# CHAPTER 5

# ACETYLENE HYDROGENATION PROCESS

## 5.1 Introduction

With the steady increase in the market value of petrochemicals, efficient operation of the acetylene-removal process has become increasingly important. Most commercial plants for remove acetylene are effectively convert the acetylene impurity to the desired specification but do not address the issue of the undesired hydrogenation of ethylene and deactivation of the catalyst and the process widely used is the catalytic hydrogenation process. Thus, this thesis is considered to study an acetylene hydrogenation process. This chapter describes an acetylene hydrogenation process and reviews a kinetic of reactions.

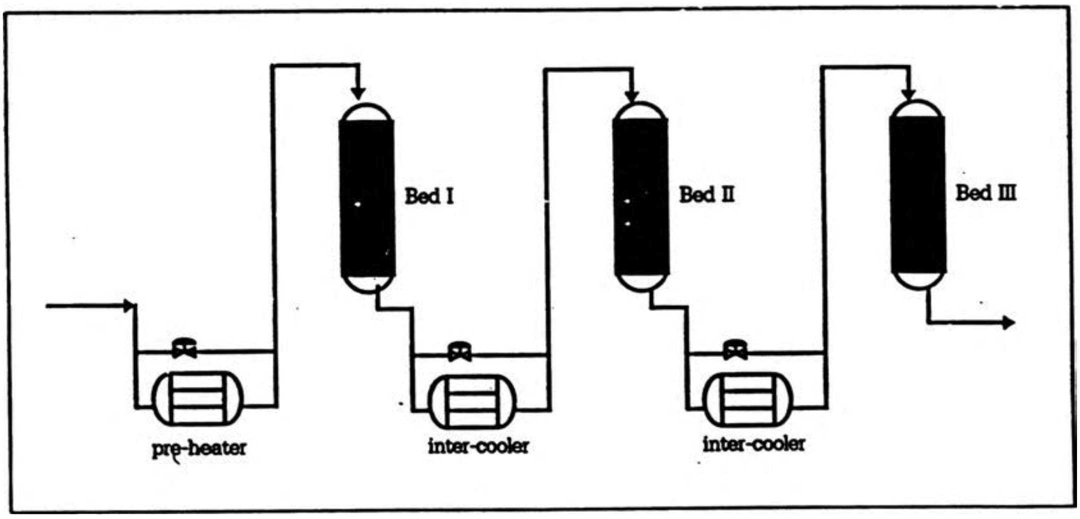

**Figure 5.1** The acetylene hydrogenation process under study in this thesis

## 5.2 The description of an acetylene hydrogenation process

The industrial acetylene-removal plant under study in this thesis is the three catalytic fixed-bed hydrogenation reactors that connected in series with pre-heater and two inter-cooler between beds. The process flow diagram shown in Figure 5.1. The bed reactor size is 3 m in diameter and 1.8 m in height as shown in Figure 5.2 and the detail specification of the reactors are:

- The volume of reactor = 10.815 $m^3$
- The volume of catalyst per bed = 10.8 $m^3$
- The catalyst type is the palladium on an alumina support
- The pressure drop per bed = 0.25 $Kg/cm^2$
- The weights of catalyst per bed = 11340 Kg

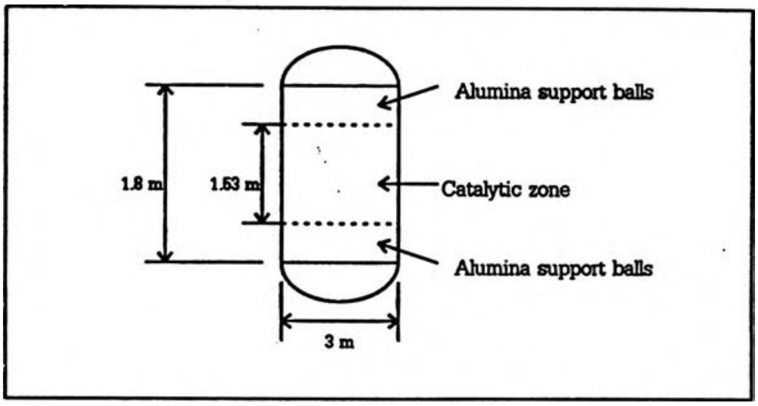

**Figure 5.2** Bed reactor

The pre-heater and inter-cooler systems are the shell and tube heat exchangers with by-pass valves and the surface area of the heat exchanger is 256.1 $m^2$. These systems are used to control the inlet bed temperature by adjust the by-pass flow.

