

Potentiometric Study of the Stability of Eu^{3+} Acetate Complexes as a Function of Pressure (1–1000 bar) at 25°C

A. V. Zotov*, L. A. Koroleva*, and E. G. Osadchii**

* *Institute of the Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry (IGEM), Russian Academy of Sciences, Staromonetnyi per. 35, Moscow, 119017 Russia*
e-mail: azotov@igem.ru

** *Institute of Experimental Mineralogy (IEM), Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia*
e-mail: euo@iem.ac.ru

Received March 18, 2004

Abstract—The stability of europium acetate complexes was examined potentiometrically at 25°C as a function of pressure in the range of 1–1000 bar. The measurements were carried out in an isothermal potentiometric cell with a liquid junction. The cell consisted of a pH glass electrode and an Ag, AgCl (3*m* KCl) reference electrode. The calibration of the cell on standard solutions has demonstrated that its electromotive force is independent of pressure. Based on pH measurements under various pressures in four acetate solutions with pH from 3 to 4.7 and containing 0.0142*m* Eu, we determined the standard partial mole volumes and the HKF parameters for the complexes $\text{Eu}(\text{Ac})^{2+}$ and $\text{Eu}(\text{Ac})_2^+$. The baric dependence of the $\Delta_f G^0$ of the third complex, $\text{Eu}(\text{Ac})_3^0$, was evaluated from correlations. The stability of all three Eu acetate complexes decreased with pressure: as the pressure was increased from 1 to 1000 bar, the constants of formation of the complexes decreased by factors of 1.5–3 at 25°C and 2–6 at 170°C.

DOI: 10.1134/S0016702906040057

INTRODUCTION

The rare earth elements (REE) have long and successfully been utilized as geochemical indicators of magmatic processes. At the same time, the mobility of REE in the Earth's crust during metamorphism, hydrothermal processes, and lithogenesis remains disputable as of yet [1, 2]. Keen interest was also attracted to the behavior of REE in aqueous solutions in the context of problems related to the safe disposal of radioactive wastes.

Numerous experiments conducted to elucidate REE complexation with various inorganic and organic ligands at 25°C and a pressure of 1 bar (see review in [2–4]) made it possible to apply thermodynamic analysis and correlation dependences to estimate the stabilities of these complexes within broad ranges of temperature and pressure [2, 5, 6].

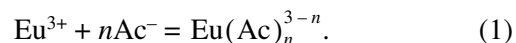
Over the past decade, data were obtained on the thermodynamic characteristics of several trace-element complexes at elevated temperatures (up to 200–300°C): chloride [7, 8], hydroxide [9], and acetate [10, 11]. However, all of these studies were conducted under low pressures and, thus, cannot clarify the influence of pressure on the stability of these complexes. Because of this, we attempted to determine experimentally the dependence of the thermodynamic characteristics of one of these types of complexes and to compare this

dependence with one predicted theoretically in compliance with the Helgeson–Kirkham–Flowers (HKF) model. For this experimental research, we selected acetate complexes of Eu to bridge the gap in our earlier potentiometric studies in this system [11].

MATERIALS AND METHODS

Theoretical Fundamentals

Earlier research [10, 12, 13] has demonstrated that Eu forms mononuclear complexes with acetate in acetate solutions at REE concentrations of <0.05 mol/l by the reaction



The thermodynamic constants of this reaction are expressed as

$$K_n = \frac{[\text{Eu}(\text{Ac})_n^{3-n}] \gamma_{\text{Eu}(\text{Ac})_n^{3-n}}}{[\text{Eu}^{3+}] [\text{Ac}^-]^n \gamma_{\text{Eu}^{3+}} \gamma_{\text{Ac}^-}^n}, \quad (2)$$

where K_n is the equilibrium constant of reaction (1), n is the number of ligands (acetate ions, Ac^-), and brackets and γ stand for, respectively, the concentrations and activity coefficients of aqueous species.

Inasmuch as the measurements were carried out in acidic solutions (pH < 5), we did not introduce correc-

