J. Chem. Eng. Data **2010,** *55,* 3779–3785

Study of Incongruent Decomposition of Calcium Carbonate by Transpiration Thermogravimetry

R. Viswanathan,* T. S. Lakshmi Narasimhan, and S. Nalini

Fuel Chemistry Division, Chemistry Group, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India

The vaporization of $CaCO_3(s)$ was studied by a transpiration method using a commercial thermogravimetric apparatus. The measurements involved the use of argon as the carrier gas for the transport of $CO_2(g)$ and derivation of its pressure in the temperature range from (650 to 790) K through many flow dependence and temperature dependence runs. The decomposition pressures of $CaCO_3(s)$ obtained in this study represent the first results from dynamic measurements at low temperatures and are in reasonable accord with those from the previously reported studies at relatively higher temperatures (dynamic method, from (950 to 1161) K; static method, (722 to 1177) K). The results from all three studies are combined to recommend the following thermodynamic parameters pertinent to the decomposition reaction $CaCO_3(s) = CaO(s) + CO_2(g)$: $\log[p(CO_2)/Pa] = -(9074 \pm 555)/(T/K) + (12.91 \pm 0.71)$ for the temperature range (650 to 1177) K; $\Delta_r H^\circ_m(298.15\ K) = (180.7 \pm 11.0)\ kJ \cdot mol^{-1}$; and $\Delta_r S^\circ_m(298.15\ K) = (161.6 \pm 8.3)\ J \cdot mol^{-1} \cdot K^{-1}$.

Introduction

In our recent paper,[1] it was described in detail how our commercial thermogravimetric apparatus had been validated for vapor pressure measurements based on the transpiration technique. Briefly, the validation efforts were all aimed at obtaining the results that will not defy the basic criterion of a good transpiration experiment that the rate of mass-loss should in general increase with an increase in the carrier gas flow rate (at least up to the end of the so-called plateau region in the apparent vapor pressure, P, versus flow rate plot). During this process, it was noted[1] that quite a number of previous transpiration thermogravimetric studies had some basic errors: (1) overestimation of vapor pressures by using a sample temperature in the calculations (instead of room temperature) when the carrier gas flow rates were measured at room temperature and used without conversion to the sample temperature and (2) lack of evidence for perfect transpiration conditions as shown by inconsistent and often erratic trends in the rate of mass loss with increasing flow rate. After the validation of our apparatus with three congruently vaporizing systems, CsI,[2] Te,[3] and TeO_2,[4–6] all of which had been studied previously by us using Knudsen effusion mass spectrometry,[2–6] the investigation of vaporization of boric acid[7] was undertaken by us using both transpiration thermogravimetry and Knudsen effusion mass spectrometry, and mutually consistent results were obtained.

Encouraged by these successful transpiration experiments,[1,7] an attempt was made by us to employ transpiration thermogravimetry to determine the Te-rich phase boundary of $RuTe_2$, the only condensed phase that exists in the binary system, (Ru + Te). The idea was that (1) due to incongruent vaporization, an initially two-phase mixture ($RuTe_2$ + Te) upon continuous vaporization would lose the excess tellurium (as $Te_2(g)$) and enter into the single-phase $RuTe_2$; (2) consequently, the rate of mass-loss (at a constant temperature and carrier gas flow rate) will be constant as long as the excess tellurium is present, and upon entry into the single-phase $RuTe_2$, it will be monotonically decreasing; and (3) the composition corresponding to the onset of the latter can be taken as the Te-rich boundary. However, mass gain was observed for most of the experiment, except when a high carrier gas flow rate was employed. Attempts with (Ru + $RuTe_2$) samples also met with similar experience, and so were (MnTe + $MnTe_2$) samples. In the case of the latter sample, the vapor pressure was nearly the same as that over elemental tellurium, although it is known from our KEMS study[8] that it is 2 orders of magnitude lower. Observation of whiskers of tellurium deposits on the reactive capillary tube explained such a result, but the reason for its occurrence remained unclear. With all our experiments on incongruently vaporizing samples yielding disconcerting results, it was decided to undertake the study of an incongruently vaporizing system that will give free-volatile molecules. Accordingly, calcium carbonate was chosen for the investigation since this substance is known to decompose to CaO(s) and $CO_2(g)$, the latter being not condensable (unlike the vapor species $Te_2(g)$ in the case of the Ru−Te or Mn−Te systems).

Stern and Weise[9] critically reviewed the literature dealing with high-temperature behavior of inorganic carbonates and tabulated the equilibrium constants for $CaCO_3$ decomposition from (298.15 to 1200) K by deducing them through a thermodynamic method. There was no mention in this review of the comprehensive CO_2 pressure measurements by Hill and Winter,[10] who used static techniques (a mercury U-manometer, a cathetometer, and a McLeod gage) to measure $p(CO_2)$ at different pressure ranges and over a large temperature range from (722 to 1177) K. Searcy and his co-workers[11–14] extensively studied the decomposition of $CaCO_3(s)$ by using single crystals and powder, all these studies essentially yielding very useful information on decomposition kinetics of $CaCO_3(s)$ rather than on the decomposition equilibrium. Gleixner and Chang[15] determined the equilibrium CO_2 decomposition pressure of a (CaO + $CaCO_3$) mixture in the temperature range from (950 to 1161) K by employing two different cyclic thermogravimetric methods. These authors used a mixture of (CO_2 + argon) flowing over the sample and took that value of $p(CO_2)$ which

---

* Corresponding author. Fax: 91 44 27480065. E-mail: rvis@igcar.gov.in.

