

## Critical review of a paper about limits of stability of carbon dioxide in terms of temperature up to 1000 °C and pressure up to 100 atm

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### Abstract

The thermal decomposition of carbon dioxide (CO<sub>2</sub>) has been dealt by many authors to determine the necessary conditions to break down the molecules of CO<sub>2</sub>, generally at very high temperature (more than 1000 K) or/and with a catalyst and at atmospheric pressure. The goal of our work was to investigate the stability range of CO<sub>2</sub> molecule as a function of temperature (less than 1000 °C) and pressure (up to 100 atm), to estimate if the CO<sub>2</sub> is a good candidate for thermal compression. The only work about thermal stability of CO<sub>2</sub> was published by M. H. LIETZKE and C. MULLINS in 1981. Our results did not match theirs. Therefore, the stability range of CO<sub>2</sub> remains unknown.

**Keywords:** Thermal decomposition; Carbon dioxide; Thermal compression; Critical conditions; Equilibrium constant

### 1. Introduction

For thermal compression application[1], it is necessary to verify the stability of the fluid when the temperature and pressure increase respectively up to 1000 °C and 100 atm (1 atm = 101325 Pa). The SPAN and WAGNER equation of state for carbon dioxide covers the fluid region from the triple point temperature to 1100 K (826.85 °C) at pressures up to 800 MPa [2]. This enables to think that the CO<sub>2</sub> could be a good candidate for thermal compression. The goal of this study was to double-check this conclusion.

The paper of LIETZKE *et al.*[3] used the three main ways of thermal decomposition of carbon dioxide to study these phenomena.



Each of these equations are respectively associated with an equilibrium constant of reaction,  $K_1$  for equation (1),  $K_2$  for equation (2) and  $K_3$  for equation (3).

Assuming  $x$  and  $y$  are respectively the mole fraction of carbon monoxide (CO) and carbon (C), the equilibrium constant can be expressed as a function of  $x$ ,  $y$  and the pressure  $P$  (the unit of  $P$  is the atm).

$$K_1 = \frac{x \sqrt{y + x/2}}{(1 - x - y) \sqrt{1 + x/2}} \sqrt{P} \quad (4)$$

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$$K_2 = \frac{(1 - x - y)(1 + x/2)1}{x^2 P} \tag{5}$$

$$K_3 = \frac{1 - x - y}{y + x/2} \tag{6}$$

To calculate the values of these equilibrium constants, LIETZKE *et al.* used the JANAF Thermodynamical tables [4]. They obtained a temperature dependent expression for these equilibrium constants. The unit of the temperature T is the Kelvin.

$$\ln K_i = \frac{a_i}{T} + b_i + c_i T + d_i T^2 \tag{7}$$

**Table 1** Coefficients of eqn (7) for  $K_1$ ,  $K_2$  and  $K_3$  from [3]

	<b>a</b>	<b>b</b>	<b>c x 104</b>	<b>d x 108</b>
$\ln K_1$	-34126.3	10.6993	-1.03294	-1.65376
$\ln K_2$	20934.7	-21.8718	3.95504	1.11121
$\ln K_3$	47309.0	0.477681	-1.90999	2.22717

The authors used the Newton-Raphson method to solve simultaneously the equations (4) and (5) at a given temperature and pressure. They specified that for region where there is no carbon precipitation, the mole fraction y equals zero. They found three regions denoted A, B and C. In region A, there is no dissociation of CO<sub>2</sub>. In region B, the three stable species are CO<sub>2</sub>, CO and O<sub>2</sub> (oxygen). In region C, the three stable species are CO<sub>2</sub>, C and O<sub>2</sub>.

**1.1. New calculations**

The NIST-JANAF Thermochemical Data [5] was used in our study to verify the coefficients of equation (7) for  $K_1$ ,  $K_2$  and  $K_3$ . A good agreement was found with the paper of LIETZKE *et al.*

In the region where no precipitation of carbon occurs, as y equals zero, exact solutions could be found for the equations (4) and (5).

