

Thermodynamics of Double Oxides

III. Study of the CaO-Ga₂O₃ System by the emf Method and X-Ray Analysis

YU. YA. SCOLIS, V. A. LEVITSKII, L. N. LYKOVA, AND
T. A. KALININA

*Laboratory of Chemical Thermodynamics and X-Ray Analysis,
Moscow State University, Moscow, 117234, USSR*

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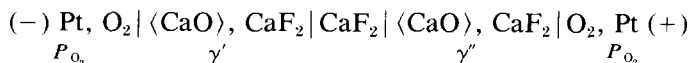
Using the methods of X-ray and differential thermal analysis, four compounds Ca₃Ga₂O₆, Ca₃Ga₄O₉, CaGa₂O₄, and CaGa₄O₇ have been found in the subsolidus region of the phase diagram of the CaO-Ga₂O₃ system. The existence of the gallate Ca₃Ga₄O₉ discovered for the first time is confirmed by experiments on measuring the emf's of galvanic cells. Changes in Gibbs energy, enthalpy, and entropy for the reactions of formation of all four calcium gallates from oxides have been determined by the emf method with a solid [F⁻]-ionic electrolyte in the range 1100-1400 K. On the basis of the data obtained the relative stability of the compounds is analyzed and the activity of calcium oxide in the system under study is calculated.

The present paper which is a continuation of the systematic studies of the authors on the thermodynamics of refractory double oxide systems gives the results of study of the phase relationships and thermodynamic properties of compounds in the CaO-Ga₂O₃ system at high temperatures. The basis for such an investigation was the absence in the literature of any thermody-

amic data characterizing the stability of phases formed in the course of crystallization of this system.

Experimental

The thermodynamic properties of gallates were determined by the emf method using electrochemical cells of the type



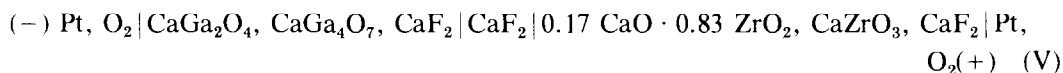
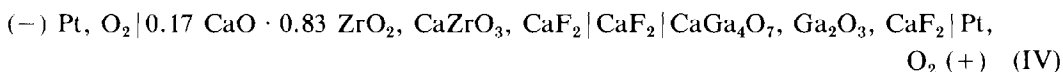
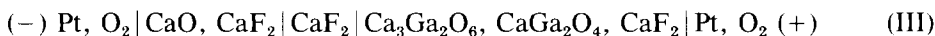
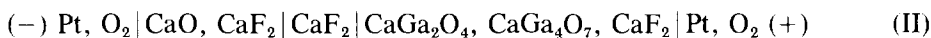
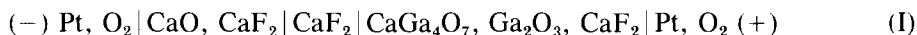
which were first proposed by Benz and Wagner (1) and which we have used to determine the thermodynamic stability of some refractory double oxide systems (see, for example, Refs. (2-4)). In cells of this type the electrodes γ' and γ'' represent

mixtures of oxide phases, coexistent with each other according to the phase diagram, with additions of calcium fluoride.

According to Ref. (5), in the CaO-Ga₂O₃ system there exist three stable compounds: Ca₃Ga₂O₆, CaGa₄O₇, and CaGa₂O₄, the last-

mentioned of which can exist in two stable and one metastable modifications. In accordance with the phase diagram of CaO-Ga₂O₃ proposed in Ref. (5), for determining

the thermodynamic properties of three calcium gallates, we have measured the emf values (*E*) of the cells



Gallates were obtained by 400-hr heat treatment in air at 1000–1100°C of stoichiometric mixtures CaCO₃ (99.9% pure) and Ga₂O₃ (99.99% pure) with double intermediate grinding. The completeness of the reaction was checked by X-ray diffraction.

The studied electrodes of cells I to V were prepared from individual phases. The mole proportion CaO:Ga₂O₃ in the electrodes under study was: for cells I and IV, 1:4 or 1:6; for cells II and V, 1:1.33; for cell III, 2:1 or 1.25:1.

