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Thermodynamics of Double Oxides
II. Study of the CoO–TiO_2 System by the emf Method

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The emf method using an oxide-ion-conducting electrolyte has been used to determine the thermodynamic properties of the CoO–TiO_2 system in the temperature range 1160–1420 K. Electrochemical reduction and oxidation of the electrodes showed that the compositional boundary for $CoTiO_{3-y}$ is near the composition $CoTiO_{2.85}$. Standard values of $\Delta H°$ and $\Delta G°$ of formation of $CoTiO_3$ and CO_2TiO_4 from oxides and elements, as well as entropies for these compounds, are presented and compared with the literature data. The discrepancy in $\Delta H°$ values of formation from oxides for some spinels obtained from emf and gas equilibrium data and by high-temperature solution calorimetry is discussed.

Introduction

The thermodynamic properties of the phases $CoTiO_3$ and Co_2TiO_4 existing in the CoO–TiO_2 system (*1*) are necessary for comparing the thermodynamic stability of compounds of the type MeTiO$_3$, Me_2TiO$_4$, MeAl$_2$O$_4$, and MeCr$_2$O$_4$ (Me = Fe, Co, Ni) in the course of their reduction by gaseous reducing agents at high temperatures. An analysis of the results of the works (*1, 2, 8–20, 12*) devoted to the determination of the thermodynamic parameters for the reactions of formation of $CoTiO_3$ and Co_2TiO_4 from oxides (ΔG°_T, ΔH°_T, ΔS°_T) by various heterogeneous equilibrium methods, the emf method, and calorimetry indicates that:

(1) for $CoTiO_3$ the discrepancy in the values of ΔH°_T and ΔS°_T in approximately the same temperature range is 6.3 kJ mole^{-1} and 6.7 J T^{-1} mole^{-1};

(2) for Co_2TiO_4 the discrepancy in ΔH°_T reaches about 20.9 kJ mole^{-1}.

An analysis of the accuracy of the published data shows that these discrepancies evidently result from systematic errors in some of the cited works which necessitates the conduct of independent experiments on the determination of the thermodynamic properties of these phases.

Experimental

The thermodynamic properties of titanates in the CoO–TiO_2 system were studied by the emf method in cells of the type

$$(-)\ \mathrm{Pt}|\underset{\mu^{\mathrm{I}}_{\langle \mathrm{O}\rangle}}{\langle \mathrm{M_IO}\rangle}|\mathrm{O}^{-2}|\underset{\mu^{\mathrm{II}}_{\langle \mathrm{O}\rangle}}{\langle \mathrm{M_{II}O}\rangle}|\mathrm{Pt}\ (+) \tag{I}$$

where $\mu^{\mathrm{I}}\langle \mathrm{O}\rangle$ and $\mu^{\mathrm{II}}\langle \mathrm{O}\rangle$ are the chemical potentials of oxygen in the electrodes $\langle \mathrm{M_IO}\rangle$ and $\langle \mathrm{M_{II}O}\rangle$ which represent oxide compounds mixed with the products of their equilibrium reduction.

Experiments were conducted in cell ar-

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rangements with a nonseparated gas space (*3*) and with a separated gas space (*4*).

Polished ceramic disks made of 0.99 ThO_2 + 0.01 CaO were used as a solid oxide-ion electrolyte in measurements of the emf in the device with a nonseparated gas space. Vacuum-tight ceramic tubes of the composition 0.85 ZrO_2 + 0.15 CaO were used in the devices with a separated gas space. To check the electrolytes for the absence of electron conductivity we have measured the emf's of the cell

$$(-)\ \mathrm{Pt}\ |\ \mathrm{Fe_{0.95}O,Fe}\ \left|\ \begin{matrix}\mathrm{ThO_2}\\ (\mathrm{CaO})\end{matrix}\ \text{or}\ \begin{matrix}\mathrm{ZrO_2}\\ (\mathrm{CaO})\end{matrix}\ \right|\ \mathrm{CoO,Co}\ |\ \mathrm{Pt}\ (+) \tag{II}$$

with the cell reaction:

$$\mathrm{CoO} + 0.95\ \mathrm{Fe} = \mathrm{Fe_{0.95}O} + \mathrm{Co}. \tag{1}$$

