



Enthalpy and Gibbs energy of formation of lanthanum dicarbide

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Abstract

Equilibrium CO partial pressures over the phase field $\text{LaO}_{1.5}(\text{s})\text{--C}(\text{s})\text{--LaC}_2(\text{s})$ between 1343 and 1638 K were obtained by employing a quadrupole mass spectrometer. The $\text{LaC}_2(\text{s})$ phase was generated in situ starting from a mixture of $\text{LaO}_{1.5}(\text{s})$ and $\text{C}(\text{s})$. The enthalpy of the reaction $\text{LaO}_{1.5}(\text{s}) + 3.5\text{C}(\text{s}) = \text{LaC}_2(\text{s}) + 1.5\text{CO}(\text{g})$ at 298 K derived by the second-law and third-law methods using thermal functions of $\text{LaC}_2(\text{s})$ derived from those of $\text{UC}_{1.94}$ and $\text{ThC}_{1.94}$ was found to be $(656.6 \pm 8.4) \text{ kJ mol}^{-1}$ and $(636.3 \pm 8.4) \text{ kJ mol}^{-1}$ (second-law), and $(673.0 \pm 3.6) \text{ kJ mol}^{-1}$ (third-law), respectively. The enthalpy of formation of $\text{LaC}_2(\text{s})$ was derived from the enthalpy of reaction and the enthalpies of formation of $\text{LaO}_{1.5}(\text{s})$ and $\text{CO}(\text{g})$ taken from the literature. The Gibbs energy of formation of $\text{LaC}_2(\text{s})$ was derived from the enthalpy of formation at 298 K and the standard entropies of $\text{LaC}_2(\text{s})$, $\text{La}(\text{s})$ and $\text{C}(\text{s})$ from the literature. The enthalpy and Gibbs energy of formation of $\text{LaC}_2(\text{s})$ at 298 K (based on thermal functions of $\text{LaC}_2(\text{s})$ derived from those of $\text{UC}_{1.94}$ and $\text{ThC}_{1.94}$) are $-(58.6 \pm 10.1)$ and $-(62.4 \pm 10.1) \text{ kJ mol}^{-1}$, respectively. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Thermodynamic data for various reactions that may occur during the irradiation of fast reactor fuels and information on the phase relationships which exist between fission product elements and the fuel are essential for predicting the chemical state of irradiated fuel. Such information is also required for interpreting data obtained in post-irradiation studies of the fuel. Even though a large amount of information is available on the chemistry of lanthanides in aqueous and organic solutions, much less is known with respect to their basic binary compounds, especially the carbides, and there is considerable discrepancy in the reported data. Owing to their high reactivity and susceptibility to hydrolysis, it is difficult to handle the rare-earth carbides. Recently, we have demonstrated a new method

[1] by which the thermodynamic data of the metal carbide phase can be derived from the equilibrium carbon monoxide pressures measured over the three-phase field (metal oxide–metal carbide–carbon). This method obviates the need for the complete conversion of the oxide to carbide. As the carbide is generated in situ, the problems due to its reactivity are circumvented. We had published our results on the U–Gd–C system based on this method earlier [2]. We have initiated a programme to generate thermodynamic data of rare-earth dicarbides by employing this method and in this paper we report our results on the lanthanum dicarbide phase.

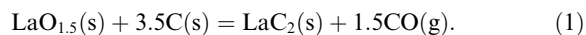
Chupka et al. [3] were the first to detect gaseous species containing lanthanum and carbon in the vapour phase from their studies on the vaporisation of metallic lanthanum from a graphite crucible by means of a Knudsen effusion mass spectrometer. Gingerich and co-workers [4–7] have obtained the thermodynamic data on various gaseous lanthanum carbide species, La_xC_y , where $x = 1\text{--}2, y = 1\text{--}8$, by employing high-temperature mass spectrometry. Jackson et al. [8] reported

