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Thermal stability of potassium carbonate near its melting point

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Abstract

The behavior of potassium carbonate was studied by thermal analysis near its melting point under 1 atm total pressure. Literature data are scant regarding the degree to which K_2CO_3 decomposes in sub- and pro-liquidus thermal environments, and reliable thermodynamic data are not available for the reaction $K_2CO_3 \rightleftharpoons K_2O + CO_2$ in the temperature range of interest. TGA and DTA analyses indicate that significant volatilization occurs below the melting point and the logarithm of the rate of volatilization is a linear function of $1/T$ above the melting point. The effect of CO_2 partial pressure was highly significant in reducing, but not eliminating, volatilization near the melting point. Graphs of $\ln[P_{CO_2} \times \text{weight loss rate}]$ vs. $(1/T)$ were linear, supporting a decomposition model rather than congruent volatilization. The melting point of K_2CO_3, as measured by DTA, is 905°C in CO_2 and 900°C in N_2. © 1998 Elsevier Science B.V.

Keywords: Potassium carbonate; K_2CO_3; Decomposition; Melting behaviour

1. Introduction

Potassium carbonate is an important industrial commodity used in a wide variety of processes and products. The specific behavior of K_2CO_3 between 700°–1000°C and under various CO_2 partial pressures was examined in the present work.

Although an enormous amount of literature exists on the physical and chemical properties of potassium carbonate, only a paucity of consistent data is available at elevated temperatures under the foregoing conditions. Therefore, the present study was conducted to elucidate the effect of temperature and atmosphere on the stability of K_2CO_3 near the melting point under various CO_2 partial pressures and 1 atm total pressure.

Of the many compounds that exist in the comprehensive K–H–C–O system, four anhydrous compounds, K_2O, $KHCO_3$, KOH, and K_2CO_3 are of principal interest under ordinary ambient environments. Potassium hydrogen carbonate, $KHCO_3$, forms under certain conditions of H_2O and CO_2 partial pressures, but it decomposes rapidly between 100° and 200°C. Potassium hydroxide, KOH, which forms under conditions of sufficient moisture and low CO_2 partial pressure, melts at 360°C and boils at 1316°C. K_2CO_3 occurs in two forms, γ and β. The γ phase transforms to the β form at 421°C and the β form is stable up to the melting point, near 900°C. The carbonate thermally decomposes at high tempera-

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tures according to the following reaction,

$$K_2CO_3 \rightleftharpoons K_2O + CO_2$$

although considerable uncertainty is reflected in the literature regarding the temperature and rate at which this reaction proceeds. Some studies [1] indicate that the reaction is negligible below the melting point of 900°C, whereas others note thermal instability [2,3] and varying degrees of dissociation [4].

Of the numerous studies on K_2CO_3, most are for mixtures of salts [5,2,6,3], or for molten salts [7]. Several studies are devoted to crystallography and phase transitions [8,9]. Only a few studies have addressed the thermal-analysis behavior of pure K_2CO_3. The study of K_2CO_3 by Reisman [3] was part of a more general investigation, and his work on potassium carbonate remains the most comprehensive examination of the high-temperature behavior of this compound. Most of Reisman's thermal-analysis experiments with the carbonates were done under 1 atm CO_2 because of "the varying degrees of dissociation they undergo at elevated temperatures." The melting temperature of K_2CO_3 was found to be 901±1°C, with a single solid–solid transition at 422±2°C. The melting temperature reduced to 891–896°C, when tested under air instead of CO_2.

Of particular interest in the present study is the degree to which K_2CO_3 volatilizes near the melting point and whether the volatilization is congruent evaporation or decomposition. As already indicated, the literature is quite vague in this regard. Although it is clear that, well above the melting point, K_2CO_3 decomposes according to Eq. (1), the thermal onset of this reaction, the degree to which it occurs, and the inhibiting effect of CO_2 overpressures have not been well documented. The only data, found in the literature, which define the vapor pressure over K_2CO_3 are given in Fig. 1 [10] and suggest a low rate of decomposition near the melting point (13 mbar is achieved only by 1200°C). Lee and Ladd [10] assumed that the decomposition reaction (Eq. (1)) was applicable. Across the entire temperature range, K_2CO_3 has low volatility rates compared to Na_2CO_3, a carbonate salt known for its significant volatility. The goal of the present study was to refine our knowledge of the decomposition behavior of K_2CO_3 by thermal-analysis studies in the presence of varying CO_2/N_2 atmospheres.

