CHAPTER II

LITERATURE REVIEWS AND ION-EXCHANGE KINETICS

2.1 Literature Reviews

Sheng and Chang (1996) studied the removal of ammonia from aqueous solution by a strongly-acid cation resin. They found that operating variables such as pH, initial ammonia concentration and temperature were highly effective on the rate of exchange. Various ion-exchange isotherms, including those of Langmuir, Freundlich, modified Langmuir and Jossens, were employed to correlate the experimental isotherm data. A mass-transfer model based on the squared driving force was adopted and found to fit well with the experimental rate.

Ion-exchange accompanied by a chemical reaction can be applied to separation processes, and it is one of the best methods to employ when the resin has no selectivity for specific ions. Appropriate chemical reactions are acid-base, redox and complex formulation (Takeda and Morita, 1996).

Mathematical models have been reported in several published papers. Prediction of ion exchange equilibrium is needed for designing and operating such an ion exchange process. Batch experiment are commonly employed to obtain the equilibrium experimental data.

Maria, et al. (1992) found that the equilibrium constant (K) was 3.04 and that the total exchange capacity was q_0 = 5.38 meq/g dried resin. The exchange of H^+ for Ag^- on a strongly-acid cation resin and the total exchange capacity increased when the superficial velocity was decreased. In this work, the equilibrium constant (K) was defined as

$$K = \frac{hq}{c(q_0 - q)} \qquad \qquad \dots(1)$$

where

h	=	concentration of hydrogen ion in the solution phase, meq/ml
c	=	concentration of sodium ion in the solution phase, meq/ml
q	=	concentration of the sodium ion in the resin, meq/ml
q_0	=	total capacity of the resin, meq/ml

All the concentrations refer to equilibrium concentrations.

The rate of exchange was assumed to be given by

$$\frac{dq}{dt} = k_1\left[c(q_0 - q) - \frac{1}{K} hq \right] \qquad \dots(2)$$

where the constant, k_1, is

$$k_1 = \frac{1}{\left(\dfrac{a}{k_L} - \dfrac{C_0}{Kk_R} \right)} \qquad \dots(3)$$

The terms of $\dfrac{a}{k_L}$ and $\dfrac{C_0}{Kk_R}$ represent the liquid resistance and solid resistance, respectively.

where

k_1	=	rate constant, ml/meq*s
K	=	equilibrium constant
k_L	=	resistance constant in the liquid phase
k_R	=	resistance constant in the resin phase
t	=	time, s
a, C_0	=	constants

Andonion (1950) performed batch experiments and integrated equation (2) to obtain

$$\ln\left[\frac{1 - E\left(\dfrac{h}{h_e}\right)}{1 - \left(\dfrac{h}{h_e}\right)}\right] = kCt \qquad\qquad .....(4)$$

where

$$E = \left[\frac{C_0 + q_0}{C_0 q_0}\right]h_e - 1 \qquad\qquad .....(5)$$

$$C = \left[C_0 q_0 - h_e(C_0 + q_0)\right]h_e \qquad\qquad .....(6)$$

in which h_e is the hydrogen ion concentration at equilibrium.

It was shown that a plot of $\ln\left[\dfrac{1 - E\left(\dfrac{h}{h_e}\right)}{1 - \left(\dfrac{h}{h_e}\right)}\right]$ against t obtained a straight line so

equation 3 is a valid expression for the rate of exchange.

Gililand and Baddour (1952) found that the equilibrium constant (K) was in the range of 1.42 -1.58, depending on the initial concentration of the aqueous solution. Analytical expressions for the breakthrough time were given, showing that the rate model can be successfully predicted from the experimental data. Equation 3 was correlated for the different particle sizes.

$$\frac{1}{kd_p^2} = \frac{1010}{Re^{0.84} + 0.049} + 720 \qquad\qquad .....(7)$$

Sujata (1952) found that the equilibrium constant (K) = 1.58 and the overall resistance can be written as

$$\frac{1}{kd_p^2} = 670\,Re^{-0.9} + 1750 \qquad\qquad .....(8)$$

where

Re = Reynolds number

k   =   rate constant

d_p =   particle diameter, mm

Successful simulation of an ion exchange process which is classified as a fixed-bed adsorption column depends mainly on the choice of an adequate mathematical model. To develop a mathematical model that describes the adsorption process, the four following steps must be included: mobile phase mass balance, external film diffusion, interparticle diffusion and adsorption kinetics. In general, the adsorption rate is much faster than the diffusion rate, so that equilibrium can be assumed at every local position(Huang, et al, 1995).

Mark, et al.(1997) studied the performance of an ion-exchange column under fixed-bed operation and introduced the WORKBENCHMAC software as a tool for data acquisition. The kinetic model of batch operation was developed for fixed-bed operation with numerical simulation.