10.1021/je100294t

yielded a symmetric mass signal with no net mass change as the equilibration pressure for the system. Each temperature cycling (between T_1 and T_2) was performed at a constant CO_2 pressure, and each $p(CO_2)$ cycling (between p_1 and p_2) was performed at a constant temperature. Oniyama and Wahlbeck[16] performed extensive thermogravimetric measurements using nitrogen as carrier gas. They employed different heating rates and different carrier gas flow rates to determine the peak temperature (temperature at which the $\mathrm{d}m/\mathrm{d}t$ vs T yielded a peak) as well as the enthalpy change and the vaporization coefficient for the decomposition reaction. The averaged $\Delta_{\mathrm{vap}}H°$ value was $(176.51 \pm 3.86)\ \mathrm{kJ \cdot mol^{-1}}$ at an average peak temperature of 980 K, while the vaporization coefficient α_{vap} was 0.0062. The low value of α_{vap} was attributed to inhibited vaporization as well as undersaturation due to apparatus design. Criado and González[17] used appropriate heating rates at four different defined pressures of CO_2 (from (~4000 to 24 500) Pa) to achieve the overlapping sections of the thermogravimetric curves corresponding to the formation and decomposition of $CaCO_3$ and thus the calculation of equilibrium constants for the decomposition of $CaCO_3$(s). The excellent agreement with the values recommended by Stern and Weise[9] was taken as support for the validity of the method employed by them. Most recently, L'vov[18] suggested the use of a thermochemical approach for a quantitative evaluation of the decomposition kinetics and puts forward the representation that the decomposition of $CaCO_3$(s) involves volatilization to $CaCO_3$(g), dissociation to CaO(g) and CO_2(g), and condensation of CaO(g) as CaO(s) due to vapor oversaturation (a factor of $3 \cdot 10^{15}$ at 810 K).[19]

With not many pressure measurements existing in the literature (and no transpiration study in the strictest sense) and the $p(CO_2)$ values reported by Hill and Winter[10] and Gleixner and Chang[15] (with static and dynamic methods, respectively) agreeing reasonably well, it was surmised that a transpiration thermogravimetric study of the decomposition of $CaCO_3$(s) with our commercial TG apparatus might not only validate the method yet again but also provide new experimental $p(CO_2)$ data at temperatures lower than hitherto done. Both these objectives were met, and the details are presented in this paper.

Experimental Section

The transpiration measurements were performed by using a Mettler Toledo TG/SDTA851 instrument, the details of which are given elsewhere.[1,7] Briefly, the apparatus has a horizontal furnace in the center of which lies the pan holder of the electronic microbalance. The carrier gas (argon in the present experiment) flows into the furnace through three inlets: the "purge gas inlet", the "protective gas inlet", and the "reactive gas inlet". As mentioned previously, it is the flow through the "reactive gas inlet" (a capillary positioned immediately in front of but slightly above the sample crucible) that facilitated best the transport of the vapor from the reaction zone in the sense that the change in the carrier gas flow rate did effect a change in the rate of mass-loss of the sample. The other two gas inlets were not blanked, but instead, a minimum and a constant flow was maintained through them. Two mass flow controllers were employed for admission of carrier gas, one exclusively for the reactive gas inlet and the other for the purge and protective gas inlets together. The carrier gas flows out of the furnace through a common outlet and a stopcock immediately outside the furnace. The overall carrier gas flow out of the furnace is measured (at room temperature) using a drum-type wet test meter (Ritter, Germany; Type 05/6), and the mass of the sample is acquired through the computer as a function of time at an intended carrier gas flow or temperature. About 200 mg of a $CaCO_3$ sample (GR grade; assay: minimum 99.0 %; Sarabhai Chemicals, India) was taken up to the brim of a lightweight cylindrical quartz crucible (~300 mg; 2 cm diameter; 1 mm depth). In all, 12 flow dependence runs (four at 720 K, five at 740 K, and three at 760 K) and 13 temperature dependence runs were conducted. All the flow dependence measurements were performed by constricting the exit stopcock opening, the constriction effected such that the resulting carrier gas flow rate for a given mass flow controller setting (for reactive gas inlet) would roughly match that deducible from an empirical relation, deduced previously from similar measurements over CsI(s) and Te(s) which provided unambiguous proof of the existence of good transpiration conditions—in terms of both $\mathrm{d}m/\mathrm{d}t$ vs $\mathrm{d}V/\mathrm{d}t$ and P vs $\mathrm{d}V/\mathrm{d}t$ plots.[1] The temperature dependence runs were performed at different conditions of exit stopcock opening (fully open or constricted to varying extents) and for different durations. The longest temperature dependence run was for 72 h involving 38 isothermal segments, the latter selected such that an overall temperature range $\Delta T = 130$ K (T/K = 660 to 790) would be covered once in the increasing, once in the decreasing, and once in the zigzag temperature directions.

Results and Discussion

The vaporization of $CaCO_3$(s) was assumed to be incongruent, according to

$$CaCO_3(s) = CaO(s) + CO_2(g) \qquad (1)$$

The most direct support for the validity of this assumption comes from the recent study of decomposition of $CaCO_3$(s) by Feng and Lombardo[20] who detected CO_2(g) as the principal gaseous species when a sample of $CaCO_3$(s) was heated (at $5\ \mathrm{K \cdot min^{-1}}$) under flowing argon. Figure 1 shows the results of three flow dependence runs, one each at 720 K, 740 K, and 760 K. The top half shows the rate of mass loss, $\mathrm{d}m/\mathrm{d}t$, at various volumetric carrier gas flow rates, $\mathrm{d}V/\mathrm{d}t$, while the bottom half shows the corresponding values of $p(CO_2)$, computed from the values of $\mathrm{d}m/\mathrm{d}t$ and $\mathrm{d}V/\mathrm{d}t$ in accordance with the following equation

$$[p(CO_2)/\mathrm{Pa}] \text{ at } (T_s/\mathrm{K}) = 4.989 \cdot 10^5 \{(\mathrm{d}m/\mathrm{d}t)/(\mathrm{mg \cdot s^{-1}})\}/\{(\mathrm{d}V/\mathrm{d}t)/(\mathrm{mL \cdot min^{-1}})\}(T_c/\mathrm{K})/\{M/(\mathrm{g \cdot mol^{-1}})\} \qquad (2)$$

where T_s = the sample temperature; T_c = temperature at which the carrier gas flow was measured (in this work, at room temperature, taken as 298.15 K); and M = mean molar mass of $CO_2 = 44.0\ \mathrm{g \cdot mol^{-1}}$. Table 1 gives a summary of results from all 12 flow dependence experiments. The least-squares fit of the values of $\mathrm{d}m/\mathrm{d}t$ against $\mathrm{d}V/\mathrm{d}t$ according to the relation $\mathrm{d}m/\mathrm{d}t = k(\mathrm{d}V/\mathrm{d}t)$ yielded positive values of R-squared (MS Excel) which is taken to indicate that proper transpiration conditions existed in all flow dependence experiments. The contribution to the flow from CO_2(g) was ignored in the calculations. In these experiments, there existed a flow range ($\Delta(\mathrm{d}V/\mathrm{d}t) \approx (13.7 \pm 5.0)\ \mathrm{mL \cdot min^{-1}}$), in which the value of $p(CO_2)$ remained reasonably stable. The mean of such stable $p(CO_2)$ values in the so-called "plateau region" is given in column 10 of Table 1 along with the standard deviation. Column 11 gives the mean value of $p(CO_2)$ at each temperature, computed from the "mean stable value" corresponding to each flow dependence experiment. The quoted uncertainties are the most probable values.

