

## Determination of Frequency Factor (Number of Collisions per second) for the Decomposition of Calcium Trioxocarbonate (IV) In Dilute Hydrochloric Acid

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**ABSTRACT:** Activation energy ( $E_a$ ) and frequency factor ( $A$ ) are important parameters use in kinetics to measure the extent of dissociation and collision of molecules respectively. The specific rate constants for the decomposition of calcium trioxocarbonate (iv) in dilute HCl at 30<sup>o</sup> and 40<sup>o</sup>C were measured using the method of collection of gases over water. Although carbon (IV) oxide is sparingly soluble in water, salting effect was applied with a view to reducing its (CO<sub>2</sub>) solubility for reliability of data. The values were found to be 4.33x10<sup>-3</sup> and 8.10x10<sup>-3</sup> respectively. The values strongly supported the suggestion that the rates of decomposition and collision of reacting species increase with increase in temperature. From the same values of  $K_1$  and  $K_2$ , the activation energy for the decomposition was similarly calculated and was found to 54.658 K.J/mol. This value enhanced the determination of the frequency factor which measures the number of collisions of the reacting species per second. This factor which was determined at 40<sup>o</sup>C was found to be 5.10x10<sup>-68</sup> per second.

**KEYWORDS:** Determination, frequency factor, decomposition, calcium trioxocarbonate (iv), hydrochloric acid.

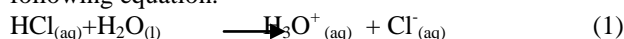
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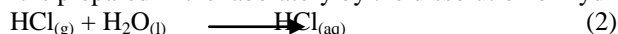
### I. INTRODUCTION

Calcium trioxocarbonate (iv), CaCO<sub>3</sub> which is the main chemical in this research, occurs naturally as deposits in the form of chalk, limestone and marble. AlanáHouse (1990). Pillars of limestone are found in caves as stalactites and stalagmites. It is also found in shells, e.g. egg shells Kaplan (2004). Calcium trioxocarbonate (iv) is a very important raw material in chemical industries. Specifically, limestone and marble, being hard are used as building materials, while chalk which is relatively soft, is used in toothpaste Ashassi-Sorkhabi et. al (2004). It is used in making glass and in the extraction of iron in the blast furnace. Domestically it is used in agriculture to neutralize the acid in the soil. It is also used in concretizing bricks and stones in building.

Hydrochloric is a strong acid which ionizes in water completely to produce hydroxonium ion according to the following equation.



It is prepared in the laboratory by the dissolution of hydrogen chloride gas in water. i.e.



The gas is passed through an inverted funnel into a beaker of cold water until the solution is saturated. The resulting solution becomes hot, and is about 36% concentrated hydrochloric acid.

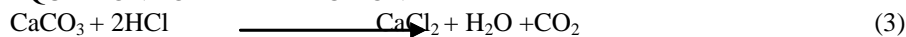
Industrially, it is used in the preservation of drugs and dyes. Similarly, it is used in cleaning or pickling of metals surface such as iron, before electroplating or galvanizing Delaney and Pierson (1976). Also, in the hydrolysis of starch to glucose. Domestically, in the form Aqua Regia is used in removing stains in glass ware. Hydrochloric acid is used as a laboratory reagent in acid – base titration, and the preparation of salts. It is also used in the chlorination of unsaturated hydrocarbons.

Carbon (iv) oxide which is the major product from the reaction of this research work is an acidic oxide and therefore should be treated with a lot of care and precaution. Its significance in the lives of plants and

animals cannot be over emphasized. The green plants utilize Carbon (iv) oxide to manufacture their own food (photosynthesis) and release oxygen as a by-product. The oxygen released by plants is utilized by animals during respiration. Carbon (iv) oxide is an oxide of group (iv) elements. It is denser than air that is why it is used both industrially and domestically.

Industrially, it is used in making fizzy drinks such as lemon and champagne Hatakeyama et al. (2009). Similarly, it is used in the manufacture of urea and washing soda. Domestically, it is used as fire extinguisher and refrigerating agent for perishable goods like ice cream and fruits. Magomet et al. (2010).

EQUATION FOR THE REACTION



Frequency factor which is an important parameter in Arrhenius equation measures the number of collisions per second of the reacting species, i.e.

$$k = Ae^{-E_a/RT}$$

Where  $k$  is the specific rate constant

$A$  is the frequency factor (number of collisions per second)

$E_a$  is the activation energy

$R$  is the gas constant

$T$  is the reacting temperature

Its (frequency factor) determination is very essential because of the roles it plays in kinetics and thermodynamics studies.

## II. MATERIAL AND METHOD

The chemicals /reagents used in this research include the followings: 2M solution of dilute hydrochloric acid (HCl), calcium trioxocarbonate (iv) (crystals),  $\text{CaCO}_3$ , common salt (NaCl) and distilled water ( $\text{H}_2\text{O}$ ).