The reference electrodes of cells I to V were obtained as described in Refs. (3, 6). CaF₂ heat treated in vacuum (~1.10⁻⁵ Torr) was added to all electrodes according to Refs. (1–4). Discs cut from optically transparent single crystals CaF₂ (diam. = 6 mm, *h* = 3–4 mm) were used as electrolyte. The conditions of reversibility of cells I to V, the apparatus design, and the experimental technique are described in Refs. (3, 4).

For studying the phase relationships, the methods of X-ray and differential thermal analysis were used. X-Ray patterns were taken at room temperature in a Guinier camera of the "Nonius" Company (CuK α radiation). Germanium was used as an in-

ternal standard. The thermoanalytical patterns T, DTA, TG, DTG were obtained simultaneously using the derivatograph of the F. Paulic, J. Paulic, and L. Erdey system, with the heating rate 8°C/min in the temperature range 25–1500°C. The mixtures CaCO₃ + Ga₂O₃ for the thermoanalysis were prepared every 5 mol%, and near the compositions, where after the previous investigations the compounds and the eutectics had been found, every 1–2 mol%.

The pellets of the mixtures were heat treated in air at 1000–1200°C for 100–700 hr with multiple intermediate grindings until a constant phase composition was obtained. The specimens with a CaO content of more than 45 mol% were heat treated in platinum crucibles and the specimens rich in Ga₂O₃, in platinum and corundum crucibles. No interaction of the specimens with the material of the crucibles was detected by X-ray method.

Results and Discussion

a. The Galvanic Cell Study of the CaO-Ga₂O₃ System

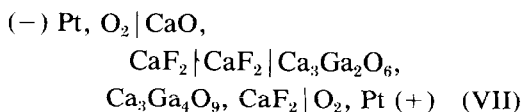
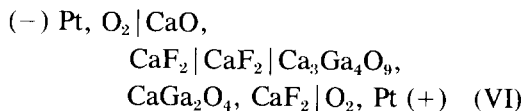
The runs with cells I and II showed that at relatively low temperatures (800–900°C)

the equilibrium potentials were established extremely slowly. The temperature rise to 1000–1100°C resulted in a slow drop of the potential due to the acceleration of diffusion of oxygen ions from the reference electrode ($a_{\langle \text{CaO} \rangle} = 1$) deep into the electrolyte and due to the resultant partial transfer of calcium oxide through the electrolyte into the electrode under study ($a_{\langle \text{CaO} \rangle} \ll 1$) (4).*

According to Ref. (4), the reference electrode $|0.17 \text{ CaO} \cdot 0.83 \text{ ZrO}_2, \text{ CaZrO}_3, \text{ CaF}_2|$ is characterized by low values of $a_{\langle \text{CaO} \rangle}$. The use of this electrode in cells IV and V enabled us to obtain the equilibrium values of E reproducible with increasing and decreasing temperature and stable in the course of experiments during $\sim(150\text{--}200)$ hr at 1173–1373 K.

In the runs on measuring the emf of cell III there was a drastic difference between the values of E depending upon the quantitative compositions of the electrodes under study. The emf values of the cell with the mole content $\text{CaO}:\text{Ga}_2\text{O}_3 = 2:1$ in the electrode were 17–21 mV in the temperature range 1100–1250 K whereas with the proportion $\text{CaO}:\text{Ga}_2\text{O}_3 = 5:4$ for the same temperature the potentials of the cell were 60–80 mV higher. Such a considerable difference between the values of E for cell III with the different content of Ga_2O_3 in the electrode under study can be explained only by the formation of a new phase in the course of prolonged electrochemical experiments (~ 200 hr). In fact, the X-ray analysis of the electrodes studied, which was made after the experiments, confirmed the occurrence of a new previously unknown phase. Thus, the data we have obtained were inconsistent with the results of in-

vestigation of the phase relationships of the $\text{CaO}\text{--}\text{Ga}_2\text{O}_3$ system, (5) and stimulated an independent study of this part of the phase diagram. As a result of the studies made, we have discovered a new compound $3 \text{ CaO} \cdot 2 \text{ Ga}_2\text{O}_3$ ($\text{Ca}_3\text{Ga}_4\text{O}_9$) which was not described earlier in the literature. In accordance with this, instead of cell III in the subsequent runs we measured the values of E of the cells



