Quick method for determination of equilibrium temperature of calcium carbonate dissociation

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Abstract A quick method for determination of equilibrium temperature of high temperature reactions, which is inexpensive and suitable for small industrial laboratories, is reported. Reaction of high temperature dissociation of calcium carbonate is used as example for quick method application. The method is based on calorimetric measurement, Hess Law, and thermodynamic calculations. The calibrated calorimeter is used to determine enthalpy change for reactions $CaCO_3(s) + HCl(l)$, $Ca(s) + 2HCl(l)$, and $CaO(s) + 2HCl(l)$. By application of Hess's energy cycle, enthalpies of formation of calcium carbonate and calcium oxide were determined. Acquired results were used to calculate enthalpy change for carbonate dissociation reaction. Calculated enthalpy change value was used for free energy change in dependence of temperature and also for equilibrium constant in dependence of temperature calculation using equations derived from basic thermodynamic equations. Using this method, equilibrium temperature for calcium carbonate dissociation reaction is found to be equal to 1154.14 K, which confirms accuracy of the method.

Keywords Calcium carbonate dissociation · Equilibrium temperature · Method

Introduction

Knowing exact equilibrium temperatures of high temperature reactions are of extreme importance especially in industrial applications. This method offers simple, yet, if properly conducted, very accurate tool for its determination.

Equilibrium temperatures of a number of high temperature dissociation reactions can be easily determined with very good accuracy using just an inexpensive calibrated reaction calorimeter or any constant pressure calorimeter, Hess law, and several equations derived from basic thermodynamic equations. In this study, this method was applied for determination of temperature equilibrium of $CaCO_3$ dissociation. Calcium carbonate dissociation is represented by reaction (1):

$$CaCO_3(s) \leftrightarrow CaO(s) + CO_2(g) \tag{1}$$
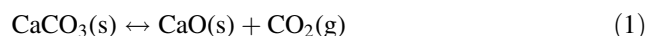
The first round explanation of calcium carbonate calcination, including its expulsion of carbon dioxide gas, was given by British chemist Joseph Black in the eighteenth century. French scientists Vicat, Debray, and Le Chatelier in the nineteenth century are credited with measuring most of the earliest fundamental data including dissociation temperature [1].

Equilibrium temperature under constant pressure for reaction (1) was subject of many investigations [2–5], mostly done in the first half of the late century. In this study, an indirect approach was used to determine enthalpy change for reaction (1) by application of Hess's energy cycle. Experimentally acquired results for the enthalpy change were used as a base for free energy change and reaction equilibrium constant calculations. Indirect methods for determination of dissociation reaction enthalpy change and equilibrium temperature could prove to be even more accurate compared with standard thermal analysis if the new controversial theories [6] concerning nature of dissociation of calcium carbonate are accurate. Thermochemical approach of activation energy determination of calcium carbonate dissociation reaction introduced by L'vov [6, 7]

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is based upon the assumption of an initial step involving evaporation of the reactant followed by condensation of low volatile calcium oxide product. Since elementary thermochemical calculations show that in all cases of formation of solid product in the process of the congruent dissociative vaporization of reactants, the equilibrium partial pressure of the main product greatly exceeds its saturation vapor pressure, and therefore causes the appearance of vapor oversaturation. The oversaturation is responsible for the transfer of condensation energy to the reactant [8]. Since this transfer of energy to the reactant directly affects molar enthalpy change of the dissociation reaction [9], if the theory is correct, equilibrium temperature of the reaction is even more difficult to determine using standard thermal analysis because the condensation energy transfer is extremely difficult to determine.
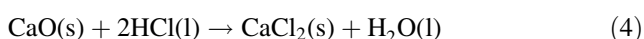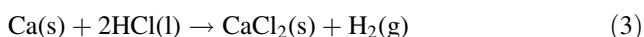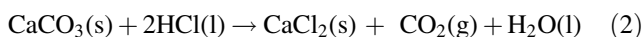
Materials and methods

Materials

Materials used in the experiments were precipitated calcium carbonate type MD600 produced by Minhduc chemical, with a purity of 99.9% and average particle size of 2.7 μm. Calcium oxide was produced by the calcination of the previously mentioned calcium carbonate in a laboratory furnace for 3 h at 950 °C. Other materials used are solid calcium *pro analysis* and 1 M chloride acid. All materials used in the experiments were tempered at 25 °C.