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thermodynamic data on lanthanum dicarbide based on their Langmuir vaporisation experiments by using a mass spectrometer. Faircloth et al. [9] have obtained the apparent vapour pressure data in the temperature range 1923–2250 K by employing the Knudsen effusion target collection method and using lanthanum dicarbide as the starting sample. The apparent vapour pressures were apportioned to the partial pressures of La(g) and LaC₂(g) from the ratio of La(g)/LaC₂(g) reported by Chupka et al. [3] Stearns et al. [10] have studied the vaporisation thermodynamics of the La–C system by employing the Knudsen effusion mass spectrometry in the temperature range 2267–2600 K. Anderson et al. [11] have obtained the thermodynamic data for lanthanum dicarbide from a study of the dicarbide/carbon two-phase region employing a solid-state galvanic cell with calcium fluoride solid electrolyte in the temperature range 900–1300 K. Meschel et al. [12] obtained the enthalpy of formation of the lanthanum dicarbide by using direct synthesis calorimetry. Meschel et al. [12] have also referred to a few other reports in which the estimates of enthalpy of formation of lanthanum dicarbide were made based on Miedema's semi-empirical model [13,14]. Gschneidner et al. [15] have compiled the thermodynamic data of all the rare-earth carbides, nitrides and sulphides, in the year 1971, based on the available data till then. Adachi et al. [16] have reviewed the available information up to 1991 on the thermodynamic as well as other physical properties of rare-earth carbides. There is also a very recent report on the electronic structure and on the calculation of thermodynamic properties of LaC₂(g) by Roszak et al. [17].

In most of the previous studies, lanthanum dicarbide was prepared either by carbothermic reduction or by mixing metal with graphite powder. In order to ensure the complete conversion of oxides to carbide the reactions were carried out at high temperatures ($T > 2300$ K), where the loss of metal vapour during the preparation could result in uncontrolled stoichiometry. In the present study, the carbide was generated in situ in a high vacuum chamber (ultimate pressure $\approx 10^{-9}$ bar) from a mixture of LaO_{1.5} and graphite according to Eq. (1):



The equilibrium carbon monoxide pressure, of the resulting phase field, LaO_{1.5}(s)–C(s)–LaC₂(s) was determined by measuring the effusion pressure of carbon monoxide from the sintered pellet by means of a quadrupole mass spectrometer (QMS) [1]. From the temperature dependence of equilibrium carbon monoxide pressures, the Gibbs energy and enthalpy of reaction (1) and subsequently for the formation of LaC₂(s) were derived.

2. Experimental

2.1. Procedure

Samples were prepared from mixtures of LaO_{1.5}(s) (purity 99.99%, M/s. Koch Light Laboratories, UK) and C(s) (purity >99.999%). The oxide was blended with graphite slightly in excess of the stoichiometric amounts. The sample was then pelletised at 25 MPa to give pellets with the dimensions 6 mm in diameter, 1 mm in thickness and weighing about 90–100 mg. The pellets were degassed at around 473 K for 12 h in vacuum before carrying out the actual experiment.

The pellets were heated rapidly at the rate of approximately 100 K min⁻¹ to the temperatures of interest by means of an induction generator in a high vacuum chamber and maintained there for short-time periods (≈ 10 min). During this time the CO(g) effusing out of the pellet through the wide-mouthed, open tantalum crucible was recorded as a function of time by using the quadrupole mass spectrometer (Spectramass, DAQ/DXM 200). After recording the decay of CO(g) for about 5 min the furnace power was lowered to zero and after about 5 min, the same pellet was heated to the next higher temperature and the experiment was continued. The steps as mentioned above were repeated until the effusion pressures crossed the limiting operating pressure of the QMS ($\approx 10^{-7}$ bar). Temperatures were measured with an optical pyrometer which was sighted onto a blackbody hole on the side of the crucible.

At the end of each experiment, the sample was analysed for the phases present by X-ray diffraction (XRD) (Debye–Scherrer) employing Cu–K α radiation. Care was taken to avoid the reaction of lanthanum carbide with air/moisture during the XRD measurements by coating the sample with xylene. The reacted pellets were also examined by means of an optical microscope in order to establish the formation of a different phase.

Four independent runs with different pellets were carried out. In one of the experiments, the sample was quenched to room temperature after it had seen the temperature of 1343 K for 5 min and subjected to XRD analysis.

2.2. Method of calculation

The equilibrium CO(g) pressure in the pellet was computed by measuring the CO(g) pressure in the high vacuum chamber as a function of time by using a QMS as described below. The CO(g) released by the carbothermic reduction of the oxide accumulates in the pores of the pellet that get sintered during the process. The effusion of the gas through the pores of the pellet causes the CO(g) pressure in the chamber, to increase to a maximum value very quickly and then to fall. This process can be described in terms of the rate of pro-

duction of CO(g) in the pellet, its release to the vacuum chamber and its ultimate removal from the vacuum chamber by the pumping action. When the rate of production of the gas inside the pellet is higher than its release from the pellet, there is an increase of pressure in the pellet. Since the rate of pumping out is very high in comparison to the rate of release to the chamber, the chamber pressure will indicate the pressure inside in the pellet.