The apparatus used are spatula, measuring cylinder, trough containing water, stop-water, retort stand, Buckner flask, delivery tube, rubber bung, syringe, electrical balance and filter paper.

### Experimental Procedure

The set up is a method adopted from the procedure for the collection and measuring of the volume of biogas Dangoggo et al. (2004). The apparatus consists of a 250cm Buckner flask corked with a rubber bung, 50cm poly vinyl chloride (PVC) rubber tube fitted to the side arm of the Buckner flask while the free end of the PVC tube was placed into an inverted measuring cylinder filled with water in a trough.

The gas ( $\text{CO}_2$ ) evolved being sparingly in water, common salt was added to the water contained in the trough in order to reduce its solubility. At this point, 0.2g of  $\text{CaCO}_3$  was accurately weighed, placed in the Buckner flask and corked with a rubber bung. 10cm<sup>3</sup> of 2M dilute HCl was pipetted out with help of a graduated syringe. Immediately the acid was injected into the Buekner flask through the cork, the stop watch was started to commence recording the time required for the decomposition to reach completion. When no gas bubbles were noted in the measuring cylinder and no down ward displacement of water, the time taken for the evolution of carbon (iv) oxide to cease was recorded. Also, the volume of water displaced was recorded as the volume of carbon (iv) oxide evolved during that period. The same procedure was repeated with 0.2g of  $\text{CaCO}_3$  and 20, 30, 40 and 50 cm<sup>3</sup> of HCl. Similarly, time and volume of carbon (iv) oxide evolved were recorded. The results are shown in table 1.

The above procedure was repeated with 0.2, 0.4, 0.6, 0.8 and 1.0g of  $\text{CaCO}_3$  keeping the volume of HCl constant at 10cm<sup>3</sup>. The results are presented in table II

Similarly, when 1.5g of  $\text{CaCO}_3$  was made to decompose in 30cm<sup>3</sup> of dilute HCl at 30<sup>0</sup>C, the data obtained is presented in table (III). The same experiment was repeated at 40<sup>0</sup>C, the result is indicated in table (iv).

## III. RESULTS

**Table I:** showing the volume of carbon (iv) oxide evolved with increasing volume of hydrochloric acid at constant mass (0.2g) of calcium trioxocarbonate.

S/N	Mass of $\text{CaCO}_3$ Used (g)	Volume of HCl used (cm <sup>3</sup> )	Volume of $\text{CO}_2$ Evolved (cm <sup>3</sup> )	Time taken (s)
1.	0.2	10	50	40
2.	0.2	20	120	30
3.	0.2	30	121	18
4.	0.2	40	120	9
5.	0.2	50	120	5

**Table II:** Showing the volume of carbon (iv) oxide evolved with increasing mass of calcium trioxocarbonate (iv) at constant volume of HCl (10cm<sup>3</sup>).

S/N	Mass of CaCO <sub>3</sub> Used (g)	Volume of HCl used (cm <sup>3</sup> )	Volume of CO <sub>2</sub> Evolved (cm <sup>3</sup> )	Time taken (s)
1.	0.2	10	50	40
2.	0.4	10	135	55
3.	0.6	10	155	70
4.	0.8	10	185	80
5.	1.0	10	195	95

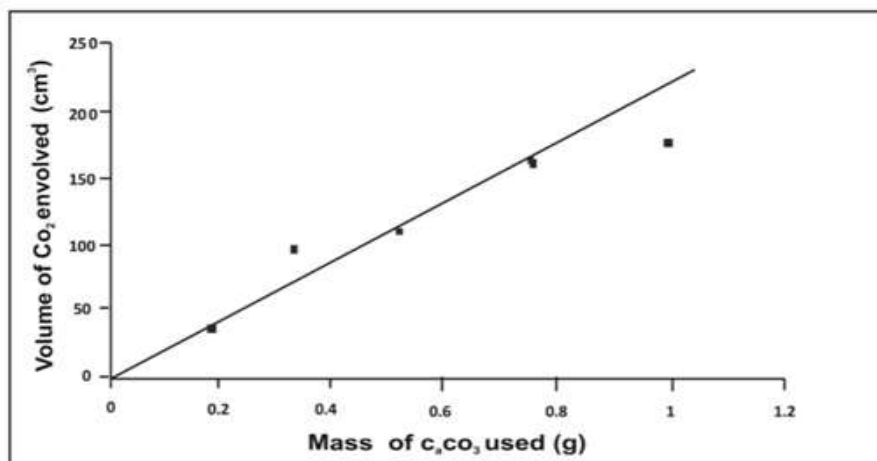
**Table III:** Showing the volume of carbon (iv) oxide evolved when 1.5g of calcium trioxocarbonate (iv) was made to decompose in 30cm<sup>3</sup> of dilute HCl after 30 seconds intervals at 30<sup>0</sup>C.