Methods

The calibrated calorimeter type Setaram C80 with a sensitivity of 30 μW/mW and resolution of 0.10 μW was used for an indirect determination of enthalpy of formation of the calcium carbonate and calcium oxide by Hess's law. To determine enthalpies of the formation of calcium carbonate and calcium oxide, enthalpies of reactions (2–4) were experimentally determined:

$$CaCO_3(s) + 2HCl(l) \rightarrow CaCl_2(s) + CO_2(g) + H_2O(l) \quad (2)$$

$$Ca(s) + 2HCl(l) \rightarrow CaCl_2(s) + H_2(g) \quad (3)$$

$$CaO(s) + 2HCl(l) \rightarrow CaCl_2(s) + H_2O(l) \quad (4)$$

Determination of the enthalpy of reaction (2)

Sample of 1 g of calcium carbonate was transferred into the calorimeter and temperature of calorimeter system was recorded. Then, 100 mL of 1 M HCl was added and the mixer was started. Temperature was recorded at 1 min interval for next 12 min.

Determination of the enthalpy of reaction (3)

Calcium was ground to the size in the range of 0–40 μm for granulometry. Sample of 1 g of calcium was transferred into the calorimeter and temperature of the calorimeter system was recorded. Then, 100 mL of 1 M HCl was added and mixer was started. Temperature was recorded at 1 min interval for next 12 min.

Determination of the enthalpy of reaction (4)

Sample of 1 g of calcium oxide was transferred into the calorimeter and temperature of the calorimeter system was recorded. Then, 100 mL of 1 M HCl was added and mixer was started. Temperature was recorded at 1 min interval for next 12 min.

Calculation

The total energy change of the system (the reaction) and the surroundings (calorimeter and solvent) is equal to 0, as shown in Eq. 5

$$q_{system} + q_{surroundings} = q_{reaction} + q_{calorimeter}$$
$$= n \cdot \Delta H + C \cdot \Delta T = 0 \quad (5)$$

where n is number of moles of the reactant, ΔH is the change of enthalpy of the chemical bonds of reaction, C is the specific molar heat capacity of the calorimeter and the solvent, and ΔT is the change of solvent temperature (water). Specific molar heat capacities of the calorimeter and solvent (water) are defined by the Eq. 6:

$$C = -(m_w c_{pw} + C_{cal}) \quad (6)$$

where m_w is the mass of water, c_{pw} is the specific heat of the solvent (water), and C_{cal} is the heat capacity of an empty calorimeter.

From Eq. 5, Eq. 7 is obtained:

$$\Delta H = -\frac{C\Delta T}{n} \quad (7)$$

The specific molar heat capacities as a function of temperature, at the constant pressure, are defined by Eq. 9 [10]:

$$C_p = a + bT + cT^{-2} \quad (9)$$

Literature data required for this method determined experimentally are shown in Table 1 [10, 11].

Table 1 Literature data

Component	$\Delta S°_{298}/\text{J K}^{-1} \text{ mol}^{-1}$	$\Delta H°_{298}/\text{kJ mol}^{-1}$	a	b	c	Temperature range/K
$CaCO_3$			24.98	0.00524	−620,000	298–1,200
CaO			10.00	0.00484	−108,000	298–1,173
CO_2		−393.769	10.55	0.00216	−204,000	298–2,500
H_2O		−285.8				
Reaction (1)	164					

The chemical reaction enthalpy (heat of reaction) is defined by the Eq. 10 [2]:

$$\Delta H°_{298} = \sum \Delta H°_{298} \text{ (products)} - \sum \Delta H°_{298} \text{ (reactants)} \tag{10}$$

