Thermodynamics of $NaHCO_3$ decomposition during Na_2CO_3-based CO_2 capture

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ABSTRACT

Amine-basedcarbon-capture technologies have been shown to be energetically expensive and to cause significant environmental and epidemiological impacts due to their volatility. Bicarbonate formation from carbon dioxide's reaction with water has been suggested as an effective alternative for capturing CO_2; however, the thermodynamics of this reaction are not well understood. This study experimentally determined the equilibrium constant of sodium bicarbonate ($NaHCO_3$) decomposition to sodium, water, and carbon dioxide; the study also compared the equilibrium constant to theoretical calculations. Using a combination of experimentation and thermodynamic relationships, the unitless equilibrium constants of the forward and reverse reactions were calculated accurately (error $<\pm9\%$ and $<\pm4\%$, respectively). Equilibrium data were calculated using enthalpy and entropy values of each component of $NaHCO_3$ decomposition at temperatures ranging from 25 to 155℃ respectively. These results offer more data essential to optimizing $NaHCO_3$ use in environmentally friendly next-generation CO_2-capture technologies.

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Introduction

Understanding equilibrium data for specific chemical reactions or compound decompositions is an essential step toward optimizing the use of these processes. Vapor–liquid equilibrium calculations for aqueous solutions containing weak electrolytes provide a reliable thermodynamic calculation method for aqueous solutions' equilibria (Edwards et al., 1978). Having equilibrium data for sodium bicarbonate could be of significant interest due to its practicality as 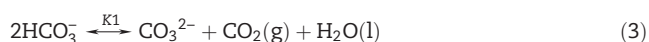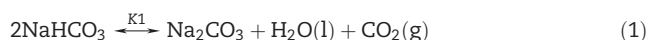a candidate sorbent used in the growing industry of CO2 capture. Alternate carbon dioxide (CO_2) capturing methods such as the use of mixed matrix membranes with multi-walled nanotubes have been studied and shown to raise selectivity of CO_2/N_2 as well as CO_2/CH_4 separations (Pohorecki and Kucharsk, 1991), but membrane CO_2 capture remains a relatively expensive technology. The use of inorganic chemical reagents such as sodium carbonate ($Na_2CO_3/NaHCO_3$) is a viable option to reduce the costs and environmental impacts of fossil fuel consumption and CO_2 capture. However, for desorption using inorganic sorbents such as $Na_2CO_3/NaHCO_3$, the process' energy consumption remains a primary challenge. The desorption process

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consumes almost 70%–80% of CO_2 during the capture process. Thus the cost to operate CO_2 capture plant is overwhelmingly dominated by energy consumption. In order to overcome this issue, the study of thermodynamic of $NaHCO_3$ decomposition is necessary.

The overall equation for $NaHCO_3$ decomposition (CO_2 desorption in this application), occurs as shown in Reaction (1) (Dutcher et al., 2011; Savage et al., 1980), which can also be described as the dissolution of $NaHCO_3$ (Reaction (2)) and subsequent decomposition of the bicarbonate ion (Reaction (3)). Similarly, CO_2 absorption, leading to the formation of $NaHCO_3$, follows the reverse of the path shown below.

$$2NaHCO_3 \xleftarrow{K1} Na_2CO_3 + H_2O(l) + CO_2(g) \tag{1}$$

$$NaHCO_3 \leftrightarrow Na^+ + HCO_3^- \tag{2}$$

$$2HCO_3^- \xleftarrow{K1} CO_3^{2-} + CO_2(g) + H_2O(l) \tag{3}$$

where $K1$ denotes as equilibrium constant based on molar concentration of CO_2.

Reaction (3) can also be described by the following series of elementary reactions (Reactions. (4)–(7)).

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \tag{4}$$

$$HCO_3^- \leftrightarrow OH^- + CO_2(g) \tag{5}$$

$$H^+ + OH^- \leftrightarrow H_2O(l) \tag{6}$$

$$2Na^+ + CO_3^{2-} \leftrightarrow Na_2CO_3 \tag{7}$$

The theoretical calculation method relies on stoichiometric coefficients as well as the calculated Gibbs free energy at each temperature of $NaHCO_3$, Na_2CO_3, H_2O, and CO_2 (Teh and Rangaiah, 2002). Experimental pressure and temperature data were recorded as aqueous $NaHCO_3$ decomposition reached equilibrium at a specific temperature; the data were used to calculate the equilibrium constant through known thermodynamic relationships. Molar volumes of each species were calculated prior to any reaction and after equilibrium was reached based on Henry's constants for the involved species.