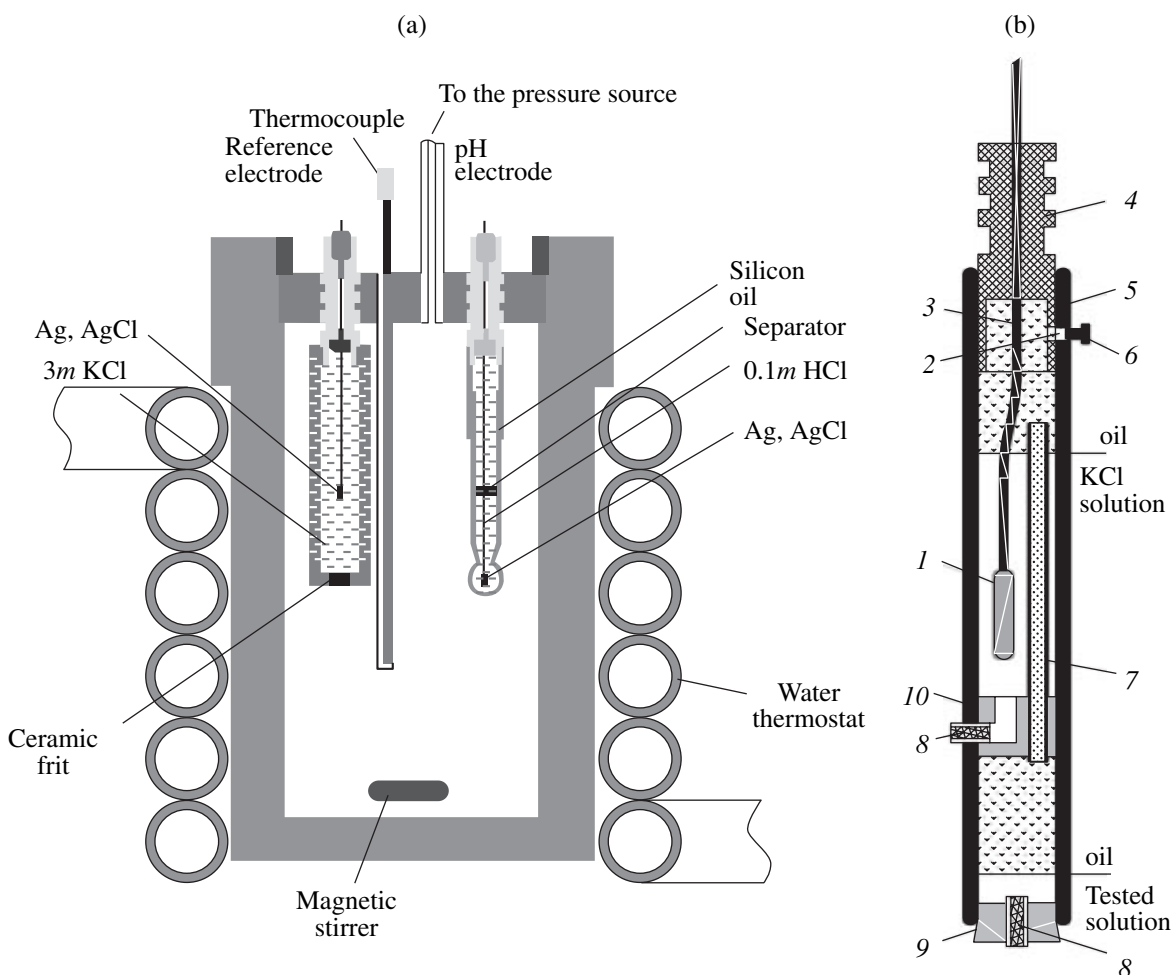


Fig. 1. Schematic illustration of the design of (a) the potentiometric cell and (b) the specialized reference electrode. (1) Ag/AgCl half-element; (2) hole for adding the internal KCl solution and oil; (3) Ag wire; (4) connector bushing and lead-in; (5) glass electrode vessel; (6, 9, and 10) rubber plugs; (7) glass tube; (8) ceramic frit.

tions for the formation of Eu hydroxyl complexes. The absence of noticeable hydrolysis under these conditions has been demonstrated for La^{3+} and Gd^{3+} [14] and, later, also for Nd^{3+} [9, 10].

Materials

The buffer and tested solutions were prepared from the following reactants: $\text{Na}(\text{CH}_3\text{COO})$ (BDH-Analar, 99.9%), glacial acetic acid CH_3COOH (99.9%), KCl (reagent-grade purity), Eu_2O_3 (Rectapur, 99.99%), and HClO_4 (reagent-grade purity, 59.5%). In addition, we used standard NBS buffer solutions with pH 4.01, 6.86, and 9.18 at 25°C , which were prepared from Fixanals (State Standard no. 8.135-74) and an 0.1M HCl Fixanal solution.

All of the solutions were prepared in distilled water, which had been boiled for 30–40 min to get rid of CO_2 .

The basic solution containing Eu [$0.45\text{M Eu}(\text{ClO}_4)_3 + 0.058\text{M HClO}_4$] was prepared by dissolving 8.7 g of Eu_2O_3 in 26.14 g of HClO_4 (59.5%) at heating and the

subsequent addition of 97.3 g of H_2O . The europium oxide was calcinated at 460°C for 2 h to remove water and carbonates. The solution thus prepared was filtered through a Schott no. 4 glass filter. The check determinations of the free HClO_4 concentration in the basic solution was conducted in two different manners: by the direct measurement of the pH of the solution diluted by a factor of 29 (pH 2.80, ionic strength of about 0.1) and by the potentiometric titration of the same diluted solution by 0.1M solution of HCl. Calculations for both of the variants yielded similar concentrations of free HClO_4 in the basic solution ($0.058 \pm 0.002\text{M}$).

Before the preparation of the solutions, the sodium acetate was dried at 200°C for 2 h and was held in an desiccator.

Methods

Potentiometric Cell and Electrodes

The potentiometric measurements were conducted at 25°C and pressures from 1 to 1000 bar, in a cell of

Table 1. pH of standard solutions at 25°C as a function of pressure (1–1000 bar)

Solution	pH				
	1 bar	186 bar	490 bar	687 bar	980 bar
0.01 <i>m</i> HCl	2.04*	2.04*	2.04*	2.04*	2.04*
0.05 <i>m</i> KC ₈ H ₅ O ₄	4.01 ^{2*}	3.96 ^{3*}	3.88 ^{3*}	3.84 ^{3*}	3.76 ^{3*}
0.025 <i>m</i> KH ₂ PO ₄ + 0.025 <i>m</i> Na ₂ HPO ₄	6.86 ^{2*}	6.77*	6.65*	6.57*	6.45*
0.01 <i>m</i> Na ₂ B ₄ O ₇	9.18 ^{2*}	9.06 ^{3*}	8.91 ^{3*}	8.82 ^{3*}	8.67 ^{3*}
0.025 <i>m</i> HAc + 0.025 <i>m</i> NaAc	4.69*	–	4.59 ^{4*}	4.56 ^{4*}	4.51 ^{4*}
0.04 <i>m</i> HAc + 0.015 <i>m</i> NaAc	4.28*	–	4.18 ^{4*}	4.15 ^{4*}	4.10 ^{4*}
0.083 <i>m</i> HAc + 0.01 <i>m</i> NaAc	3.80*	–	3.71 ^{4*}	3.68 ^{4*}	3.63 ^{4*}

* Values of pH were calculated based on Slop98.

^{2*} NBS scale of buffer solutions.

^{3*} Based on the data of Kryukov and Zarubina [15].

^{4*} Our data in this paper.

VT8 Ti alloy. The design of the cell is schematically shown in Fig. 1. The temperature was measured by a chromel–alumel thermocouple and was maintained constant (within $\pm 0.2^\circ\text{C}$) by a UT-2 liquid thermostat. The pressure was set up by a hand-operated hydraulic press and was measured by a D100 strain sensor and an OBMGv1-160 (0–1600 kgs/cm², class 1.6) manometer, which were calibrated on a MP-2500 deadweight pressure gage. The accuracy of the measurements was ± 10 bar for the pressure range of 200–1000 bar. The solution was stirred by a magnetic stirrer.

The e.m.f., pressure, and temperature of the potentiometric cell were measured by a computer-operated multichannel meter (designed by N.N. Zhdanov at the Institute of Experimental Mineralogy, Russian Academy of Sciences). The input resistance of the measuring potentiometer was very high ($>10^{12} \Omega$), the potentiometric channels were galvanically isolated from the electronic unit, the resolution was 0.1 mV, and the error was ± 5 mV. The measurements were conducted in an isothermal cell with a liquid junction, which consisted

