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# Physical Chemistry

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## Abstract

## Full Text

*Physical Chemistry*

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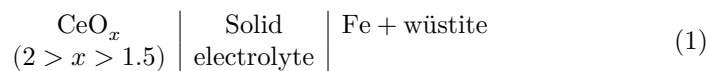
# THERMODYNAMIC PROPERTIES OF CERIUM OXIDES

The thermodynamic properties of compounds of the rare-earth elements have as yet been studied very little. This also applies to cerium.

The aim of our work was to obtain thermodynamic data which, together with those already available in the literature, would make it possible to give a sufficiently complete thermodynamic characterization of the cerium–oxygen system. The literature contains the following information on the thermodynamic properties of cerium oxides and metallic cerium. Parkinson, Simon, and Spedding <sup>(1)</sup> measured the low-temperature heat capacity of metallic cerium and obtained the value of its standard entropy ( $S_{298}^0 = 16.64$  e.u.). Spedding, McKeown, and Daane measured the heat capacity of metallic cerium at high temperatures <sup>(2)</sup>. Westrum and Beall \* measured the heat capacity of  $\text{CeO}_2$  at low temperatures and gave  $S_{298}^0 = 14.89$  e.u.. Huber and Holley <sup>(3)</sup>, by combustion of metallic cerium in a calorimetric bomb for the reaction  $\text{Ce} + \text{O}_2 \rightarrow \text{CeO}_2$ , found  $\Delta H_{298}^0 = -260.18$  kcal.

Earlier, we measured by the mixing method in a massive calorimeter the high-temperature heat capacity of  $\text{CeO}_2$  <sup>(4)</sup> and  $\text{Ce}_2\text{O}_3$  <sup>(5)</sup>, and with the aid of a calorimetric bomb for the reaction  $\text{Ce}_2\text{O}_3 + 1/2\text{O}_2 \rightarrow 2\text{CeO}_2$  obtained  $\Delta H_{298}^0 = -85.43$  kcal <sup>(6)</sup>.

In the present work the thermodynamic properties of cerium oxides were studied in the composition interval  $\text{CeO}_2\text{--CeO}_{1.5}$ . For this purpose we used the method of e.m.f. with a solid electrolyte, recently proposed by Kiukkola and Wagner <sup>(7)</sup>, and also measured the equilibrium constants of cerium oxides with hydrogen. In <sup>(8)</sup> a new, more convenient apparatus implementation of the Kiukkola-Wagner method is described, which we used in the present work in measuring the e.m.f. of a cell of the form:



Mixed crystals in the  $\text{ThO}_2\text{--La}_2\text{O}_3$  system, possessing purely ionic conductivity, were used as the electrolyte. The electrolyte was checked for the absence of

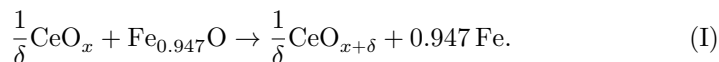
electronic conductivity, and the Fe + wüstite electrodes were prepared in the same way as in (7).

The CeO electrodes were pressed at a pressure of 10 t/cm<sup>2</sup> from a mixture of corresponding amounts of CeO<sub>2</sub> and Ce<sub>2</sub>O<sub>3</sub>. Preliminary annealing of the pellets was not required, since the 5–7 hr needed to heat the cell to the required temperature proved sufficient for the formation of the oxide CeO from the mixture. The oxygen content in the specimen was determined after the e.m.f. measurement by the “active oxygen” method (9).

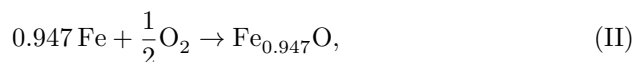
In view of the extreme pyrophoricity of CeO, all manipulations with it during removal of the pellet from the apparatus and transfer of it to the flask for analysis of the oxygen content were carried out in an argon atmosphere.

\* E. F. Westrum, A. F. Beall, private communication—will be published in J. Chem. Phys., 1961.

The values of the equilibrium emf of cell (1) correspond to the change in the isobaric potential ( $\Delta\bar{G}_I^0 = -2FE$ )\* of the current-producing reaction:



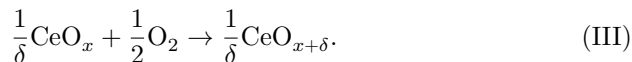
Combining  $\Delta\bar{G}_I^0$  with  $\Delta\bar{G}_{II}^0$  for the reaction of formation of wüstite from the elements



for which, according to the data of Darken and Gurry (10) and Peters and Möbius (11),

$$\Delta G_{II} = -63570 + 16.06T \quad (1073 - 1270^\circ\text{K}),$$

makes it possible to calculate the differential ( $\Delta\bar{G}_{III}^0$ ) of the reaction