The feed stream of an acetylene hydrogenation process is a cracked gas from the cracking furnaces that produce acetylene as by-product of high temperature pyrolysis reactions. An acetylene hydrogenation reactors must remove almost all acetylene from a cracked gas and the reactors effluent must contain less than 0.3 ppmv of acetylene in order to meet a specification of 1ppmv in the ethylene product. The cracked gas contains sufficient hydrogen to hydrogenate all acetylene to ethylene. In addition to acetylene, the cracking furnaces also produce methyl acetylene (MA) and a

C3 diolefin called propadienes (PD). Both MA and PD are hydrogenated in the acetylene hydrogenation reactors as same as acetylene and ethylene. Approximately 80 percent of the MA and 20 percent of the PD to propylene. The undesired reaction is hydrogenation of ethylene to ethane.

### 5.3 Kinetic of an acetylene hydrogenation reaction: A review

The old kinetic study of acetylene hydrogenation is a study about catalytic hydrogenation of acetylene dared back to 1899, when nickel catalyst was studied (Sabatier and Senderens, 1899). Nickel is good but, for an acetylene hydrogenation reaction, the palladium support catalyst is better (Cremer *et al.*, 1941). The main reactions involve in an acetylene hydrogenation process are (Godinez *et al.*, 1996):

1. Alkynes and diolefins hydrogenation

   Acetylene (Ac) hydrogenation

   $C_2H_2$ + $H_2$ ----> $C_2H_4$ $\Delta Hr$ = -163.61 KJ/mol

   Methyl acetylene (MA : $C_3H_4$) hydrogenation

   MA + $H_2$ ----> $C_3H_6$ $\Delta Hr$ = -164.86 KJ/mol

   Propadiene (PD : $C_3H_4$) hydrogenation

   PD + $H_2$ ----> $C_3H_6$ $\Delta Hr$ = -171.55 KJ/mol

2. Olefins hydrogenation

   Ethylene (Eth) hydrogenation

   $C_2H_4$ + $H_2$ ----> $C_2H_6$ $\Delta Hr$ = -130.63 KJ/mol

Many several kinetic models of acetylene hydrogenation reaction and the side reactions are presented continuously till today. Most kinetic results are given in a power rate equation from with hydrogen and acetylene pressures as the only variables. Some researches find that the rate of acetylene hydrogenation is zero order in acetylene and first order in hydrogen (McGown *et. al.*, 1977 ,and Moses *et. al.*, 1984). However, the rate order in hydrogen depends on the reaction temperature, for example, the first order in hydrogen is valid for hydrogenation at 0 - 30 C, whereas a reaction order of 1.4 is recorded at 125 C (Bond and Wells, 1965).

The one important topics is the mechanism of the reaction on a surface of catalyst. The two different active sites of catalyst are presented and this is an important way to explain the selectivity properties of acetylene hydrogenation (McGown *et. at.*, 1983). The hydrogenation of acetylene and ethylene are proceeded on the different type of active sites (Bos *et. al* .,1993). The first type of site is active for both acetylene and ethylene hydrogenation with being some 2000 times more strongly adsorbed than ethylene. The second type of site is responsible only for ethylene hydrogenation in the present of acetylene. It is this second type of site which more readily poisoned by carbon monoxide (Michael *et. al* .,1991). Hydroge may be adsorbed in the form of hydrogen atoms. The reversible formation of this half - hydrogenated intermediate follows from a study of the distribution of deuterium (D) in deuterated ethylene formed in hydrogenation of acetylene with $D_2$ (Bond and Wells, 1966). A simplified reaction sequence could thus be written:

$$H^2 + 2^* \Leftrightarrow 2H^*$$
$$C_2H_2 + 2^* \Leftrightarrow C_2H_2^{**}$$
$$C_2H_2^{**} + H^* \Leftrightarrow C_2H_3^{**} + {}^*$$
$$C_2H_3^{**} + H^* \Leftrightarrow C_2H_4^* + 2^*$$
$$C_2H_4^* \Leftrightarrow C_2H_4 + {}^*$$