If y equals zero, the equation (4) becomes:

$$K_1 = \frac{x \sqrt{x/2}}{(1 - x) \sqrt{1 + x/2}} \sqrt{P} \tag{8}$$

then

$$K_1(1 - x) \sqrt{1 + x/2} = x \sqrt{x/2} \sqrt{P} \tag{9}$$

$$K_1^2(1 - x)^2(1 + x/2) - x^2(x/2)P = 0 \tag{10}$$

$$K_1^2(1 - 2x + x^2)(1 + x/2) - x^3 P/2 = 0 \tag{11}$$

Finally:

$$x^3 + x \left( \frac{3K_1^2}{P - K_1^2} \right) + \frac{2K_1^2}{K_1^2 - P} = 0 \tag{12}$$

To solve equation 12, which takes the form  $x^3 + px + q = 0$ , it is necessary to calculate the discriminant:

$$\Delta_{K_1} = \left( \frac{2K_1^2}{K_1^2 - P} \right)^2 + \frac{4}{27} \left( \frac{3K_1^2}{P - K_1^2} \right)^3 \tag{13}$$

If  $\Delta_{K_1}$  is positive or equal zero, the only one real root of equation (12) is:

$$x = \sqrt[3]{-\frac{q}{2} - \sqrt{\left(\frac{q}{2}\right)^2 + \left(\frac{p}{3}\right)^3}} + \sqrt[3]{-\frac{q}{2} + \sqrt{\left(\frac{q}{2}\right)^2 + \left(\frac{p}{3}\right)^3}} \quad (14)$$

$$\text{with } p = \frac{3K_1^2}{P - K_1^2} \text{ and } q = \frac{2K_1^2}{K_1^2 - P} \quad (15)$$

And, if y equal zero, the equation (5) becomes:

$$K_2Px^2 = (1 - x) \left(1 + \frac{x}{2}\right) \quad (16)$$

Then, comes:

$$\left(\frac{1}{2} + PK_2\right)x^2 + \frac{1}{2}x - 1 = 0 \quad (17)$$

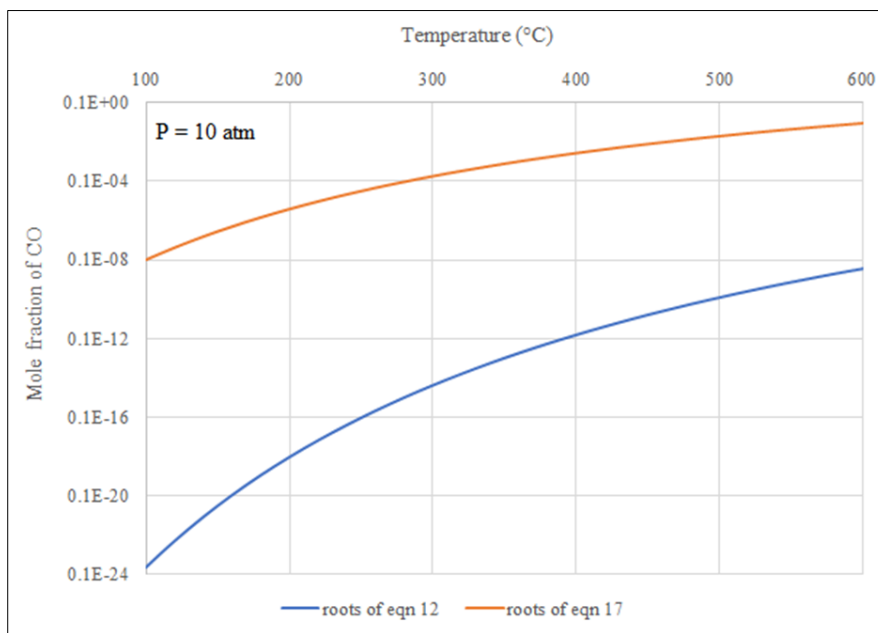
The discriminant of this equation is:

$$\Delta_{K_2} = \left(\frac{1}{2}\right)^2 + 4\left(\frac{1}{2} + PK_2\right) \quad (18)$$

If  $\Delta_{K_2}$  is positive, there are two real roots, one positive and one negative. The only physically meaningful exact is the positive one.

$$x = \frac{-b + \sqrt{\Delta_{K_2}}}{2a} \quad (19)$$

$$\text{with } a = \frac{1}{2} + PK_2, \quad b = \frac{1}{2} \quad (20)$$



**Figure 1** Roots (mole fraction of CO) of equations (12) and (17) at a pressure of 10 atm and temperature between 100 °C and 600 °C