1. Materials and methods

1.1. Materials

$NaHCO_3$ (99.9% pure) and Na_2CO_3 (99.9% lab-grade pure) were purchased from Fisher Scientific and United States Welding Inc., respectively. Purified, distilled water was supplied by the chemical stock room at the University of Wyoming.

1.2. Apparatus

As shown in Fig. 1 and Appendix A Fig. S1, gas was fed from a CO_2 cylinder controlled by a flow controller and mass sensor before entering the reactor. $NaHCO_3$ decomposition and formation reactions occurred in a 0.5-L stainless-steel reactor that was monitored by a thermocouple and pressure transducer connected to a recorder. The contents of the reactor were heated and stirred by a hot plate and stirrer, respectively. Lastly, the pressure vent was used to inject CO_2 into the reactor during the reverse reaction.

1.3. Experimental procedure

1.3.1. Forward reaction
Sodium bicarbonate (10–50 g) and water (450 mL) were mixed inside the reactor. The reactor was then sealed, and the reactor's pressure was recorded until equilibrium was reached at the set temperature (25–155°C).

1.3.2. Reverse reaction
Sodium carbonate (10–50 g) and water (450 mL) were mixed inside the reactor, followed by evacuation of the reactor using an air pump. CO_2 was then injected into the reactor, and the reactor's temperature and pressure were recorded until equilibrium was reached.

1.4. Theoretical equilibrium constant calculation

Theoretical equilibrium constant values, K_{cal}, were calculated using tabulated values of Gibbs free energy (ΔG) in kcal/mol, entropy (ΔS) in cal/K·mol, and enthalpy (ΔH) in kcal/mol according to the relationship between Gibbs free energy and the equilibrium constant (Eq. (8)). The Gibbs free energy of an overall reaction was calculated using the definition of Gibbs free energy (Eq. (9)). The overall enthalpy and entropy of formation were calculated (Eqs. (10) and (11)) based on the enthalpy and entropy of each chemical component at standard temperature as found in the Handbook of Thermochemical Data for Compounds and Aqueous Species (Barner and Scheuerman, 1978), using linear interpolation for K_{cal} values at non-standard temperatures:

$$K_{cal} = e^{\frac{-\Delta G_{rxn}}{RT}} \tag{8}$$

$$\Delta G_{rxn} = \Delta H_{rxn} - T\Delta S_{rxn} \tag{9}$$

$$\Delta H_{rxn} = \sum_{prod}\Delta H - \sum_{react}\Delta H \tag{10}$$

$$\Delta S_{rxn} = \sum_{prod}\Delta S - \sum_{react}\Delta S \tag{11}$$

where the subscripts rxn, prod and react refer to all reactions, products and reactants of a reaction, respectively; R is the gas constant, and T is the temperature of the reaction.

This set of calculations was used to determine the theoretical equilibrium constants for $NaHCO_3$ decomposition in aqueous solution (Reaction (3)) and as a solid (Reaction (1)).

Calculated equilibrium constants at all comparable temperatures were similar to those previously reported (Keener et al., 1985). This suggests the results for the $K_{cal,(3)}$ calculations are reliable and can be used as a baseline for comparison with experimental data for decomposition in an aqueous solution.