Time (sec)	30	60	90	∞
Volume of CO <sub>2</sub> evolved (cm <sup>3</sup> )	75	130	170	290
Specific rate constant (k) calculated	4.33x10 <sup>-3</sup>	4.33.x10 <sup>-3</sup>	4.22x10 <sup>-3</sup>	-

**Table iv:** Showing the volume of carbon (iv) oxide evolved when 1.5g of calcium trioxocarbonate (iv) was made to decompose in 30cm<sup>3</sup> of HCl after 30 seconds intervals at 40<sup>0</sup>C.

Time (sec)	30	60	90	∞
Volume of CO <sub>2</sub> evolved (cm <sup>3</sup> )	175	275	334	410
Specific rate constant (k) calculated	8.00x10 <sup>-3</sup>	8.10x10 <sup>-3</sup>	8.1x10 <sup>-3</sup>	-

**Figure I:** A plot of volume of carbon (iv) oxide against mass of CaCO<sub>3</sub>



**Figure II:** A plot of volume of carbon (iv) oxide against volume of HCl (cm<sup>3</sup>)

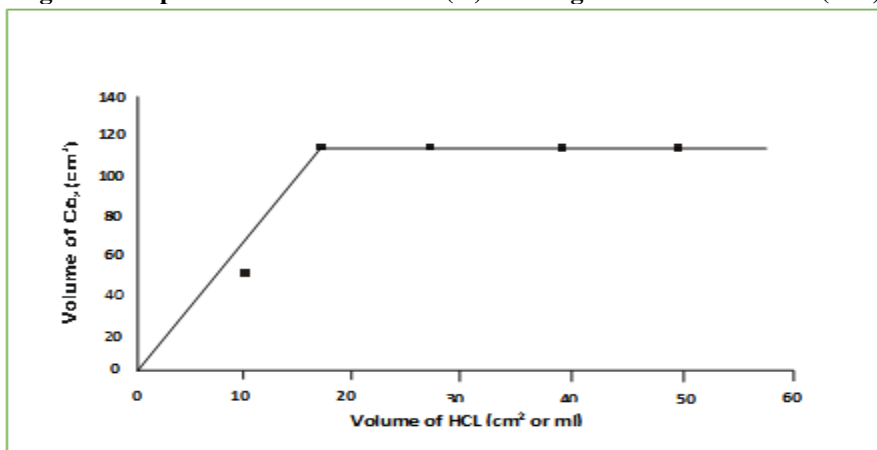
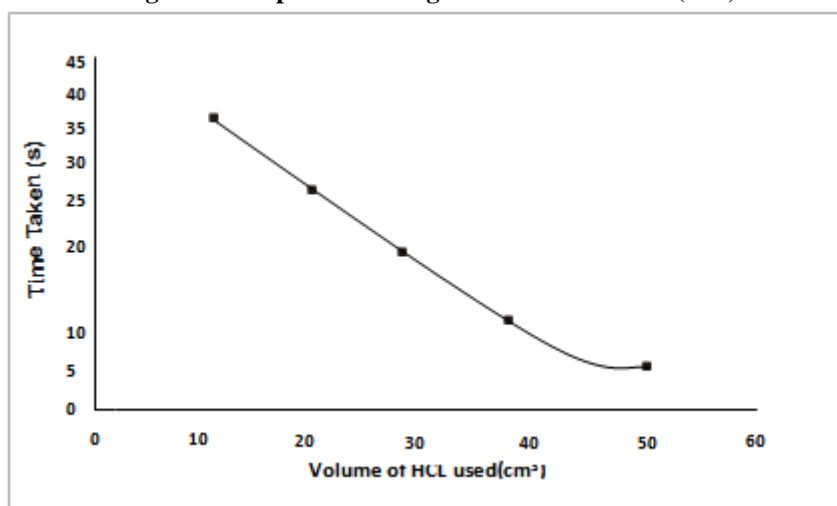


Figure III: A plot of time against volume of HCl (cm<sup>3</sup>).

#### IV. DISCUSSION

Considering the fact that the method used is based on collection of gases over water, however, gases like nitrogen (N), oxygen (O<sub>2</sub>) and carbon (iv) oxide (CO<sub>2</sub>) are sparingly soluble in water. Therefore, reasonable amount of common salt (NaCl) was dissolved in water in order to reduce the solubility of CO<sub>2</sub> in it (water). The strategy adopted was to decompose 0.2, 0.4, 0.6, 0.8 and 1.0g of calcium trioxocarbonate (iv) using fixed volume (10cm<sup>3</sup>) of hydrochloric. The volume of carbon (iv) oxide evolved in each case was measured using the apparatus described earlier.