The change of the specific molar heat capacity, at constant pressure, as function of the temperature is defined by Eq. 11 [10]:

$$\Delta C_p = \Delta a + \Delta bT + \frac{\Delta c}{T^2} \tag{11}$$

The chemical reaction enthalpy (heat of reaction), at the defined temperature, is defined by Eq. 12 [10]:

$$\Delta H°_T = \Delta H°_{298} + \int_{298}^{T} \Delta C_p dT \tag{12}$$

The integration of Eq. 12 gives Eq. 13:

$$\Delta H°_T = \Delta H°_{298} + \Delta a(T - 298) + \Delta b \cdot \frac{1}{2}(T^2 - 298^2) + \Delta c \cdot (-1) \cdot \left(\frac{1}{T} - \frac{1}{298}\right) \tag{13}$$

The change of the free energy of reaction, as a function of the temperature, is defined by the expression (14) [10]:

$$\Delta G°_T = \Delta H°_T - T\Delta S°_T \tag{14}$$

By combining previous equation, the expression (15) for the change of free energy, at a specific temperature becomes [10]:

$$\Delta G°_T = \Delta H°_0 - \Delta aT \ln T - \frac{1}{2}\Delta bT^2 - \frac{1}{2}\Delta c \cdot \frac{1}{T} + yT \tag{15}$$

or

$$\Delta G°_T = \left(\Delta H°_{298} - \Delta a \cdot 298 - \frac{1}{2}\Delta b \cdot (298)^2 + \Delta c \cdot \frac{1}{298}\right) - \Delta aT \ln T - \frac{1}{2}\Delta bT^2 - \frac{1}{2}\Delta c \cdot \frac{1}{T} + yT \tag{16}$$

where y is constant of integration.

The constant of integration, y, can be determined by knowing the standard free energy, according to expression (17):

$$y = \frac{-\Delta H°_0 + \Delta aT \ln T + \frac{1}{2}\Delta bT^2 + \frac{1}{2}\Delta c \cdot \frac{1}{T} - \Delta G°_{298}}{298} \tag{17}$$

So, by determining standard enthalpy change at 298 K and by knowing entropy change at 298 K, free energy change on an entire temperature range can be easily calculated using Eq. 16

Free energy change is in close correlation with equilibrium constant of the dissociation reaction as explained in following Eqs. 18–24. This correlation enables simple determination of equilibrium temperature of the calcium carbonate dissociation reaction on various outside pressures as shown in Fig. 4.

For the generalized chemical reaction

$$aA + bB \Leftrightarrow cC + dD \tag{18}$$
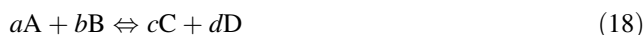
Chemical equilibrium constant may be described by the components concentration as shown in Eq. 19

$$K_c = \frac{c_C^c \cdot c_D^d}{c_A^a \cdot c_B^b} \tag{19}$$

and via components partial pressure as shown in Eq. 20

$$K_p = \frac{p_C^c \cdot p_D^d}{p_A^a \cdot p_B^b} \tag{20}$$

For reaction (1), the chemical equilibrium constant via components partial pressure is expressed by Eq. 21

$$K_p = \frac{pCaO \cdot pCO_2}{pCaCO_3} \tag{21}$$

Because $CaCO_3$ and CaO are in a solid state, the equilibrium constant of reaction (1) is given with expression (22):

$$K_p = pCO_2 \tag{22}$$

The relation between change of free energy and equilibrium constant is defined by expression (23), (24), [10]:

$$\Delta G = \Delta G^\circ + RT \ln K \qquad (23)$$

$$\Delta G_T^\circ = -RT \ln K \qquad (24)$$

Results and discussion

Temperature values recorded at time intervals for each examined reaction are shown in Table 2.

Based on data from Table 3, graph of temperature change as a function of time was constructed using a spreadsheet program (Figs. 1, 2, 3).