As expected, the $K_{cal,(1)}$ values were much larger than $K_{cal,(3)}$ at higher temperatures (above 75°C) because the heat required to initiate the reaction is not lost to the solution in the case of solid decomposition (Tables 1 and 2). Thus, the decomposition
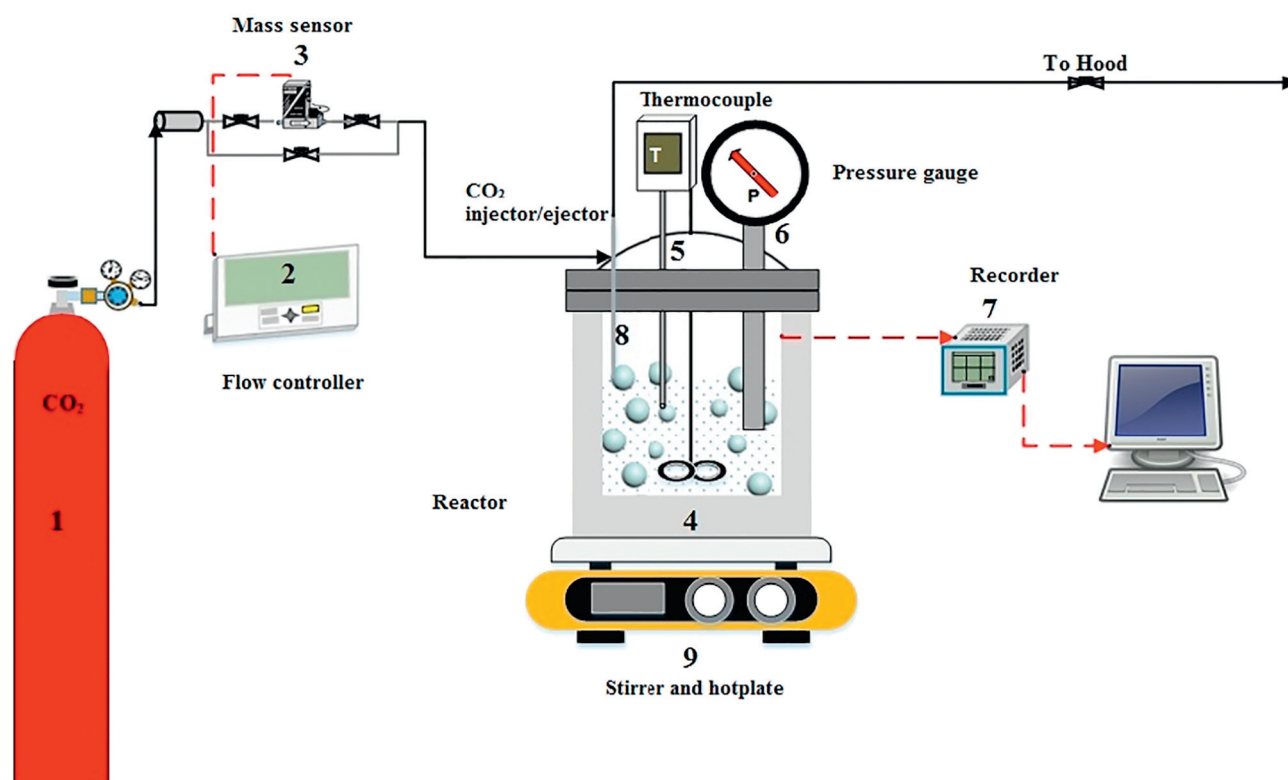
Fig. 1 – Schematic diagram of experimental set-up.