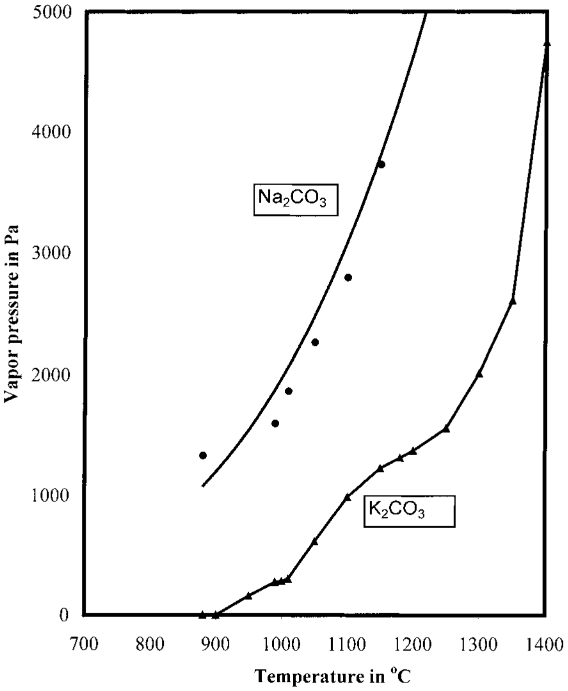

Fig. 1. Vapor pressure of alkali carbonates.

2. Thermodynamic assessment of K_2CO_3 decomposition

Prior to commencing experimental studies, an assessment of the behavior of K_2CO_3 and related compounds was conducted using thermodynamic properties from the literature. Considering the presence of CO_2 overpressure and the existence of small amounts of ambient H_2O, ≈20 pertinent chemical equations were identified in the K–O–H–C system. Of these, the following four were selected as relevant to the heating of K_2CO_3 under the experimental conditions:

$$K_2CO_3 \rightleftharpoons K_2O + CO_2 \quad (1)$$

$$K_2O + H_2O \rightleftharpoons 2KOH \quad (2)$$

$$K_2CO_3 + CO_2 + H_2O \rightleftharpoons 2KHCO_3 \quad (3)$$

$$2KOH + CO_2 \rightleftharpoons K_2CO_3 + H_2O \quad (4)$$

The stability of K_2CO_3 and the degree to which other compounds listed in Eqs. (1)–(4) exist under given conditions can best be identified outside the laboratory by evaluating thermodynamic quantities. To accomplish this preliminary task, the free energies for each reaction, $\Delta_r G$, were determined by calculations using the most recent and reliable data from the literature [11]. $\Delta_r G^0$ for reaction $aA+bB=cC+dD$ was calculated in the standard way, viz.:

$$\Delta_r G^0(298\,\mathrm{K}), l = \Delta_f G^0(\text{products}) - \Delta_f G^0(\text{reactants}) \qquad (5)$$

The standard free energies of formation of principal compounds addressed in this study are given in Table 1. To calculate ΔG_r^0 for reactions at temperatures other than 298 K, Eq. (6) was used:

$$\Delta_r G^0(T) = \Delta_r G^0(298\,\mathrm{K}) + \int_{298\,\mathrm{K}}^{T} \Delta C_p \mathrm{d}T' - T \int_{298\,\mathrm{K}}^{T} \frac{\Delta C_p}{T'} \mathrm{d}T' \qquad (6)$$

where ΔC_p is calculated from the heat capacities of the products and reactants. In practice, it was most convenient to obtain $\Delta_r G^0(T)$ from the following polynomial expression,

$$\Delta_r G^0(T) = a + bT + cT(\ln T - 1) \qquad (7)$$

using the well-established coefficients, a, b, and c, from Table 1.