Thirty values of E_{II} obtained in the interval 1100–1420 K are described by the equation

$$E_{\mathrm{II}}(\pm 0.0018) = 0.1459\ (\pm 0.0066) + 3.37(\pm 0.25) \times 10^{-5}\ T,\ \mathrm{V}$$

and are in good agreement with other independent measurements of the emf of this cell (*5*). The values of $\bar{t}_{\mathrm{ion}}$ for the electrolytes used, which were calculated from the values of E of cell II and from the calorimetric data for $Fe_{0.95}O$ and CoO (*11*), were found to be 1.00 ± 0.01. This points to the absence of a noticeable fraction of electron conductivity at oxygen pressures which are set over the mixture $Fe_{0.95}O$ + Fe.[1]

Using the dependence from Ref. (*6*)

$$\Delta G^{\circ}/\mathrm{kJ\ mole^{-1}} \pm 0.3 = -265.3\ (\pm 0.8) + 65.52\ (\pm 0.63) \times 10^{-3} \times T$$

for the formation of wüstite from elements and the dependence of E_{II} on T, for the reaction

$$\mathrm{Co} + \tfrac{1}{2}\,\mathrm{O_2} = \mathrm{CoO} \tag{2}$$

for the interval 1100–1420 K we obtain

$$\Delta G_2^{\circ}/\mathrm{kJ\ mole^{-1}} \pm 0.4 = -236.8 + 72.4 \times 10^{-3}\ T.$$

The enthalpy and entropy change of this reaction for the middle of the temperature range covered is:

$$\Delta H_2^{\circ}\ (1260\ \mathrm{K}) = -(236.8 \pm 1.7)\ \mathrm{kJ\ mole^{-1}}$$

$$\Delta S_2^{\circ}\ (1260\ \mathrm{K}) = -(72.4 \pm 0.8)\ \mathrm{J\ T^{-1}\ mole^{-1}}.$$

The values are in good agreement with the high-temperature parameters of the reaction (2) recommended in Refs. (*7, 11*).

For studying the thermodynamic properties of cobalt titanates in the interval 1150–1420 K we have measured the emf's of the cells

$$(-)\mathrm{Pt}\ |\ \mathrm{Fe_{0.95}O,Fe}\ \left|\ \begin{matrix}\mathrm{ThO_2}\\ (\mathrm{CaO})\end{matrix}\ \text{or}\ \begin{matrix}\mathrm{ZrO_2}\\ (\mathrm{CaO})\end{matrix}\ \right|\ \mathrm{CoTiO}_x\ |\ \mathrm{Pt}\ (+) \tag{III}$$

$$(-)\mathrm{Pt}\ |\ \mathrm{Fe_{0.95}O,Fe}\ \left|\ \begin{matrix}\mathrm{ThO_2}\\ (\mathrm{CaO})\end{matrix}\ \right|\ \mathrm{CoTiO_3,Co,Co_2TiO_4}\ |\ \mathrm{Pt}\ (+) \tag{IV}$$

where the index for oxygen (x) is 2.75, 2.80, 2.85, 3.0.

Cobaltous oxide was obtained by the decomposition of $Co(NO_3)_2$ (chemically pure grade) in a vacuum of 10^{-5} Torr at

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[1] According to the available data (*1, 2, 8–10*) and the data obtained in the present paper the partial oxygen pressures over the equilibrium products of the partial reduction of $CoTiO_3$ and Co_2TiO_4 are higher than P_{O_2} over the mixture $Fe_{0.95}O$ + Fe.

1100°C. Cobalt titanates $CoTiO_3$ and Co_2TiO_4 were synthesized in air at 1200°C from CoO and TiO_2 (rutile of chemically pure grade) for 200 hr with intermediate grinding in an agate mortar after 50 hr. To protect the phases from traces of reducing agents in the gas phase, crucibles with specimens were covered by a platinum cup with CoO powder. The investigated electrodes $CoTiO_x$ of the above-mentioned compositions were prepared from the corresponding amounts of CoO, Co, and TiO_2 (rutile) by prolonged (300 hr) heating in vacuum at 1323–1373 K with an intermediate grinding after each 50 hr. The X-ray powder analysis of the heated specimens carried out in a Guinier camera has shown that:

(1) the specimens of the compositions $CoTiO_{2.75}$ and $CoTiO_{2.80}$ represent a heterogeneous mixture of three phases: defect cobalt metatitanate $CoTiO_{3-y}$ (where y is the deficit of oxygen), TiO_2 (rutile), and Co;

(2) the specimens of the compositions $CoTiO_{2.85}$ and $CoTiO_3$ represent homogeneous phases and have the structure of ilmenite. An analysis of the specimens $CoTiO_{2.85}$ and $CoTiO_3$ for the content of oxygen was carried out before and after the experiments by weighing the initial and oxidized specimens up to the stoichiometric composition $CoTiO_3$. Oxidation was carried out in a current of dried oxygen at 900°C for 50 hr as was described in Ref. (*21*). As a result, the following values for the index for oxygen were obtained: $x = 2.86 \pm 0.01$ and $x = 3.00 \pm 0.01$, respectively.

The electrodes of cell IV were prepared from the mixture of Co_2TiO_4, $CoTiO_3$, and Co-powder and were heated in evacuated double silica ampoules at 1050°C for 200 hr. After the experiments, the phase composition of all electrodes was examined by X-ray diffraction.

Measurements of the emf in cell III with the oxygen index $x = 2.75$ or 2.80 were made in the device with a nonseparated gas space and with $x = 2.85$ or 3.00 in the device with a separated gas space.

Preliminary experiments in the device with a nonseparated gas space showed that the measured potentials are sensitive to the presence of traces of reducing agents in the gas phase. The experimentally observed partial reduction of the surfaces of the electrodes resulted in a slow drift of the potentials. In order to avoid this, before the experiments the cell area was fitted with a special silica cover in the expanded upper part of which held small pieces of CoO near the bottom of the cell. The preliminary evacuation of the device in the course of heating was carried out through a system of adsorption traps cooled with liquid N_2. The experiments were conducted in an atmosphere of spectrally pure argon.

In the present work we have measured the values of E over a small temperature range 1150 K $\leq T \leq$ 1415 K and approximated the obtained dependences for E by the linear equations

$$E(\pm t_{0.05} \times S^*) = a\ (\pm t_{0.05} \times \alpha) + (\pm t_{0.05} \times \beta) \times T, \quad \text{(V)}$$

where S^* is the root mean-square error of the calculated value of E, α and β are the errors in the terms a and b, and $t_{0.05}$ is the Student criterion for the confidence limit of 95% probability.

Results

For experiments in which the reduction of electrode surfaces was ruled out, the equilibrium values of the potentials were established practically instantaneously, were stable with time, and were independent of the way of reaching the temperature. The constant values of the emf for each temperature were held from 3 to 12 hr, and the deviation of the measured potentials from their mean values did not exceed 0.0005 V.

TABLE I

EXPERIMENTAL VALUES FOR THE CELLS ARE DESCRIBED BY THE EQUATIONS $E = a + bT(\mathrm{K})$[a]

Cell	x	a	$b \times 10^5$	$\pm t_{0.05} \times S^*$	$\pm t_{0.05} \times \alpha$	$\pm t_{0.05} \times \beta$	T_1	T_2
III	3	0.1721	−3.00	0.0022	0.0242	1.96	1165	1290
III	2.85	−0.0098	9.29	0.0010	0.0070	0.52	1163	1320
III	2.80	−0.0156	9.68	0.0010	0.0080	0.64	1150	1340
III	2.75	−0.0164	9.73	0.0015	0.0071	0.57	1168	1331
IV	—	0.0717	5.57	0.0021	0.0088	0.65	1210	1415

[a] Given here also are the errors $t_{0.05} \times S^*$, $t_{0.05} \times \alpha$, and $t_{0.05} \times \beta$ of the quantities E, a, and b and the temperature range T_1 and T_2 covered.