The measured potentials of cells IV, V, VI, and VII in the chosen temperature ranges reached their equilibrium values several hours after the admission of oxygen into the reactor. The cells were held at constant temperature, as a rule, from 1 to 5 hr and sometimes up to 7–10 hr. At two relatively low temperatures 1083 and 1163 K, in order to check for constancy of the equilibrium potentials in time, cell VII was held for 62 and 56 hr, respectively. Sudden changes in temperature led to the deviation of the measured potentials from their equilibrium values by no more than 2–3 mV, the equilibrium values of E being reestablished rather rapidly (from 20–30 min at higher temperatures to 1–2 hr at low temperatures). With gradual temperature changes (10–15°/hr) the measured potentials were practically similar to the values of E kept constant in time, which indicates that they correspond to the equilibrium values and allows them to be used for calculating the thermodynamic properties of calcium gallates. To illustrate the behavior of the studied cells in time, Fig. 1 gives part of the kinetic curve obtained in one

* The appearance of partial electron conductivity (σ_e) in the CaF_2 electrolyte saturated with calcium oxide at $T \geq 1273$ K is not excluded either. According to Ref. (7), the fraction of σ_e in CaO crystals at 1273 K is $\sim 35\%$.

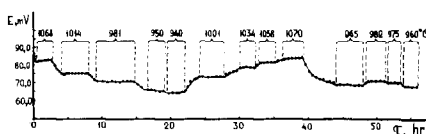
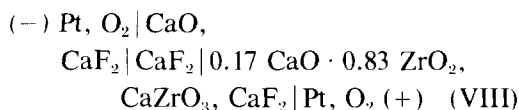


FIG. 1. Part of the kinetic curve of one of the runs with the cell Pt, O₂ | Ca_{0.17}Zr_{0.83}O_{1.83}, CaZrO₃, CaF₂ | CaF₂ | CaGa₄O₇, Ga₂O₃, CaF₂ | Pt, O₂.

of the runs with cell IV. Parallel runs were carried out with different batches of the electrodes. The temperature dependences of the emf's of cells IV to VII are given in Fig. 2 and the coefficients of the equations $E = a + b \times T$ are listed in Table I.

The dependences $E = f(T)$ for cells I and II were found by combining the experimentally determined dependences $E = f(T)$ for cells IV and V with the corresponding equation $E = f(T)$ for the cell



borrowed from Ref. (6).

The thermodynamic parameters of the cell reactions of cells I, II, VI, and VII

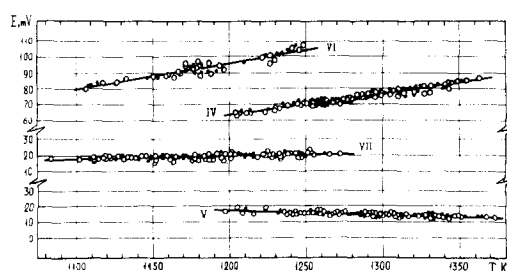
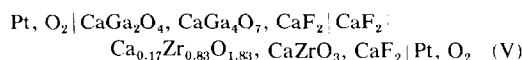
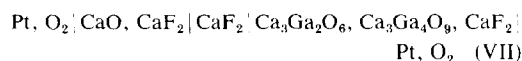
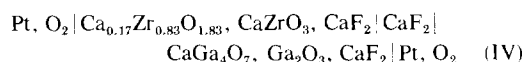
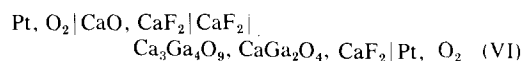


FIG. 2. The temperature dependence of the emf's of the cells



○, The emf values kept constant in time; ●, the emf values measured during gradual temperature changes (10–15°/hr).

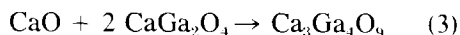
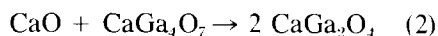
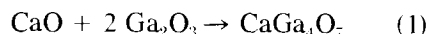


TABLE I
The COEFFICIENTS OF THE EQUATIONS $E = a + b \times T$ (mV) FOR CELLS (I–VIII)^a

Cell	n^b	a	$b \times 10^2$	$\pm t_{0.05} \times \sigma_E$	$\pm t_{0.05} \times \sigma_a$	$\pm t_{0.05} \times \sigma_b \times 10^2$	$T_1 \div T_2, (\text{K})$
IV	143(49)	-98.3	13.50	2.8	8.0	0.62	1204–1363
V	114(60)	+47.0	-2.46	1.5	4.5	0.35	1193–1373
VI	48(29)	-101.0	16.41	4.7	20.4	1.72	1107–1248
VII	172(75)	-1.9	1.81	2.2	4.4	0.37	1083–1273
VIII ^c		+191.9	2.47	2.0	4.9	0.97	1200–1500
I ^d		+93.6	15.97	3.4	9.4	1.15	1204–1363
II ^d		-144.9	4.93	2.5	6.7	1.03	1197–1373