2.2 Theoretical Consideration of Ion-Exchange Kinetics

There are generally three basic modes in operating ion-exchange processes: batchwise, fixed-bed and fluidized-bed. Therefore, the development of the kinetic expression will be dependent upon the mode of operation of the ion-exchange unit. This part of the work is to develop adequate mathematical models to describe the exchange rate of cation resins.

2.2.1 Batchwise Operation

This mode of application is by far the simplest but also the most inefficient. The operation is such tha the whole of the electrolyte solution is contacted with a mass of ion-exchange resins. Therfore, the aqueous phase is homogeneous. For the exchange of sodium ions in solution with hydrogen ions in the resin phase, the process is represented by the exchange equation:

$$RSO_3H + NaCl \rightleftharpoons RSO_3Na + HCl$$

RSO_3H and RSO_3Na are in the resin phase and NaCl and HCl are in the solution phase.

Simple material balances for both ions can be written as

Hydrogen ion balance:

$$V_Rq = V_Lh \qquad \qquad .....(9)$$

Sodium ion balance:

$$V_Lc_0 = V_Rq + V_Lc \qquad \qquad .....(10)$$

where

V_R = volume occupied by the resin bed, ml

V_L = volume occupied by the liquid bed, ml

c_0 = initial concentration of sodium chloride, meq/ml

h = concentration of hydrogen ion in the solution phase, meq/ml

q = concentration of sodium ion in the resin, meq/ml

c = concentration of sodium ion in the solution phase, meq/ml

2.2.2 Fluidized-bed Operation (upflow direction)

For fluidized-bed operation, one can assume perfect mixing. It is generally modeled as having no spatial variations in concentration, temperature and reaction rate. Therefore, at any location, sodium ion concentrations in the liquid(c) and on the resin (q) are uniform throughout the column. It simply says that the rate of desorption of H^+ equals the rate adsorption of Na^+, namely, $\dfrac{dq}{dt}$.

The void fraction of the bed can be calculated for any known height, H, from:

$$\varepsilon = 1 - \left(1 - \varepsilon_0\right)\frac{H_0}{H} \quad\quad .....(11)$$

where

ε	=	bed void fraction
ε_0	=	compacted bed void fraction, taken as 0.41 in this study
H	=	height of fluidized bed
H_0	=	height of compacted bed

2.2.3 Fixed-Bed Operation(Downflow Direction)

The operation of an ion-exchange unit by passing downwards a solution through the resin bed achieves most efficiently the goal that would take many stepwise stages of a batchwise method. The uppermost portion of the column constantly contacts fresh electrolyte whereas the lower portions contact the electrolyte not adsorbed by the upper exchanger. This procedure permits the

resin bed to become fully exhausted at the top first and then gradually downwards. The process was performed with a uniformly packed column of constant cross-section and under constant flow rate.

2.3 Description of Process Kinetic Models

The mechanism of ion exchange is expressed by the governing equations, which can be solved analytically or numerically. The solution is valid if it is compatible with the experimental data. The assumptions made in the derived equation are:

1. The mechanisms that limit the transport of ions from the liquid phase to the resin phase are diffusion in the resin and eddy diffusion in the liquid phase;

2. The driving force involve in the mass transfer is expressible in terms of concentrations, and chloride ions in the solution do not affect the process;

3. The influence of counter diffusion of the exchange ion from the resin to the solution is neglected;

4. There are no gradients in the resin, so the concentration in the resin is uniform;

5. Equilibrium exists at the liquid-solid interface;

6. The resin particles are uniform.

These assumptions are necessary to simplify for the rate expression. Also, the following assumptions are made regarding the experimental apparatus in this study:

1. The exchange process takes place uniformly throughout the packed column.

2. Only the two cations (hydrogen and sodium) involve the exchange process; thus the influence of anion transfer was neglected.

3. The volume of the resin is constant without swelling and shrinking effects.

4. Wall effects are insignificant in the exchange process.

2.3.1 Modeling Response Time of pH Electrode

The response time of a pH electrode influences the experimental data obtained from a standard experiment setup. The hydrogen ions at the exit cannot be instantaneously measured by the pH electrode. There will be a significant time delay between the actual value and the measured values. The experiment conducted with continuous flow operation can be simply shown in Figure 2.1.
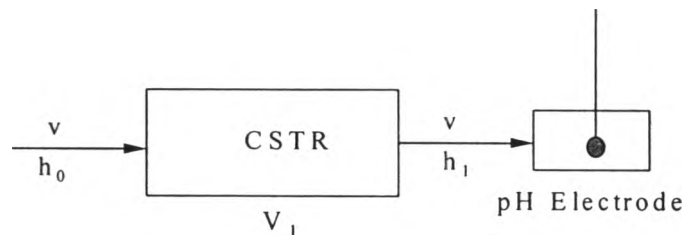

Figure 2.1 Representation of the response time experiment.