The other important term for kinetic model is catalyst activity profile or catalyst deactivity. For an acetylene hydrogenation process, the one of undesired reaction is the polymerization of acetylene to from the green oil. Green oil is the catalyst poison. The catalyst deactivity dependent upon the amount of the green oil produced that can be written as:

$$\theta = 1/(1+ K_D\sum \text{Green oil produced}) \tag{5.1}$$

and the deactivity phenomenon occurs only on the sites responsible for the hydrogenation of acetylene (Michael *et. at.*, 1991). However, the catalyst activity can model in the different way such as:

$$-d\vartheta / dt = K_D(P_{reactant})^n \theta^d \quad (5.2)$$

where $K_D$ is in the form of an Arrhenuis expression (Corella *et. al.,* 1988). The best known of catalyst activity could find out the good catalytic reaction model (Corella *et. al.,* 1988).

Many researches report the kinetic model of the acetylene hydrogenation reaction in the sense of the Langmuir - Hinshelwood model that developed for an acetylen reactor control will be :

$$R_{C2H2} = k_1 P_{H2}^{\ n1} P_{C2H2}^{\ n2} / W \quad (5.3)$$

$$W = (1 + A_{H2} P_{H2}^{\ n3} + A_{C2H2} P_{C2H2}^{\ n4} + A_{CO} P_{CO}^{\ n5})^{m} \quad (5.4)$$

where $k_1$ was a rate constant of the Arrhenuis type (Nasi *et. al.,*1985).

In the recent years, the concept of the Langmuir - Hinshelwood kinetics is widely used in the sense of the acetylene hydrogenation reaction and the other side reactions (e.g. : Wilfred *et.al.,* 1990,Michael *et. al.,* 1991, and Schbib *et. al.,* (1993,1994,1996)). For this thesis, the Langmuir - Hinshelwood kinetics is considered to use to develop the kinetic models and check against the industrial data. The detail of the simulation models and the result are presented in the next chapter.

### 5.4 Kinetic of a catalyst reaction

A catalyst is a substance that effects the rate of a reaction but emerges from the process unchanged. On the chemical side, a catalyst usually changes a reaction rate by promoting a different molecular path ("mechanism") for the reaction. A catalyst changes only the rate of a reaction. It dose not affect the equilibrium.

#### 5.4.1 Steps in a catalytic reaction

The general mechanism of a heterogeneous catalytic reaction can be broken down into the sequence of individual steps shown in Table 5.1 and pictured in Figure 5.3 for an isomerization.

**Table 5.1** Steps in a catalytic reaction

| Steps | Description |
|---|---|
| 1 | Mass transfer (diffusion) of the reactant(s)(e.g., species A) from the bulk fluid to the external surface of the catalyst pellet |
| 2 | Diffusion of the reactant(s) from the pore mouth through the catalyst pores to the immediate vicinity of the internal catalyst surface |
| 3 | Adsorption of the reactant(s) onto the catalyst surface |
| 4 | Reaction on the surface of the catalyst (e.g., A-------->B) |
| 5 | Desorption of the product(s)(e.g., B) from the surface |
| 6 | Diffusion of the product(s) from the interior of the pellet to the pore mouth at the external surface |
| 7 | Mass transfer of the products from the external pellet surface to the bulk fluid |

The overall rate of reaction is equal to the rate of the slowest step in the mechanism. When the diffusion steps (1, 2, 6, and 7 in Table 5.1 ) are very fast compared with the reaction steps (3, 4, and 5) the concentrations in the immediate vicinity of the active sites are indistinguishable from those in the bulk fluid. In this situation, the transport or diffusion steps do not affect the overall rate of the reaction. In other situation, if the reaction steps are very fast compared with the diffusion steps, mass transport dose affect the reaction rate. In a system where diffusion from the bulk fluid to the catalyst surface or to the mouths of catalyst pores affects the rate, changing the flow conditions past the catalyst should change the overall rate.

There are many variations on the theme in Table 5.1 . Sometimes, of course, there are two reactants necessary for a reaction to occur, and both of these may undergo the steps listed above. Other reactions between two substances have only one of them adsorbed.