T(°C)	H₂O(l)		CO₂(g)		CO₃²⁻		HCO₃⁻		ΔH	ΔS	ΔG	$K_{cal,(3)}$
	ΔH	ΔS	ΔH	ΔS	ΔH	ΔS	ΔH	ΔS				
25	−68.30	16.70	−94.10	51.10	−161.90	−3.60	−165.40	26.80	6.50	10.60	3.34	0.003565
30	−68.26	17.00	−94.10	51.24	−162.42	−5.72	−165.54	26.32	6.30	9.88	3.30	0.004144
35	−68.22	17.30	−94.10	51.38	−162.94	−7.84	−165.68	25.84	6.10	9.16	3.28	0.004739
40	−68.18	17.60	−94.10	51.52	−163.46	−9.96	−165.82	25.36	5.90	8.44	3.26	0.005333
45	−68.14	17.90	−94.10	51.66	−163.98	−12.08	−165.96	24.88	5.70	7.72	3.24	0.005911
50	−68.10	18.20	−94.10	51.80	−164.50	−14.20	−166.10	24.40	5.50	7.00	3.24	0.006459
55	−68.06	18.46	−94.10	51.94	−165.02	−16.38	−166.18	23.98	5.18	6.06	3.19	0.007491
60	−68.02	18.72	−94.10	52.08	−165.54	−18.56	−166.26	23.56	4.86	5.12	3.15	0.008527
65	−67.98	18.98	−94.10	52.22	−166.06	−20.74	−166.34	23.14	4.54	4.18	3.13	0.009535
70	−67.94	19.24	−94.10	52.36	−166.58	−22.92	−166.42	22.72	4.22	3.24	3.11	0.010482
75	−67.90	19.50	−94.10	52.50	−167.10	−25.10	−166.50	22.30	3.90	2.30	3.10	0.011337
80	−67.88	19.76	−94.10	52.64	−167.60	−27.34	−166.54	21.94	3.50	1.18	3.08	0.012357
85	−67.86	20.03	−94.10	52.79	−168.12	−29.67	−166.58	21.57	3.08	0.02	3.08	0.013226
90	−67.84	20.28	−94.10	52.92	−168.61	−31.88	−166.62	21.21	2.69	−1.10	3.09	0.013873
95	−67.82	20.54	−94.10	53.06	−169.11	−34.09	−166.66	20.86	2.29	−2.20	3.10	0.014372
100	−67.80	20.80	−94.10	53.20	−169.60	−36.30	−166.70	20.50	1.90	−3.30	3.13	0.014656
105	−67.76	21.03	−94.10	53.32	−170.00	−37.92	−166.88	19.83	1.90	−3.23	3.12	0.015705
110	−67.72	21.26	−94.10	53.44	−170.40	−39.54	−167.06	19.16	1.90	−3.16	3.11	0.016813
115	−67.68	21.49	−94.10	53.56	−170.80	−41.16	−167.24	18.49	1.90	−3.09	3.10	0.017985
120	−67.64	21.72	−94.10	53.68	−171.20	−42.78	−167.42	17.82	1.90	−3.02	3.09	0.019223
125	−67.60	21.95	−94.10	53.80	−171.60	−44.40	−167.60	17.15	1.90	−2.95	3.07	0.020529
130	−67.56	22.18	−94.10	53.92	−172.00	−46.02	−167.78	16.48	1.90	−2.88	3.06	0.021908
135	−67.52	22.41	−94.10	54.04	−172.40	−47.64	−167.96	15.81	1.90	−2.81	3.05	0.023363
140	−67.48	22.64	−94.10	54.16	−172.80	−49.26	−168.14	15.14	1.90	−2.74	3.03	0.024896
145	−67.44	22.87	−94.10	54.28	−173.20	−50.88	−168.32	14.47	1.90	−2.67	3.02	0.026513
150	−67.40	23.10	−94.10	54.40	−173.60	−52.50	−168.50	13.80	1.90	−2.60	3.00	0.028215
155	−67.35	23.31	−94.10	54.52	−174.24	−54.68	−168.60	13.35	1.51	−3.55	3.03	0.028405

Table 1 – Theoretical equilibrium constants for aqueous NaHCO₃ decomposition.

ΔH (kcal/mol): enthalpy; ΔS (cal/(K·mol)): entropy; ΔG (kcal/mol): Gibbs free energy; T: temperature (oC); Kcal,(3): equilibrium constant.

Table 2 – Theoretical equilibrium constants for solid NaHCO₃ decomposition.