**Table 1**

Composition of preparation			Composition of preparation		
CeO <sub>x</sub>	Temp., °K	E, V	CeO <sub>x</sub>	Temp., °K	E, V
CeO <sub>1,581</sub>	1038	0,4166	CeO <sub>1,702</sub>	1065	0,3599
CeO <sub>1,581</sub>	1156	0,3912	CeO <sub>1,702</sub>	1136	0,3448

Composition of preparation			Composition of preparation		
CeO <sub>x</sub>	Temp., °K	E, V	CeO <sub>x</sub>	Temp., °K	E, V
CeO <sub>1,581</sub>	1273	0,3714	CeO <sub>1,702</sub>	1263	0,3237
CeO <sub>1,582</sub>	1052	0,4141	CeO <sub>1,746</sub>	967,5	0,3640
CeO <sub>1,582</sub>	1145	0,3951	CeO <sub>1,746</sub>	1066	0,3461
CeO <sub>1,582</sub>	1267	0,3722	CeO <sub>1,746</sub>	1129	0,3365
CeO <sub>1,597</sub>	972	0,4304	CeO <sub>1,746</sub>	1220	0,3238
CeO <sub>1,597</sub>	1076	0,4090	CeO <sub>1,746</sub>	1282	0,3181
CeO <sub>1,597</sub>	1120	0,4006	CeO <sub>1,782</sub>	1038	0,2747
CeO <sub>1,597</sub>	1226	0,3781	CeO <sub>1,782</sub>	1133	0,2394
CeO <sub>1,597</sub>	1254	0,3745	CeO <sub>1,782</sub>	1165	0,2275
CeO <sub>1,663</sub>	1018	0,3995	CeO <sub>1,782</sub>	1272	0,1856
CeO <sub>1,663</sub>	1047	0,3954	CeO <sub>1,870</sub>	1057	0,1526
CeO <sub>1,663</sub>	1058	0,3929	CeO <sub>1,870</sub>	1086	0,1448
CeO <sub>1,663</sub>	1139	0,3782	CeO <sub>1,870</sub>	1134	0,1290
CeO <sub>1,663</sub>	1228	0,3620	CeO <sub>1,870</sub>	1233	0,0940
CeO <sub>1,663</sub>	1272	0,3543	CeO <sub>1,890</sub>	1061	0,1145
CeO <sub>1,700</sub>	1020	0,3674	CeO <sub>1,890</sub>	1079	0,1093
CeO <sub>1,700</sub>	1089	0,3532	CeO <sub>1,890</sub>	1208	0,0502
CeO <sub>1,700</sub>	1180	0,3360	CeO <sub>1,96</sub>	1033	0,1084
CeO <sub>1,700</sub>	1250	0,3240	CeO <sub>1,96</sub>	1089	0,0820
CeO <sub>1,700</sub>	1282	0,3200	CeO <sub>1,96</sub>	1138	0,0542
			CeO <sub>1,96</sub>	1253	-0,0186

Table 1 gives the results of measurement of the emf of cell (1) at various temperatures. For each of the studied compositions CeO<sub>x</sub>, over the entire temperature interval in which the measurements were made, *E* varies linearly with temperature according to the equation  $E = a + bT$ .

**Table 2**

Composition	$-b$					Composition	$-b$						
	$a$ in $E_V = E_V = \Delta G_{III}^0 - \Delta G_{III}^0 - \lg P_{O_2}(\text{atm})$	$10^4$ in	$-a_1$ in	$b_1$ in	$-A$ in		$B$ in	$a$ in	$10^4$ in	$-a_1$ in	$b_1$ in	$-A$ in	$B$ in
	$a + bT$	$a + bT$	$a_1 + b_1T$	$a_1 + b_1T$	$\frac{A}{T} + B$	$\frac{A}{T} + B$	$a + bT$	$a + bT$	$a_1 + b_1T$	$a_1 + b_1T$	$\frac{A}{T} + B$	$\frac{A}{T} + B$	
1,581	0,6460	1,929	91	24,96	40	10,91	1,746	0,4845	1,307	85	22,09	37	9,65
			980		200					920		550	
1,582	0,6360	2,096	92	25,73	40	11,24	1,782	0,6714	3,816	94	33,66	41	14,51
			900		600					540		310	