The experimental results for cells III and IV are given in Table I and in Fig. 1. Changes in the Gibbs energies, enthalpies, and entropies of the cell reactions of these cells for homogeneity region

$$1/\delta\ \mathrm{CoTiO}_x + 0.95\ \mathrm{Fe} = \mathrm{Fe}_{0.95}\mathrm{O} + 1/\delta\ \mathrm{CoTiO}_{x-\delta} \quad (\delta \rightarrow \mathrm{O}) \qquad (3)$$

and for two heterogeneity regions

$$\frac{1}{x-2}\mathrm{CoTiO}_x + 0.095\ \mathrm{Fe} = \mathrm{Fe}_{0.95}\mathrm{O} + \frac{1}{x-2}\mathrm{Co} + \frac{1}{x-2}\mathrm{TiO}_2 \qquad (4)$$

$$\mathrm{Co}_2\mathrm{TiO}_4 + 0.95\ \mathrm{Fe} = \mathrm{Fe}_{0.95}\mathrm{O} + \mathrm{CoTiO}_3 + \mathrm{Co} \qquad (5)$$

calculated using the date of Table I are tabulated in Table II.

Let us discuss in more detail the experimental data for the phases CoTiO_x. The emf's of cell III with $x = 2.75$ and 2.80 agree with each other within the experimental error, which indicates that the specimens of the compositions $\mathrm{CoTiO}_{2.75}$ and $\mathrm{CoTiO}_{2.80}$ belong to the same phase field. In order to define the boundary of the stability region (y) of the phase CoTiO_{3-y}, the values of E were measured in the apparatus with a separated gas space and the electrochemical oxidation and reduction of the electrode of the composition $\mathrm{CoTiO}_{2.85}$ were carried out. The values of E from cell III with the electrode $\mathrm{CoTiO}_{2.85}$ agree within the error with the emf values obtained for cell III with the electrodes of the compositions $\mathrm{CoTiO}_{2.75}$ and $\mathrm{CoTiO}_{2.80}$ corresponding to the heterogeneous region (marked with diamonds in Fig. 1).

An analysis of the curves of electrochemical oxidation and reduction $E = f(\tau)$ (Fig. 1a) and of Table III shows that after pro-

TABLE II

CHANGES IN THE GIBBS ENERGY, ENTHALPY, AND ENTROPY OF THE CELL REACTIONS (3), (4), AND (5) OF CELLS III AND IV[a]

Cell	x	$-\Delta H^\circ_T$	ΔS°_T	$\pm\Delta(\Delta G^\circ)$	$\pm\Delta(\Delta H^\circ_T)$	$\pm\Delta(\Delta S^\circ_T)$	T_1/K	T_2/K
III	3.00	33.2	−5.8	0.4	4.7	3.8	1165	1290
	2.85	−1.9	17.9	0.2	1.4	1.0	1163	1320
	2.80	−3.0	18.7	0.2	1.5	1.2	1150	1340
	2.75	−3.2	18.8	0.3	1.4	1.1	1168	1332
IV	—	13.8	10.8	0.4	1.7	1.3	1210	1415

[a] $\Delta G^\circ_T = \Delta H^\circ_T - T \times \Delta S^\circ_T$, kJ mole^{-1}.

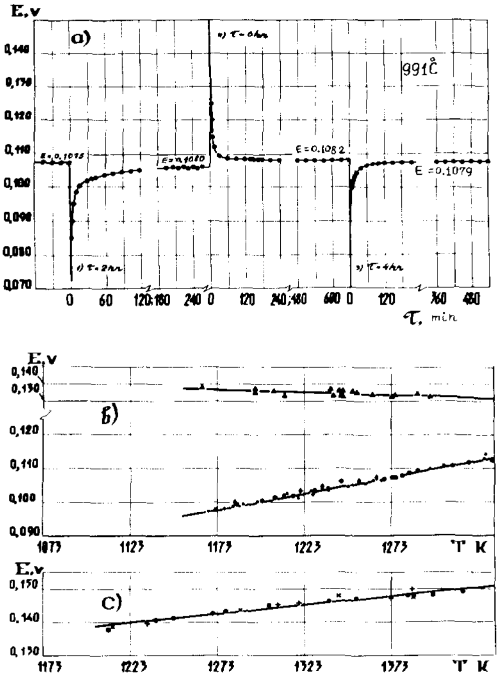

FIG. 1. (a) Curves of electrochemical oxidation and reduction of the electrodes of the cell ($E = F(\tau)$)

$$(+)\mathrm{Pt} \mid \mathrm{CoTiO_{2.85}} \mid \mathrm{ZrO_2(CaO)} \mid \mathrm{Fe_{0.95}O,Fe} \mid \mathrm{Pt}(-)$$