T(°C)	$H_2O(g)$		$CO_2(g)$		CO_3^{2-}		HCO_3^-		ΔH	ΔS	ΔG	K_{cal}	$K_{reported}$
	ΔH	ΔS	ΔH	ΔS	ΔH	ΔS	ΔH	ΔS					
25	−57.80	45.10	−94.10	51.10	−270.30	33.20	−226.40	24.40	30.60	80.60	6.57	0.000015	0.0000140
50	−57.90	45.80	−94.10	51.80	−270.30	35.30	−226.40	26.10	30.50	80.70	4.42	0.001022	N/A
75	−57.90	46.40	−94.10	52.50	−270.20	37.40	−226.50	27.80	30.80	80.70	2.70	0.020064	0.023
80	−57.92	46.50	−94.10	52.64	−270.46	37.78	−226.62	28.12	30.76	80.68	2.27	0.039495	N/A
90	−57.96	46.70	−94.10	52.92	−270.98	38.54	−226.86	28.76	30.68	80.64	1.40	0.144587	N/A
95	−57.98	46.80	−94.10	53.06	−271.24	38.92	−226.98	29.08	30.64	80.62	0.96	0.269317	N/A
100	−58.00	46.90	−94.10	53.20	−271.50	39.30	−227.10	29.40	30.60	80.60	0.52	0.493220	0.45
105	−58.01	47.01	−94.10	53.32	−271.50	39.67	−227.10	29.71	30.59	80.58	0.12	0.853916	N/A
110	−58.02	47.12	−94.10	53.44	−271.50	40.04	−227.10	30.02	30.58	80.56	−0.29	1.456980	N/A
115	−58.03	47.23	−94.10	53.56	−271.50	40.41	−227.10	30.33	30.57	80.54	−0.69	2.451330	N/A
120	−58.04	47.34	−94.10	53.68	−271.50	40.78	−227.10	30.64	30.56	80.52	−1.10	4.069037	N/A
125	−58.05	47.45	−94.10	53.80	−271.50	41.15	−227.10	30.95	30.55	80.50	−1.50	6.667206	N/A
130	−58.06	47.56	−94.10	53.92	−271.50	41.52	−227.10	31.26	30.54	80.48	−1.91	10.788678	N/A
135	−58.07	47.67	−94.10	54.04	−271.50	41.89	−227.10	31.57	30.53	80.46	−2.31	17.249014	N/A
140	−58.08	47.78	−94.10	54.16	−271.50	42.26	−227.10	31.88	30.52	80.44	−2.71	27.259745	N/A
145	−58.09	47.89	−94.10	54.28	−271.50	42.63	−227.10	32.19	30.51	80.42	−3.12	42.601167	N/A
150	−58.10	48.00	−94.10	54.40	−271.50	43.00	−227.10	32.50	30.50	80.40	−3.52	65.862108	64.00
155	−58.11	48.09	−94.10	54.52	−271.48	43.36	−227.10	32.79	30.51	80.39	−3.91	98.924747	N/A

$K_{reported}$ is the values of which obtained from "Thermal Decomposition of Sodium Bicarbonate"(Keener et al., 1985).

of sodium bicarbonate in an aqueous solution cannot happen as easily as it does in solid decomposition.

2. Results and discussion

2.1. Experimental equilibrium constants of NaHCO₃ decomposition

2.1.1. Analyzing experimental data
Experimentally determined equilibrium constant values of Reaction (3) under different temperatures were calculated according to the following equation:

$$K_{(3)} = K_1 = \frac{a_{CO_2} a_{H_2O} a_{Na_2CO_3}}{a_{NaHCO_3}^2} \tag{12}$$

where $K_{(3)}$ refers to the equilibrium constant of Reaction (3), and a_i corresponds to the activity of species 'i'.

The activity of gaseous and aqueous species is approximated by their partial pressure and concentration, respectively. It is assumed that only air, water, and carbon dioxide are present in the gas phase. The partial pressure of air (P_{air} in psi) at room temperature was estimated by taking the average of the first 10 pressure data points, which assumes the reaction had not begun by this time, and that only air was in the gas phase. Water was assumed to act as an ideal gas in equilibrium with the liquid water, so the Antoine equation (Eq. (13)) was used to approximate its saturation vapor pressure (with Antoine coefficients A = 8.07131, B = 1730.63, and C = 233.426):

$$\log_{10} P_{water}(T) = A - \frac{B}{C + T} \tag{13}$$

where $P_{water}(T)$ (psi) and T (°C) refer to saturation vapor pressure and temperature in of water respectively.

The partial pressure of CO_2 (P_{CO_2} in psi) was then calculated using Dalton's Law of Partial Pressure (Eq. (14)),

$$P_{total} = \sum_i P_i = P_{CO_2} + P_{air} + P_{H_2O} \tag{14}$$

where P_{total} (psi) is the measured pressure in the chamber, and P_i (psi) is the partial pressure of gas 'i'. The partial pressure of CO_2 was then used to calculate the moles of CO_2 in the gas phase using the ideal gas law, as shown below:

$$n_{CO_2,gas} = \frac{P_{CO_2} V_{head}}{RT_R} \tag{15}$$

where $n_{CO_2, gas}$ (mol), V_{head} (L), R (0.08205736(L × atm)/(mol × K)) and T_R (°C), refer to the moles of CO_2 in the gas phase, the volume of the headspace, the ideal gas constant, and the temperature of the reactor headspace, respectively.