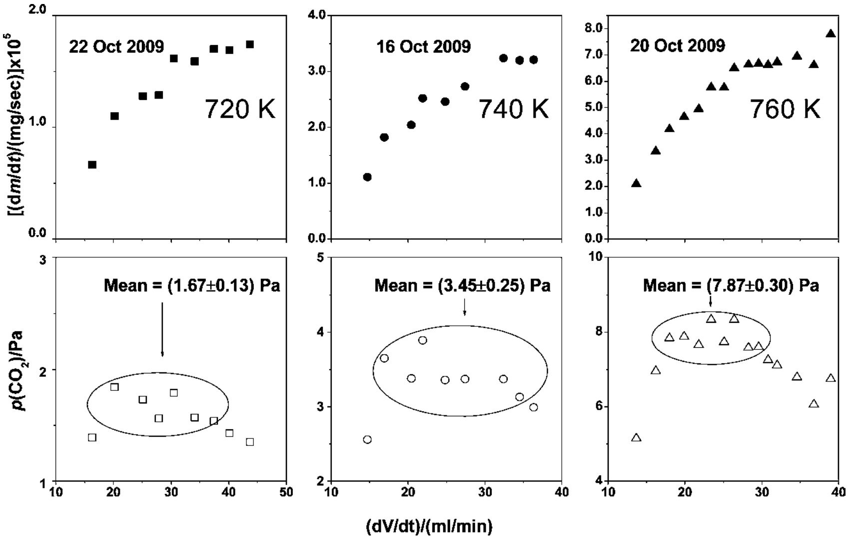

Figure 1. Results of typical flow dependence transpiration experiments on $CaCO_3$ decomposition at 720 K, 740 K, and 760 K. Variation of rate of mass loss with volumetric flow rate (top half). Corresponding variation of apparent vapor pressure $p(CO_2)$ with volumetric flow rate (bottom half).

Table 1. Results from the Flow Dependence Experiments on $CaCO_3$(s) Decomposition

			flow region covered				plateau region			
T/K	run no.	date	$mL \cdot min^{-1}$	no. of points	k in $(dm/dt) = k(dV/dt)$	R(squared)	$mL \cdot min^{-1}$	no. of points	mean p/Pa	mean p/Pa at T/K
720	8	21 Oct 2009	16.9 to 35.2	7	$4.92 \cdot 10^{-7}$	0.84	20.3 to 35.2	6	1.69 ± 0.15	
	9	22 Oct 2009	16.3 to 40.1	9	$4.53 \cdot 10^{-7}$	0.81	20.2 to 37.4	6	1.67 ± 0.13	1.92 ± 0.43
	10	25 Nov 2009	8.2 to 27.6	18	$5.81 \cdot 10^{-7}$	0.80	11.0 to 25.8	12	2.09 ± 0.23	
	11	26 Nov 2009	9.0 to 27.9	17	$5.85 \cdot 10^{-7}$	0.82	13.6 to 20.6	8	2.22 ± 0.12	
740	1	09 Oct 2009	10.3 to 27.3	8	$1.28 \cdot 10^{-6}$	0.88	10.3 to 27.3	8	4.40 ± 0.40	3.52 ± 0.92
	2	12 Oct 2009	14.7 to 46.6	8	$8.73 \cdot 10^{-7}$	0.80	16.0 to 35.5	5	3.40 ± 0.22	
	3	13 Oct 2009	18.0 to 36.1	10	$9.14 \cdot 10^{-7}$	0.79	20.2 to 36.1	8	3.14 ± 0.45	
	4	15 Oct 2009	13.1 to 29.3	9	$9.46 \cdot 10^{-7}$	0.85	13.1 to 29.3	9	3.20 ± 0.33	
	5	16 Oct 2009	14.7 to 36.3	10	$9.46 \cdot 10^{-7}$	0.85	16.9 to 34.5	7	3.49 ± 0.21	
760	6	19 Oct 2009	15.3 to 37.4	11	$2.19 \cdot 10^{-6}$	0.69	19.0 to 29.0	7	8.17 ± 0.39	8.36 ± 0.78
	7	20 Oct 2009	13.7 to 39.0	15	$2.13 \cdot 10^{-6}$	0.86	18.0 to 29.6	8	7.87 ± 0.30	
	12	27 Nov 2009	11.0 to 31.0	15	$2.59 \cdot 10^{-6}$	0.51	21.7 to 24.0	2	9.04 ± 0.03	

The reason for the dip in the $p(CO_2)$ at flow rates lower than that of the plateau region (see Figure 1) is not known. Such a dip was also observed by Opila in the transpiration study of the Cr−O−H system.[21] In all our previous studies with other systems,[1,7] it was observed that the apparent pressures increase steeply at flow rates below that of the plateau region.

The mean $p(CO_2)$ values given in Table 1 (column 11) at 720 K, 740 K, and 760 K were input to obtain a $p-T$ relation

$$\log[p(CO_2)/Pa] = -(8732 \pm 1024)/(T/K) + (12.39 \pm 1.38) \quad (3)$$

The main purpose of deducing the above equation was to use it for pressure calibration (as described below) in temperature dependence runs which contained measurements at T as high as 790 K and T as low as 650 K. Ideally, one would have liked to cover the whole temperature range solely through flow dependence runs. However, since measurement at low temperatures would consume very long duration even for one flow rate (given the criterion set by us that the mass loss at each flow rate should be at least 0.015 mg), covering many flow rates might not be practically feasible (given the situation that a change in the flow rate has to be effected manually). At high temperatures, the problem of surface depletion could arise (due to a high rate of mass loss) when the sample had to be at the same temperature for almost a day.