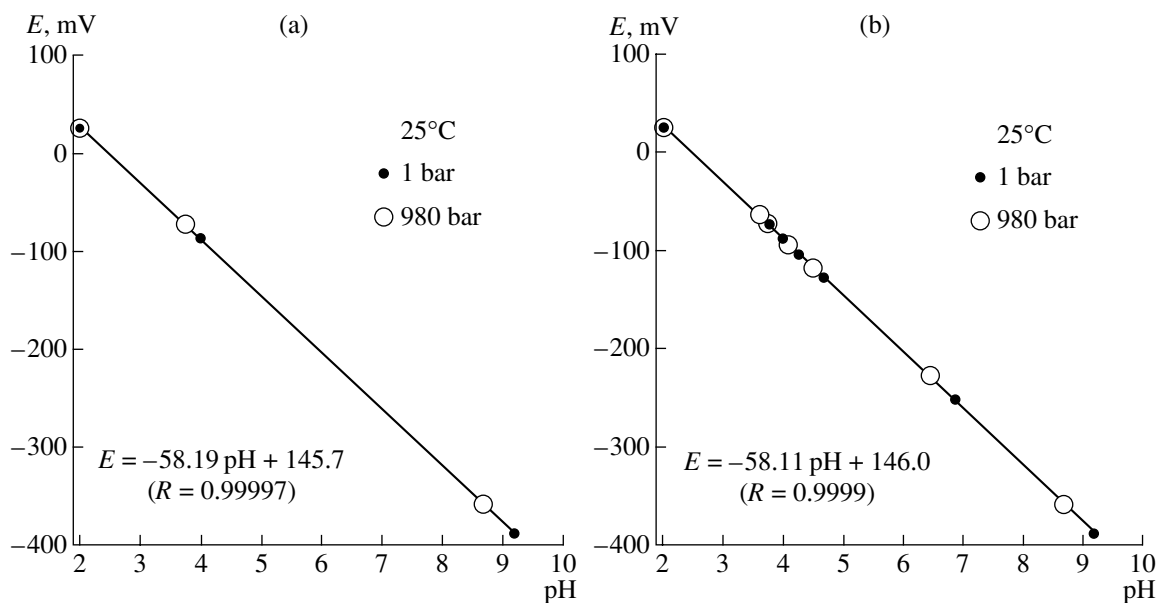


Fig. 2. *E* (e.m.f.) vs. pH calibration plots for 25°C and pressures of 1 and 980 bar constructed using NBS buffer solutions and (a) 0.01*m* HCl and (b) all solutions (Table 1), including acetate buffers.

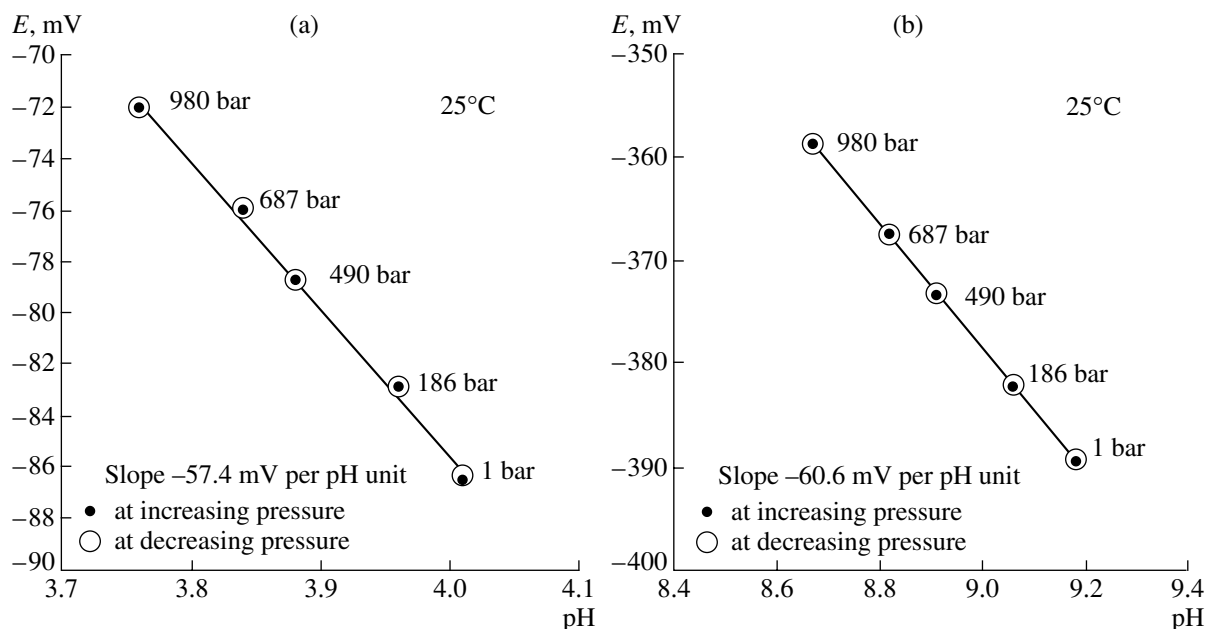


Fig. 3. Dependence of the measured E (e.m.f.) on pH at 25°C for (a) biphilate and (b) borate NBS buffers at pressures from 1 to 980 bar. Symbols correspond to results obtained by approaching pressure from below and above.

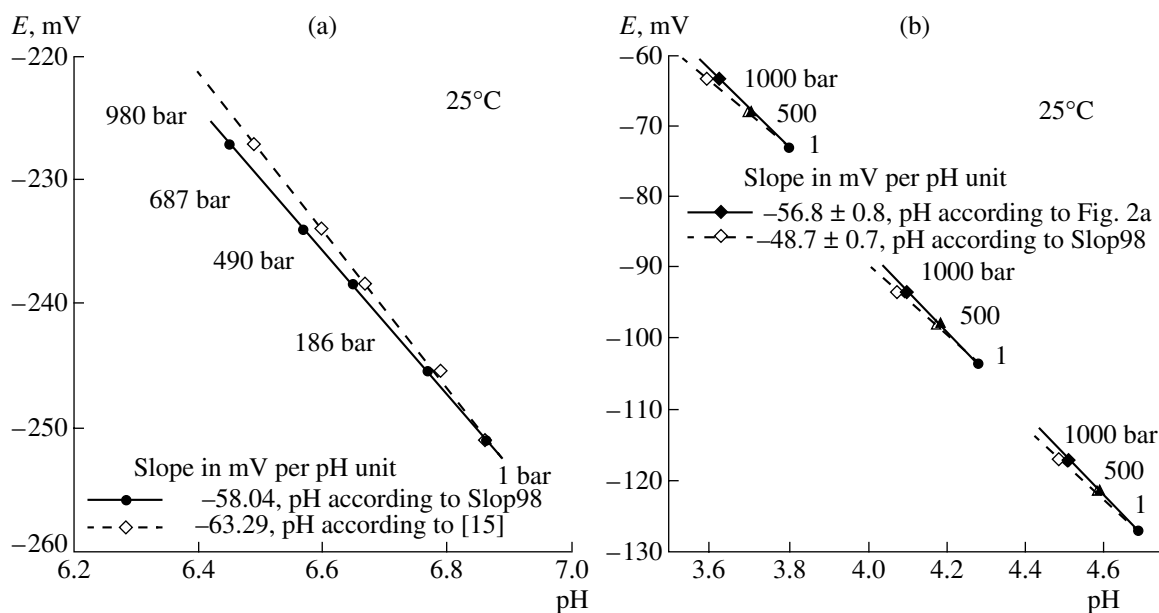
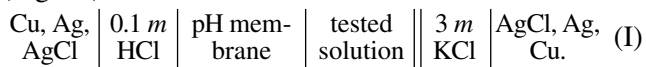


Fig. 4. Dependence of the measured E (e.m.f.) on pH at 25°C for (a) phosphate and (b) tri-acetate buffers at pressures from 1 to 980–1000 bar. The values of pH were determined by various methods: calculated based on thermodynamic data from Slop98, assumed according the experimental data [15], and based on the calibration shown in Fig. 2.

of a glass pH electrode and a Cl–Ag reference electrode (Fig. 1a)



We commonly simultaneously used two glass electrodes, whose design is demonstrated in Fig. 1. The sensitive membranes were manufactured at the Izmeri-

tel'naya Tekhnika Research and Production Company, using electrode glass no. 45. The internal half-element was a Cl–Ag electrode in 0.1M HCl solution.