For a chemical reaction involving gas-phase species not at equilibrium, the relation between the free energy for the reactions, $\Delta_r G(T)$, the standard free energy of the reaction, $\Delta_r G^0$, and the partial pressures of gaseous reactants and products at temperature T is given by:

$$\Delta_r G(T) = \Delta_r G^0(T) + RT \ln \frac{(P_c/P_t)^c (P_d/P_t)^d}{(P_a/P_t)^a (P_b/P_t)^b} \qquad (8)$$

where the pressures in parentheses represent the partial pressure of each gaseous component, and P_t the total pressure. Given partial pressures and temperature, the free energy change of the reaction, $\Delta_r G$ can be calculated.

Consider the reaction, $K_2CO_3+CO_2+H_2O \rightleftharpoons 2KHCO_3$ as an example:

$$\Delta_r G(T) = \Delta_r G^0(T) + RT \ln \frac{1}{P_{H_2O} P_{CO_2}} \qquad (9)$$

or,

$$\begin{aligned}\Delta_r G(T) &\equiv \Delta_r G^0(T) - RT \ln P_{H_2O} P_{CO_2} \\ &= -115450 - 136.53T + 88.06T \\ &\quad (\ln T - 1) - 8.3144(T) \ln(P_{H_2O} P_{CO_2})\end{aligned} \qquad (10)$$

At T=298 K, and $P_{CO_2} \equiv P_{H2O} = 0.1$ bar, $\Delta_r G = -21.7$ kJ mol^{-1}, thus indicating the reaction is favorable for the forward direction under these conditions. For general purposes, it is desirable to know the locus of points in the parametric space of T, P_{H_2O} and P_{CO_2} in which $\Delta_r G$=0, thus defining the boundary between favorable forward- and back-reactions. The loci of $\Delta_r G$=0 points, for the three important reactions illustrated in Fig. 2(A)–(C), are useful and significant curves since they define the regions above and below the line, where $\Delta G<0$ and $\Delta G>0$, and as such are regions in which products or reactants will be observed. Using this type of analysis, KOH and $KHCO_3$ were precluded from any further consideration as compounds present near the melting point under the thermal conditions and atmospheres of interest, as illustrated by Fig. 2(A) and (B).

Fig. 2(C) illustrates that $\Delta_r G>0$ for the K_2CO_3 decomposition reaction (1) for all temperatures shown and, thus, the reaction will not proceed in the forward direction. However, the thermodynamic data for reaction (3) only apply below 880°C, since the published data for K_2O are not available for higher temperatures. Extrapolation of the data in Table 1 to higher temperatures leads to obvious error. For example, calculation for $\Delta_r G$ for $P_{CO_2} = 1.3$ mbar at 900°C yields +117 kJ mol^{-1} and at 1200°C, $\Delta_r G$=+38 kJ mol^{-1}, indicating non-spontaneous forward-reactions under temperature conditions which surely promote the forward reaction. Thus, the thermodynamic approach to evaluating reaction (1) was limited to temperatures <880°C and no estimate was obtained by thermodynamic calculations in the temperature range of interest.

3. Thermogravimetric analysis (TGA)

To further define the behavior of K_2CO_3 near the melting point, thermogravimetric analysis was per-

Table 1
Standard free energies for principal reactions

Compound or reactions	$\Delta_r G^0$(298 K) (kJ mol^{-1}) (Ref. [12])	$\Delta_r G^0$ (298 K) (kJ mol^{-1}) (calculated, Ref. [1])	$\Delta_r G^0$ (298 K) (kJ mol^{-1}) (average value)	Factors for $\Delta_r G^0(T)$		
				intercept factor, a/ (J mol^{-1})	T factor, b/ (J mol^{-1} K^{-1})	T(ln $T-1$) factor, c/ (J mol^{-1} K^{-1})
K_2O (s)+H_2O (g)=2KOH (s,α)	−208.68	−203.00	−205.84	−240680	10.31	24.72
K_2O (s)+H_2O (g)=2KOH (s,β)		−204.44	−204.44	−244960	352.09	−46.00
K_2O (s)+H_2O (g)=2KOH (l)		−195.95	−195.95	−233740	384.55	−54.86
K_2CO_3 (s)=K_2O (s)+CO_2 (g) $T<880^\circ$	350.56	347.01	348.78	386670	8.38	−30.12
$K_2CO_3+CO_2+H_2O$ =2$KHCO_3$	−45.74	−32.70	−39.22	−115450	−136.53	88.06
2KOH (l)+CO_2 (g)=K_2CO_3(s)+H_2O(g)	−141.88	−144.00	−142.94	−152930	−392.93	84.98
C+CO_2=2CO	120.08	119.93	120.01	−172270	−124.96	−10.79
2C+O_2=2CO	−274.3	−275.60	−274.95	−223400	−175.30	0
2CO+O_2=2CO_2	−514.45	−527.87	−521.16	−576571	248.15	−11.19
C+O_2=CO_2	−394.38	−394.35	−394.37	−394100	−0.84	0
2H_2+O_2=2H_2O	−457.18	−459.34	−458.26	−492000	109.6	0