(1) reduction; (2) oxidation; (3) reduction. (b) The dependences $E = f(T)$ for electrochemical cells

$$(+)\mathrm{Pt} \mid \mathrm{CoTiO}_x \left| \begin{matrix}\mathrm{ThO_2}\\ \mathrm{(CaO)}\end{matrix} \text{ or } \begin{matrix}\mathrm{ZrO_2}\\ \mathrm{(CaO)}\end{matrix} \right| \mathrm{Fe_{0.95}O,Fe} \mid \mathrm{Pt}(-)$$

Symbols: /, $x = 3.00$; ◈, $x = 2.8$; ●, ⊙, $x = 2.75$; 2.80; △, ◈, ●, E-values kept constant at T = const; ⊙, E-values measured during gradual changes in T, x = 2.75; 2.80. (c) The dependence $E = f(T)$ for electrochemical cell

$$(+)\mathrm{Pt} \mid \mathrm{Co_2TiO_4,CoTiO_3,Co} \mid \mathrm{ThO_2(CAO)} \mid \mathrm{Fe_{0.95}O,Fe} \mid \mathrm{Pt}(-)$$

Symbols: ⊙, E kept constant at T = const; +, x, E during gradual changes in T.

longed reduction[2] ($\tau = 2$ hr) the emf value for the electrode of the composition $\mathrm{CoTiO_{2.85-\gamma}}$ ($E = 0.1060$ V) is found to be 1.5 mV below the initial equilibrium value ($E = 0.1075$ V) for the composition $\mathrm{CoTiO_{2.85}}$ and corresponds to the value of E for the $\mathrm{CoTiO_{2.75}}$ electrode. Thus the initial phase $\mathrm{CoTiO_{2.85}}$ lost part of its oxygen (γ) and converted to the "phase" $\mathrm{CoTiO_{2.85-\gamma}}$ which can be considered as a heterogeneous mixture of cobalt metatitanate $\mathrm{CoTiO_{3-y}}$ maximally depleted of oxygen, Co, and $\mathrm{TiO_2}$. The subsequent electrochemical oxidation of the specimen of composition $\mathrm{CoTiO_{2.85-\gamma}}$ during 6 hr at the same temperature led to the emf value ($E = 0.1082$ V) exceeding both E for the composition $\mathrm{CoTiO_{2.75}}$ ($E = 0.1066$ V) and the initial value of E corresponding to the composition $\mathrm{CoTiO_{2.85}}$, i.e. ($E_{\mathrm{CoTiO_{2.75}}} < E_{\mathrm{CoTiO_{2.85}}} < E_{\mathrm{CoTiO_{2.85-\gamma+\beta}}}$). Finally, reduction of the specimen $\mathrm{CoTiO_{2.85-\gamma+\beta}}$ during 4.5 hr gave the value of E equal to 0.1080 V which is somewhat smaller than $E(\mathrm{CoTiO_{2.85-\gamma+\beta}})$ but greater than E ($\mathrm{CoTiO_{2.85}}$) at the same temperature. The results obtained are in good agreement with the data (2) and allow one to conclude that within the accuracy of the experimental data the boundary of the homogeneity region is near the composition $\mathrm{CoTiO_{2.85}}$. Then the cell reaction of the cell (III) with the electrode of the composition $\mathrm{CoTiO_{2.85}}$ will be

$$\begin{aligned} &1.176\,\mathrm{CoTiO_{2.85}} \\ &\quad + 0.95\,\mathrm{Fe} = \mathrm{Fe_{0.95}O} + 1.176\,\mathrm{Co} \\ &\qquad\qquad + 1.176\,\mathrm{TiO_2}. \end{aligned} \tag{6}$$

Taking the value 0.15 for the parameter y in the formula of $\mathrm{CoTiO_{3-y}}$ and using $\Delta G^{\circ}_{\mathrm{FeO}}$ of the reaction of formation of wüstite from elements from Ref. (6), we calculated changes in the integral Gibbs energy of the reaction

$$\mathrm{Co} + \mathrm{TiO_2} + \tfrac{1}{2}\,\mathrm{O_2} = \mathrm{CoTiO_3}. \tag{7}$$

For this purpose, on the basis of experimental data, we plotted isotherms $\Delta\bar{G}^{\circ}_{\frac{1}{2}\mathrm{O_2}}(x)$ for the four compositions studied at five temperatures (Fig. 2). The graphical integration $\Delta\bar{G}^{\circ}_{\frac{1}{2}\mathrm{O_2}}(x)$ over x allowed us to find $\Delta G^{\circ}_{\mathrm{T}}$ of

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[2] Oxidation and reduction were carried out at a fixed current of 700 μA at a fixed temperature of 991°C.