The reference electrode was a Cl–Ag electrode in 3M KCl solution. The constant outflow of the electrolyte through the liquid junction under any pressure was ensured by the design of the electrode (Fig. 1a), which included a Teflon bellows. The stable outflow of the

Table 2. Measured pH of buffer acetate solutions at 25°C and pressures of 1–1000 bar

Solution	P , bar	$\Delta E = E_P - E_{P=1}$	$\Delta \text{pH} = \text{pH}_P - \text{pH}_{P=1}$	$\text{pH}_{P, \text{exper}} = \text{pH}_{P=1} + \Delta \text{pH}$	$\Delta_f G(\text{HAc}_{(\text{aq})})$, kJ/mol	pH_P, calc
0.025m HAc + 0.025m NaAc	1			4.688 ^{1*}	-396.476 ^{2*}	
	490	5.7 ± 0.3	-0.098 ± 0.005	4.590	-393.965	4.591
	687	7.6 ± 0.3	-0.131 ± 0.005	4.557	-392.990	4.558
	980	10.4 ± 0.4	-0.179 ± 0.007	4.509	-391.555	4.509
0.04m HAc + 0.015m NaAc	1			4.277 ^{1*}	-396.476 ^{2*}	
	490	5.5 ± 0.4	-0.095 ± 0.007	4.182	-393.975	4.183
	687	7.4 ± 0.3	-0.127 ± 0.005	4.150	-393.010	4.151
	980	10.3 ± 0.3	-0.177 ± 0.005	4.100	-391.565	4.101
0.083m HAc + 0.01m NaAc	1			3.800 ^{1*}	-396.476 ^{2*}	
	490	5.2 ± 0.2	-0.089 ± 0.003	3.711	-394.000	3.710
	687	7.2 ± 0.3	-0.124 ± 0.005	3.676	-393.020	3.676
	980	10.1 ± 0.4	-0.174 ± 0.007	3.626	-391.575	3.627

^{1*} Values of pH were calculated based on Slop98.

^{2*} Slop98.

Table 3. Standard thermodynamic characteristics and HKF parameters of HAc_(aq) and acetate complexes of Eu

Thermodynamic characteristics		HAc _(aq)	Eu(Ac) ²⁺	Eu(Ac) ₂ ⁺	Eu(Ac) ₃ , aq
$\Delta_f G_{298}^0$	(cal mol ⁻¹)	-94760	-229579	-320303	-409817
S_{298}^0	(cal mol ⁻¹ K ⁻¹)	42.70	-13.97	18.26	50.60
$C_{P, 298}^0$	(cal mol ⁻¹ K ⁻¹)	40.3	50.1	151.1	235.5
V_{298}^0	(cm ³ mol ⁻¹)	52.1	11.78	67.15	119.6
$a_1 \times 10$	(cal mol ⁻¹ bar ⁻¹)	9.3004	3.8683	11.0548	18.1311
$a_2 \times 10^{-2}$	(cal mol ⁻¹)	12.5937	1.6633	19.2109	36.4884
a_3	(cal K mol ⁻¹ bar ⁻¹)	0.3270	5.0962	-1.8009	-8.5918
$a_4 \times 10^{-4}$	(cal K mol ⁻¹)	-3.3494	-2.8478	-3.5732	-4.2874
c_1	(cal mol ⁻¹ K ⁻¹)	42.0760	47.3933	97.1602	144.1841
$c_2 \times 10^{-4}$	(cal K mol ⁻¹)	-1.5417	7.1730	27.7439	44.9368
$\omega \times 10^{-5}$	(cal mol ⁻¹)	-0.1500	1.2998	0.2676	0.0

KCl solution, which was ensured by the preliminary extension of the bellows, notably reduced the diffusion potential. We also used a reference electrode of special design [Patent of Russian Federation no. 2003117512/28(019200), E.G. Osadchii and A.V. Zotov of June 17, 2003). In this electrode (Fig. 1b), inner solution outflow was maintained by the buoyancy force of the buoyant oil in communicating vessels. This electrode can operate for a long time under any external pressure.

Electrode Calibration

The electrode system was calibrated at 25°C and at pressures of 1–1000 bar against the 0.01m HCl solution and two NBS buffer solutions (biphthalate and borate). The pH values of these solutions as a function of pressure are listed in Table 1. The calibration plots (Figs. 2a, 3a, 3b) indicate that the linear dependence between the measured e.m.f. and pH is independent of pressure. The slope of the lines in the diagram (Fig. 2a) is equal to -58.19 mV per pH unit and is close to the theoretical

Table 4. Measured pH of acetate solutions containing 0.0142*m* Eu(ClO₄)₃ and 0.00187*m* HClO₄ at 25°C and pressures of 1, 490, and 980 bar

Acetate solution	<i>P</i> , bar	ΔE $= E_P - E_{P=1}$	$\Delta \text{pH}_{\text{exper}}$ $= \text{pH}_P - \text{pH}_{P=1}$	$\text{pH}_{P=1, \text{exper}}$	$\text{pH}_{P=1, \text{calc}}^*$	$\text{pH}_P = \text{pH}_{P=1, \text{calc}} + \Delta \text{pH}_{\text{exper}}$	pH_P, calc
0.080 <i>m</i> HAc + 0.00968 <i>m</i> NaAc	1			3.21	3.189		3.189
	490	2.3 ± 0.3	-0.040 ± 0.005			3.149	3.152
	980	4.6 ± 0.2	-0.079 ± 0.003			3.110	3.109
0.048 <i>m</i> HAc + 0.0145 <i>m</i> NaAc	1			3.63	3.626		3.626
	490	2.7 ± 0.3	-0.046 ± 0.005			3.580	3.580
	980	5.3 ± 0.3	-0.091 ± 0.005			3.535	3.529
0.024 <i>m</i> HAc + 0.024 <i>m</i> NaAc	1			4.23	4.230		4.230
	490	3.6 ± 0.3	-0.062 ± 0.005			4.168	4.173
	980	6.8 ± 0.3	-0.117 ± 0.005			4.113	4.113
0.02 <i>m</i> HAc + 0.04 <i>m</i> NaAc	1			4.62	4.631		4.631
	490	4.0 ± 0.3	-0.069 ± 0.005			4.562	4.561
	980	8.0 ± 0.2	-0.138 ± 0.003			4.493	4.494

* Based on the data from [11].

one corresponding to the Nernst law (-59.16). The deviation of the experimental points from the straight line do not exceed 1.2 mV and are independent of both pH and pressure. This implies that the pressure effect on the standard electrode potential of the cell (I) can be neglected within the examined pressure range of 1–1000 bar.