Table 2 Temperature change at time intervals for the reactions (2–4)

Time/min	Temperature/°C		
	Reaction (2)	Reaction (3)	Reaction (4)
1	25.00	25.00	25.00
2	25.28	54.12	32.22
3	25.26	54.03	32.18
4	25.23	53.62	32.11
5	25.17	53.51	31.98
6	25.14	53.23	31.78
7	25.13	53.10	31.56
8	25.12	52.98	31.49
9	25.12	52.73	31.38
10	25.10	52.01	31.21
11	25.10	51.82	31.18
12	25.07	51.55	31.02

Table 3 Enthalpy change for the reactions (2–4)

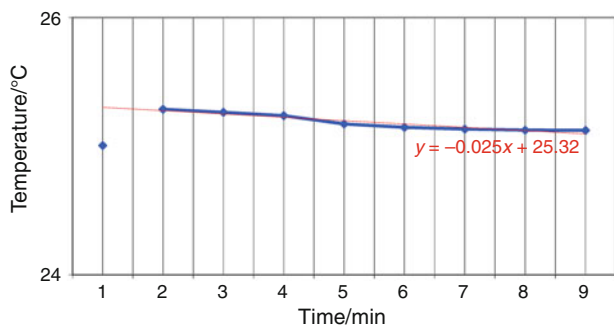| Reaction	$\Delta H^\circ{}_{298}$/kJ mol^{-1}
(2)	13.534
(3)	539.892
(4)	191.249

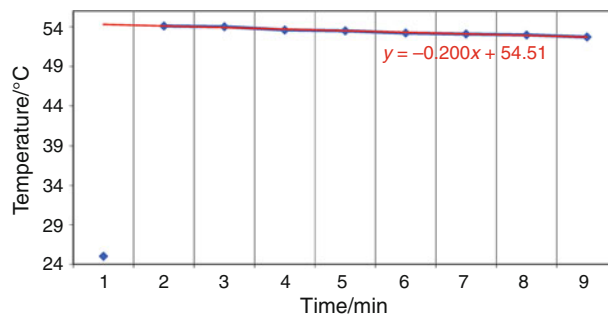**Fig. 1** Temperature change as a function of time for reaction (2)

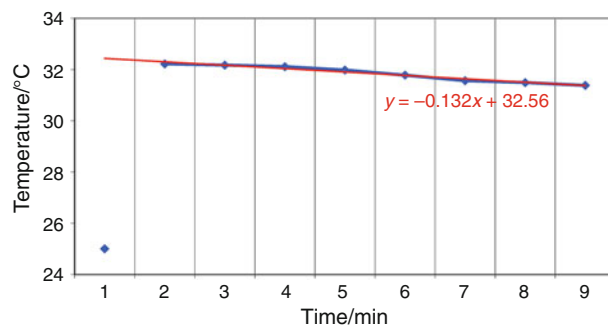**Fig. 2** Temperature change as a function of time for reaction (3)

Fig. 3 Temperature change as a function of time for reaction (4)

Table 4 Enthalpies of formation of components

Component	Formula	State	$\Delta H^\circ{}_{298}$/kJ mol^{-1}
Calcium carbonate	$CaCO_3$	Solid	−1,205
Calcium oxide	CaO	Solid	−634.422

Table 5 Heat capacity of the calorimeter and its content

Reaction	C/J K^{-1}
(2)	458.371
(3)	459.585
(4)	459.124

Table 6 Enthalpy change for reaction (1) obtained experimentally

Reaction	$\Delta H^\circ{}_{298}$/kJ mol^{-1}
(1)	177.684

Table 7 Coefficients Δa, Δb, and Δc for reaction (1)