Ionic strength (I) and the Henry's constant (k_H) were solved iteratively (Eqs. (16) and (17)),

$$k_H(T) = \frac{k_H^o \exp\left(C_H\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right)}{10^{bI}}$$

or

$$\log(\gamma) = \log\left(\frac{k_H^o \exp\left(C_H\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right)}{k_H}\right) = bI \tag{16}$$

$$I = 0.5 \sum c_i z_i^2 \tag{17}$$

where k_H^o is the Henry's constant for CO_2 in pure water at reference temperature T_{ref} = 298.15°C; C_H ($= \frac{-\Delta_{sol}H}{R} = 2400$ K) is the temperature dependence of Henry's constant for CO_2 (where $\Delta_{sol}H$ is the enthalpy of dissolution in kcal/mol); γ is the activity coefficient of salt ions, and b (0.0975 L/mol) is the salting-out coefficient. In Eq. (17), c_i and z_i (mol/L) refer to the concentration and reaction coefficients of solvated species 'i',
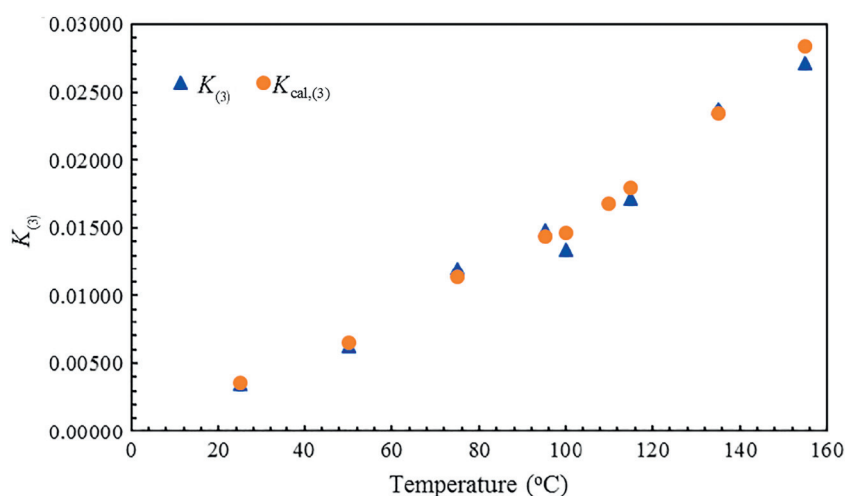
Fig. 2 – Comparison of the experimental forward reaction equilibrium constant values of Reaction (3) ($2HCO_3^- \leftrightarrow CO_3^{2-} + CO_2(g) + H_2O(l)$, $K_{(3)}$) to those calculated ($K_{cal,(3)}$) at different temperatures.

respectively. The concentrations of the solvated species were then determined according to Eqs. (18)–(21):

$$c_{CO_2} = \frac{n_{CO_2,sol}}{V_{sol}} = k_H(T_R)P_{CO_2} \tag{18}$$

$$n_{CO_2,form} = n_{CO_2,gas} + n_{CO_2}(aq) \tag{19}$$

$$n_{Na_2CO_3,form} = n_{CO_2,form} \tag{20}$$

$$n_{NaHCO_3,rem} = \frac{m_{NaHCO_3,added}}{MW_{NaHCO_3}} - 2n_{CO_2,formed} \tag{21}$$

where $n_{CO_2, form}$, $n_{CO_2}(aq)$, $n_{Na_2CO_3, form}$, $n_{NaHCO_3, rem}$, $m_{NaHCO_3, added}$, V_{sol}, $n_{CO_2, sol}$ and MW_{NaHCO_3} refer to number of moles of CO_2 formed from reaction, number of moles of CO_2 in the liquid phase, number of Moles of Na_2CO_3 formed during reaction, number of moles of $NaHCO_3$ remaining after reaction, number of moles of $NaHCO_3$ added, volume of the solution in L, number of moles of CO_2 dissolved in solution and molecular weight of $NaHCO_3$ in g/mol respectively.