Using the calibration of the electrode cells, we measured the pH of the phosphate NBS buffer and three acetate buffers at pressures of up to 1000 bar (Table 1).

The pH values experimentally determined for the phosphate buffer under elevated pressures (up to 1000 bar) are in good agreement with the pH calculated by the GIBBS computer program [16, 17] on the basis of thermodynamic data on all aqueous species from the Slop98 database (Fig. 4a). At the same time, they notably differ from the pH values measured by Kryukov and Zarubina [15], but the reasons for these discrepancies remain unexplained.

The pH values of the acetate buffers measured under elevated pressures are inconsistent with the data calculated based on thermodynamic constants from the Slop98 database (Fig. 4b). In view of the necessity of making consistent the experimental and calculated pH values, we had to revise the thermodynamic parameters for acetic acid [HAc_(aq)] presented in Slop98.

Thermodynamic Characteristics of HAc_(aq)

The results of our pH measurements in the acetate buffer solutions depending on pH are listed in Table 2. In order to improve the accuracy of the calculations, we used not the pH values *per se* but their changes with increasing pressure as compared to the pH value at 1 bar. In recalculating the measured ΔE values to ΔpH ,

we assumed that the slope of the line corresponding to the dependence in the ΔE vs. pH diagram is equal to -58.2 mV per pH unit. Then, using the UT-HEL [18]

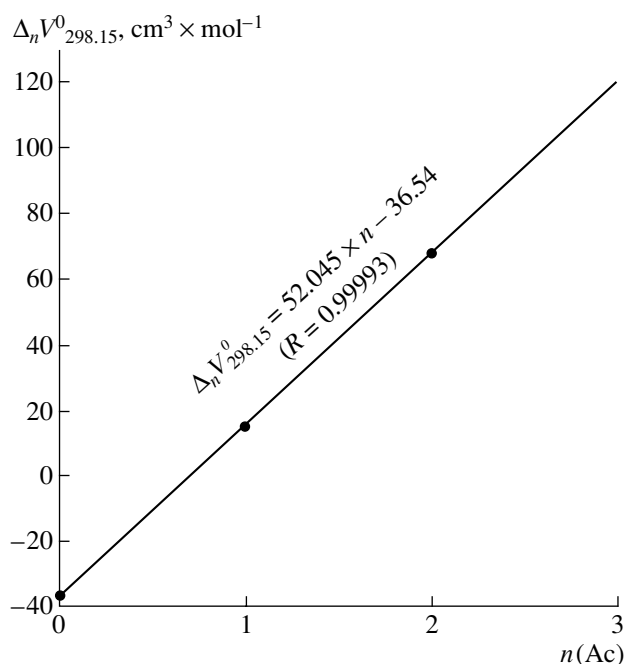


Fig. 5. Linear correlation between the nonsolvation contribution to the standard partial molar volume ($\Delta_n V_{298.15}^0$) for the Eu ion and its two acetate complexes [Eu(Ac)²⁺ and Eu(Ac)₂⁺] and the number of the ligands (acetate ions) in the complex. Symbols correspond to calculated values: for $n = 0$ —according to Slop98 and $n = 1$ and 2 according to experimental data (Table 5). The intersection of the approximation line and the vertical axis at $n = 3$ corresponds to $\Delta_n V_{298.15}^0$ for Eu(Ac)_{3(aq)}}.

Table 5. Calculated values of the solvation ($\Delta_s V_{298.15}^0$) and nonsolvation ($\Delta_n V_{298.15}^0$) contributions to the molar volumes $V_{298.15}^0$ of Eu^{3+} and Eu acetate complexes

Eu ion and complexes	Born parameter $\omega \times 10^{-5}$, cal/mol	Molar volume, cm^3/mol		
		$V_{298.15}^0$	$\Delta_s V_{298.15}^{0*}$	$\Delta_n V_{298.15}^{02*}$
Eu^{3+}	2.3161	-42.0 ^{3*}	-5.72	-36.28
$\text{Eu}(\text{Ac})^{2+}$	1.2998	11.78 ^{4*}	-3.21	14.99
$\text{Eu}(\text{Ac})_2^+$	0.2676	67.15 ^{4*}	-0.66	67.81
$\text{Eu}(\text{Ac})_{3, \text{aq}}$	0.0	119.6	0.0	119.6 ^{5*}

* $\Delta_s V_{298.15}^0 = \omega Q = -\omega 2.46848 \times 10^{-5}$ [24].

2* $\Delta_n V_{298.15}^0 = V_{298.15}^0 - \Delta_s V_{298.15}^0$.

3* Based on data from Slop98.

4* Our data in this paper.

5* Obtained by a linear extrapolation (Fig. 5) to $n = 3$.

computer program, we minimized the discrepancies between the experimental and calculated values of the Gibbs function for the neutral $\text{HAc}_{(\text{aq})}$ species and refined the coefficients (a_1 – a_4) of the HKF equation that specifies the baric dependence of this function. In this procedure, we preserved the reliably established value of the molar volume accepted in Slop98 and optimized the a_1 and a_2 parameters. The optimization procedure allowed us to achieve consistence between the measured and calculated pH values within 0.001 (Table 2). The refined HKF parameters of $\text{HAc}_{(\text{aq})}$ and the calculated pH values of the acetate buffers are listed in Tables 3 and 1.

Measurement Accuracy

Figure 2b demonstrates the measured e.m.f. values for all of the used buffer solutions and 0.01M HCl at 1 and 980 bar. In an e.m.f. vs. pH diagram, they are approximated by a straight line with a slope of -58.11 mV per pH unit, which is close to the theoretically predicted value. The maximum deviation of the

experimental points from the fitted straight line was, regardless of pressure, 1.5–2 mV, which corresponds to a pH inaccuracy of 0.03 units. The differences between the pH values determined by the two glass electrodes never exceeded 0.02. Based on the calibrations, we evaluated the accuracy of our pH measurements throughout the whole pressure interval (from 1 to 1000 bar) at ± 0.03 pH units.

However, the precision of the measurements in the same solution depending on pressure is much better (Table 2). The variations in the pH of the solution with changing pressure (from 1 to 1000 bar) were determined accurate to ± 0.3 – 0.4 mV or ± 0.005 – 0.007 pH units. Ignoring the changes in the diffusion potential with pressure changes, it can be assumed that

$$\Delta \text{pH} = \text{pH}_P - \text{pH}_{1 \text{ bar}} = -(E_P - E_{P=1 \text{ bar}})/58.11. \quad (3)$$

The error of the ΔpH measurements did not exceed ± 0.01 pH units.