The pressure, p_{eff} , of CO(g) in the chamber (after subtracting the background pressure) at 298 K, as recorded by the QMS, was plotted against the time, t . The CO(g) pressure increased to a maximum value initially and then decreased exponentially. The decay portion of the curve was fitted to an exponential function of the form [1]

$$p_{\text{eff}} = p_0 e^{-kt}, \quad (2)$$

p_0 and k are the constants derived from the least-square fitting of this data. k is termed as the decay factor and is a constant for a given sample at that temperature. p_0 is the maximum CO(g) pressure. From the values of p_0 and k for a particular temperature, the equilibrium CO(g) pressure, p_{CO} , for that temperature was calculated according to the equation

$$p_{\text{CO}} = p_0 T k^{-1} C. \quad (3)$$

The derivation of the above-mentioned equation is reported in our previous paper [1]. k is the rate of effusion of CO(g) from the pellet. T is the temperature of the pellet and C is a constant, $C = S/T''$, where S is the rate of removal of gas from the chamber and T'' is the ambient temperature. For our system the nominal value of C is approximately equal to unity.

3. Results

Table 1 gives the equilibrium pressures of carbon monoxide, p_{CO} , calculated as described above in the temperature range 1343–1638 K. The decay factors obtained from the plot of p_{eff} versus time at each temperature of measurement and the derived equilibrium carbon monoxide pressures are also given in Table 1. The carbon monoxide pressure was plotted as a function of $1/T$ in Fig. 1 and fitted to a straight line by the method of least squares, to get the expression

$$\ln p_{\text{CO}} = -(50130 \pm 658)/T + (22.9 \pm 0.4), \quad (4)$$

where p_{CO} is indicated in bar.

Table 1

Equilibrium CO(g) pressure (p_{CO}) over the phases $\text{LaO}_{1.5}(\text{s})\text{--C}(\text{s})\text{--LaC}_2(\text{s})$ derived from the effusion pressure of CO (p_0) and decay factor (k) by using Eq. (3) and the Gibbs energy and enthalpy of reaction (1) as a function of temperature

Runs	Temperature (K)	Pressure (p_0) (bar)	Decay factor (K) (s^{-1})	Equilibrium pressure (P_{CO}) (bar)	$\Delta_r G_{\text{T}}^\circ$ of reaction (1) (kJ mol^{-1})	$\Delta_r H_{298}^\circ$ of reaction (1) ^a at 298 K (kJ mol^{-1})
Run 1	1343	1.26E-10 ^b	0.3462	4.98E-7	243.6	650.3
	1403	4.52E-10	0.2122	2.99E-6	222.5	647.9
	1443	8.48E-10	0.1309	9.35E-6	208.4	655.7
	1593	4.76E-9	0.0408	1.86E-4	170.7	653.4
	1603	2.53E-9	0.0173	2.34E-4	167.1	655.6
Run 2	1343	1.47E-10	0.3771	5.19E-7	242.3	649.6
	1408	4.64E-10	0.2118	3.09E-6	222.8	649.8
	1458	1.31E-9	0.1483	1.29E-5	204.7	661.1
	1603	2.12E-9	0.0144	2.36E-4	166.9	649.7
	1628	6.41E-9	0.0393	2.66E-4	167.1	649.6
Run 3	1353	1.53E-10	0.3019	6.86E-7	239.5	654.1
	1398	3.55E-10	0.1976	2.51E-6	224.8	652.7
	1498	1.47E-9	0.1054	2.09E-5	201.3	655.7
	1638	1.75E-8	0.0568	5.03E-4	155.1	648.7
Run 4	1373	2.62E-10	0.3154	1.14E-6	234.3	652.2
	1408	4.88E-10	0.2199	3.12E-6	222.6	646.8
	1498	1.38E-9	0.0989	2.10E-5	201.2	655.6
	1628	2.25E-8	0.0912	4.02E-4	158.7	652.7
	1633	1.99E-8	0.0735	4.11E-4	157.3	652.8

Average $\Delta_r H_{298}^\circ$ of reaction 1 = $(651.6 \pm 3.6) \text{ kJ mol}^{-1}$

^a Third-law results based on Gibbs energy functions of $\text{LaC}_2(\text{s})$ derived from those of $\text{CaC}_2(\text{s})$.