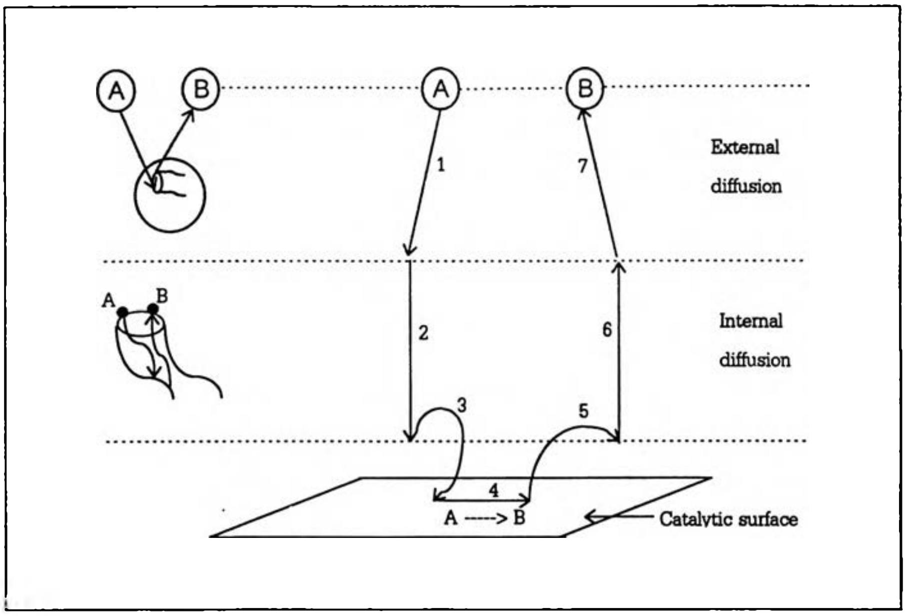

**Figure 5.3** Steps in a heterogeneous catalytic reaction.

### 5.4.2 Synthesizing a rate law, mechanism, and rate-limiting step

This section wish to develop rate law for heterogeneous catalytic reactions that are not diffusion limited. Thus the remained steps are :

1. Adsorption of reactant(s) on the catalytic surface
2. Surface reaction
3. Desorption of product(s) from the catalytic surface

If the chemical reaction is :

$$A \text{ ------------> } B + C$$

and if product C is not adsorbed, the total concentration of sites is

$$C_{total} = C_v + C_{A.S} + C_{B.S} \tag{5.5}$$

where

$C_{total}$ = the total concentration of sites, sites/weight

$C_v$ = the concentration of free sites

$C_{A.S}$ = the A specie adsorbed sites

$C_{B.S}$ = the B specie adsorbed sites

The rate expression for the adsorption of A is

$$r_{AD} = k_A P_A C_v - k_{-A} C_{A.S} \tag{5.6}$$

$$r_{AD} = k_A (P_A C_v - (C_{A.S}/K_A)) \tag{5.7}$$

with the adsorption equilibrium constant $K_A$

$$K_A = k_A/k_{-A} \tag{5.8}$$

The rate law for the surface reaction is

$$r_S = k_S C_{A.S} - k_{-S} P_C C_{B.S} \tag{5.9}$$

$$r_S = k_S (C_{A.S} - (P_C C_{B.S}/K_S)) \tag{5.10}$$

with the surface reaction equilibrium constant $K_S$

$$K_S = k_S/k_{-S} \tag{5.11}$$

The rate of product B desorption is

$$r_D = k_D C_{B.S} - k_{-D} P_B C_v \tag{5.12}$$

$$r_D = k_D (C_{B.S} - (P_B C_v/K_D)) \tag{5.13}$$

To find the rate law, all reaction steps that are not the rate-limiting step have vary large rate constant(k) and can set

$$r_{(AD, S, D)}/k_{(A, S, D)} \approx 0 \tag{5.14}$$

and then solve all equations for rate law, for example

**Example 5.1** When the adsorption of A is the rate-limiting step.

By assuming that this step is rate limiting, thus, the reaction rate constant of this step (in this case $k_A$) is small with respect to the rate constants of the other steps (in this case $k_S$ and $k_D$). The rate of adsorption is