Calculation Techniques

In this publication, the thermodynamic characteristics of species in aqueous solutions are described by the widely used Helgeson–Kirkham–Flowers state equation [19]. The standard state of aqueous species is assumed to be hypothetical 1m (molal) ideal solution, and the activity coefficient of water is assumed to be equal to one.

The pH of the standard solutions were calculated by the GIBBS computer program from the HCh program package [16, 17]. The thermodynamic properties of all species except $\text{HAc}_{(\text{aq})}$ were borrowed from the Slop98 database (the parameters of $\text{HAc}_{(\text{aq})}$ were refined as

Table 6. $\Delta_f G$ of Eu acetate complexes at 25°C and a pressure of 1 bar [11] and pressures of 490 and 980 bar (calculated from experimental data)

P , bar	$\Delta_f G$, kJ/mol		
	$\text{Eu}(\text{Ac})^{2+}$	$\text{Eu}(\text{Ac})_2^+$	$\text{Eu}(\text{Ac})_{3, \text{aq}}$
1	-960.559	-1340.148	-1714.674
490	-959.954	-1336.954	-1709.026
980	-959.298	-1333.900	-1703.689

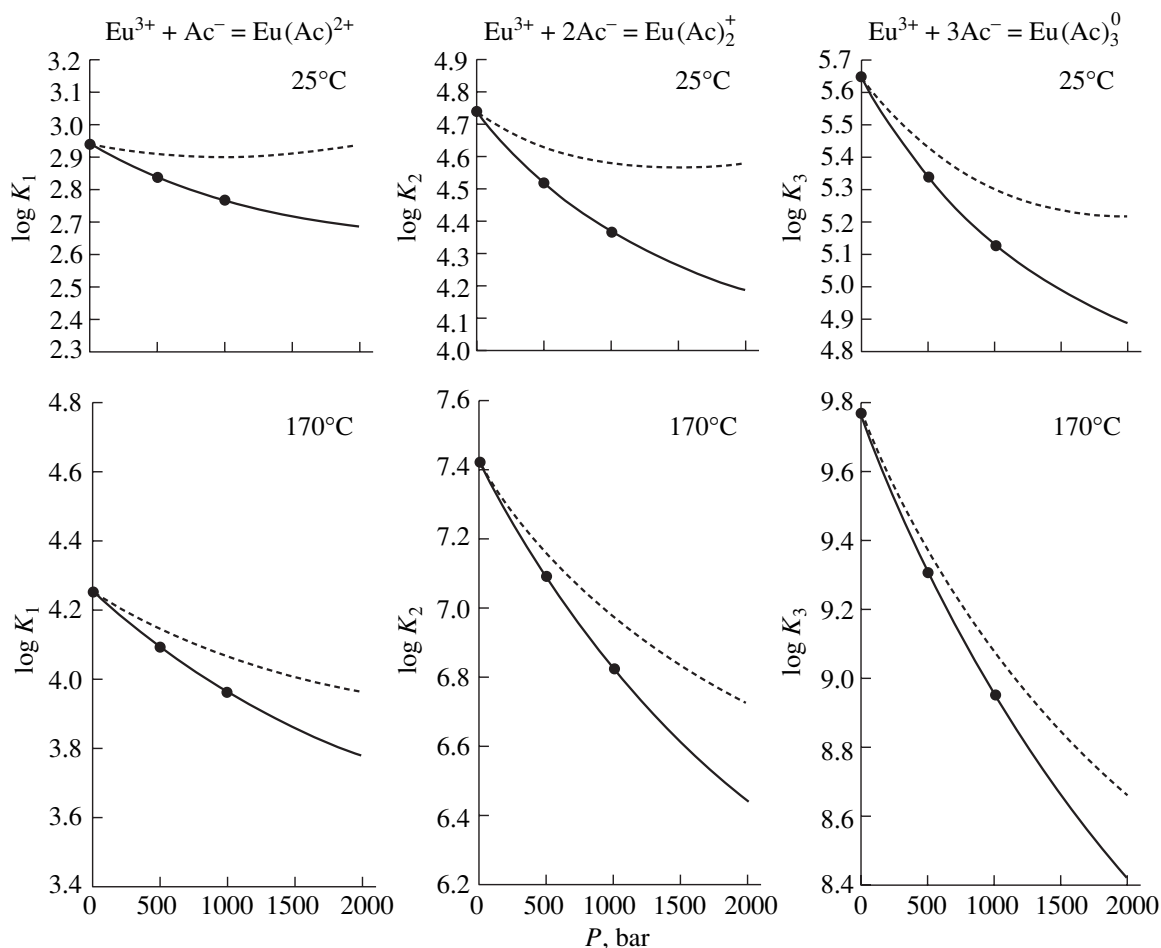


Fig. 6. Logarithm constant of the formation of Eu acetate complexes as a function of pressure at 25 and 170°C. Symbols correspond to experimental data, solid lines are their approximations according to the calculated thermodynamic characteristics of the Eu acetate complexes (Table 3). Dashed lines were calculated based on data from the Slop98 thermodynamic database.

described above). The pH of the biphthalate and borate buffers were not calculated but assumed from the results of direct potentiometric measurements of Kryukov and Zarubina [15]. However, the database contains no data on phthalic acid, therefore the baric parameters presented in Slop98 for boron hydroxide should obviously be revised. The baric parameters of $\text{HAc}_{(\text{aq})}$ were refined by the UT-HEL program [18].

The Gibbs standard free energy for Eu acetate complexes were calculated using the iteration technique by the GIBBS program. We studied the following aqueous species: CH_3COOH^0 , CH_3COO^- , $\text{NaCH}_3\text{COO}^0$, $\text{Na}(\text{CH}_3\text{COO})_2^-$, Eu^{3+} , $\text{Eu}(\text{CH}_3\text{COO})_2^{2+}$, $\text{Eu}(\text{CH}_3\text{COO})_2^+$, $\text{Eu}(\text{CH}_3\text{COO})_3^0$, Cl^- , HCl^0 , Na^+ , H^+ , OH^- , and H_2O . The thermodynamic parameters of all species except those of CH_3COOH^0 and Eu-Ac complexes were compiled from the Slop98 database, which was developed for the SUPCRT98 program package [2, 4, 5, 20, 21]. As the initial estimates for the Eu-Ac complexes and CH_3COOH^0 , we used data from [11] and from Table 3

in this paper. In the calculations, we used Cl^- in place of ClO_4^- . The activity coefficients of charged species were calculated by the extended Debye-Hückel equation. The ion-size parameter \tilde{a} was adopted equal to 4.5 Å for all species. We also assumed that the activities of all neutral species are equal to one. Note that the inaccuracies of the thermodynamic parameters of Na-Ac complexes practically do not affect the final results because of the relatively low concentrations of Na^+ in the standard and tested solutions.