^b Read as 1.26×10^{-10} .

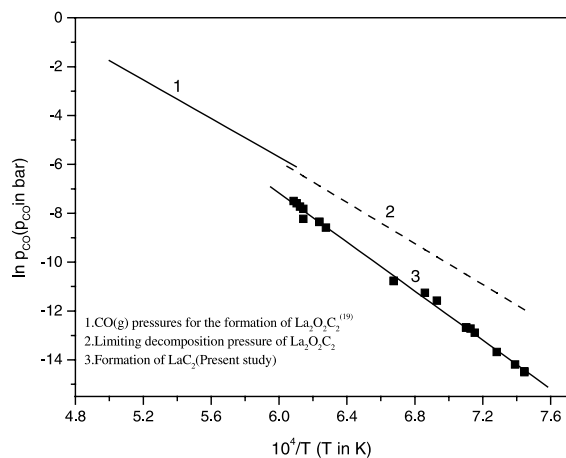


Fig. 1. A plot of equilibrium CO(g) pressure as derived for reaction (1) against reciprocal temperature.

The Gibbs energy of reaction (1) at different temperatures was then derived from the respective equilibrium constants. The Gibbs energy of formation of $\text{LaC}_2(\text{s})$ at various temperatures was derived from the Gibbs energy of reaction (1) by using appropriate Gibbs energy data for formation of $\text{LaO}_{1.5}(\text{s})$ and $\text{CO}(\text{g})$, from the literature [18]. A comparison of the Gibbs energy of formation of $\text{LaC}_2(\text{s})$ with literature reports is given in Fig. 2.

The second-law enthalpy of reaction (1) at the midtemperature of measurement was obtained from the slope of the $\ln p_{\text{CO}}$ versus $1/T$ curve. This was converted to the enthalpy of formation of the reaction at 298 K by taking the enthalpy increments of $\text{LaO}_{1.5}(\text{s})$, $\text{C}(\text{s})$ and $\text{CO}(\text{g})$ from the literature [18]. Thermodynamic functions for $\text{LaC}_2(\text{s})$ were estimated as suggested by Faircloth et al. [9] and Stearns et al. [11], from the results on isomorphous $\text{CaC}_2(\text{s})$ by employing the relations

$$(H_T^\circ - H_{298}^\circ)_{\text{LaC}_2(\text{s})} = (H_T^\circ - H_{298}^\circ)_{\text{CaC}_2(\text{s})} - (H_T^\circ - H_{298}^\circ)_{\text{Ca}(\text{s})} + (H_T^\circ - H_{298}^\circ)_{\text{La}(\text{s})}$$

Table 2

Estimated enthalpy increments and Gibbs energy functions of $\text{LaC}_2(\text{s})$ at 1 bar from the thermal functions of CaC_2 , $\text{UC}_{1.94}$ and $\text{ThC}_{1.94}$

T (K)	Based on $\text{CaC}_2(\text{s})$		Based on $\text{UC}_{1.94}(\text{s})$		Based on $\text{ThC}_{1.94}(\text{s})$	
	$(H_T^\circ - H_{298}^\circ)$ (kJ mol ⁻¹)	$(G_T^\circ - H_{298}^\circ)/T$ (J K ⁻¹ mol ⁻¹)	$(H_T^\circ - H_{298}^\circ)$ (kJ mol ⁻¹)	$(G_T^\circ - H_{298}^\circ)/T$ (J K ⁻¹ mol ⁻¹)	$(H_T^\circ - H_{298}^\circ)$ (kJ mol ⁻¹)	$(G_T^\circ - H_{298}^\circ)/T$ (J K ⁻¹ mol ⁻¹)
1000	59.0	-122.5	40.3	-144.4	57.8	-136.3
1200	69.6	-132.5	54.2	-151.1	72.8	-145.7
1400	85.1	-141.0	68.1	-157.6	87.9	-155.1
1600	100.7	-149.0	82.0	-164.2	102.9	-164.5
1800	116.7	-159.5	95.9	-170.8	118.0	-173.9