^a n is the number of pairs of the experimental values E and T ; $t_{0.05} \times \sigma_E$, $t_{0.05} \times \sigma_a$, and $t_{0.05} \times \sigma_b$ are the confidence intervals of the quantities E , a , and b , and $(T_1 \div T_2, \text{K})$ are the temperature measuring ranges for cells I, II, and IV to VIII.

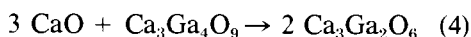
^b Given in parentheses is the number of experimental values of E kept constant in time.

^c According to the data of Ref. (6).

^d Found by combining the values belonging to cells IV and V with the values for cell VIII.

TABLE II
CHANGES IN THE GIBBS ENERGY, ENTHALPY, AND ENTROPY OF CELL REACTIONS 1-4 OF CELLS I, II, VI,
AND VII AT 1100-1400 K

Cell	Reaction	$\Delta G^\circ = f(T)$ (kcal mole ⁻¹)	$\delta(\Delta G^\circ)$ (kcal mole ⁻¹)	$\Delta H^\circ 1250$ K (kcal mole ⁻¹)	$\Delta S^\circ 1250$ K (cal T ⁻¹ mole ⁻¹)
I	1	$-4.32-7.37 \times 10^{-3} \times T$	± 0.16	-4.3 ± 0.4	7.4 ± 0.5
II	2	$-6.68-2.27 \times 10^{-3} \times T$	± 0.12	-6.7 ± 0.3	2.3 ± 0.5
VI	3	$+4.66-7.57 \times 10^{-3} \times T$	± 0.22	$+4.7 \pm 0.9$	7.6 ± 0.8
VII	4	$+0.26-2.57 \times 10^{-3} \times T$	± 0.30	$+0.3 \pm 0.6$	2.6 ± 0.5



were found from the equations $E = a + b \times T$ using the known relationships: $\Delta G^\circ = -nFE(T)$; $\Delta H^\circ = -nF(E - T \partial E/\partial T)$ = $-nF\bar{u}$; $\Delta S^\circ = nF(\partial E/\partial T)_p = nFb$, where n is the number of equivalents of F^- ions transferred through the cell and F is Faraday's constant. The results are presented in Table II. In Table III the values of the Gibbs energies of reaction (1) obtained from the most stable emf values at the initial stage of one of the successful experiments with cell I (column 3) are compared with the values found from the emf of cell IV (column 4). The agreement within the given errors of the values listed in columns 3 and 4 of

TABLE III

COMPARISON OF THE GIBBS ENERGY VALUES OF
THE REACTION $\text{CaO} + 2\text{Ga}_2\text{O}_3 \rightarrow \text{CaO} \cdot 2\text{Ga}_2\text{O}_3$ ^a

T (K)	Holding time E of cell I (hr)	$-\Delta G^\circ$ (kcal)	
		Calculation from E for cell I	Calculation from E for cell IV
1296	0.5	13.6 ± 0.2	13.9 ± 0.2
1281	3.5	13.6 ± 0.2	13.8 ± 0.2
1254	1.0	13.3 ± 0.2	13.6 ± 0.2
1251	2.0	13.2 ± 0.2	13.5 ± 0.2

^a Obtained from the emf's of the cells Pt, O₂|CaO, CaF₂|CaF₂|CaO · 2Ga₂O₃, Ga₂O₃, CaF₂|Pt, O₂ (I) and Pt, O₂|CaZrO₃, 0.17 CaO · 0.83 ZrO₂, CaF₂|CaF₂|CaO · 2Ga₂O₃, Ga₂O₃, CaF₂|Pt, O₂ (IV).

Table III additionally confirms the reliability of the results of determination of the thermodynamic properties of the gallates CaGa₄O₇ and CaGa₂O₄ from the emf's of cells IV and V.