Table 2 gives the details pertinent to temperature dependence runs. These runs served to examine (1) how the dm/dt values varied with temperature under various conditions of carrier gas flow and (2) how the rate of mass loss varied with time at some randomly selected temperatures, reached in increasing or decreasing temperature directions. The duration at any temperature was kept such that the total mass loss would be at least 0.015 mg. The least-squares-fitted relation between dm/dt vs temperature obtained in each run is given in Table 2. Since the temperature dependence measurements could be performed wholly through a computer (unlike the flow dependence measurements), low temperatures were more readily accessible for collecting meaningful results, and thus, the results of flow and temperature dependence measurements together can yield a $p(CO_2)-T$ relation that encompasses many data points and a larger temperature range (∼140 K) than does eq 3. The following approach was employed: (1) for each run, the value of dm/dt at its mean temperature T_m was computed from the relations given in Table 2, and the $p(CO_2)$ at T_m was deduced from eq 3; (2) a normalization factor f was then deduced as $[p(CO_2)/(dm/dt)]$ at T_m; and subsequently (3) the $p(CO_2)$ corresponding to every dm/dt value was computed as $[f\,(dm/dt)]$. Table 2 gives the value of f for each run and the other details with regard to each temperature dependence run. Figure 2 shows the values of $p(CO_2)$ so computed (200 points from 13 temperature dependence runs). The $p-T$ relation obtained

Table 2. Details of Temperature Dependence Runs on $CaCO_3$(s) Decomposition

run no.	date	temp range K	flow $mL \cdot min^{-1}$	no. of points	T_m K	$\log[(dm/dt), mg \cdot s^{-1}] = -A/T + B$ A	B	$f = (p/Pa)/(dm/dt)$
1[a]	26 and 27 Oct 2009	720 to 780	19	4	750	9515 ± 1386	8.34 ± 1.85	$1.24 \cdot 10^5$
2[c]	4 and 5 Nov 2009	700 to 780	54	17	740	9433 ± 252	8.26 ± 0.34	$1.20 \cdot 10^5$
3[c]	5 and 6 Nov 2009	670 to 780	56	20	725	10458 ± 219	9.53 ± 0.30	$1.72 \cdot 10^5$
4[b]	6 to 9 Nov 2009	660 to 780	105	18	720	10943 ± 285	10.17 ± 0.40	$1.94 \cdot 10^5$
5[a]	9 to 12 Nov 2009	650 to 780	33	19	715	9841 ± 162	8.70 ± 0.23	$1.76 \cdot 10^5$
6[a]	18 to 23 Nov 2009	670 to 790	30	12	730	9686 ± 118	8.52 ± 0.16	$1.52 \cdot 10^5$
7[a]	23 to 25 Nov 2009	690 to 790	20	18	740	9726 ± 263	8.56 ± 0.36	$1.48 \cdot 10^5$
8[a]	25 and 26 Nov 2009	720 to 780	17	4	750	9510 ± 23	8.27 ± 0.03	$1.43 \cdot 10^5$
9[a]	26 and 27 Nov 2009	690 to 790	18	20	740	9724 ± 92	8.55 ± 0.13	$1.53 \cdot 10^5$
10[a]	27 to 30 Nov 2009	650 to 790	22	9	720	9740 ± 167	8.60 ± 0.24	$1.54 \cdot 10^5$
11[b]	3 and 4 Dec 2009	680 to 790	113	16	735	9037 ± 159	7.76 ± 0.22	$1.10 \cdot 10^5$
12[b]	4 to 7 Dec 2009	660 to 790	113	38	725	9148 ± 80	7.83 ± 0.11	$1.35 \cdot 10^5$
13[b]	11 to 13 Dec 2009	660 to 790	113	5	725	9883 ± 124	8.94 ± 0.17	$1.08 \cdot 10^5$

[a] Exit stopcock constriction optimum for transpiration. [b] Exit stopcock completely opened. [c] Exit stopcock constriction intermediate.

from these $p(CO_2)$ values in the temperature range (650 to 790) K is

$$\log[p(CO_2)/Pa] = -(9702 \pm 63)/(T/K) + (13.72 \pm 0.09) \quad (4)$$

The second law enthalpy change for reaction 1 corresponding to the above relation is (185.8 ± 1.2) $kJ \cdot mol^{-1}$ at $T_m = 720$ K. With the auxiliary thermal functions from Knacke et al.,[22] the second law enthalpy change at $T = 298.15$ K is (189.4 ± 1.2) $kJ \cdot mol^{-1}$. Though this value is about 19 $kJ \cdot mol^{-1}$ higher than that deducible from the basic eq 3 which has been employed for pressure calibration, they both agree within uncertainties. The third-law evaluation of the results with Gibbs energy functions from Knacke et al.[22] yield the mean value of (178.5 ± 1.0) $kJ \cdot mol^{-1}$ at $T = 298.15$ K.

The $p-T$ relations deducible from the $p(CO_2)$ values given by Hill and Winter[10] and by Gleixner and Chang[15] are

$$\text{ref 10: } \log[p(CO_2)/Pa] = -(8772 \pm 28)/(T/K) + (12.51 \pm 0.03) \quad (5)$$

$$\text{ref 15: } \log[p(CO_2)/Pa] = -(8748 \pm 88)/(T/K) + (12.51 \pm 0.08) \quad (6)$$

The second- and third-law evaluation of these results with the thermal functions from Knacke et al.[22] yield at $T = 298.15$ K: (176.4 ± 0.5 and 178.9 ± 0.8) $kJ \cdot mol^{-1}$ (Hill and Winter, second-law, third-law); (175.8 ± 1.7 and 179.0 ± 0.5) $kJ \cdot mol^{-1}$ (Gleixner and Chang, second-law, third-law).

The results of the present study together with those of Hill and Winter[10] and Gleixner and Chang[15] yield

$$\log[p(CO_2)/Pa] = -(9074 \pm 555)/(T/K) + (12.91 \pm 0.71) \quad (7)$$

The coefficients in the above relation were obtained by taking the mean of the coefficients in eqs 4, 5, and 6. This approach amounts to giving equal weights to the three sets of data (present study, ref 10, and ref 15) that were combined. Figure 2 shows all the data points and the straight line representing eq 7. The uncertainties in the coefficients of eq 7 were deduced by error propagation using the standard deviation of the mean and the uncertainties in the coefficients of the component equations.