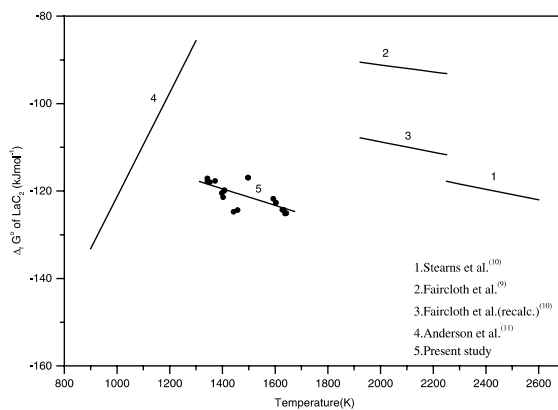


Fig. 2. A comparison of Gibbs energy of formation of $\text{LaC}_2(\text{s})$ obtained in the present study (calculated from thermal functions of CaC_2) with literature reports.

$$\begin{aligned} ((G_T^\circ - H_{298}^\circ)/T)_{\text{LaC}_2(\text{s})} &= ((G_T^\circ - H_{298}^\circ)/T)_{\text{CaC}_2(\text{s})} \\ &\quad - ((G_T^\circ - H_{298}^\circ)/T)_{\text{Ca}(\text{s})} \\ &\quad + ((G_T^\circ - H_{298}^\circ)/T)_{\text{La}(\text{s})} \end{aligned}$$

and were tabulated in Table 2. The $\Delta_r H_T^\circ$ ($T = 1490$ K) and $\Delta_r H_{298}^\circ$ were found to be (632.1 ± 8.4) and (641.1 ± 8.4) kJ mol⁻¹, respectively. The errors are derived from the standard deviation of the data. Similarly the third-law enthalpy of reaction (1) was derived from the CO pressures at each temperature and Gibbs energy functions of $\text{LaO}_{1.5}(\text{s})$, $\text{C}(\text{s})$, $\text{CO}(\text{g})$ from the literature [18] and that of $\text{LaC}_2(\text{s})$ estimated as mentioned above. The third-law enthalpy values calculated at each temperature of measurement are listed in Table 1. The average of the enthalpy of reaction derived using the third-law method was found to be (651.6 ± 3.6) kJ mol⁻¹. The enthalpy increments and Gibbs energy functions of $\text{LaC}_2(\text{s})$ were also calculated by using the corresponding thermal functions of $\text{UC}_{1.94}$ [18] and $\text{ThC}_{1.94}$ [18] and used for deriving the enthalpy of reaction using the second-law and third-law methods. The calculated thermal functions of LaC_2 based on those of $\text{UC}_{1.94}$ and $\text{ThC}_{1.94}$ are also listed in Table 2. The enth-

Table 3
A comparison of the enthalpies of formation of $\text{LaC}_2(\text{s})$ with the literature data

Method/technique	$\Delta_f H^\circ$ at 298K (kJ mol ⁻¹)			Reference
	Second-law	Third-law	Selected	
Langmuir evaporation	-151 ± 16		-151 ± 16	Jackson et al. [8]
Knudsen effusion	-79.5	-61.1	-79.5	Faircloth et al. [9]
	-92 ^a	-	-92 ^a	
Knudsen effusion MS	-89 ± 24	58.5 ± 22	- 89 ± 24	Stearns et al. [10]
EMF	-240	-87.4	-87.4	Anderson et al. [11]
Calorimetry			- 80.8 ± 4.2	Meschel et al. [12]
Calculation			-207	De Boer et al. [13]
Calculation			-180	Niessen et al. [14]
CO pressure				Present study
	-90.6 ± 8.4	-80.1 ± 3.6		(from CaC_2) ^b
	-75.1 ± 8.4	-57.8 ± 3.6		(from $\text{UC}_{1.94}$) ^b
	-95.4 ± 8.4	-59.5 ± 3.6	- 58.6 ± 10.1 ^c	(from $\text{ThC}_{1.94}$) ^b

^a Results of Faircloth et al. [9] as recalculated by Stearns et al. [10].

^b The thermal functions of $\text{LaC}_2(\text{s})$ for calculation in the present study were derived from the corresponding thermal functions as mentioned. The thermal functions used for calculation by other workers are based on thermal functions $\text{CaC}_2(\text{s})$.