TABLE III

RESULTS OF ELECTROCHEMICAL REDUCTION AND OXIDATION OF THE ELECTRODE $CoTiO_{2.85}$

Composition of the electrode	Conditions of experiment			$E_{exp.} \pm \Delta E$ (V)	E_{calc} (V)
		Time (hr)	t (°C)		
$CoTiO_{2.85}$	Argon, separated gas space	—	991	0.10751 ± 0.00004	0.1076 ± 0.0005
$CoTiO_{2.85-\gamma}$	Reduction of the phase $CoTiO_{2.85}$	2.0	991	0.10604 ± 0.00003	—
$CoTiO_{2.85-\gamma+\beta}$	Oxidation of the phase $CoTiO_{2.85-\gamma}$	6.0	991	0.10823 ± 0.00005	—
$CoTiO_{2.85-\gamma+\beta-\alpha}$	Reduction of the phase $CoTiO_{2.85-\gamma+\beta}$	4.5	991	0.10790 ± 0.00003	—
$CoTiO_{2.75}$	Vacuum, nonseparated gas space	—	991		0.1066 ± 0.007

the reaction (7)

$$\Delta G_7^\circ/\text{kJ mole}^{-1} \pm 1.0 = -264.8 + 82.0 \times 10^{-3} \times T/\text{K}.$$

The heat and entropy change of this reaction for the middle of the temperature range covered is:

$$\Delta H_7^\circ\,(1250\text{ K}) = -(264.8 \pm 1.3)\text{ kJ mole}^{-1};$$
$$\Delta S_7^\circ\,(1250\text{ K}) = -(82.0 \pm 0.8)\text{ J T}^{-1}\text{ mole}^{-1}.$$

Using $\Delta G^\circ(T)$ for reaction (2) for the reaction

$$CoO + TiO_2 = CoTiO_3 \qquad (8)$$

we obtain: $\Delta G_8^\circ/\text{kJ mole}^{-1} \pm 1.3 = -28.9 + 9.6 \times 10^{-3} \times T/\text{K}$, where for $T = 1250$ K

$$\Delta H_8^\circ = -(28.9 \pm 2.1)\text{ kJ mole}^{-1};$$
$$\Delta S_8^\circ = -(9.6 \pm 1.7)\text{ J T}^{-1}\text{ mole}^{-1}.$$

Taking into account the dependences given in Table II and the dependences of the reactions (1), (5), and (8) obtained above, for the reaction

$$2\,CoO + TiO_2 = Co_2TiO_4 \qquad (9)$$

we have $\Delta G_9^\circ/\text{kJ mole}^{-1} \pm 1.5 = -43.9 + 13.4 \times 10^{-3} \times T/\text{K}$, where ΔH_9° (1310 K) $= -(43.9 \pm 3.3)$ kJ mole^{-1}; ΔS_9° (1310 K) $= -(13.4 \pm 2.5)$ J T^{-1} mole^{-1}.

Table IV gives standard values for the

TABLE IV

THERMODYNAMIC PROPERTIES OF COBALT TITANATES AT 298.15 K[a]

Titanate	$-\Delta H^\circ$(ox.) (kJ mole^{-1})	$-\Delta G^\circ$(ox.) (kJ mole^{-1})	$-\Delta H_f^\circ$ (kJ mole^{-1})	$-\Delta G_f^\circ$ (kJ mole^{-1})	S° (JT^{1} mole^{-1})
$CoTiO_3$	27.6 ± 3.3	25.9 ± 3.8	1212.9 ± 4.6	1129.3 ± 5.0	97.5 ± 4.6
Co_2TiO_4	46.0 ± 4.2	41.0 ± 4.6	1466.9 ± 5.0	1358.9 ± 7.1	139.3 ± 5.0

[a] Since the data on the high-temperature values of the heat capacities of $CoTiO_3$ and Co_2TiO_4 are absent we assumed that their $C_P = f(T)$ are equal to the heat capacities of $FeTiO_3$ and Fe_2TiO_4. The data on the thermodynamic properties of CoO and TiO_2 are taken from Refs. (*11*, *28*).

