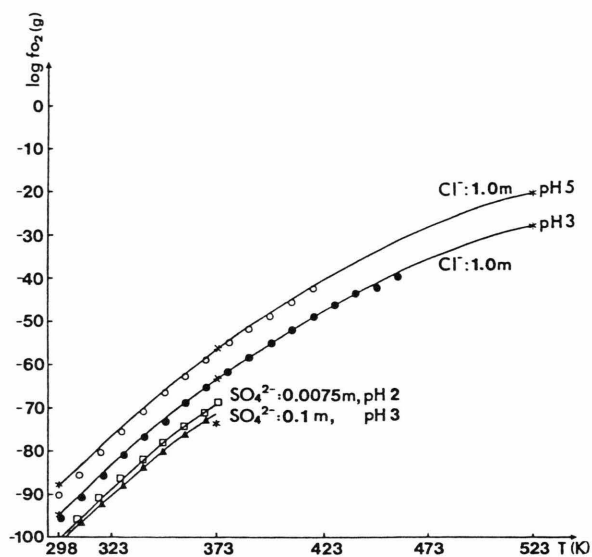
Fig. 9. log f_{O_2} of reaction (1) as function of T at the corresponding saturation pressure.

which are connected with a smooth curve. log K in (1 a) is calculated from the redox potential of reaction (2) and the negative values of the redox potentials of reaction (19) determined in this work. At pH 3, there is excellent agreement between the experimental results of this work and the values of Sverjensky. At pH 5 there is a deviation of about 2 orders of magnitude at 298 K, which decreases rapidly with increasing temperature, and a fairly good agreement is observed above 373 K. This deviation is probably due to the formation of hydroxo complexes which may have been considered as negligible at low temperature in the calculation of Sverjensky. The extended line with equal activities of Eu^{3+} and Eu^{2+} in 0.1 m sulfate solution (see [1]) yields log $f_{O_2} = -73.5$ at pH 3 and the given $T = 373$ K and $p = 1$ bar which is again about 2 orders of magnitude lower than the values found in this work. Sverjensky considered the formation of only mono sulfato complexes of Eu^{3+}. At such high sulfate activity, the formation of the more stable trisulfato complexes has been reported by Bilal and Koß [21].

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