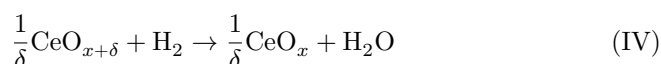
Composition	$E_V = E_V = \Delta \bar{G}_{III}^0 - \Delta \bar{G}_{III}^0 - \lg P_{O_2} \lg(P_{O_2})_{(atm)}$					$E_V = E_V = \Delta \bar{G}_{III}^0 - \Delta \bar{G}_{III}^0 - \lg P_{O_2} \lg(P_{O_2})_{(atm)}$							
	$a$ in $a +$ $b_1 T$	$10^4$ in $a_1 +$ $b_1 T$	$-a_1$ in $a_1 +$ $b_1 T$	$b_1$ in $a_1 +$ $b_1 T$	$-A$ in $\frac{A}{T} +$ $B$	$B$ in $\frac{A}{T} +$ $B$	$a$ in $a +$ $b_1 T$	$10^4$ in $a_1 +$ $b_1 T$	$-a_1$ in $a_1 +$ $b_1 T$	$b_1$ in $a_1 +$ $b_1 T$	$-A$ in $\frac{A}{T} +$ $B$	$B$ in $\frac{A}{T} +$ $B$	
1,597	0,620	1,960	92	25,10	40	10,97	1,870	0,511	3,380	87	31,67	38	13,8
			170		280					160		090	
1,663	0,584	2,810	90	24,40	39	10,66	1,890	0,587	0,450	90	36,59	39	16,00
			516		560					640		610	
1,700	0,549	1,799	88	24,36	38	10,64	1,960	0,715	5,850	96	43,04	42	18,81
			920		860					590		209	
1,702	0,561	1,803	89	24,41	38	10,67							
			020		900								

Table 2 gives the coefficients  $a_1, b_1$  of this equation for  $CeO_x$  preparations with  $x$  from 1,581 to 1,96. The same table gives the coefficients

\* A bar over the top denotes differential thermodynamic quantities referred to the oxide of the given composition  $CeO_x$ .

$a_1$  and  $b_1$  of the equation  $\Delta \bar{G}_{III}^0 = a_1 + b_1 T$  for reaction (III), and the coefficients  $A$  and  $B$  of the equation  $\lg P_{O_2(atm)} = \frac{A}{T} + B$ , which relates the dissociation pressure of cerium oxide of a given composition  $CeO_x$  to temperature.

Measurement of the equilibrium constants  $K_p = \frac{p_{H_2O}}{p_{H_2}}$  for the reduction reaction of cerium oxides  $CeO_x$  by hydrogen



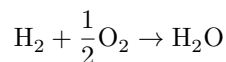
was carried out by the circulation method in an apparatus described in (12).

Because of the pyrophoric nature of the intermediate cerium oxides, either  $CeO_2$  or  $Ce_2O_3$  was taken for measurement of the equilibrium constants; the composition of the equilibrium oxide was then determined by subsequent oxidation to  $CeO_2$ . All operations were carried out in a chamber with purified nitrogen.

Combining the found values

$$\Delta \bar{G}_{IV}^0 = -RT \ln K_p$$

with  $\Delta \bar{G}_V^0$  of the reaction of formation of water vapor



$$(\Delta G_V^0 = -59000 + 13.38 T \text{ according to (13)}) \quad (\text{V})$$

also makes it possible to calculate  $\Delta \bar{G}_{\text{III}}^0$ . The results of measurements of the equilibrium constants of reaction (IV) and the values of  $\Delta G_{\text{III}}^0$  and  $\lg P_{\text{O}_2}$  calculated from them are given in Table 3.

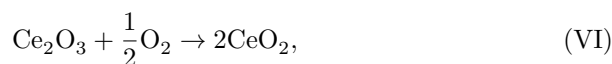
**Table 3**

Composition of the prepara- tion $\text{CeO}_x$	Equilibrium tempera- ture, °K	$K_p =$ $\frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}}$	$\Delta G_{\text{IV}}^0$ , cal	$\Delta \bar{G}_{\text{III}}^0$ , cal	$\lg P_{\text{O}_2}$ , atm
1.837	1168	0.0152	9710	-53 100	-19.9
1.852	1167	0.0280	8290	-51 680	-19.4
1.875	1166	0.0311	8040	-51 430	-19.3
1.887	1168	0.0633	6410	-49 800	-18.6
1.829	1251	0.0968	5820	-48 000	-16.7
1.884	1255	0.144	4880	-47 090	-16.4
1.921	1255	0.625	1170	-43 400	-15.1

**Fig. 1.** Curves of the dependence of the dissociation pressure of cerium oxides on composition. Recorded by different methods: *a* –e.m.f., *b* –equilibrium, *c* –Bauer’ s data.

By the time our work was completed, Brauer (14) had published data on the dissociation pressure of cerium oxides obtained by the dynamic method. A comparison of Brauer’ s data with ours is shown in Fig. 1. As follows from Fig. 1, the form of the isotherms characterizing the dependence of the dissociation pressure of the oxides on composition over the entire temperature range studied is the same for us as for Brauer. Consequently, our data confirm the phase relationships established by Brauer in this system. The discrepancy between the values of  $\lg P_{\text{O}_2}$  from our data and from Brauer’ s data does not exceed 1.5-2%. Taking into account the difference in methods, such agreement of the data should be considered good.