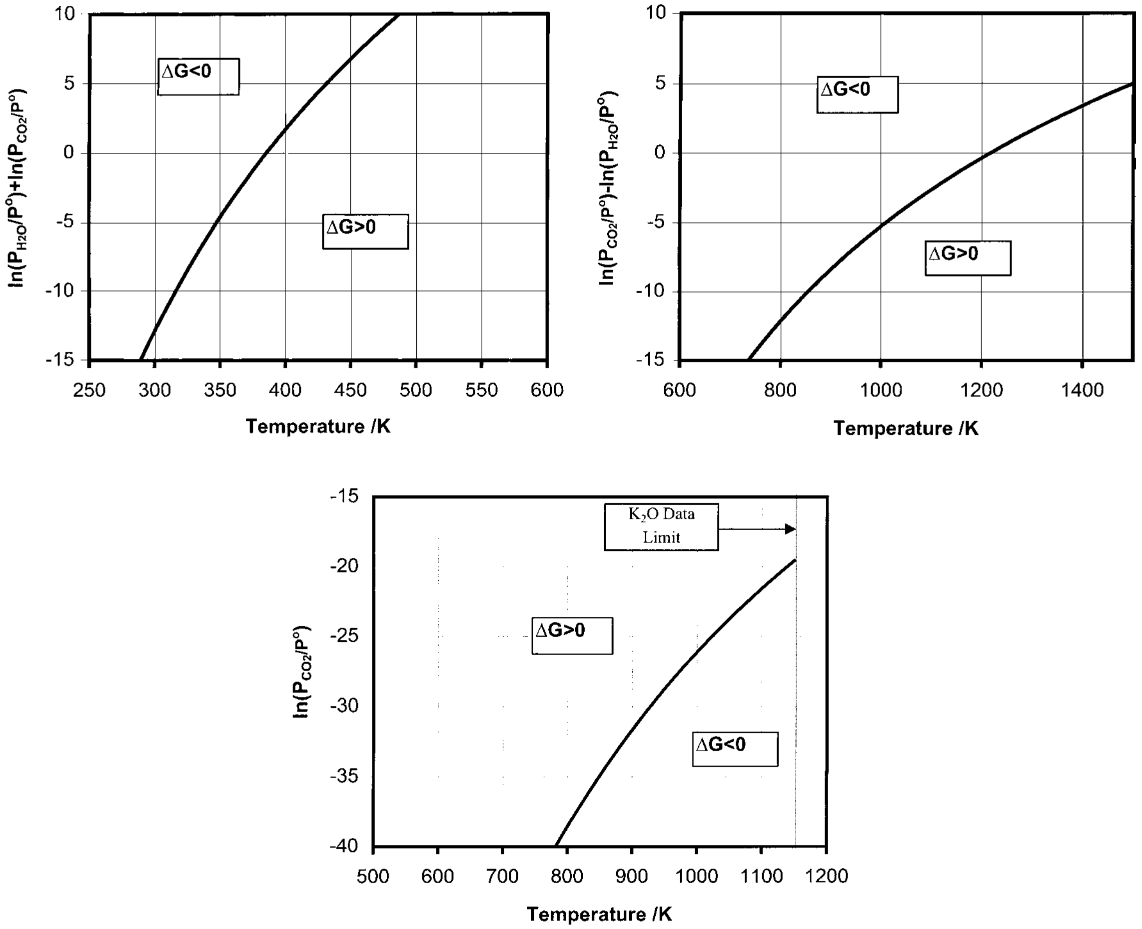

Fig. 2. (A) Regions of favorable forward- and back-reactions based on free energy calculations. $K_2CO_3+CO_2+H_2O\rightleftharpoons 2KHCO_3$. (B) Regions of favorable forward- and back-reactions based on free energy calculations. $2KOH_{(liq)}+CO_2\rightleftharpoons K_2CO_3+H_2O$. (C) Regions of favorable forward- and back-reaction based on free energy calculations. $K_2CO_3\rightleftharpoons K_2O+CO_2$.