The isotherms of the activity of CaO in the subsolidus region of the CaO-G₂O₃ system, which were calculated using the data of Table I, are presented in Fig. 3. As is evident, the phase diagram falls into five heterogeneous regions, in which case in the temperature range covered as the concentration of calcium oxide decreases its activity falls off from unity to $\sim 5 \times 10^{-3}$.

b. Study of the Phase Relationships in the CaO-Ga₂O₃ System

T-X diagram of the CaO-G₂O₃ system (Fig. 4) was constructed in a wide temperature range on the basis of the data of the X-

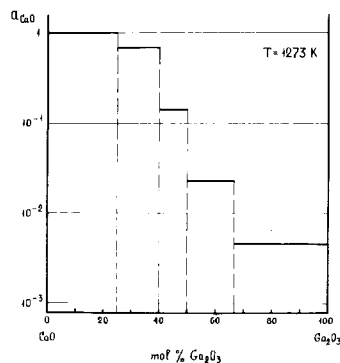


FIG. 3. The dependence of the activity of calcium oxide on its content in the $x \text{CaO} + y \text{Ga}_2\text{O}_3$ system.

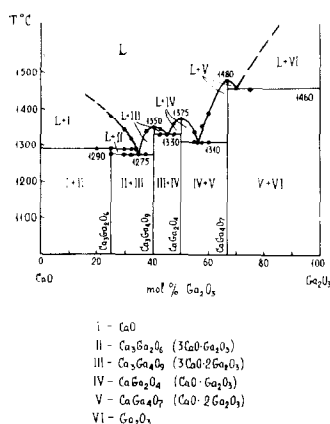


FIG. 4. The phase diagram of the CaO-Ga₂O₃ system.

ray and high-temperature differential thermal analysis. Each point on Fig. 4 is the mean value of the results of two to four DTA patterns obtained in different runs for the specimens of the same compositions of different batches of samples. In the system four individual compounds were found: Ca₃Ga₂O₆, Ca₃Ga₄O₉, CaGa₂O₄, and CaGa₄O₇. No noticeable regions of solid solutions were detected. Three compounds Ca₃Ga₄O₉, CaGa₂O₄, and CaGa₄O₇ melt congruently at 1350, 1375, and 1480°C, respectively, and Ca₃Ga₂O₆ melts incongruently with the decomposition into CaO and liquid at 1290°C. In the system four eutectics were found: 70 mol% Ga₂O₃ with a melting temperature of 1460°C; 56.5 mol% Ga₂O₃ (1310°C); 45 mol% Ga₂O₃ (1330°C), and 35 mol% Ga₂O₃ (1275°C).

The most significant distinction between our data and the data of Ref. (5) relates to the region of compositions with CaO concentration of more than 50 mol% where we found the formation of a compound Ca₃Ga₄O₉; there is a considerable difference between the temperature and the composition of the eutectic richest in calcium oxide and the temperature of the incongruent melting of Ca₃Ga₂O₆.

The X-ray pattern of the powder

Ca₃Ga₂O₆ was interpreted under the assumption of rhombic syngony with the elementary cell parameters given in Table V. The correctness of identification, apart from the good agreement between $\rho_{\text{exp}} = 3.46$ and $\rho_{\text{calc}} = 3.47$, is confirmed by the value of the criterion of De Wolff (8) $M_{20} = 20$.

The phase Ca₃Ga₄O₉ is not identical with the so called metastable modification *m*-CaGa₂O₄ described in Ref. (5) (the forma-