$$-r_A = r_{AD} = k_A (P_A C_v - (C_{A.S}/K_A)) \tag{5.15}$$

The either of $C_v$ or $C_{A.S}$ cannot measure and must replace these variables in the rate equation with measurable quantities in order for the equation to be meaningful. For this case, $k_A$ is small and $k_S$ and $k_D$ are large. Consequently, the ratios $r_S/k_S$ and $r_D/k_D$ are very small (approximately zero), whereas the ratio $r_A/k_A$ is relatively large. The surface reaction rate expression is

$$r_S = k_S (C_{A.S} - (P_C C_{B.S}/K_S)) \tag{5.16}$$

$$r_S/k_S = C_{A.S} - (P_C C_{B.S}/K_S) \approx 0 \tag{5.17}$$

and solve equation (5.17) for $C_{A\,S}$

$$C_{A.S} = P_C C_{B.S}/K_S \tag{5.18}$$

To be able to express $C_{A.S}$ solvely in terms of the partial pressures of the species present, and then must evaluate $C_{B.S}$. The rate of desorption is

$$r_D = k_D(C_{B.S} - (P_B C_v/K_D)) \tag{5.19}$$

$$r_D/k_D = C_{B.S} - (P_B C_v/K_D) \approx 0 \tag{5.20}$$

and then solve equation (5.20) for $C_{B.S}$

$$C_{B.S} = P_B C_v/K_D \tag{5.21}$$

After combining equations (5.18) and (5.21), obtain

$$C_{A.S} = P_C P_B C_v/K_S K_D \tag{5.22}$$

Replacing $C_{A\,S}$ in the rate equation by equation (5.15), and then factoring $C_v$, obtain

$$r_{AD} = k_A(P_A\text{-}(\,P_C P_B/K_S K_D K_A))C_v \tag{5.23}$$

And then use equation (5.5) to find $C_v$ in term of the measurable quantities. Obtain

$$C_t = C_v + (P_C P_B/K_S K_D)C_v + (P_B/K_D)C_v \tag{5.24}$$

$$C_v = C_t/(1 + P_C P_B/K_S K_D + P_B/K_D) \tag{5.25}$$

Combining equations (5.23) and (5.25), can find the rate law for the reaction, assuming that the adsorption rate is the rate-limiting step, is

$$-r_A' = r_{AD} = k_A(P_A\text{-}(\,P_C P_B/K_S K_D K_A))C_v \tag{5.26}$$

$$-r_A' = \frac{C_t k_A \left(P_A - P_C P_B / K_S K_D K_A\right)}{1 + P_C P_B / K_S K_D + P_B / K_d} \tag{5.27}$$

For an other case, the rate law can find by change the r/k values for approximately zero. And then solve all equations by the same proceeding for the solution.

### 5.4.3 Langmuir-Hinshelwood kinetics

The other way to find the rate law for the heterogeneous catalytic reaction is making assumptions and producing the rate law by used the Langmuir-Hinshelwood kinetics concept.

The Langmuir-Hinshelwood kinetics is:

**Langmuir-Hinshelwood model**

The reactant(s) must be adsorbed on the catalytic surface and then the reaction between the reactant(s) occurs at the surface to form product(s) as the follow equations

$$A + B \dashrightarrow C$$

The assumptions are :

1. The two reactants are absorbed on active catalytic sites

$$A + \theta \dashrightarrow \theta_A$$

$$B + \theta \dashrightarrow \theta_B$$

2. The rate of reaction depends on the surface concentration fraction of A and B($\theta_A$ and $\theta_B$). The rate equation is :

$$-r_A = k\,\theta_A\theta_B \qquad (5.28)$$

3. The product C is not absorbed.

Where

$\theta$ = the fraction concentration of free active site

$\theta_A$ = the fraction concentration of site with A

$\theta_B$ = the fraction concentration of site with B

Using the Langmuir absorption mechanism can find the $\theta_A$ and $\theta_B$ as:

$$\text{rate of absorption} = \text{rate of desorption} \qquad (5.29)$$

$$k_A\theta P_A = k_A'\theta_A \qquad (5.30)$$

$$k_A(1-\theta_A-\theta_B)\,P_A = k_A'\theta_A \qquad (5.31)$$

$$k_A(1-\sum\theta)\,P_A = k_A'\theta_A \qquad (5.32)$$

$$\theta_A = (k_A/k_A')\,P_A(1-\sum\theta) \qquad (5.33)$$

$$\theta_A = K_AP_A(1-\sum\theta) \qquad (5.34)$$

like $\theta_A$ :