The thermodynamic quantities characterizing the reaction



were found by graphical integration of the isotherms  $\Delta \bar{G}_{\text{III}}^0$ —composition  $\text{CeO}_x$  at  $1.5 \leq x \leq 2$  for temperatures of 973, 1073, 1173, and 1273°K. The values of  $\Delta G_{\text{VI}}^0$  found are given in Table 4. On the basis of these data and the value  $(\Delta H_{298})_{\text{VI}} = -85.43$  kcal (6), taking into account the dependence of the heat capacity of  $\text{CeO}_2$

and  $\text{Ce}_2\text{O}_3$  on temperature (<sup>4,5</sup>), an equation was obtained for  $\Delta G_{\text{VI}}^0$  in the temperature interval 298–1273° K.

$$\Delta G_{\text{VI}}^0 = -85500 - 4.007 \lg T + 1.495 \cdot 10^{-3} T^2 - \frac{0.47 \cdot 10^5}{T} + 35.8T.$$

**Table 4**

Temp., °K	$-\Delta G_{\text{VI}}^0$ , cal, by integration	$-\Delta G_{\text{VI}}^0$ , cal, by equation	$-\Delta S_{\text{VI}}^0$ , e.u.
298.2		77 800	25.6
973.2	61 690	60 940	25.0
1073.2	59 150	58 400	25.2
1173.2	55 990	55 900	25.3
1273.2	52 670	53 400	25.5

Table 4 gives the values of  $\Delta G_{\text{VI}}^0$  and  $\Delta S_{\text{VI}}^0$ , calculated on the basis of this equation.

Having obtained  $(\Delta S_{298}^0)_{\text{VI}}$  and taking, according to (<sup>1</sup>), for cerium  $S_{298}^0 = 16.64$  e.u. and for  $\text{CeO}_2$   $S_{298}^0 = 14.89$  e.u. (<sup>2</sup>), we find  $(S_{298}^0)_{\text{Ce}_2\text{O}_3} = 30.8$  e.u.

Having this value and the other data given earlier in the article, it is not difficult to calculate all the thermodynamic quantities characterizing the reaction



**Table 5**

Oxide	$\Delta G_{298}^0$ , kcal/mole	$\Delta H_{298}^0$ , kcal/mole	$S_{298}^0$	$\Delta G_T^\circ, \Delta H_T^\circ, C_p$
Ce <sub>2</sub> O <sub>3</sub>	-412.3	-435.0	30.8	$\Delta G_T^0 =$ $-434189 +$ $0.88 T \lg T -$ $3.83 \cdot$ $10^{-3} T^2 +$ $0.40 \cdot$ $10^{-6} T^3 -$ $\frac{1.41 \cdot 10^5}{T} +$ $74.02 T$ $(\text{cal/mole}) \Delta H_T^0 =$ $-434189 -$ $0.38 T +$ $3.83 \cdot$ $10^{-3} T^2 -$ $0.79 \cdot$ $10^{-6} T^3 -$ $\frac{2.82 \cdot 10^5}{T}$ $(\text{cal/mole}) C_p$ of oxide $= 23.31 +$ $1.26 \cdot 10^{-2} T$ $(\text{cal/deg} \cdot$ mole)(298-1003°K)

Oxide	$\Delta G_{298}^0$ , kcal/mole	$\Delta H_{298}^0$ , kcal/mole	$S_{298}^0$	$\Delta G_T^\circ, \Delta H_T^\circ, C_p$
CeO <sub>2</sub>	-245.1	-260.2	14.9	$\Delta G_T^0 =$ $-259845 -$ $1.54 T \lg T -$ $1.16 \cdot$ $10^{-3} T^2 +$ $0.20 \cdot$ $10^{-6} T^3 -$ $\frac{0.94 \cdot 10^5}{T} +$ $54.90 T$ (cal/mole) $\Delta H_T^0 =$ $-259845 -$ $0.68 T +$ $1.16 \cdot$ $10^{-3} T^2 -$ $0.39 \cdot$ $10^{-6} T^3 -$ $\frac{1.88 \cdot 10^5}{T}$ (cal/mole) $C_p$ of oxide $= 14.59 +$ $4.89 \cdot 10^{-3} T$ (cal/deg · mole)(298-1003°K)

Table 5 compiles the thermodynamic properties of CeO<sub>2</sub> and Ce<sub>2</sub>O<sub>3</sub> obtained in the present work and previously known from the literature.

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*Note: Figure translations are in progress. See original paper for figures.*

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