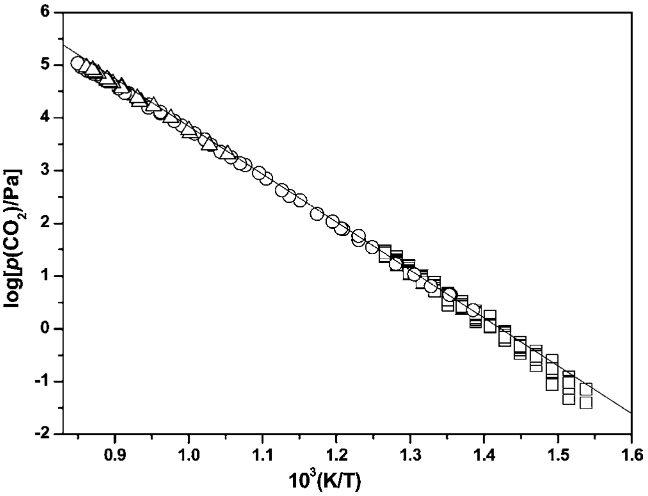

Figure 2. $p(CO_2)$ corresponding to the incongruent vaporization reaction $CaCO_3(s) = CaO(s) + CO_2(g)$ as a function of temperature. Present study: □, 200 points from temperature dependence runs; ■, 3 points from flow dependence runs. Reference 10: ○, 43 points. Reference 15: Δ, 23 points.

Table 3 gives the values of $p(CO_2)$ calculated from eqs 3 to 7 (experimental values) as well as those recommended in the NBS report by Stern and Weise[9] (calculated from thermodynamic data) at some selected temperatures from (700 to 1100) K. There is reasonably good agreement among the values considering the uncertainties in the measurements and extrapolations. Equation 7 is recommended, which represents the experimental values of this work, Hill and Winter,[10] and Gleixner and Chang.[15] That the values deduced from eq 7 agree very well with those given in the NBS report[9] gains merit in view of the statement made in the NBS report that measurement of meaningful decomposition pressures is difficult.

Table 4 gives some information pertinent to the temperature dependence experiments but actually more so to the finer aspects of our transpiration measurements using the commercial TG apparatus. The results corresponding to measurements at each temperature are given in Table 4. While $T = 650$ K was accessed once each in two runs, $T = 720$ K was accessed 22 times in a total of 13 runs. The mean $p(CO_2)$ values given in column 5 of Table 4 show that the relative standard deviation in the mean $p(CO_2)$ at a given T is ≤ 15 % at $T \geq 680$ K, ~30 % at (660 and 670) K, and ~40 % at 650 K. When the $p(CO_2)$ values were calculated by using eq 2 (and the dV/dt given in column 4 of Table 2), the means of such values (column 6 of Table 4) are not only lower but also have large relative standard deviations, (60 to 90) %, at all temperatures. The same

Table 3. Comparison of $p(CO_2)$ Values over $CaO(s) + CaCO_3(s)$

		$p(CO_2)$/Pa at T =				
ref	remarks	700 K	800 K	900 K	1000 K	1100 K
this work	eq 3 [flow dependence runs; (720 to 740) K]	$8.2 \cdot 10^{-1}$	$3.0 \cdot 10^{1}$	$4.9 \cdot 10^{2}$	$4.5 \cdot 10^{3}$	$2.8 \cdot 10^{4}$
	eq 4 [temperature dependence runs; (650 to 790) K]	$7.2 \cdot 10^{-1}$	$3.9 \cdot 10^{1}$	$8.7 \cdot 10^{2}$	$1.0 \cdot 10^{4}$	$7.9 \cdot 10^{4}$
	eq 7 [refs 10 and 15 data combined; (650 to 1177) K]	$8.9 \cdot 10^{-1}$	$3.7 \cdot 10^{1}$	$6.8 \cdot 10^{2}$	$6.9 \cdot 10^{3}$	$4.6 \cdot 10^{4}$
ref 10	eq 5 [(722 to 1177) K]	$9.5 \cdot 10^{-1}$	$3.5 \cdot 10^{1}$	$5.8 \cdot 10^{2}$	$5.5 \cdot 10^{3}$	$3.4 \cdot 10^{4}$
ref 15	eq 6 [(950 to 1161) K]	1.0	$3.8 \cdot 10^{1}$	$6.2 \cdot 10^{2}$	$5.8 \cdot 10^{3}$	$3.6 \cdot 10^{4}$
NBS report	tabulated equilibrium constant values	$9.1 \cdot 10^{-1}$	$3.8 \cdot 10^{1}$	$6.6 \cdot 10^{2}$	$6.4 \cdot 10^{3}$	$4.1 \cdot 10^{4}$
ref 9	LS fit [of 5 values from (700 to 1100) K][a]	$9.4 \cdot 10^{-1}$	$3.7 \cdot 10^{1}$	$6.5 \cdot 10^{2}$	$6.4 \cdot 10^{3}$	$4.2 \cdot 10^{4}$

[a] $\log[p(CO_2)/\text{Pa}] = -8952/(T/\text{K}) + 12.76$. This relation yields $p(CO_2) = 1$ atm = 101325 Pa at T = 1154 K, while eqs 3 to 7 yield $p > (CO_2) = 1$ atm = 101 325 Pa at T = 1183 K (eq 3), 1114 K (eq 4), 1169 K (eq 5), 1166 K (eq 6), and 1148 K (eq 7).