EXPERIMENTAL RESULTS

Table 4 summarizes the results of our potentiometric measurements in acetate solutions with Eu at 25°C and pressures from 1 to 1000 bar. The values of $\Delta_f G$ for two Eu acetate complexes, $\text{Eu}(\text{Ac})_2^{2+}$ and $\text{Eu}(\text{Ac})_2^+$, were computed by iterations in such a manner that the pH values calculated at 490 and 980 bar corresponded to the experimental values. Then we optimized the param-

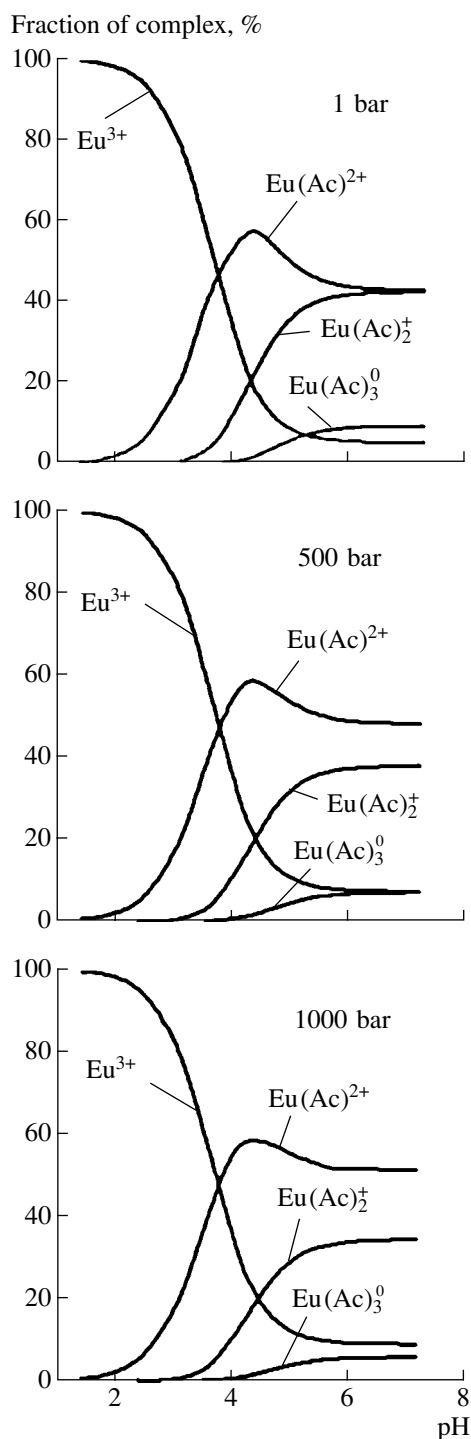


Fig. 7. Distribution of Eu^{3+} and Eu acetate complexes at 25°C as functions of pH at various pressures (1, 500, and 1000 bar). The solution contained 0.001m $\text{Eu}(\text{ClO}_4)_3$, 0.05m NaAc, and variable amounts of HClO_4 and NaClO_4 (ionic strength was close to 0.12).

eter a_1 by the UT-HEL program [18] to determine the new values for the molar volume and the baric parameters a_1 – a_4 for both complexes with regard for the “internal” correlations between them [22]. The volumes

newly obtained for the two charged acetate complexes allowed us to estimate the molar volume of the neutral complex $\text{Eu}(\text{Ac})_3^0$ by the linear correlation between the nonsolvation contribution to its value and the number of ligands, as was proposed by Hovey [23]. The results of these estimates are presented in Fig. 5 and Table 5. The procedure described above was resumed until the calculated pH value for all of the four solutions at 490 and 980 bar coincided with the experimental values accurate to 0.005 pH units (Table 4). The corresponding computed $\Delta_f G$ values for the acetate complexes at 490 and 980 bar are listed in Table 6. The refined thermodynamic and HKF parameters of the acetate complexes (computed by iterations) are listed in Table 3.

DISCUSSION

Our thermodynamic data presented in Table 5 were utilized to calculate the equilibrium constants of the formation of three Eu acetate complexes as functions of pressure (Fig. 6). The logarithms of all three constants decrease with increasing pressure, with this effect pronounced the more clearly, the greater the number of ligands in the complex. For comparison, this diagram also demonstrates the constants calculated from the data of Zotov et al. [11] that were used in the baric characteristics of complexes from the Slop98 thermodynamic database. The differences between the experimentally determined formation constants of acetate Eu complexes and those predicted based on Slop98 are greater (as large as 0.15–0.35 logarithmic units at a pressure of 1000 bar) at lower temperatures and decrease with increasing temperature.

Figure 7 presents the calculated fractions of Eu^{3+} and three Eu complexes depending on pH at 25°C and pressures of 1, 500, and 1000 bar. In these calculations, we assumed that the solutions contained 0.001m $\text{Eu}(\text{ClO}_4)_3$, 0.05m NaAc, and variable concentrations of HClO_4 and NaClO_4 at an ionic strength of approximately 0.12. As can be seen from the diagram, in spite of the noticeable changes in the complex formation constants with pressure (by factors of 1.5–2), the distribution of Eu^{3+} and its acetate complexes varies insignificantly. The only noteworthy change is the mild increase in the fraction of $\text{Eu}(\text{Ac})^{2+}$ with increasing pressure. This seems to be explained by the simultaneous increase in the dissociation constant of acetic acid. It is thus reasonable to suggest that, during the concurrent formation of Eu complexes with CH_3COO^- and Cl^- ions, the relative stability of the acetate complexes should increase relative to that of the chloride complexes with increasing pressure. However, the reliable comparison of complexes with different ligands at increasing pressure requires further experimental studying.

CONCLUSIONS

Our potentiometric measurements allowed us to determine the molar volumes and baric HKF parameters of two Eu acetate complexes: Eu(Ac)²⁺ and Eu(Ac)₂⁺. Using these values of the molar volumes and the corresponding correlations, we calculated the baric characteristics of the third neutral complex (Eu(Ac)₃⁰).

The stability of all Eu acetate complexes was determined to diminish with increasing pressure: as the pressure increases from 1 to 1000 bar, the formation constants of these complexes decrease by factors of approximately 1.5–3 at 25°C and 2–6 at 170°C. This effect is more significant, the greater the number of the ligands.

It is worth noting that a notable increase in the constants with pressure practically does not affect the distribution of dissolved Eu between the Eu³⁺ ion and its acetate complexes, i.e., a pressure increase (to 1–2 kbar) does not result in any radical Eu redistribution.

At the same time, there are significant discrepancies between the baric characteristics of Eu acetate complexes determined experimentally and predicted on the basis of known correlations in the widely used Slop98 thermodynamic database. For example, the difference between the molar volumes of Eu acetate complexes are as great as 8–12 cm³/mol. Our research demonstrates the necessity for conducting new experiments aimed at determining the baric characteristics of other REE complexes.

ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research, project no. 03-05-64788.