TABLE IV
X-RAY POWDER DATA FOR Ca₃Ga₄O₉

<i>l</i>	<i>d</i>	10 ⁴ / <i>d</i> ² exp	<i>hkl</i>	10 ⁴ / <i>d</i> ² calc.
5	10.89	84.35	100	84.35
60	5.317	353.8	010	353.8
20	4.782	437.4	110	438.2
20	4.498	494.2	11 $\bar{1}$	495.2
10	4.271	548.2	111	548.6
15	3.802	692.0	210	691.2
30	3.630	758.8	300; 10 $\bar{3}$	759.2; 758.0
10	3.587	777.2	202	779.0
40	3.479	826.0	112	826.6
30	3.297	919.9	103; 21 $\bar{2}$	918.2; 919.4
20	3.266	937.3	30 $\bar{2}$	934.0
70	3.000	1112	310; 11 $\bar{3}$	1112; 1111
10	2.974	1131	212	1133
20	2.832	1246	203	1251
100	2.805	1271	30 $\bar{3}$; 113	1273; 1271
90	2.789	1285	21 $\bar{3}$	1284
10	2.754	1318	10 $\bar{4}$	1317
40	2.657	1416	020	1415
20	2.609	1469	40 $\bar{2}$	1471
30	2.582	1501	120	1499
40	2.556	1531	104	1531
10	2.534	1558	12 $\bar{1}$	1556
10	2.498	1603	213	1605
5	2.437	1683	41 $\bar{1}$	1682
3	2.389	1752	220; 303	1753
3	2.370	1781	304; 221; 12 $\bar{2}$	1779; 1782; 1780
10	2.342	1823	21 $\bar{4}$	1817
30	2.303	1886	221; 114; 122	1889; 1885; 1887
5	2.182	2103	313	2107
10	2.147	2169	12 $\bar{3}$	2173
5	2.110	2246	214	2245

TABLE V
CRYSTAL STRUCTURE PARAMETERS OF THE COMPOUNDS IN CaO-Ga₂O₃ SYSTEM

Compound	Syngony	a(Å)	b(Å)	c(Å)	α°	β°	γ°
Ca ₃ Ga ₂ O ₆	Rhombic	11.50(1)	11.27(1)	10.4(1)	—	—	—
Ca ₃ Ga ₄ O ₉	Monoclinic	11.03(1)	5.317(2)	11.07(1)	—	99.10(1)	—
CaGa ₂ O ₄ (I)	Rhombic	10.53(4)	7.745(2)	9.013(3)	—	—	—
CaGa ₂ O ₄ (II)	Monoclinic	7.992(3)	8.830(4)	10.585(6)	—	94.72(2)	—
CaGa ₄ O ₇	Monoclinic	13.16(2)	9.119(3)	5.625(7)	—	105.4(5)	—

tion of *m*-CaGa₂O₄ was established by the authors of Ref. (5) in the range of compositions including 40 mol% Ga₂O₃). The basic lines on X-ray patterns of these phases do not coincide and the conditions of the formation of Ca₃Ga₄O₉ and *m*-CaGa₂O₄ are also different. The X-ray pattern of Ca₃Ga₄O₉ was interpreted under the assumption of monoclinic syngony (see Table IV). The possible elementary cell parameters are presented in Table V. The reasonable agreement between $\rho_{\text{exp}} = 3.98$ and $\rho_{\text{calc}} = 4.22$ and the value of the De Wolf criterion $M_{20} = 17$ assures us of the correctness of the interpretation.

The calcium monogallate under all chosen conditions of synthesis was obtained in the form of a mixture of two modifications: rhombic and monoclinic (Table V). The elementary cell parameters are close to those found in Refs. (9-11). By varying the conditions of heat treatment of the specimens it became possible to obtain X-ray

patterns containing predominantly lines of a particular modification. No thermal effects indicative of the presence of polymorphic transformation were observed on the differential thermal curve up to the melting temperature of CaGa₂O₄. Since the structures of both phases are similar and differ only in the orientation of the double tetrahedrons of GaO₄ in six-membered rings it is possible that the melting temperatures of both modifications are very similar.

The melting temperature and the elementary cell parameters of CaGa₄O₇ are in good agreement with the data of Refs. (5, 12).

The liquidus line in the region rich in calcium oxide (20-30 mol% Ga₂O₃) is more sloping than it might be expected taking into account the high melting temperature of CaO. This may be due either to the existence of a miscibility gap or to the difficulty of equilibration of the samples in determination of the liquidus line of the CaO-rich region from DTA patterns, as

TABLE VI
THERMODYNAMIC FUNCTIONS OF THE REACTIONS OF FORMATION OF CALCIUM GALLATES FROM OXIDES AT 1100-1400K

Compound	$\Delta G^\circ = f(T)$, (kcal/mole)	$\pm \delta(\Delta G^\circ)$	$-\Delta G^\circ_2$ (kcal/mole)		$-\Delta H^\circ_{1273\text{K}}$ (kcal/mole)	$\Delta S^\circ_{1273\text{K}}$ (cal/mole · K)
			1173 K	1373 K		
Ca ₃ Ga ₂ O ₆	$-3.04-9.89 \times 10^{-3} \times T$	0.21	14.64	16.62	3.0 ± 0.6	9.9 ± 0.6
Ca ₃ Ga ₄ O ₉	$-6.34-17.21 \times 10^{-3} \times T$	0.30	26.53	29.97	6.3 ± 1.1	17.2 ± 1.1
CaGa ₂ O ₄	$-5.50-4.82 \times 10^{-3} \times T$	0.10	11.15	12.12	5.5 ± 0.3	4.8 ± 0.4
CaGa ₄ O ₇	$-4.32-7.37 \times 10^{-3} \times T$	0.16	12.96	14.44	4.3 ± 0.4	7.4 ± 0.5