formed with TGA equipment[2] having 1 μg resolution, 2 μg sensitivity, ±5 μg accuracy, and thermal precision of 0.5°C. Thermal calibration was verified using the melting point of a silver standard (mp=961.9°C). Gravimetric calibration was verified by calcium oxalate decomposition.

After careful calibration of the instrument, a series of TGA runs were made in atmospheres ranging from pure CO_2 to pure N_2. Certified K_2CO_3[3] was placed on platinum pans in the TGA and typical sample weights were 30 mg. The geometric surface area of the sample was 0.64 cm^2 and the sample chamber was purged with gas continuously during the experiments at the rate of 1 l min^{-1}. Specimens were heated at a rate of 20°C min^{-1} to ≈850°C, where a 10°C ramp was initiated leading to a 45 min isothermal period near the melting point. Successive isotherms at ≈950°C and 1000°C were reduced to 30 min duration to prevent excessive volatilization and reduction of the geometric surface area. Weight-loss curves were recorded during these periods as shown in Table 2 and Fig. 3.

The TGA curves were analyzed using the analysis software provided with the thermal analysis equip-

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[2] TA Instruments, New Castle, Delaware, 302-427-4000, Model TGA 951.

[3] Fisher Scientific, Fairlawn, NJ 07410, 201-796-7100.

Table 2
TGA data for K_2CO_3 tests at elevated temperatures in CO, N_2, and mixed CO_2/N_2 atmospheres (total pressure=1.01 bar; geometric surface area of sample=0.64 cm^2)

CO_2 pressure/ bar	Temperature/		Sample weight/ (mg)	Rate of weight loss/ (μg min^{-1})
	K	C		
0.0	1154	881	41.982	3.67
0.0	1185	912	41.982	11.53
0.0	1210	937	41.982	24.16
0.0	1183	910	42.045	10.14
0.0	1221	948	42.045	28.41
0.0	1264	991	42.045	80.05
0.0	1186	913	42.484	9.52
0.0	1225	952	42.484	32.50
0.0	1268	995	42.484	90.19
0.4	1181	908	40.563	10.65
0.4	1219	946	40.563	21.10
0.4	1264	991	40.563	46.32
0.4	1186	913	41.187	8.28
0.4	1225	952	41.187	19.81
0.4	1268	995	41.187	46.91
0.7	1187	914	41.133	6.07
0.7	1226	953	41.133	13.50
0.7	1226	953	40.519	9.93
0.7	1269	996	41.133	34.53
0.7	1270	997	40.519	23.30
1.0	1155	882	41.364	0.91
1.0	1175	902	27.521	3.94
1.0	1184	911	38.847	5.16
1.0	1185	912	41.364	2.97
1.0	1189	916	41.222	3.03
1.0	1201	928	27.521	6.26
1.0	1211	938	41.364	4.67
1.0	1222	949	38.847	8.78
1.0	1228	955	41.222	9.85
1.0	1231	958	27.521	11.31
1.0	1267	994	38.847	19.49
1.0	1272	999	41.222	25.14

ment. The natural logarithm of the weight loss, expressed as μg min^{-1}, was calculated and plotted vs. $1/T$ in Fig. 4 for pure CO_2 and pure N_2 atmospheres. Graphical representation of this form permits estimation of the activation energy of the process from the slope. Indeed, the relationship was linear throughout the temperature range studied and the slope of the best fit line was calculated by linear regression. The slope, $-Q/R$, was $-40101\ K^{-1}$ for nitrogen atmosphere and $-35611\ K^{-1}$ for CO_2 atmosphere. Standard errors were $1391\ K^{-1}$ and $3784\ K^{-1}$, respectively. Thus, activation energies, Q, for the volatilization processes were determined to be ≈300 kJ mol^{-1}.