Table 4. Mean $p(CO_2)$ at Different Temperatures Obtained in Various Temperature Dependence Runs

T/K	run no. (no. of times measurement performed at this temperature in the given run)	total no. of points	total no. of runs	mean p/Pa (with normalization)	mean p/Pa (without normalization)	p/Pa from recommended relation eq 7
650	5(1), 10(1)	2	2	$(5.6 \pm 2.2) \cdot 10^{-2}$	$(4.7 \pm 3.4) \cdot 10^{-2}$	$8.9 \cdot 10^{-2}$
660	10(1), 12(1), 13(2), 4(2), 5(2)	8	5	$(1.0 \pm 0.3) \cdot 10^{-1}$	$(4.5 \pm 3.8) \cdot 10^{-2}$	$1.5 \cdot 10^{-1}$
670	3(1), 4(1), 5(1), 6(2), 10(2), 12(2)	9	6	$(1.6 \pm 0.5) \cdot 10^{-1}$	$(8.9 \pm 5.4) \cdot 10^{-2}$	$2.3 \cdot 10^{-1}$
680	3(1), 4(2), 5(2), 6(2), 11(1), 12(3)	11	6	$(3.0 \pm 0.5) \cdot 10^{-1}$	$(1.2 \pm 0.7) \cdot 10^{-1}$	$3.7 \cdot 10^{-1}$
690	3(1), 4(1), 5(1), 7(1), 9(2), 11(1), 12(3)	10	7	$(4.6 \pm 0.6) \cdot 10^{-1}$	$(2.4 \pm 1.7) \cdot 10^{-1}$	$5.7 \cdot 10^{-1}$
700	2(2), 3(2), 4(3), 5(3), 6(2), 7(3), 9(2), 11(1), 12(3)	21	9	$(7.6 \pm 0.8) \cdot 10^{-1}$	$(4.3 \pm 2.6) \cdot 10^{-1}$	$8.9 \cdot 10^{-1}$
710	2(2), 3(2), 4(1), 5(1), 7(1), 9(1), 11(1), 12(3)	12	8	1.2 ± 0.2	$(6.3 \pm 5.5) \cdot 10^{-1}$	1.3
720	1(1), 2(2), 3(2), 4(1), 5(1), 6(1), 7(2), 8(3), 9(2), 10(2), 11(1), 12(3), 13(1)	22	13	1.8 ± 0.2	1.3 ± 0.8	2.0
730	2(2), 3(2), 4(1), 5(1), 7(1), 9(2), 11(1), 12(3)	13	8	2.8 ± 0.2	1.4 ± 1.0	3.0
740	1(1), 2(2), 3(2), 4(1), 5(1), 6(2), 7(4), 9(2), 11(1), 12(3)	19	10	4.0 ± 0.4	2.7 ± 1.6	4.4
750	2(2), 3(2), 4(1), 5(1), 7(1), 9(2), 11(2), 12(3)	14	8	6.1 ± 0.6	3.1 ± 2.3	6.5
760	1(1), 2(2), 3(2), 4(1), 5(1), 6(1), 7(1), 9(2), 11(2), 12(3)	16	10	8.1 ± 0.8	5.1 ± 3.5	9.3
770	2(2), 3(2), 4(1), 7(2), 9(2), 10(2), 11(2), 12(3)	16	8	13.0 ± 1.2	7.5 ± 5.2	13.4
780	1(1), 2(1), 3(1), 4(2), 5(2), 6(1), 7(2), 8(1), 9(2), 11(2), 12(3)	18	11	18.7 ± 2.0	12.1 ± 8.4	18.9
790	6(1), 7(1), 9(1), 10(1), 11(1), 12(2), 13(2)	9	7	26.5 ± 2.2	16.1 ± 11.7	26.5

information is displayed in Figure 3 which shows the primary dm/dt values (Figure 3a) and the deduced $p(CO_2)$ values (Figure 3b without normalization and Figure 3c with normalization) in various temperature dependence runs. The relatively high scatter seen in Figure 3b is attributed to the lack of proper transpiration conditions when appropriate constriction is not effected to the carrier gas flow at the exit point. There apparently are three bands, the high flow rates (runs 4 and 11 to 13) yielding low $p(CO_2)$ values, the low flow rates (runs 1 and 5 to 10) yielding high $p(CO_2)$ values, and the intermediate flow rates (runs 2 and 3) yielding intermediate $p(CO_2)$ values. That all three bands do display nearly similar temperature dependence leads to confirmation of the inference made by us previously[1] that the transpiration measurements performed with commercial TG apparatuses could yield meaningful vaporization enthalpy values but are more likely to yield low vapor pressures if care is not exercised to ascertain the increase in dm/dt with dV/dt at least up to the so-called "unsaturation" region.

The second- and third-law enthalpy values corresponding to the combined results shown in Figure 2 and eq 7 (this study and refs 10 and 15) are: (173.7 ± 10.6) kJ·mol^{-1} (second-law, T = 914 K); (182.6 ± 10.6) kJ·mol^{-1} (second-law, T = 298.15 K); (178.8 ± 1.2) kJ·mol^{-1} (third-law, T = 298.15 K). We seek to recommend for reaction 1, $\Delta_r H^o_m(298.15\text{ K}) = (180.7 \pm 11.0)$ kJ·mol^{-1} (the mean of second and third law values) and $\Delta_r S^o_m(298.15\text{ K}) = (161.6 \pm 8.3)$ J·mol^{-1}K^{-1} (deduced from eq 7). These values are in accord with $\Delta_r H^o_m(298.15\text{ K}) = 178.3$ kJ·mol^{-1} and $\Delta_r S^o_m(298.15\text{ K}) = 160.4$ J·mol^{-1}K^{-1} (deduced from the $S^o_m(298.15\text{ K})$ values) given in the NBS report.[9]

The main reason mentioned in the NBS report[9] for suspecting the direct measurement of decomposition pressures as unreliable was the appearance of "pseudoequilibrium' which shows up as different constant pressures at a given temperature depending on whether the equilibrium is approached from above or below. Accordingly, some isothermal segments to be attained in the increasing or decreasing temperature directions were included in our experiments. Table 5 gives the details of how the dm/dt varied with time at three temperatures (700 K, 740 K, and 660 K). The time segments chosen were ~500 min (at T = 660 K), ~60 min (at T = 700 K), and ~20 min (at T = 740 K) based on the criteria that each time segment should correspond to at least 0.015 mg of mass loss or 15 min of duration. This criteria ensured that the values of dm/dt (slope of mass vs time least squares fit) were obtained with reasonably good precision (R-squared > 0.95). A nearly similar rate of mass loss (dm/dt) at all time segments at a constant temperature and the reproducibility of the dm/dt values irrespective of whether the temperature was reached in the increasing or the decreasing temperature directions were taken to indicate that the equilibrium was attained in these measurements without being affected by kinetic difficulties. It needs to be mentioned here that in one of the experiments (run 13 of Table 2), attainment of T = 660 K from room temperature resulted in a dm/dt value that was as high as $1.0 \cdot 10^{-5}$ mg·s^{-1} (after an hour) which decreased monotonically with time to $1.3 \cdot 10^{-6}$ mg·s^{-1} (in 8 h). This value is not very different from those obtained subsequently at T = 660 K, when the same temperature was reached from 790 K or 720 K (see Table 5).