^c Recommended value with the overall estimated error in the measurement.

alpy of the reaction derived using the second-law method was found to be (656.6 ± 8.4) and (636.3 ± 8.4) kJ mol⁻¹, respectively. The average third-law enthalpy of the reaction was determined to be (673.8 ± 3.6) and (672.2 ± 3.6) kJ mol⁻¹, respectively.

The enthalpy of formation of $\text{LaC}_2(\text{s})$ at 298 K was derived from the enthalpy of reaction (1), derived using the second-law and third-law methods and the values for the enthalpy of formation of $\text{LaO}_{1.5}(\text{s})$, $\text{C}(\text{s})$ and $\text{CO}(\text{g})$ from the literature [18]. The estimated error in the pressure measurements for different samples heated to the same temperature is less than 5%, based on our data. However, admitting even a higher error in pressure measurements (±50%) and temperature measurements (±3 K), the overall estimated error is only about 10.1 kJ mol⁻¹. Data on the enthalpy of formation of $\text{LaC}_2(\text{s})$ at 298 K available in the literature are compared with those obtained in the present study (calculated using the thermal functions of CaC_2 , $\text{UC}_{1.94}$ and $\text{ThC}_{1.94}$) in Table 3.

4. Discussion

The XRD pattern of the sample at the end of the measurement indicated the presence of the three-phase mixture $\text{LaO}_{1.5}(\text{s})$, $\text{LaC}_2(\text{s})$ and $\text{C}(\text{s})$. The same was observed in one of the samples which was quenched after seeing a temperature of 1343 K, the minimum of the temperature range of the present measurements. The lattice parameters of LaC_2 were deduced to be $a = 395$ pm and $c = 657$ pm. This is taken as confirmation of the sample to be a three-phase mixture $\text{LaO}_{1.5}(\text{s})$ – $\text{LaC}_2(\text{s})$ – $\text{C}(\text{s})$ in the entire temperature range of measurement.

One of the problems of preparing the carbide by carbothermic reduction is the possibility of formation of an oxycarbide. While $\text{La}_2\text{O}_2\text{C}_2(\text{s})$ has a monoclinic structure, $\text{LaC}_2(\text{s})$ has a tetragonal structure. The absence of peaks due to $\text{La}_2\text{O}_2\text{C}_2(\text{s})$ in the XRD pattern in the present study indicated that the measurements were carried out in the phase field $\text{LaO}_{1.5}(\text{s})$ – $\text{LaC}_2(\text{s})$ – $\text{C}(\text{s})$ and not in $\text{LaO}_{1.5}(\text{s})$ – $\text{La}_2\text{O}_2\text{C}_2(\text{s})$ – $\text{C}(\text{s})$. Butherus and Eick [19] have measured the $\text{CO}(\text{g})$ partial pressures over the three-phase field $\text{LaO}_{1.5}(\text{s})$ – $\text{La}_2\text{O}_2\text{C}_2(\text{s})$ – $\text{C}(\text{s})$ in the temperature range 1640–2040 K. The variation of p_{CO} as a function of temperature, reported by them are compared with those obtained in the present study in Fig. 1. It can be seen from the plot that the p_{CO} pressure obtained in the present study is lower in the entire temperature range of measurement. For example at 1600 K, p_{CO} over the three-phase field $\text{LaO}_{1.5}(\text{s})$ – $\text{La}_2\text{O}_2\text{C}_2(\text{s})$ – $\text{C}(\text{s})$ is 1.2×10^{-3} bar ($\ln p_{\text{CO}} = -6.737$) as compared to 2.2×10^{-4} bar ($\ln p_{\text{CO}} = -8.431$) over the phase field $\text{LaO}_{1.5}(\text{s})$ – $\text{LaC}_2(\text{s})$ – $\text{C}(\text{s})$. The limiting pressures for the decomposition of $\text{La}_2\text{O}_2\text{C}_2(\text{s})$ to $\text{LaC}_2(\text{s})$ have been calculated based on the results from the present study and those of Butherus et al. [19] and have been plotted in Fig. 1. The lower p_{CO} pressures obtained in the present study in comparison to the calculated limiting pressures are taken as further confirmation of absence of the oxycarbide phase. The presence of another oxycarbide, $\text{La}_4\text{O}_3\text{C}$ has also been reported by Butherus et al. [20], but no systematic study on the vapour pressures is available for comparison.

