

Kinetic



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We can use many of Technique or methods for separating of compounds or mixtures . and we can by those methods studying of kinetic for reactions , determine of reaction rate and reaction order . some of those methods are : mass spectrometric , spectrometric and Chromatographic Methods . But in this paper I just talk about chromatographic method . exactly, gas chromatography .

Chromatography: Few methods of chemical analysis are truly specific to a particular analyte. It is often found that the analyte of interest must be separated from the myriad of individual compounds that may be present in a sample. As well as providing the analytical scientist with methods of separation, chromatographic techniques can also provide methods of analysis .

Chromatography involves a sample (or sample extract) being dissolved in a mobile phase (which may be a gas, a liquid or a supercritical fluid). The mobile phase is then forced through an immobile, immiscible stationary phase. The phases are chosen such that components of the sample have differing solubility in each phase.

A component which is quite soluble in the stationary phase will take longer to travel through it than a component which isn't very soluble in the stationary phase but very soluble in the mobile phase. As a result of these differences in mobilities , sample components will become separated from each other as they travel through the stationary phase.

Gas chromatography methods that are used for studying first-order reaction kinetics by gas chromatography : (1) classical kinetic methods where

samples of batch-wise kinetic studies are analyzed by enantioselective gas chromatography, (2) stopped-flow methods performed on one chiral column, (3) stopped-flow methods performed on an achiral column or empty capillary coupled in series with two chiral columns, (4) on-flow method performed on an achiral column coupled in series with two chiral columns, and (5) reaction gas chromatography, known as a dynamic gas chromatography.

The following procedures have been developed to determination peak areas of reaction constituents in such complex chromatograms: (i) methods based on computer-assisted simulations of chromatograms where the kinetic activation parameters for the interconversion of enantiomers are obtained by iterative comparison of experimental and simulated chromatograms, (ii) stochastic methods based on the simulation of Gaussian distribution functions and using a time-dependent probability density function, (iii) approximation function and unified equation, (iv) computer-assisted peak deconvolution methods.

Fast reaction : Reaction between metal carbonate and acid.- Reaction between calcium carbonate and hydrochloric acid :  $\text{CaCO}_3 + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2$  Reaction between reactive metal and water .-reaction between lithium and water :  $2\text{Li} + 2\text{H}_2\text{O} \rightarrow 2\text{LiOH} + \text{H}_2$  Combustion .-combustion of magnesium in oxygen .  $2\text{Mg} + \text{O}_2 \rightarrow 2\text{MgO}$  Precipitation (double decomposition )-precipitation of silver (I) chloride :  $\text{AgNO}_3 + \text{HCl} \rightarrow \text{AgCl} + \text{HNO}_3$

Rate : The rate can be measured using apparatus on the rightrate of reaction =  $d[\text{CaCl}_2] / t$  , or  $d[\text{CO}_2] / t$  or  $d[\text{H}_2\text{O}]$  the rate can be decrease or increase

with change of temperature , concentration , pressure , surface area or size of molecules . concentration : when the concentration is decrease the rate decrease . example : 3 g of calcium carbonate react with 5 g of hydrochloric acid to produce 3 g of carbon dioxide in 10s at 25C and 1atm. rate =  $-\frac{d[\text{CaCO}_3]}{t} = -\frac{d[3]}{10}$  .

But we decrease of concentration of calcium carbonate to 2 . rate =  $-\frac{d[2]}{10}$  . pressure and temperature : also when decrease the pressure or temperature the rate decrease . example : 3 g of calcium carbonate react with 5 g of hydrochloric acid to produce 3 g of carbon dioxide in 10s at 25C and 1atm. rate =  $-\frac{d[\text{CaCO}_3]}{t} = -\frac{d[3]}{10\text{s}}$  . but the time is increase to 20s , because the pressure decrease to 0.5 and temperature decrease to 15 , so the rate =  $-\frac{d[3]}{20\text{s}}$  .

In a chemical reaction the reactant decrease over time and product increase over time . The rate will decrease over time as the hydrochloric acid is used up (its concentration decreases)The graph in after page shows the volume of gas produced over time in the reaction between HCl and CaCO<sub>3</sub> . All three reactions result in the same amount of CO<sub>2</sub> gas being produced; however the higher the concentration of HCl, the faster the rate of reaction, thus the less time it takes for the reaction to be complete .

The table below shows the time taken to produce 50cm<sup>3</sup> of CO<sub>2</sub> for each concentration of HCl : Rate of reaction / cm<sup>3</sup> of CO<sub>2</sub> s<sup>-1</sup> Time take to produce 50 cm<sup>3</sup> of CO<sub>2</sub>/1s Concentration of HCl /mold m<sup>-3</sup>

30.86	58	2.00	42
120	2.00	21	235
0.5			

From the results in the table above, it can be worked out that the rate of reaction is directionally proportional to the concentration of hydrochloric acid, so if you halve the concentration of HCl will be halved, if you quarter the concentration, the rate will be quartered .  $\text{rate} = k [\text{HCl}]^1$  Order : The order of a reaction is not necessarily an integer.

The following orders are possible : Zero: A zero order indicates that the concentration of that species does not affect the rate of a reaction . Negative integer: A negative order indicates that the concentration of that species INVERSELY affects the rate of a reaction . Positive integer: A positive order indicates that the concentration of that species DIRECTLY affects the rate of a reaction .

Non-Integer: Non-integer orders, both positive and negative, represent more intricate relationships between concentrations and rate in more complex reactions. So, in The reaction of calcium carbonate with hydrochloric acid is said to be first order with respect to hydrochloric acid . This is because the rate depends upon the concentration of hydrochloric acid to the power one .

Technique : we can measure of rate of carbon dioxide by gas chromatography , gas chromatography can separating of compound by boiling point , and you can analyze results on your computer and measuring of rate of CO<sub>2</sub> . and you can determine of rate by flow reaction that may be is easier method .