The values of  $K_1$  and  $K_2$  are calculated by using the equation (7). At the temperature of 282°C (555.15 K) and a pressure of 10132.5 Pa (0.1 atm), the value of  $x$ , calculated by equation (14) equals  $5.191990 \times 10^{-15}$  (six significant figures are provided for ease of validation). The equation (19) gives a value of  $x$  equal at  $1.028603 \times 10^{-3}$ . When  $y$  equals zero, the

mole fraction of  $O_2$  is the half of mole fraction of  $CO$  ( $x$ ), therefore equals  $2.595995 \times 10^{-15}$  with  $x$  from equation (14). In the paper of LIETZKE *et al.*, at these temperature and pressure, the mole fraction of  $CO$  equals  $5.19 \times 10^{-15}$  and the mole fraction of  $O_2$  equals  $2.60 \times 10^{-15}$ . The solutions found by equation (14) are identical to those found by LIETZKE *et al.*, but cannot be considered as points of the boundary curves. The two curves below (Fig. 1) show the roots of equation (12) and (17) for a pressure of 10 atm. It is challenging to understand how LIETZKE *et al.* could have found, when there is no precipitation of carbon ( $y = 0$ ), the same value of mole fraction of  $CO$  ( $x$ ), by using Newton-Raphson method.

Provided the absence of carbon precipitation, the mole fraction of  $CO$ , between 0.01 atm and 100 atm and 0 °C to 1000 °C, can be calculated. For some values, it is necessary to add an easy method - easy because the partial derivation of  $K_1$  (equation 4) at constant pressure is always positive - to increase the precision of the root. It is required because the root of equation (12) uses square and cubic roots which are not always exactly calculated by Excel (enough to fig. 1) or visual studio C++ (used for Fig. 2). For example, the double or long double used by visual studio C++ are 8-bit format and it is not enough to have a difference between  $K_1$  calculated by equation 8, and  $K_1$  calculated by equation 7, less than  $1.0 \times 10^{-6} \% ((K_{1eqn7} - K_{1eqn8})/K_{1eqn8})$ .