The effect of CO_2 partial pressure was highly significant in reducing the rate of volatilization in this experiment, supporting the generally recognized nature of the volatilization process. At ≈1000°C, the rate of volatilization in pure N_2 (90 μg min^{-1}) is nearly four times the rate under pure CO_2 (25 μg min^{-1}). The relationship between the rate of weight loss and the CO_2 partial pressure is an important one since it sheds light on whether the volatilization from K_2CO_3 solid or liquid is congruent sublimation or evaporation, or whether the decomposition reaction is occurring. The difference is important with regard to the chemical behavior of the vapor phase in certain industrial processes and products. If Eq. (1) represents the volatilization process, then at equilibrium:

$$-\Delta_r G^0 = RT \ln\left[\frac{a_{K_2O} P_{CO_2}}{a_{K_2CO_3}}\right] \tag{11}$$

where a_{K_2O} and $a_{K_2CO_3}$ represent the activities of those phases. If the activity of K_2CO_3 is constant and the volatilized K_2O is part of the weight loss, then a plot of $\ln[P_{CO_2} \times \text{weight loss rate}]$ vs. $[1/T]$ should be linear. Fig. 5 presents the CO_2-dependent weight loss data in this form with a linear best-fit line. The quality of the regression fit, R^2=0.91, provides support to the decomposition model. Indeed, if congruent volatilization were occurring, the rate of weight loss would be independent of P_{CO_2}. The slope of the line, an estimate of $-\Delta_r G^0/R$, is $-32{,}433\ K^{-1}$, or $\Delta_r G^0 \sim 270$ kJ mol^{-1}.

The issue of congruent or incongruent volatilization of K_2CO_3 could perhaps be best resolved by X-ray diffraction analysis of the volatilization products. Unfortunately, this approach presents serious experimental obstacles which, which could not be overcome in the present work. The high reactivity of K_2O with moisture and collection substrate materials near 900°C, the dissociation of K_2O, and the reversible nature of reaction (1) all confound the collection and identification of decomposition products. Given these difficulties, the authors believe the use of CO_2 overpressures to be the most practical approach to probing the thermal behavior of K_2CO_3 at high temperatures.

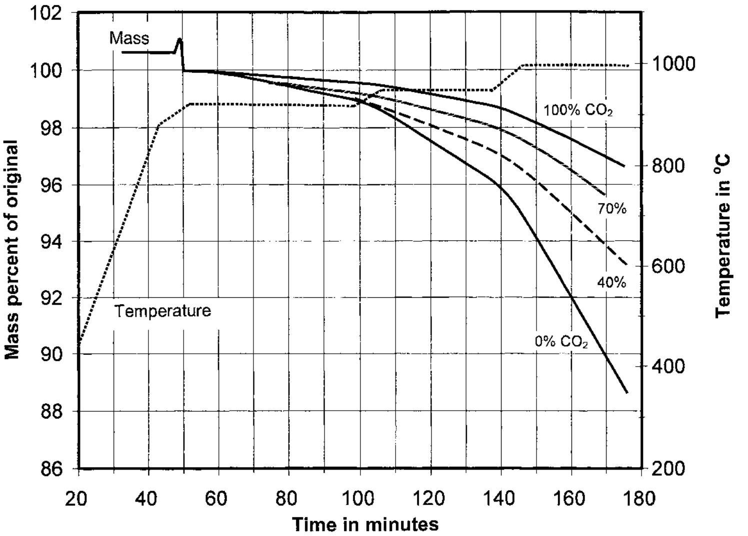

Fig. 3. Thermogravimetric analysis of K_2CO_3 under varied CO_2/N_2 atmospheres.

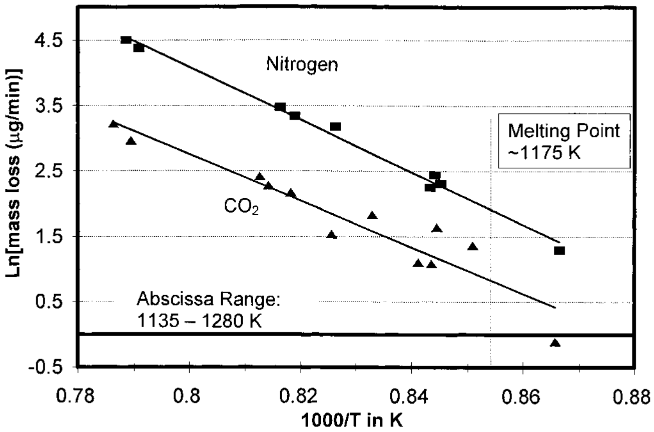

Fig. 4. Volatile weight loss from K_2CO_3 during thermal analysis at elevated temperatures under varied CO_2/N_2 atmospheres.