Combining Eqs. (16)–(21), the ionic strength can rewritten as

$$I = 0.5 \sum c_i z_i^2 = 0.5\left(c_{CO_3^{2-}}(-2)^2 + c_{Na^+}(+1)^2 + c_{HCO_3^-}(-1)^2\right)$$

$$I = 0.5\left(\frac{4n_{Na_2CO_3,form} + 2n_{Na_2CO_3,form} + 2n_{NaHCO_3,rem}}{V_{sol}}\right) \tag{22}$$

After converging on a solution for ionic strength and Henry's constant, the equilibrium constant ($K_{eq, C}$) was calculated.

$$K_{eq,P} = \frac{\frac{n_{Na_2CO_3,form}}{V_{sol}}P_{CO_2}}{\left(\frac{n_{NaHCO_3,rem}}{V_{sol}}\right)^2} = \frac{n_{Na_2CO_3,form}P_{CO_2}V_{sol}}{\left(n_{NaHCO_3,rem}\right)^2} \tag{23}$$

$$K_{eq,C} = K_{(3)} = \frac{\frac{n_{Na_2CO_3,form}}{V_{sol}}\frac{n_{H_2O}}{V_{sol}}\frac{n_{CO_2,sol}}{V_{sol}}}{\left(\frac{n_{NaHCO_3,rem}}{V_{sol}}\right)^2} = \frac{n_{Na_2CO_3,form}\,n_{H_2O}\,n_{CO_2,sol}}{V_{sol}\left(n_{NaHCO_3,rem}\right)^2} \tag{24}$$

2.1.2. Confirmation of forward reaction

All the variance between $K_{cal,(3)}$ and $K_{(3)}$ were less than ±9% (Fig. 2). Therefore, experimental data suggests the calculated equilibrium constant, $K_{cal,(3)}$, is reliable (Table 1). The reverse reaction was analyzed similarly. (See Table 3.)

2.2. Reverse reaction

2.2.1. Analyzing experimental data

The equilibrium constant for the reverse reaction ($K_{(3)}'$) at different temperatures was calculated according to Eq. (25):

$$K_{(3)}' = K_2 = \frac{a_{NaHCO_3}^2}{a_{CO_2}a_{H_2O}a_{Na_2CO_3}} \tag{25}$$

where the concentration of each component at equilibrium was obtained from the measured pressure, solubility of CO_2 in water (Carroll et al., 1991), and saturation pressure of water (Keener et al., 1985) at a given temperature once equilibrium was reached as described by the following process.

After the reactor was evacuated, CO_2 was introduced to the vessel, and the pressure (P_{CO2} in psi) was calculated using Dalton's Law of Partial Pressures where the saturation pressure

Table 3 – Comparison between the experimental ($K_{(3)}$) and calculated ($K_{cal,(3)}$) forward reaction equilibrium values at different temperatures.

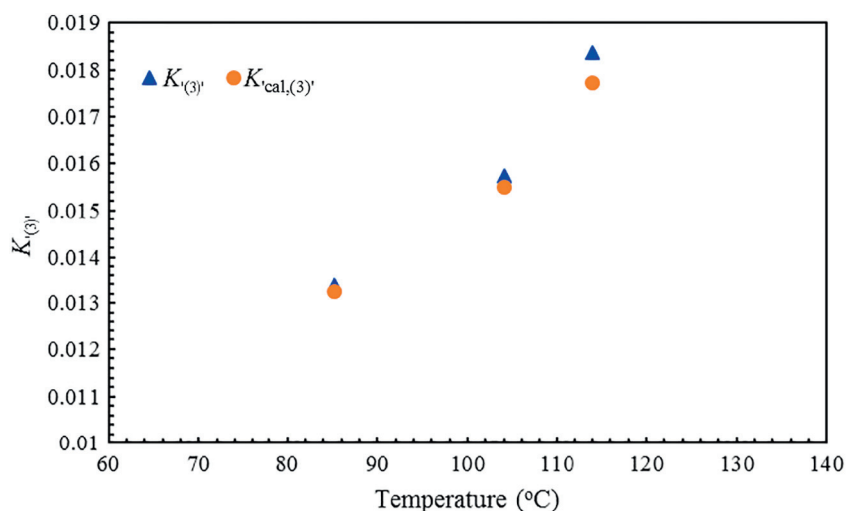| Temperature (°C)	$K_{(3)}$	$K_{cal, (3)}$	Error (%)
25	0.00350	0.00356	1.82
50	0.00621	0.00646	3.87
75	0.01200	0.01134	5.85
95	0.01480	0.01437	2.98
100	0.01340	0.01466	8.57
115	0.01720	0.01799	4.36
135	0.02380	0.02336	1.87
155	0.02710	0.02841	4.59

Fig. 3 – Differences between the calculated ($K_{cal,\ (3)'}$) and experimental ($K_{(3)'}$) reaction equilibrium constant values derived from equilibrium data of reverse reaction Reaction (3) at different temperatures.

of water is estimated using the Antoine Equation, as shown in Eq. (26) (Lisal et al., 2004):

$$P_{CO_2} = P_{T,final} - P_{water}(T_R) \qquad (26)$$

where $P_{T,\ final}$ and $P_{water}(T_R)$ refer to final pressure in psi and saturation pressure of water in psi, respectively.