Figure I: revealed a linear or direct relationship between the volume of carbon (iv) oxide produced and the mass of (CaCO<sub>3</sub>) decomposed. This indicated that there was an increase in the volume of carbon (iv) oxide evolved with a corresponding increase in the amount of calcium trioxocarbonate (iv). This confirmed the assumption that it (CaCO<sub>3</sub>) is a limiting reagent in this reaction. Furthermore, since the volume of HCl remained constant, it is reasonable to suggest that the decomposition processes are dependent on the mass of CaCO<sub>3</sub>.

In figure II, there was an initial increase in the volume of CO<sub>2</sub> evolved with a corresponding increase in the volume of HCl up to 20cm<sup>3</sup>. However, further increase of the volume of HCl above 20cm<sup>3</sup> generated practically constant volume of CO<sub>2</sub>. Three possibilities could be suggested for this incident. i.e.

- It implies that 20cm<sup>3</sup> of HCl was necessary and sufficient to ensure a complete decomposition of 0.2g of CaCO<sub>3</sub>.
- Also it is suggested that the excess HCl beyond 20cm<sup>3</sup> had no effect on the decomposition and
- It clearly demonstrated the fact that CaCO<sub>3</sub> is the limiting reagent in the decomposition reaction as suggested earlier.

Figure III disclosed an inverse relationship between the time taken for the completion of the reaction and the volume of HCl used. In other word, there was a decrease in the time of production of CO<sub>2</sub>. Clearly, this means that excess HCl fastened the decomposition process. This could possibly be due to the fact that more volume of HCl provided more surface area for reacting with CaCO<sub>3</sub>; Therefore the higher the volume of HCl, the higher the rate of reaction (consumed less time for the decomposition).

Table III. Highlighted increase in the volume of CO<sub>2</sub> generated when 1.5g of CaCO<sub>3</sub> was made to decompose in 30cm<sup>3</sup> of HCl at 30<sup>0</sup>C within an interval of 30 seconds. The evolution of CO<sub>2</sub> continued to increase up to the end of the reaction and the total volume of CO<sub>2</sub> evolved was 290cm<sup>3</sup> at this time (infinity). Also the values of specific rate constant (k) calculated at various time intervals were found to be constant at 4.33 x 10<sup>-3</sup> when the following first order equation was used.

$$\text{i.e. } k = \frac{1}{t} \log \frac{V_{\infty}}{V_{\infty} - V_t}$$

Where k is the specific rate constant V<sub>t</sub> is the volume of CO<sub>2</sub> evolved at any time t and V<sub>∞</sub> is the final volume of CO<sub>2</sub> evolved when the reaction is completed. V<sub>∞</sub> - V<sub>t</sub> is a measure of the decomposed CaCO<sub>3</sub> remaining at time t. The reaction was assumed to be a first order based on the fact that the volume of CO<sub>2</sub> evolved is independent of the volume of HCl, but directly proportional to the mass of CaCO<sub>3</sub> (from previous experiments).

When the same experiment was repeated at 40<sup>0</sup>C, the volumes of CO<sub>2</sub> produced at similar time interval (30 seconds), continued to increase at higher values than at 30<sup>0</sup>C as contained in table IV. This is possibly due to

the fact that increase in temperature leads to increase in the kinetic energy (K.E) of the reacting species which consequently led to the increase in their rate of decomposition and collisions. Furthermore, based on the same reason, the values of specific rate constant (k) doubled that obtained at 30<sup>0</sup>C. i.e. 8.00x10<sup>-3</sup>. From the values of specific rate constants obtained at 30<sup>0</sup> and 40<sup>0</sup> C, the value of activation energy (Ea) was calculated using the following equation. i.e.

$\log \frac{k_2}{k_1} = \frac{E_a}{2,302RT} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$  and was found to be 54.658kj, where k<sub>1</sub> and k<sub>2</sub> are the specific rate constants obtained at 30<sup>0</sup> and 40<sup>0</sup>C respectively. (Ea) is activation energy while R is the gas constant and T the absolute (k) temperature.

From the value of activation energy (Ea) calculated, the value of frequency factor (A) at 40<sup>0</sup>C, was determined using the following Arrhenius equation. i.e.

$\log k = \frac{E_a}{2,302RT} + \log A$  and it was found to be 5.10x10<sup>-68</sup> per second.

## V. CONCLUSION

During the decomposition, it was confirmed that CaCO<sub>3</sub> is a limiting agent and HCl catalyzed the process. Decrease in the decomposition time with increase in the volume of HCl confirmed its (HCl) role as a catalyst. Constant values of specific rate constant obtained at 30<sup>0</sup> and 40<sup>0</sup>C indicated that the decomposition is first order reaction. Increased values of specific rate constant with increase in temperature supported the argument that increases in temperature increases the rate of decomposition and number of collision per second.

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