$$\theta_B = K_BP_B(1-\sum\theta) \qquad (5.35)$$

$$\Sigma\theta = \theta_A+\theta_B \qquad (5.36)$$

$$\Sigma\theta = (1-\Sigma\theta)(K_AP_A+K_BP_B) \qquad (5.37)$$

$$(1-\Sigma\theta) = 1/(1+K_AP_A+K_BP_B) \qquad (5.38)$$

Replacing and in the rate equation by equation (5.28). Obtain

$$-r_A = k\,K_AP_AK_BP_B/(1+ K_AP_AK_BP_B)^2 \tag{5.39}$$

If the product is adsorbed on catalytic surface, the reaction need the free site near $\theta_A$ and $\theta_B$ for the product adsorbing. Thus the rate equation may be written in form as

$$-r_A = k\theta_A\theta_B(1-\Sigma\theta) \tag{5.40}$$

Replacing, $\theta_A$, $\theta_B$ and $(1-\Sigma\theta)$ in the rate equation by equation (5.40) . Obtain

$$-r_A = k\,K_AP_AK_BP_B/(1+ K_AP_AK_BP_B)^3 \tag{5.41}$$

For the reaction that the reaction A must break in free atom before to form the product C, the rate of adsorption or desortion depend on $\theta^2$ or $\theta_A^2$ like :

$$r_{AD} = k_A(1-\theta_A-\theta_B)^2P_A \tag{5.42}$$

$$r_D = k_A\theta_A^2 \tag{5.43}$$

thus

$$\theta_A = (K_AP_A)^{0.5}(1-\Sigma\theta) \tag{5.44}$$

$$\Sigma\theta = (1-\Sigma\theta)((K_AP_A)^{0.5}+ K_BP_B) \tag{5.45}$$

$$(1-\Sigma\theta) = 1/(1+(K_AP_A)^{0.5}+ K_BP_B)) \tag{5.46}$$

the rate equation is

$$-r_A = k\,K_AP_AK_BP_B/(1+ (K_AP_A)^{0.5} + K_BP_B)^3 \tag{5.47}$$

## 5.5 Collection and analysis of rate data: to determine the reaction order and rate constant

Four methods of analyzing data are presented: the differential, the integral, the initial rate, and half-life methods. The methods of half-life and initial rates require experiments at many different initial conditions to determine the rate order and rate constant. On the other hand, with either the methods of integral and differential, it carries out only one experiment to find the rate order and rate constant with respect to one of reactants.

### 5.5.1 The differential method

This method is applicable when the reaction rate is essentially a function of the concentration of only one reactant: e.g., if, for the decomposition reaction

$$A \dashrightarrow \text{products}$$

or

$$A+B \dashrightarrow \text{products}$$

$$-r_A = kC_A^n \tag{5.48}$$

By combining the mole balance and rate law given by equation (5.48), obtain

$$-\frac{dC_A}{dt} = kC_A^n \tag{5.49}$$

After taking the natural logarithm of both sides of equation (5.49), obtain

$$ln(-\frac{dC_A}{dt}) = \ln k + n \ln C_A \tag{5.50}$$

Plot $ln(-\frac{dC_A}{dt})$ versus $lnC_A$ to find $k$ and $n$ and to obtain the derivative $-\frac{dC_A}{dt}$ must differentiate the concentration-time data by graph method that involves plotting $-\frac{DC_A}{Dt}$ as a function of time, and then using equal-area differentiation to obtain $-\frac{dC_A}{dt}$.