The partial pressure of CO_2 was then used to calculate the moles of CO_2 in the gas phase using the ideal gas law (Eq. (27)) and was subsequently used to determine the amount of CO_2 in solution (Eq. (28)):

$$n_{CO_2,gas} = \frac{P_{CO_2} V_{head}}{R T_R} \qquad (27)$$

$$n_{CO_2,sol} = p^* n_{total} \qquad (28)$$

where p^* is the percentage of CO_2 in solution based on the solubility of CO_2 in water, and n_{total} is the total number of mole of CO_2, respectively.

The total amount of CO_2 (mol) reacted during the reaction ($n_{CO_2,\ reacted}$) was calculated by performing a mass balance on the system, where $n_{CO_2}^i$ is the initial amount of CO_2 introduced to the reactor:

$$n_{CO_2,reacted} = n_{CO_2}^i - n_{CO_2,gas} - n_{CO_2,sol} \qquad (29)$$

Based on the reaction stoichiometry, the amount of $NaHCO_3$ formed were twice the amount of CO_2 reacted. The amount of Na_2CO_3 remaining were calculated using the reaction stoichiometry and a mass balance, as illustrated in Eqs. (30) and (31):

$$n_{Na_2CO_3,rem} = \frac{m_{Na_2CO_3,added}}{MW_{Na_2CO_3}} n_{CO_2,reacted} \qquad (30)$$

$$n_{NaHCO_3,form} = 2 n_{CO_2,reacted} \qquad (31)$$

The equilibrium constant ($K_{eq,C}'$) was then calculated according to Eq. (32), with the correlation between the forward ($K_{(3)}$) and reverse reaction equilibrium constants ($K_{(3)'}$) shown in Eq. (33):

$$K_{eq,C}' = K_{(3)'} = \frac{\left(\frac{n_{NaHCO_3,form}}{V_{sol}}\right)^2}{\frac{n_{Na_2CO_3,rem}}{V_{sol}} \frac{n_{H_2O}}{V_{sol}} \frac{n_{CO_2,sol}}{V_{sol}}} = \frac{\left(n_{NaHCO_3,form}\right)^2 V_{sol}}{n_{Na_2CO_3,rem}\ n_{H_2O}\ n_{CO_2,sol}} \qquad (32)$$

$$K_{Eq.(3)} = \frac{1}{K_{Eq.(3)'}} \qquad (33)$$

2.2.2. Confirmation reaction or reverse reaction
The differences between the calculated ($K_{cal,\ (3)'}$) and experimental $K_{(3)'}$ values shown in Fig. 3 were not significant, ($<\pm4\%$) and were most likely due to instrumental or human calculation error (Table 4). Therefore, the calculated $K_{cal,\ (3)'}$ was once again reinforced as a reliable and accurate equilibrium constant for sodium bicarbonate decomposition in aqueous solution.

3. Conclusions

In this experiment, the equilibrium constants of the forward and reverse reactions were calculated accurately (error $<\pm9\%$

Table 4 – Comparison between the calculated ($K_{cal,\ (3)'}$) and experimental ($K_{(3)'}$) derived reverse reaction data at different temperatures.

Temperature (°C)	$K_{(3)'}$	$K_{cal,\ (3)'}$	Error (%)
85.2	0.01338	0.01326	0.88
104	0.01575	0.01549	−1.65
114	0.01838	0.01775	−3.56

ΔH (kcal/mol): enthalpy; ΔS (cal/(K·mol)): entropy; ΔG (kcal/mol): Gibbs free energy; T: temperature (°C); $K_{cal,(3)}$: equilibrium constant.

and <±4%, respectively) using a combination of experimental and thermodynamic relationships, suggesting their reliability as accurate equilibrium constants for sodium bicarbonate decomposition at temperatures ranging from 25 to 155°C.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jes.2018.07.005.

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