The necessary simultaneous ordinary differential equations are:

H$^+$ balance on CSTR

$$\frac{dh_1}{dt} = \frac{v}{V_1}\left[h_0 - h_1\right] \qquad .....(12)$$

where

h_1 = H$^+$ concentration in the solution leaving the CSTR, meq/ml

h_0 = entering H$^+$ concentration, meq/ml

v = volumetric flow rate of the solution, ml/s

V = total volume of CSTR, ml

Response time of the pH electrode

$$\frac{dh_m}{dt} = \alpha_e \left(h_1 - h_m \right)$$ .....(13)

with the initial conditions,

$h_1(0) = 0$ .....(14)

$h_m(0) = 0$ .....(15)

where

h_m = H$^+$ concentration measured by the pH electrode, meq/ml

α_e = constant in the response-time model for the pH electrode

2.3.2 Modeling no Adsorption with Upflow Operation

Case I one CSTR and one PFR in series(as be shown in Figure 2.2)
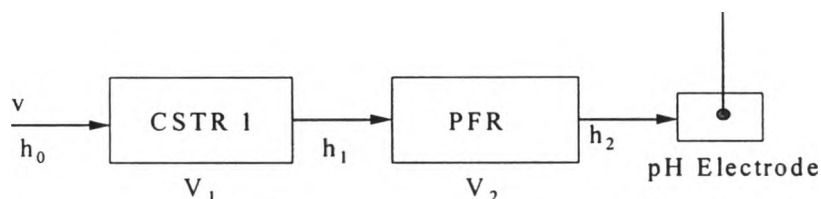
Figure 2.2 Representation of no adsorption experiment as a CSTR and PFR in series together with a pH electrode.

Theory

H^+ balance on CSTR is described as:

$$\frac{dh_1}{dt} = \frac{v}{V_1}(h_0 - h_1) \qquad \qquad \dots\dots(16)$$

Effect of plug flow reactor can be described a:

$$h_2 = h_1(t - t_r) \qquad \qquad \dots\dots(17)$$

where

$$t_r = \frac{v}{V_2}$$

Response time of pH electrode

$$\frac{dh_m}{dt} = \alpha_e(h_2 - h_m) \qquad \qquad \dots\dots(18)$$

where

h_m = H^+ concentration measured by pH electrode, meq/ml

h_2 = H^+ concentration in the solution leaving the PFR, meq/ml

h_1 = H^+ concentration in the solution leaving the CSTR, meq/ml

h_0 = entering H^+ concentration, meq/ml

v = volumetric flow rate of the solution, ml/s

V_1 = total volume of CSTR, ml

V_2 = total volume of PFR, ml

α_e = constant in the response-time model for the pH electrode

The solution of the governing equations

The analytical solution of equation 16 and equation 17 can be written as:

$$h_2(t) = \begin{bmatrix} 0; & t<t_r \\ \\ h_0\left[1 - e^{\left(-\frac{v}{V_1}(t-t_r)\right)}\right]; & t>=t_r \end{bmatrix} \quad ....(19)$$

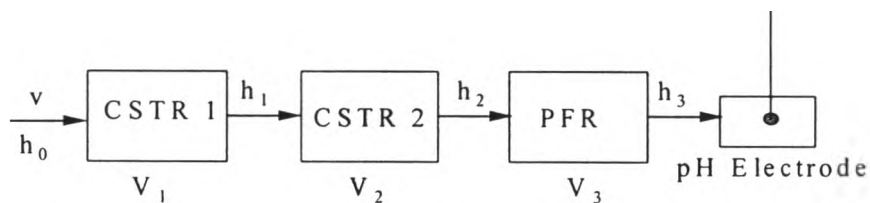## Case II Two CSTRs and one PFR in series (as shown in Figure 2.3)

Figure 2.3 Representation of modeling of no adsorption as two CSTRs and a PFR in series together with a pH electrode.

Theory

Let each CSTR have the same volume:

$$V_1 = V_2 = \frac{V_{CSTR}}{2}$$

$$\alpha = 2\left[\frac{v}{V_{CSTR}}\right]$$

The general solution for h_2 is

$$h_2 = h_0 + \beta e^{-\alpha t} + \gamma t e^{-\alpha t} \qquad \qquad .....(20)$$

A H^+ balance on CSTR 2 gives

$$\frac{dh_2}{dt} + \alpha h_2 = \alpha h_0\left[1 - e^{-\alpha t}\right] \qquad \qquad .....(21)$$

From equation 20 and equation 21

$$\gamma = -\alpha h_0$$

Substitution in equation 20 then gives

$$h_2 = h_0 + \beta e^{-\alpha t} - \alpha h_0 t e^{-\alpha t} \qquad \qquad .....(22)$$