Reaction	(1)
Δa	−4.43
Δb	0.00176
Δc	308,000

Fig. 4 Free energy change and equilibrium constant as function of temperature for reaction (1)
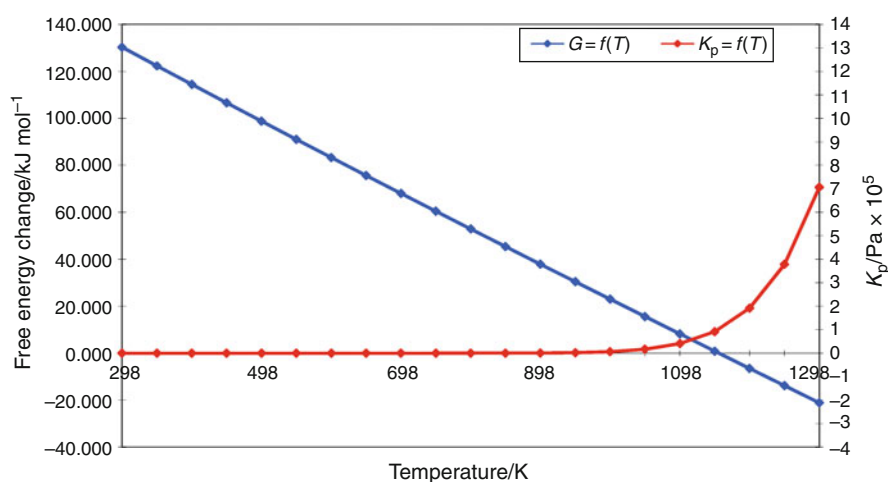
Graphs $\Delta T = f(T)$ from Figs. 1, 2 and 3 are processed in a way that regression lines in the graphs are extrapolated back to zero time (the time when the reactants were mixed in the calorimeter), in order to obtain a temperature difference (ΔT) value that is independent of temperature losses caused by calorimeter design.

Obtained temperature difference value (ΔT) was used in Eq. 5 for calculation of enthalpy change for the reactions 2–4).

Calculated values for enthalpy change for the reactions (2–4) are shown in Table 3.

Hess's law states that the energy change for any chemical or physical process is independent of pathway or number of steps required to complete the process.

Hess's law allows enthalpy change for a reaction to be calculated by performing arithmetic operations on chemical equations with known ΔH values.

By application of Hess's energy cycle, experimental determination of enthalpies for reactions 2–4) along with known values for enthalpy of formation of carbon dioxide (gas) and water (liquid) were used for the calculation of the enthalpies of formation of calcium carbonate and calcium oxide.

The enthalpies of formation of calcium carbonate and calcium oxide obtained experimentally are shown in Table 4.

The enthalpy of formation data shown in Tables 5 and 6 was used in Eq. 6 to obtain value for enthalpy change for reaction (1).

Values for enthalpy change for reaction (1) obtained experimentally are shown in Table 6.

Data from Table 1 were used to calculate Δa, Δb, and Δc for reaction (1).

Coefficients Δa, Δb, and Δc for reaction (1) are shown in Table 7.

Equations 11 and 16 were used to calculate equilibrium constant and free energy change as a function of temperature for reaction (1).

Calculation values are shown in Fig. 4.

The change of the free energy is a straight line that intersects temperature axis at 1154.14 K. At that temperature, reaction (1) is in equilibrium state at atmospheric pressure ($K_p = 1$). Equilibrium temperatures at outside pressures other than atmospheric can be extrapolated accordingly.

The value of the equilibrium temperature obtained by this study is compared with values from literature (Table 8).

It is visible that results concerning exact equilibrium temperature of calcium carbonate dissociation reaction obtained using this method are in agreement with available literature data, especially with works of Tamaru and with equilibrium temperature published by Southard [4, 5].

Table 8 Equilibrium temperature values

Temperature/K	Source from literature
1154.14	This study
1171.15	Johnston [2]
1170.15	Smyth and Adams [3]
1155.15	Tamaru et al. [4]
1155.15	Southard and Royster [5]

Conclusions

Equilibrium temperature, under atmospheric pressure, obtained by this method is 1154.14 K. Enthalpy change of calcium carbonate dissociation reaction obtained by the experimental part of the method is 177.684 kJ mol^{-1}. Although the experiment, or the method, has been conducted using relatively simple laboratory equipment, obtained result coincides with available literal data. Since this method uses

an indirect approach for determination of reaction enthalpy change, any inaccuracy that could be result of condensation energy transfer is impossible. The method allows quick determination of equilibrium temperature and could be very suitable for industrial laboratory usage.

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