4. Differential thermal analysis [DTA]

Differential thermal analysis was conducted concurrently with the TGA studies to determine the melting point of K_2CO_3 under N_2 and CO_2 atmospheres. DTA equipment[4] with an accuracy of ±1°C, sensitivity of 0.5°C, and thermal resolution of 0.1°C was calibrated with a silver standard mp=961.9°C. The sample size was ≈90 mg. A total of 16 experiments were conducted to determine the melting point under CO_2 and N_2, as shown in Table 3. Rapid heating rates of 20°C min^{-1} were used up to 850°C, where the apparatus was held for equilibration. From this point onward, heating was commenced at the specified heating rate to 920°C at which time the sample was cooled at the same rate to 880°C. The endotherm and exotherms of melting and freezing were measured and the software onset utility was used to determine the precise point of the melting or freezing process. The values achieved during heating and cooling tend to converge on a single value as the heating rate

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[4] Scanning calorimeter 912 equipped with 1600o C DTA cell. TA Instruments, New Castle, DE, 302-427-4000.

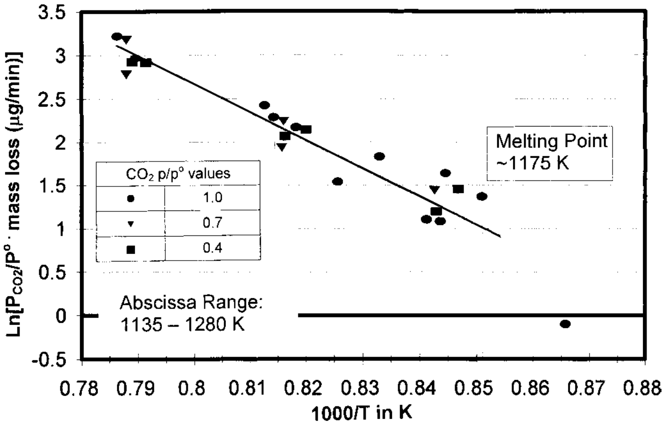

Fig. 5. Volatile weight loss from K_2CO_3 during thermal analysis at elevated temperatures. The effect of CO_2 partial pressure on decomposition.

Table 3
Experimental design for melting point determination

Test	Heating rate/ (°C/min)	Direction	Atmosphere	Replication
1.	2	heating	nitrogen	2
2.	2	cooling	nitrogen	2
3.	1	heating	nitrogen	2
4.	1	cooling	nitrogen	2
5.	2	heating	carbon dioxide	2
6.	2	cooling	carbon dioxide	2
7.	1	heating	carbon dioxide	2
8.	1	cooling	carbon dioxide	2

approaches zero. The differences in melting point values obtained by heating and cooling at 1°C min^{-1} were quite small, <1°C, and these melting point values were averaged to produce the reported results. The melting points were determined to be 905°C under CO_2 and 900°C under nitrogen.

5. Summary and conclusions

Thermal analysis of potassium carbonate was conducted at 1 atm total pressure between 880° and 1000°C to elucidate the behavior of the solid and the liquid, particularly with respect to volatilization. Available thermodynamic data are not valid in this temperature range and were of little use in predicting behavior for this particular reaction. Thermogravimetric analysis in pure N_2 revealed weight loss from K_2CO_3 below the melting point and a linear relationship between the logarithm of weight loss and reciprocal temperature in the temperature range studied. Substitution of CO_2 for N_2 reduced the rate of volatilization but measurable losses still occurred at all temperatures. Based on the temperature and CO_2 partial pressure dependence of the weight loss, the results support a K_2CO_3 decomposition model rather than a congruent sublimation/evaporation model. The melting points of $K2_CO_3$ were 905°C in CO_2 and 900°C in N_2.

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