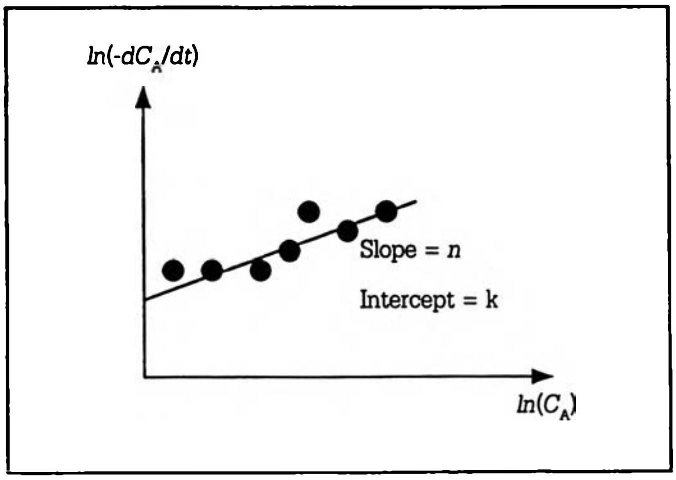

**Figure 5.4** Differential method to determine reaction oder and rate constant

### 5.5.2 Integral method

To determine the reaction order and rate constant by integral method, must guess the reaction order, integrate the differential equation, and plot reactant concentration versus time. The appropriate plot of the reactant concentration-time should be linear. For the example reaction

A -------> products

the mole balance is

$$-\frac{dC_A}{dt} = r_A \tag{5.51}$$

if, the reaction order is a zero order

$$-\frac{dC_A}{dt} = -k \tag{5.52}$$

integrating with $C_A = C_{A0}$ at $t = 0$, obtain

$$C_A = C_{A0} - kt \tag{5.53}$$

a plot of the concentration of A versus time will be linear with slope ($-k$ ). If the reaction order is not a zero order, a plot will be not linear. Then we must guess a new reaction order, integrate the differential equation, and plot reactant concentration versus time again to look for the appropriate function of concentration corresponding to rate law that is linear with time.

### 5.5.3 Method of initial rates

The method that is to determine the reaction order and rate constant by making a series of experiments that is carried out at different initial conditions($C_{A0}$) and the initial rate of reaction($-r_{A0}$) that is determine for each run. For example, if the rate law is in the form

$$-r_{A0} = kC_{A0}^{\,n} \tag{5.54}$$

the slope of a plot of $ln(-r_{A0})$ versus $lnC_{A0}$ will give the reaction order $n$ and the intercept will give the rate constant value $k$ .

### 5.5.4 Method of half-live

The half-life of reaction($t_{1/2}$ ) is defined as the time at takes for the concetration of the reactant to fall to half of its initial value. By determine the half-life of reaction as a function of the initial concentration, the reaction order and the rate constant can be determined. If there two reactants involved in the chemical reaction, the experimenter will use the method of excess in conjunction with the method of half-lives in order to arrange the rate law in form

$$-r_A = kC_A^n \tag{5.55}$$

a mole balance on A is

$$-\frac{dC_A}{dt} = -r_A = kC_A^n \tag{5.56}$$

integrating with $C_A = C_{A0}$ at $t = 0$, obtain

$$t = \frac{1}{k(n-1)}\left(\frac{1}{C_A^{n-1}} - \frac{1}{C_{A0}^{n-1}}\right) = \frac{1}{kC_{A0}^{n-1}(n-1)}\left[\left(\frac{C_{A0}}{C_A}\right)^{n-1} - 1\right] \tag{5.57}$$

The half-life time is defined as $t = t_{1/2}$ when $C_A = (1/2)C_{A0}$ . Substituting for $C_A$ in equation (5.57) gives

$$t_{\frac{1}{2}} = \frac{2^{n-1} - 1}{k(n-1)}\left(\frac{1}{C_{A0}^{n-1}}\right) \tag{5.58}$$

For the method of half-lives, taking the natural logarithm of both sides of equation (5.58)

$$\ln t_{\frac{1}{2}} = \ln\frac{2^{n-1} - 1}{k(n-1)} + (1-n)\ln C_{A0} \tag{5.59}$$

The slope of a plot of $\ln t_{1/2}$ as a function of $\ln C_{A0}$ is

$$\text{slope} = (1-n) \tag{5.60}$$

and the intercept is

$$\text{intercept} = \ln\frac{2^{n-1} - 1}{k(n-1)} \tag{5.61}$$

### 5.6 Summary

This chapter presents the reviews of an acetylene hydrogenation process, the catalytic reaction mechanism and the method to achieve the rate law. All of the knowledge that presented is used to develop the model of an acetylene hydrogenation process. The developed model, the simulation results and the conclusions about the model are continuously presented in the next chapter.