The second-law and third-law enthalpies of the reaction (1), calculated by using the thermal functions of LaC_2 derived from CaC_2 , obtained from the present study are in good agreement with each other. As can be

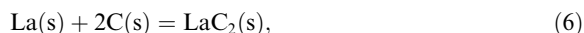
seen from Table 1, there is no significant temperature-dependent variation of the third-law enthalpy of reaction indicating the reliability of the thermodynamic data obtained. A comparison of the Gibbs energy of formation of $\text{LaC}_2(\text{s})$ obtained in the present study, calculated using the thermal functions of $\text{LaC}_2(\text{s})$ derived from those of $\text{CaC}_2(\text{s})$, with the literature reports is given in Fig. 2. From the figure it is obvious that there is a lot of scatter in the reported data. The results of Anderson et al. [11] show a very steep temperature variation of the Gibbs energy of formation, much unlike the results of all others. As this variation is indicative of the entropy, the slope of their data is probably in error. The results of Faircloth et al. [9] indicate a higher Gibbs energy of formation, but the recalculated results (done by Stearns et al. [10]) are within the limits of the experimental error of Stearns et al. [10]. The Gibbs energy of formation of $\text{LaC}_2(\text{s})$ obtained in the present study is also within the error limits of Stearns et al. [10].

The enthalpy of formation of $\text{LaC}_2(\text{s})$ as calculated by second-law and third-law methods, using the thermal functions of $\text{LaC}_2(\text{s})$ as derived from those of $\text{CaC}_2(\text{s})$, is compared with other literature references in Table 3. Faircloth et al. [9] apportioned the total pressure data as that of p_{La} and p_{LaC_2} by taking the ratio of LaC_2/La as reported by Chupka et al. [3] which is about 0.66 at 2500 K. The second-law and third-law enthalpy of the reaction



derived by Faircloth et al. [9] differed by 18.4 kJ mol^{-1} (see Table 3). They have chosen the enthalpy of formation obtained by the second-law method as the recommended value. Faircloth et al. [9] have obtained the $\text{LaC}_2(\text{s})\text{--C}(\text{s})$ phases by heating the mixture of lanthanum and graphite in a Knudsen cell at temperature above 2300 K. At such temperatures, the possibility of variation of the C-rich boundary is envisaged. The thermodynamic data derived by Faircloth et al. [9] are from total pressure measurements and are sensitive to the ratio of $\text{LaC}_2(\text{g})/\text{La}(\text{g})$ used to derive the partial pressures. Stearns et al. [10] recalculated the partial pressure of La by employing the $\text{LaC}_2(\text{g})/\text{La}(\text{g})$ ratio obtained from their mass spectrometric measurements, which is about 0.59 at 2500 K, which yielded the second-law enthalpy of formation to be -92 kJ mol^{-1} . This value is in good agreement with the second-law enthalpy of formation recommended in the present study. The difference between second-law and third-law enthalpies of reaction (5) is about 33 kJ mol^{-1} , which is reflected in the enthalpy of formation data as indicated in Table 3. Stearns et al. [10] have attributed such a large difference to the estimated thermal functions of $\text{LaC}_2(\text{s})$ and preferred the second-law value for the recommended value. In the present study, the agreement between second-law

and third-law data for the reaction (1) (calculated with the thermal functions of $\text{LaC}_2(\text{s})$ derived from those of CaC_2) as well as for the formation reaction (6),



derived from it, is good, ruling out the possibility of the thermal functions alone being responsible for the disparity. According to the La–C phase diagram [21] the $\text{LaC}_2(\text{s})$ phase exhibits a considerable amount of non-stoichiometry at high temperatures. The homogeneity range becomes significant around 1600 K. Faircloth et al. [9] reported the composition of the lanthanum dicarbide phase to be as high as $\text{LaC}_{2.66}$ at 2380 K. Such a change in the composition of lanthanum dicarbide could contribute to the difference in the second-law and third-law enthalpies of the reaction. That could be the reason for the difference in the second-law and third-law enthalpies of Stearns et al. [10].

Faircloth et al. [9] have referred to the enthalpies of formation of $\text{LaC}_2(\text{s})$ obtained by Jackson et al. [8] to be $-(151 \pm 16) \text{ kJ mol}^{-1}$ based on the Langmuir evaporation technique using mass spectrometry. Such a high negative enthalpy of formation indicates the non-equilibrium nature of their study.