CaO is known to dissolve slowly in oxide melts.

c. The Thermodynamic Stability of Calcium Gallates

The thermodynamic functions of the reactions of formation of calcium gallates from oxides at elevated temperatures were obtained by suitable combining of the dependences $\Delta G^\circ = f(T)$ and of the values ΔH_T° and ΔS_T° of reactions 1-4 listed in Table II. The results are presented in Table VI. As can be seen from this table, the heats of formation from oxides for all four calcium gallates are relatively small. A considerable decrease in Gibbs energy in the course of formation of these compounds from oxides is due to the entropy term. The increase of the entropy in the formation of calcium gallates from oxides qualitatively agrees with the decrease in the symmetry of the formed structures of gallates as compared with initial oxides.

As is evident from Fig. 5, the negative ΔG_T° values for all four gallates increase with temperature. It should be noted that the compounds coexistent with pure oxides are thermodynamically less stable than the

compounds Ca₃Ga₄O₉ and CaGa₂O₄ belonging to the middle of the phase diagram of the CaO-Ga₂O₃ system. As regards the stability of Ca₃Ga₄O₉ and CaGa₂O₄, it is approximately equal. This indicates that in the interaction of calcium oxide with Ga₂O₃ the formation of Ca₃Ga₄O₉ or CaGa₂O₄ is thermodynamically more favorable than the formation of other gallates.

The diagram of the heats of formation of calcium gallates from oxides (Fig. 5) is of somewhat different character. The heat of formation of CaGa₂O₄ per gram formula of this complex oxide is twice or thrice as high as the heats of formation of the remaining three gallates. Noteworthy is the concave character of the curve of change of the values ΔH_T° as a function of the composition $n\text{CaO} \cdot m\text{Ga}_2\text{O}_3$ near the compounds Ca₃Ga₂O₆, Ca₃Ga₄O₉, and CaGa₂O₄. This means that the reactions of formation of these compounds from the neighboring (according to the phase diagram) phases are endothermic. Nevertheless, due to the significant increase of the entropy, the occurrence of these reactions at sufficiently high temperatures turns out to be thermodynamically possible. The last fact is illustrated by the convex character of the curve of change of the values ΔG_T° over the whole range of the compositions $n\text{CaO} \cdot m\text{Ga}_2\text{O}_3$. It should be noted, however, that at temperatures below $\sim 400^\circ\text{C}$ the value of ΔG_T° for the reaction of formation of Ca₃Ga₄O₉ from the neighboring phases (CaGa₂O₄ and Ca₃Ga₂O₆) is positive. Hence, with a fairly slow cooling of the sintered specimens the gallate Ca₃Ga₄O₉ can fully or partly decompose into Ca₃Ga₂O₆ and CaGa₂O₄. It is not unlikely that precisely this circumstance prevented the authors of Ref. (5) from discovering and identifying the phase Ca₃Ga₄O₉.

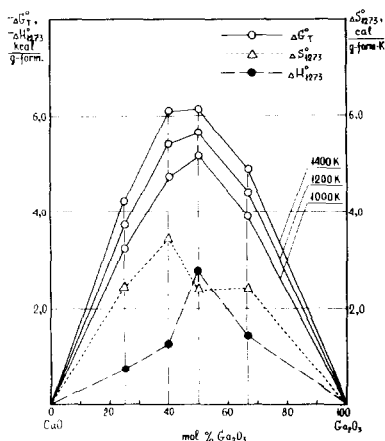


FIG. 5. Changes in the Gibbs energy, enthalpy (kcal g-form⁻¹) and entropy (cal g-form⁻¹ K⁻¹) for the reactions of formation of compounds in the CaO-Ga₂O₃ system from oxides.

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