REFERENCES

1. R. I. Grauch, "Rare Earth Elements in Metamorphic Rocks," in *Geochemistry and Mineralogy of Rare Earth Elements*, Ed. by B. R. Lipin and G. A. McKay (Mineral. Soc. Am., Washington, 1989), pp. 147–167.
2. J. Haas, E. L. Shock, and D. Sassani, "Rare Earth Elements in Hydrothermal Systems: Estimates of Standard Partial Molal Thermodynamic Properties of Aqueous Complexes of the REE at High Pressures and Temperatures," *Geochim. Cosmochim. Acta* **59**, 4329–4350 (1995).
3. S. A. Wood, "The Geochemistry of the Rare Earth Elements and Yttrium: 1. Review of Available Low-Temperature Data for Inorganic Complexes and the Inorganic Speciation of Natural Waters," *Chem. Geol.* **82**, 159–186 (1990).
4. E. L. Shock and C. M. Koretsky, "Metal–Organic Complexes in Geochemical Processes: Calculation of Standard Partial Molal Thermodynamic Properties of Aqueous Complexes at High Pressures and Temperatures," *Geochim. Cosmochim. Acta* **57**, 4899–4922 (1993).
5. S. A. Wood, "The Geochemistry of the Rare Earth Elements and Yttrium: 2. Theoretical Predictions of Speciation in Hydrothermal Solutions to 350°C at Saturation Water Pressure," *Chem. Geol.* **88**, 99–125 (1990).
6. E. L. Shock, "Organic Acids in Hydrothermal Solutions: Standard Molal Thermodynamic Properties of Carboxylic Acids and Estimates of Dissociation Constants at High Temperatures and Pressures," *Am. J. Sci.* **V**, 496–580 (1995).
7. C. H. Gammons, S. A. Wood, and A. E. Williams-Jones, "The Aqueous Geochemistry of the Rare Earth Elements and Yttrium: VI. Stability of Neodymium Chloride Complexes from 25 to 300°C," *Geochim. Cosmochim. Acta* **60**, 4615–4630 (1996).
8. A. A. Migdisov, A. E. Williams-Jones, and O. M. Suleimenov, "Solubility of Chlorargyrite (AgCl) in Water Vapor at Elevated Temperatures and Pressures," *Geochim. Cosmochim. Acta* **63**, 3817–3827 (2002).
9. S. A. Wood, D. A. Palmer, D. J. Wesolowski, and P. Ben-zeth, "The Aqueous Geochemistry of the Rare Earth Elements and Yttrium: XI. The Solubility of Nd(OH)₃ and Hydrolysis of Nd³⁺ from 30 to 290°C at Saturated Water Vapor Pressure with in-Situ pH_m Measurements," in *Water–Rock Interactions, Ore Deposits, and Environmental Geochemistry: A Tribute to David A. Crear*, Ed. by R. Hellmann and S. A. Wood, *Geochem. Soc. Spec. Publ.*, No. 7, 229–256 (2002).
10. S. A. Wood, D. J. Wesolowski, and D. A. Palmer, "The Aqueous Geochemistry of the Rare Earth Elements: IX. A Potentiometric Study of Nd³⁺ Complexation with Acetate in 0.1 Molal NaCl Solution from 25 to 225°C," *Chem. Geol.* **167**, 231–253 (2000).
11. A. V. Zotov, B. R. Tagirov, I. I. Diakonov, and K. V. Ragnarsdottir, "A Potentiometric Study of Eu³⁺ Complexation with Acetate Ligand from 25 to 170°C at P_{sat}" *Geochim. Cosmochim. Acta* **66**, 3599–3613 (2002).
12. A. Sonesson, "On the Chemistry of the Tervalent Rare Earth Ions: I. The Acetate Systems of Lanthanum, Cerium, Neodymium, and Gadolinium," *Acta Chem. Scand.* **12**, 165–181 (1958).
13. I. Grenthe, "On the Stability of the Acetate, Glycolate, and Thioglycolate Complexes of Tervalent Europium and Americium," *Acta Chem. Scand.* **16**, 1695–1712 (1962).
14. S. Deberdt, S. Castet, J.-L. Dandurand, et al., "Experimental Study of La(OH)₃ and Gd(OH)₃ Solubilities (25 to 150°C), and La-Acetate Complexing (25 to 80°C)," *Chem. Geol.* **151**, 349–372 (1998).
15. P. A. Kryukov and S. A. Zarubina, "Determination of the pH of Some Reference Buffer Solutions under Pressures up to 1030 × 10⁵ Pa and Temperatures from 0 to 25°C," *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim.*, No. 2, 56–66 (1982).
16. Yu. V. Shvarov, "Algorithmization of the Numeric Equilibrium Modeling of Dynamic Geochemical Processes," *Geokhimiya*, No. 6, 646–652 (1999) [*Geochem. Int.* **37** (6), 571–576 (1999)].
17. Y. Shvarov and E. Bastrakov, *A Software Package for Geochemical Equilibrium Modeling. User's Guide* (Australian Geological Survey Organization, Department of Industry, Science, and Resources, 1999).

18. Yu. V. Shvarov, *UT-HEL: A Program for Calculation of the HKF Characteristics of Water Particles, Version 2* (Geol. Fak. Mosk. Gos. Univ., Moscow, 1995), unpublished [in Russian].
19. H. C. Helgeson, D. H. Kirkham, and G. C. Flowers, "Theoretical Prediction of the Thermodynamic Behavior of Aqueous Electrolytes at High Pressures and Temperatures: IV. Calculation of Activity Coefficients, Osmotic Coefficients, and Apparent Molal and Standard and Partial Molal Properties to 600°C and 5 kb," *Am. J. Sci.* **281**, 1249–1516 (1981).
20. J. M. Johnson, E. H. Oelkers, and H. C. Helgeson, "SUPCRT92: A Software Package for Calculating the Standard Molal Thermodynamic Properties of Minerals, Gases, Aqueous Species, and Reactions from 1 to 5000 bars and 0–1000°C," *Comput. Geosci.* **18**, 899–947 (1992).
21. E. L. Shock, D. A. Sassani, M. Wills, and D. A. Sverjensky, "Inorganic Species in Geologic Fluids: Correlations among Standard Molal Thermodynamic Properties of Aqueous Ions and Hydroxide Complexes," *Geochim. Cosmochim. Acta* **61**, 907–950 (1997).
22. E. L. Shock and H. C. Helgeson, "Calculation of the Thermodynamic and Transport Properties of Aqueous Species at High Pressures and Temperatures: Correlations Algorithms for Ionic Species," *Geochim. Cosmochim. Acta* **52**, 2009–2036 (1988).
23. J. K. Hovey, Ph. D. Thesis (Univ. Alberta, Edmonton, 1988).
24. J. C. Tanger and H. C. Helgeson, "Calculation of the Thermodynamic and Transport Properties of Aqueous Species at High Pressures and Temperatures: Revised Equations of State for the Standard Partial Molal Properties of Ions and Electrolytes," *Am. J. Sci.* **288**, 19–98 (1988).