It was satisfying that the measurements on $CaCO_3$ decomposition could be taken down to T = 650 K, although the uncertainty in the $p(CO_2)$ values measured is high. The lowest temperature in the previously reported vapor pressure measurements was 722 K with the static method[10] and 950 K with the dynamic method.[15] The good agreement among the results of all the three studies indicated that the results corresponding to the temperature range of (650 to 790) K were not affected by the possible phase transformations in $CaCO_3(s)$.

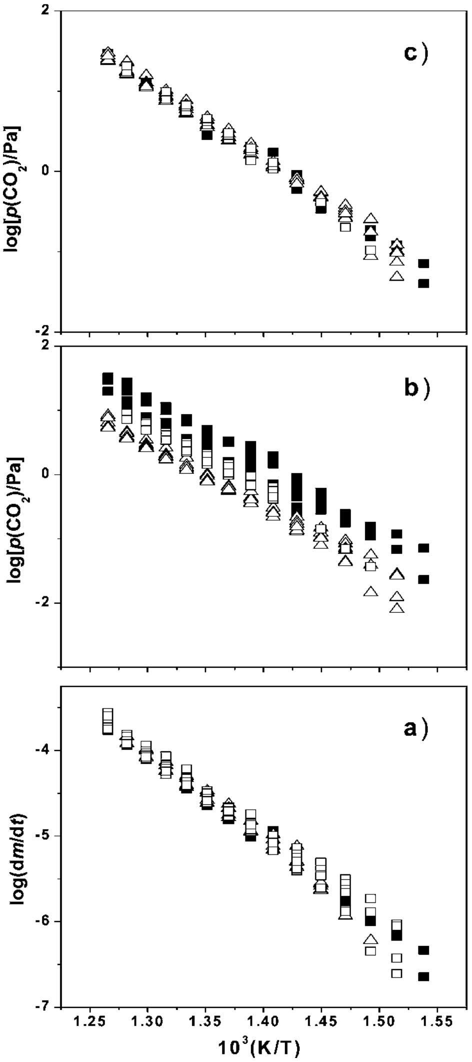

Figure 3. Results of temperature dependence transpiration experiments. (a) Measured dm/dt vs dV/dt; (b) $p(CO_2)$, deduced according to eq 2, vs dV/dt; (c) $p(CO_2)$ computed as [f(dm/dt)] (see Table 2 for values of f). □, exit stopcock completely opened; ■, exit stopcock constriction optimum; Δ, exit stopcock constriction intermediate.

Table 5. Results of Time Dependence Experiments on $CaCO_3$ Decomposition at Different Temperatures

			segment		
T/K	previous T/K	direction of T change	dt/min (each segment)	no.	dm/dt (mg·s^{-1})
Temperature Dependence Run No. 7; 23 to 25 Nov 2009					
700	740	decreasing	∼60 min	1	$4.2 \cdot 10^{-6}$
				2	$4.7 \cdot 10^{-6}$
				3	$4.9 \cdot 10^{-6}$
				4	$4.9 \cdot 10^{-6}$
				5	$5.1 \cdot 10^{-6}$
				6	$4.7 \cdot 10^{-6}$
				7	$4.9 \cdot 10^{-6}$
	660	increasing	∼60 min	1	$4.4 \cdot 10^{-6}$
				2	$4.1 \cdot 10^{-6}$
				3	$4.7 \cdot 10^{-6}$
				4	$4.7 \cdot 10^{-6}$
				5	$4.3 \cdot 10^{-6}$
740	700	increasing	∼20 min	1	$2.6 \cdot 10^{-4}$
				2	$2.7 \cdot 10^{-4}$
				3	$2.5 \cdot 10^{-4}$
				4	$2.5 \cdot 10^{-4}$
				5	$2.7 \cdot 10^{-4}$
				6	$2.7 \cdot 10^{-4}$
	780	decreasing	∼20 min	1	$2.6 \cdot 10^{-4}$
				2	$2.7 \cdot 10^{-4}$
				3	$2.7 \cdot 10^{-4}$
				4	$2.6 \cdot 10^{-4}$
				5	$2.6 \cdot 10^{-4}$
				6	$2.6 \cdot 10^{-4}$
Temperature Dependence Run No. 13; 11 to 13 Dec 2009					
660	790	decreasing	∼500 min	1	$9.7 \cdot 10^{-7}$
				2	$1.1 \cdot 10^{-6}$
				3	$8.8 \cdot 10^{-7}$
				4	$8.5 \cdot 10^{-7}$
				5	$9.9 \cdot 10^{-7}$
	720	decreasing	∼500 min	1	$8.5 \cdot 10^{-7}$
				2	$8.3 \cdot 10^{-7}$

The present study served to confirm that our commercial TG apparatus can yield reliable vapor pressures for an incongruently vaporizing system as well. The reason for not succeeding in the transpiration measurements on the Mn−Te or Ru−Te samples which were supposed to vaporize incongruently losing preferentially the component tellurium is not clear. It might be that an oxygen impurity in the commercial argon (purity 99.995 %) used as carrier gas would have reacted with the samples to form oxides of Mn or Ru thus resulting in continuous mass gain initially. However, once the mass loss began to be observed, the two systems behaved differently, the reason for which is also not clear. In the case of Mn−Te samples, oxidation of the MnTe or $MnTe_2$ phase could have induced liberation of free tellurium, its diffusion followed by subsequent deposit in the downstream in the flow of the argon carrier gas, and thus the rate of mass loss becomes the same as that over elemental tellurium. In the case of the Ru−Te samples, the excess and free Ru might have been oxidized in preference to the $RuTe_2$ phase, and the rate of mass loss was governed by competing oxidation reaction and vaporization loss of the Ru + $RuTe_2$ phase field and thus was lower than that due to the latter reaction alone. Unless these experiments are run again using purified argon gas, the above reasoning cannot be substantiated. An experiment is planned to be conducted on a sample of NiO + $Ni_2Te_3O_8$, the Knudsen effusion mass spectrometric study of which[23] led to the inference that it would vaporize incongruently by losing the component TeO_2. The hope is that the presence of a separate NiO phase in the sample might facilitate the occurrence of the incongruent vaporization of the $Ni_2Te_3O_8$ phase (which would lead to mass loss due to TeO_2 removal) in preference to the oxidation of Ni of this phase (which would lead to mass gain). In the meanwhile, the weighing capability of the electronic balance is going to be upgraded from (1 to 5) g so that cells will permit use of a larger surface area for samples, which in turn could make the plateau region extend to higher flow rates.