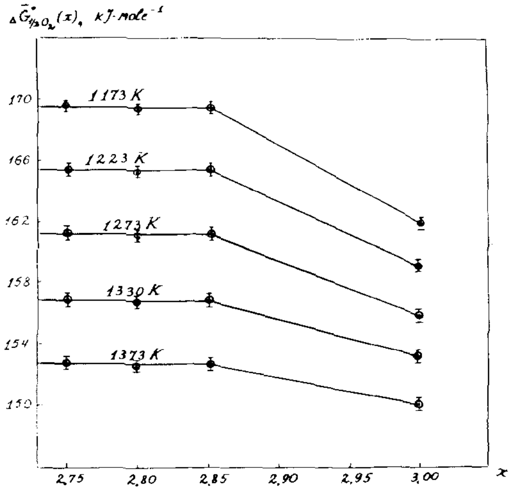

FIG. 2. The dependence of the partial Gibbs energy $\Delta\bar{G}_{\frac{1}{2}O_2} \mp \times)$ for CoTiO$_x$ ($2.75 < x \leq 3.00$).

enthalpies, entropies, and Gibbs energies of formation of CoTiO$_3$ and Co$_2$TiO$_4$ from oxides and elements. In the literature, there are no data for the thermodynamic properties of CoTiO$_3$ and Co$_2$TiO$_4$ at 298.15 K. It is of interest to compare the results of the present paper with the data obtained at high temperatures by other workers. Comparison of the values ΔG°_{T}, ΔH°_{T}, and ΔS°_{T} obtained in the present paper for the reaction (8) with the data given in the literature shows that our values agree within the errors with the results of the works (*1, 2, 8–10*). It should be noted however that the specimens investigated in Ref. (*8*) by the emf method with a separated gas space, by the thermogravimetric method (*1, 10*) and by the heterogeneous equilibrium method (*9*) involved an excess of TiO$_2$ and Co. In all these studies, specimens were preheated at high temperatures in vacuum in the course of preparation of the electrodes or were held for a long time at a constant temperature and at a partial oxygen pressure close to the equilibrium for cobalt metatitanate mixed with Co and TiO$_2$. Therefore the thermodynamic values obtained in Refs. (*1, 8–10*) should be ascribed to reactions involving defect cobalt metatitanate (CoTiO$_{2.85}$) rather than the stoichiometric CoTiO$_3$. If we assume that the homogeneity region is absent, i.e., stoichiometric CoTiO$_3$ coexists with Co and TiO$_2$, then it follows from our data that

$$\Delta G^{\circ\prime}_{8}/\text{kJ mole}^{-1} \pm 0.6 = -31.3\ (\pm 1.9) + 12.3\ (\pm 1.4) \times 10^{-3} \times T/\text{K}.$$

As is evident, the values ΔG°_{8} calculated taking into account the homogeneity region of CoTiO$_3$ and without account of it ($\Delta G^{\circ\prime}_{8}$) quite well agree with each other. The cause of good agreement lies in the fact that the contribution of the homogeneity region to the quantity ΔG°_{8} is small. This explains why, incorrectly writing both the cell reaction involving Co and TiO$_2$ and the reaction of reduction of CoTiO$_3$ to TiO$_2$ and Co,[3] the authors of Refs. (*1, 8–10*) nevertheless obtained reasonable values of Gibbs energy changes.

Our values ΔG°_{9} for formation of cobalt orthotitanate Co$_2$TiO$_4$ from oxides agree within the errors with the data of Refs. (*1, 8, 10*). Noteworthy is a significant difference between the values of ΔH°_{9} obtained in our work and in Ref. (*12*) by high-temperature solution calorimetry (Table V). A similar situation is encountered for the compounds CoAl$_2$O$_4$, NiAl$_2$O$_4$, and NiCr$_2$O$_4$ isostructural with Co$_2$TiO$_4$. The noted discrepancy cannot be connected with the difference between temperatures at which the values of ΔH°_{T} were obtained but is, evidently, indicative of the presence of systematic errors either in the data of Refs. (*12, 13*) or in the results of the present paper and Refs. (*1, 8, 10*). The

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[3] If one neglects the homogeneity region for CoTiO$_3$, the cell reaction of cell III with "electrode" |CoTiO$_3$,Co,TiO$_2$| may be written as: CoTiO$_3$ + 0.95 Fe = Fe$_{0.95}$ + Co + TiO$_2$. In reality CoTiO$_{2.85}$ coexists with Co and TiO$_2$ and the overall cell process involving this phase will be reaction (6).