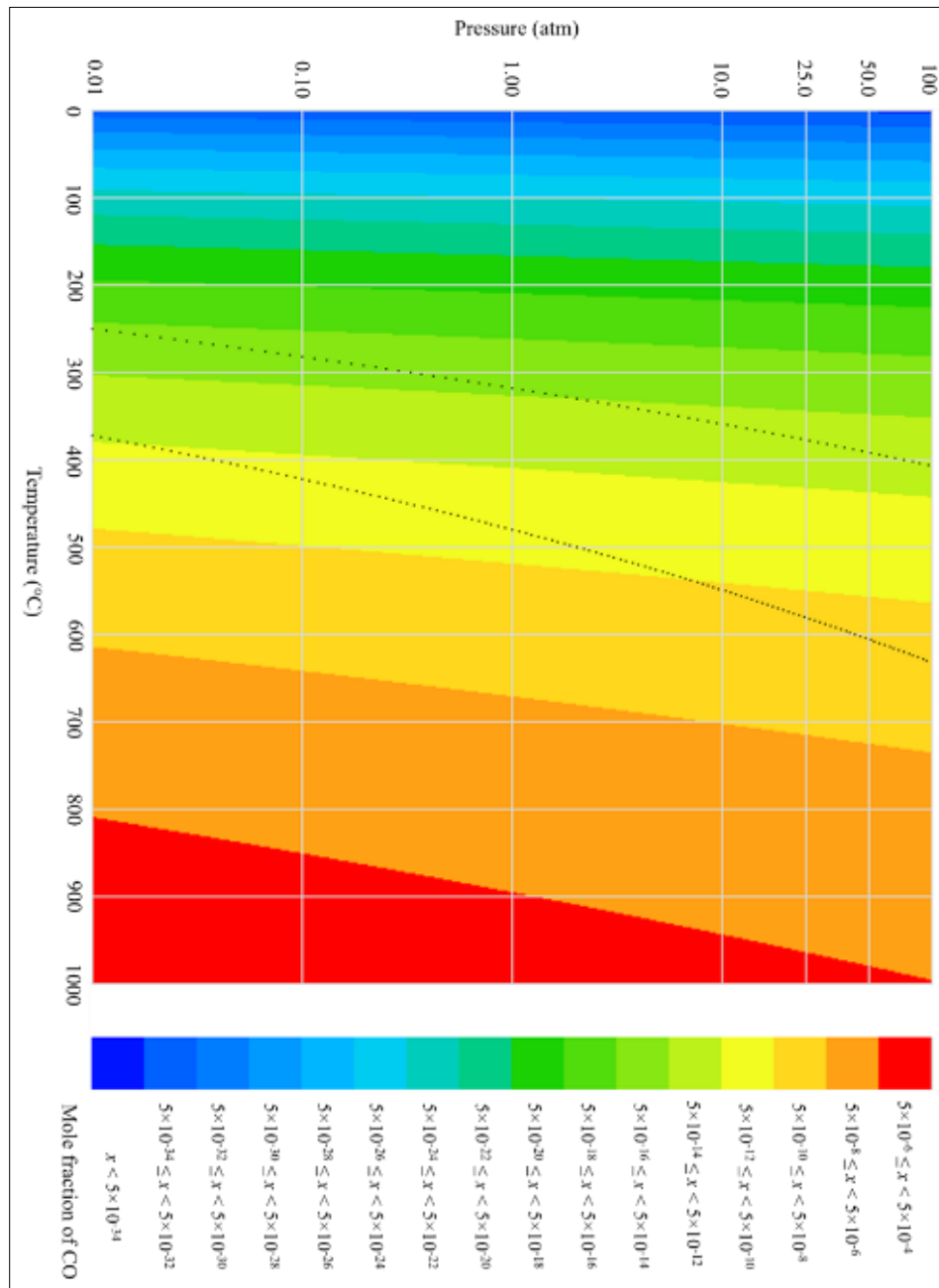


Figure 2 Roots (mole fraction of CO) of equation (12) from 0 °C to 1000°C and from 0.01 atm to 100 atm

On Fig. 2 the boundary curves between region A and region B and between region B and region C, proposed by LIETZKE *et al.*, are drawing (black dots). Fig. 2 shows that these curves should not be considered as boundary curves, but simply calculation values. The table 2 compare the values of LIETZKE *et al.* and the new calculations. The new calculations found the same results but only by using the equation (12). Many significant figures are provided for ease of validation.

**Table 2** Moles of CO produced by dissociation of 1 mole of CO<sub>2</sub> along the phase boundary curves versus [3] and roots of eq (12) for same pressures and temperatures

P (atm)	Values of table [3] from [3]		New calculations			
	Range of stability (°C)	Moles of CO	T (°C)	Moles of CO	T (°C)	Moles of CO
100	407 – 632	$9.59 \times 10^{-13} - 3.84 \times 10^{-9}$	407	$9.59028 \times 10^{-13}$	632	$3.84144 \times 10^{-9}$
10	359 – 549	$1.64 \times 10^{-13} - 6.59 \times 10^{-10}$	359	$1.63622 \times 10^{-13}$	549	$6.59141 \times 10^{-10}$
1	318 – 480	$2.92 \times 10^{-14} - 1.13 \times 10^{-10}$	318	$2.91471 \times 10^{-14}$	480	$1.13205 \times 10^{-10}$
10 <sup>-1</sup>	282 – 422	$5.19 \times 10^{-15} - 1.97 \times 10^{-11}$	282	$5.19199 \times 10^{-15}$	422	$1.97129 \times 10^{-11}$
10 <sup>-2</sup>	250 – 372	$9.14 \times 10^{-16} - 3.38 \times 10^{-12}$	250	$9.14368 \times 10^{-16}$	372	$3.37541 \times 10^{-12}$
10 <sup>-3</sup>	221 – 329	$1.54 \times 10^{-16} - 5.88 \times 10^{-13}$	221	$1.53839 \times 10^{-16}$	329	$5.88214 \times 10^{-13}$
10 <sup>-4</sup>	196 – 291	$2.86 \times 10^{-17} - 9.98 \times 10^{-14}$	196	$2.85606 \times 10^{-17}$	291	$9.97590 \times 10^{-14}$
10 <sup>-5</sup>	173 – 258	$5.06 \times 10^{-18} - 1.76 \times 10^{-14}$	173	$5.06022 \times 10^{-18}$	258	$1.75916 \times 10^{-14}$

## 2. Conclusion

The stability of CO<sub>2</sub> as function of temperature and pressure was studied. The work of LIETZKE *et al.* published in 1981 was used as a reference. The new calculations results mentioned earlier are not identical with those calculated by LIETZKE *et al.* This is one of the consequences of the increase in computing resources. The use of data extracted from JANAF to calculate the value of the equilibrium constant of the reaction (generally denoted K) can be questioned. The data taken from JANAF are about the equilibrium constant of formation (generally denoted  $K_f$ ). The values of  $K_i$  calculated by equation (7) do not have unit.  $K_1$  in equation (4) and  $K_2$  in equation (5) have respectively atm<sup>1/2</sup> and atm<sup>-1</sup> as units. Consequently, the verification of the thermal stability of carbon dioxide requires a specific study.

## Compliance with ethical standards

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### Disclosure of conflict of interest

The author declares the following interest/personal relationships which may be considered as potential competing interest:

Bruno FALCON has worked for BOOSTHEAT since February 2015. Therefore, he has been paid to perform this study and draft this paper.

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