Anderson et al. [11] have used an EMF technique for determining the thermodynamic data of rare-earth dicarbides. There is a large disagreement between the second-law $-(240 \text{ kJ mol}^{-1})$ and third-law $-(87.4 \text{ kJ mol}^{-1})$ results in this study (see Table 3). Anderson et al. [11] analysed their data in detail to explain this difference and recommended their third-law value. This value is in agreement within the error limits with that in the present study. As indicated by the authors themselves, caution should be exercised in using galvanic cells to determine reliable thermochemical information for refractory materials.

The enthalpy of formation reported by Meschel et al. [12] is in good agreement with that obtained by the third-law method in the present study. They calculated the enthalpy of formation at 298 K from the difference in the measured enthalpy of the reaction $\text{La}(\text{s}) + 2\text{C}(\text{s}) = \text{LaC}_2(\text{s})$ at 1473 K and the measured enthalpy increment associated with $\text{LaC}_2(\text{s})$ going from 298 to 1473 K. Meschel et al. [12] reported 1–2% of $\text{LaO}_{1.5}(\text{s})$ being present in their final samples. It may be difficult to estimate the influence of small amounts of $\text{LaO}_{1.5}(\text{s})$ present in the final sample of Meschel et al. [12], on the $\Delta_f H^\circ$ derived by them. The enthalpy of formation of $\text{LaC}_2(\text{s})$ computed by De Boer et al. [13] and Niessen et al. [14] based on Miedema's semi-empirical model are very low (negative). It can be seen that our results (calculated using the thermal functions of $\text{LaC}_2(\text{s})$ as derived from those of CaC_2) compare very well with the values reported in the literature.

It is pointed out that all the researchers had calculated the thermal functions of LaC_2 based on those of CaC_2 . In view of the proximity of the lanthanides to actinides like U, Th and the similarity in their properties, it is more appropriate to calculate the enthalpy of formation of $\text{LaC}_2(\text{s})$ based on the thermal functions of $\text{UC}_{1.94}$ and $\text{ThC}_{1.94}$ by using the second-law and third-law methods. The thermal functions are reliable even though these carbides are hypostoichiometric. The enthalpy of formation of LaC_2 at 298 K calculated using thermal functions of $\text{UC}_{1.94}$ is $-(75.1 \pm 8.4) \text{ kJ mol}^{-1}$ (second-law) and $-(57.8 \pm 3.6) \text{ kJ mol}^{-1}$ (third-law). The enthalpy of formation of LaC_2 at 298 K calculated based on thermal functions of $\text{ThC}_{1.94}$ is $-(95.4 \pm 8.4) \text{ kJ mol}^{-1}$ (second-law) and $-(59.5 \pm 3.6) \text{ kJ mol}^{-1}$ (third-law). It is observed that the enthalpy of formation of $\text{LaC}_2(\text{s})$ depends more on the origin of thermal functions of $\text{LaC}_2(\text{s})$.

As mentioned earlier, the calculated results based on thermal functions of $\text{LaC}_2(\text{s})$ derived from the thermal functions of $\text{UC}_{1.94}$ and $\text{ThC}_{1.94}$ are more reliable. It can be seen that the enthalpy of formation of LaC_2 at 298 K by the third-law method using thermal functions of $\text{LaC}_2(\text{s})$ derived from those of $\text{UC}_{1.94}$ and $\text{ThC}_{1.94}$ are in good agreement. Hence, the average of these two results, $-(58.6 \pm 10.1) \text{ kJ mol}^{-1}$, is chosen to be the recommended value for $\Delta_f H_{298}^\circ$ of $\text{LaC}_2(\text{s})$.

5. Summary

A method based on the measurement of equilibrium CO pressures over the three-phase field of $\text{LaO}_{1.5}(\text{s})$, $\text{C}(\text{s})$ and $\text{LaC}_2(\text{s})$ of the La–C–O system, starting from a $\text{LaO}_{1.5}(\text{s})$ and $\text{C}(\text{s})$ mixture, enabled the determination of the thermodynamic data on $\text{LaC}_2(\text{s})$. The enthalpy of formation and the Gibbs energy of formation of $\text{LaC}_2(\text{s})$ at 298 K recommended in the present study are $-(58.6 \pm 10.1) \text{ kJ mol}^{-1}$ and $-(62.4 \pm 10.1) \text{ kJ mol}^{-1}$, respectively. It can be seen that the present technique allows the Gibbs energy measurements at much lower temperatures in comparison to other reports.

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