TABLE V

HEATS OF FORMATION OF SOME SPINELS FROM OXIDES AND THEIR ENTROPIES AT 298.15 K

Compound	$-\Delta H^\circ$ (kJ mole^{-1})	S° (J T^{-1} mole^{-1}) (298 K)	Method[a]	Reference
$CoAl_2O_4$	37.2 ± 1.0 (973 K)	—	1	*12*
	50.6 ± 3.8 (1300 K)	—	2	*14*
	59.0 ± 5.9 (1250 K)	—	3	*18*
$NiAl_2O_4$	3.1 ± 1.0 (973 K)	—	1	*12*
	23.4 ± (1350 K)	—	2	*14*
	22.6 ± 1.6 (1300 K)	—	3	*15*
$NiCr_2O_4$	5.3 ± 0.8 (1173 K)	—	1	*13*
	54.0 ± 4.2 (1250 K)	—	2	*16*
	59.8 ± 2.1 (1230 K)	—	2	*17*
Fe_2TiO_4	41.4 ± 3.3 (298 K)[b]	167.4	2	*31*
	41.0 ± 2.5 (298 K)[b]	169.9 ± 3.3	2	*20*
		168.9 ± 1.0	1	*7*
	41.0 ± 3.3 (298 K)[b]	166.8	3	*32*
$FeTiO_3$	26.8 ± 2.1 (298 K)[b]	104.2 ± 3.9	2	*19, 29*
	27.2 ± 2.1 (298 K)[b]	107.1 ± 3.6	3	*19, 29*
	27.6 ± 2.1 (298 K)[b]	105.9 ± 1.3	1	*23, 24*
Fe_2SiO_4	37.2 ± 3.8 (298 K)[b]	147.7 ± 4.2	2	*25*
	32.6 ± 3.8 (298 K)[b]	151.5 ± 4.2	3	*19, 30*
	34.3 ± 4.6 (298 K)	148.1 ± 2.1	1	*26, 27*
Co_2TiO_4	25.3 ± 0.8 (973 K)	—	1	*12*
	43.1 ± 4.2 (973 K)	139.3 ± 5.0	2	Present study

[a] 1, Calorimetry; 2, emf method with $|O^{2-}|$-conducting electrolyte; 3, equilibrium with gas mixtures $CO + CO_2$ or $H_2 + H_2O$ (gas).

[b] The values obtained by third law treatment.

causes of this discrepancy are not yet fully clear. It is worth noting, however, that the data on the thermodynamic properties of compounds of the type $FeTiO_3$, Fe_2TiO_4, and Fe_2SiO_4 obtianed in Refs. (*19, 20, 25, 29–32*) by the emf and equilibrium methods agree quite well with each other and with the values of the heats and entropies of these compounds, determined from solution calorimetry at 298 K and from the low-temperature heat capacities (see Table V).

For the independent test of the technique used in the present study we carried out the third law treatment of the emf values of cell II. Calculation of the heat of the reaction (1) at 298.15 K for each of the 30 values of E is indicative of the absence of a noticeable drift in the current values of ΔH_2° (298.15 K). The mean value ΔH_2° (298.15 K) $= -238.9 \pm 1.3$ kJ mole^{-1} is in good agreement with the calorimetric value (ΔH_2° (298.15 K) $= -240.2 \pm 1.3$ kJ mole^{-1}) recommended by the CODATA Task Group. Thus, the given data prove the reliability of the emf method with $ZrO_2(CaO)$ or $ThO_2(CaO)$ electrolyte. In connection with the foregoing, systematic errors may exist in the method of high-temperature solution calorimetry. One of these may be associated with the uncertainty of the initial state of substances (*22*) and also with the different final state of the calorimetric system during the solution of free oxides (CoO, NiO, TiO_2, Al_2O_3, Cr_2O_3 etc.) and double oxides based on them in complex oxide solvents.

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