Literature Cited

(1) Viswanathan, R.; Lakshmi Narasimhan, T. S.; Nalini, S. Vapor Pressure Measurements by Mass-Loss Transpiration Method with a Thermogravimetric apparatus. *J. Phys. Chem. B* **2009**, *113*, 8362.

(2) Viswanathan, R.; Hilpert, K. Mass Spectrometric Study of Vaporization of Cesium Iodide and Thermochemistry of $(CsI)_2(g)$ and $(CsI)_3(g)$. *Ber. Busenges. Phys. Chem.* **1984**, *88*, 125.

(3) Viswanathan, R. PhD. Thesis: Studies on Binary Systems of Tellurium with Chromium and Molybdenum by using Knudsen Effusion Mass Spectrometry. University of Madras, India, 1991.

(4) Lakshmi Narasimhan, T. S.; Sai Baba, M.; Balasubramanian, R.; Nalini, S. Vaporisation Studies on Tellurium dioxide: A Knudsen Effusion Mass Spectrometric study. *J. Nucl. Mater.* **1997**, *247*, 28.

(5) Lakshmi Narasimhan, T. S. Ph.D. Thesis: Vaporisation and Phase Diagram Studies on MnTe, TeO_2 and Mn-Te-O Systems by Knudsen Effusion Mass Spectrometry. University of Madras, India, 2000.

(6) Lakshmi Narasimhan, T. S.; Sai Baba, M.; Viswanathan, R. Vaporization Behavior of $TeO_2(s)$: a Quantitative Vaporization-Knudsen Effusion Mass Spectrometric Study. *Thermochim. Acta* **2005**, *427*, 137.

(7) Balasubramanian, R.; Lakshmi Narasimhan, T. S.; Viswanathan, R.; Nalini, S. Investigation of the Vaporization of Boric acid by Transpira-

tion Thermogravimetry and Knudsen Effusion Mass Spectrometry. *J. Phys. Chem. B* **2008**, *112*, 13873.
(8) Lakshmi Narasimhan, T. S.; Sai Baba, M.; Balasubramanian, R.; Nalini, S.; Viswanathan, R. Vaporization Studies on (Manganese + Tellurium) with x(Te) > 0.5 by Knudsen Effusion Mass Spectrometry. *J. Chem. Thermodyn.* **2002**, *34*, 103.
(9) Stern, K. H.; Wise, E. L. High Temperature Properties and Decomposition of Inorganic Salts. Part 2. Carbonates. NSRDS-NBS 30, Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (US). 1969.
(10) Hill, K. J.; Winter, E. R. S. Thermal Dissociation Pressure of Calcium Carbonate. *J. Phys. Chem.* **1956**, *60*, 1361.
(11) Beruto, D.; Searcy, A. W. Use of Langmuir Method for Kinetic Studies of Decomposition Reactions: Calcite ($CaCO_3$). *J. Chem. Soc., Faraday Trans. I* **1974**, *70*, 2145.
(12) Beruto, D.; Searcy, A. W. Calcium oxides of High Reactivity. *Nature* **1976**, *263*, 221.
(13) Roberts, J. A., Jr.; Jacobson, N. S.; Searcy, A. W. Kinetics of Transport of CO_2 through porous CaO and BaO Formed by Carbonate Decomposition. *J. Chem. Phys.* **1978**, *69*, 5562.
(14) Darroudi, T.; Searcy, A. W. Effect of CO_2 Pressure on the Rate of Decomposition of Calcite. *J. Chem. Phys.* **1978**, *69*, 5562.
(15) Gleixner, R. A.; Chang, Y. A. Cyclic Thermogravimetric Methods for the Study of the Decomposition of Carbonates - $CaCO_3$. *Met. Trans. B* **1985**, *16*, 743.
(16) Oniyama, E.; Wahlbeck, P. G. Application of Transpiration Theory to TGA data: Calcium Carbonate and Zinc Chloride. *Thermochim. Acta* **1995**, *250*, 41.
(17) Criado, J. M.; González, M. Determination of the Equilibrium Dissociation Pressure of Inorganic Solids from TG: Application to the Calculation of the Enthalpy Change of the Reaction $Pb_3O_2CO_3 \Leftrightarrow 3PbO + CO_2$. *Thermochim. Acta* **1998**, *318*, 265.
(18) L'vov, B. V. Thermochemical Approach to Solid-State Decomposition Reactions Against the Background of Traditional Theories. *J. Therm. Anal. Calorim.* **2009**, *96*, 487.
(19) L'vov, B. V. Role of Vapor Oversaturation in the Thermal Decomposition of Solids. *J. Therm. Anal. Calorim.* **2009**, *96*, 321.
(20) Feng, K.; Lombardo, S. J. Kinetic Analysis from Dilatometry and Mass Spectrometry Measurements of the Decomposition and Sintering of Calcium Carbonate. *J. Ceram. Proc. Res.* **2002**, *3*, 101.
(21) Personal communication from E. J. Opila on the results of: Opila, E. J.; Myers, D. L.; Jacobson, N. S.; Nielsen, I. M. B.; Johnson, D. F.; Olminsky, J. K.; Allendorf, M. D. Theoretical and Experimental Investigation of the Thermochemistry of $CrO_2(OH)_2(g)$. *J. Phys. Chem. A* **2007**, *111*, 1971.
(22) Knacke, O.; Kubaschewki, O.; Hesselmann, K. *Thermochemical properties of Inorganic Substances*, 2nd ed.; Springer Verlag: Berlin, 1991.
(23) Unpublished data from the study performed in the authors' laboratory.

Received for review March 26, 2010. Accepted July 2, 2010.

JE100294T