From the initial condition

$$h_2 = 0$$

then equation 22 becomes

$$h_2 = h_0\left(1 - e^{-\alpha t} - \alpha e^{-\alpha t}\right) \qquad \qquad .....(23)$$

Effect of plug flow reactor

$$h_3(t) = h_1(t - t_r) \qquad \qquad .....(24)$$

Response time of pH electrode

$$\frac{dh_m}{dt} = \alpha_e(h_3 - h_m) \qquad \qquad .....(25)$$

where

$$t_r = \frac{v}{V_3}$$

h_m = H^+ concentration measured by pH electrode, meq/ml

h_3 = H^+ concentration in the solution leaving the PFR, meq/ml

h_2 = H$^+$ concentration in the solution leaving the CSTR, meq/ml

h_1 = H$^+$ concentration in the solution leaving the CSTR, meq/ml

h_0 = entering of H$^+$ concentration, meq/ml

v = volumetric flow rate of the solution, ml/s

V_1 = total volume of CSTR 1,ml

V_2 = total volume of CSTR 2, ml

V_3 = total volume of PFR, ml

α_e = constant in the response-time model for the pH electrode

α, β, γ = constants

2.3.3 Modeling a Batch Operation

After obtaining the response time of pH electrode, the calculated values of c, q and q_0 can be tabulated by performing material balance.
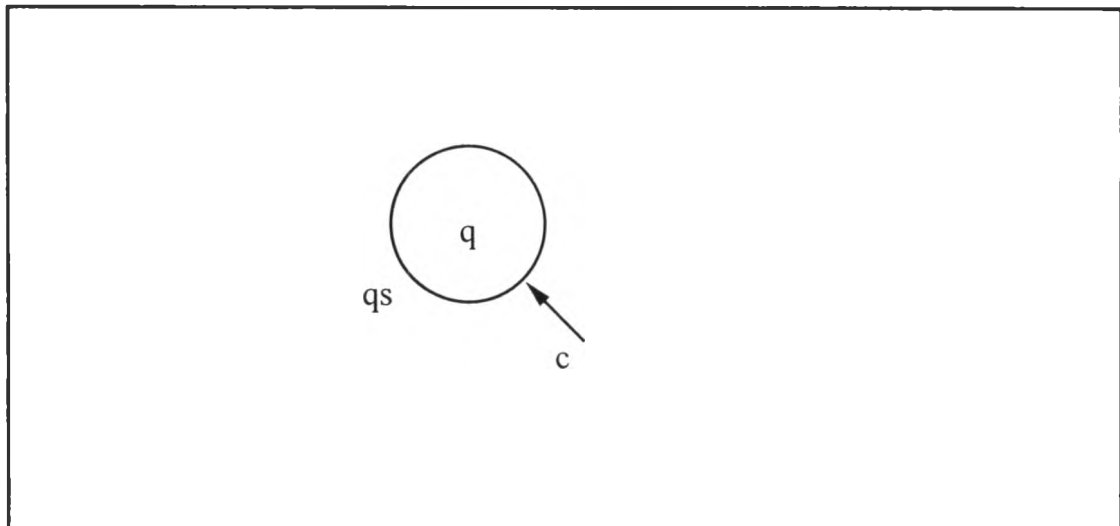

Figure 2.4 Notation for sodium ion concentration.

As shown in Figure 2.4, avoiding the complication with the mass transfer resistance both in liquid and solid phase, the simplifying assumption is made to ignore the concentration gradient within the resin. The rate of exchange is proportional to the driving force and is written as

Rate of Exchange = Rate coefficient*Driving force

$$\frac{dq}{dt} \quad = \quad k_1(q_s\text{-}q) \quad\quad\quad .....(26)$$

The driving force term is denoted by q_s -q.

Also, paralleling the concept of relative volatility for a binary mixture in the equilibrium system, the ratio of sodium ion concentration to hydrogen ion concentration on the surface of the resin is assumed to be proportional to the corresponding ratio in the liquid.

$$\frac{q_s}{q_0 - q_s} = \frac{k_2 c}{h} \quad\quad\quad .....(27)$$

Eliminating q_s from equation 26 then yields:

$$\frac{dq}{dt} = k_1 \left[\frac{q_0}{1 + \dfrac{h}{k_2 c}} - q \right] \quad\quad\quad .....(28)$$

where

k_1 = rate constant. s^{-1}

k_2 = relative volatility coefficient

q_s = concentration of the sodium ion on the surface of the resin, meq/ml

The constants k_1 and k_2 can then be determined in order to give the best fit of the data.

2.3.4 Modeling Adsorption with Upflow Operations

The theory developed here is applied to the ion-exchange column performed under fluidized-bed operation. The three previous experiments included:

i. No adsorption modeling with

a) A CSTR (Continuous Stirred Tank Reactor), which is compatible with the notation of the fluidized bed in which perfect mixing occurs.

b) A plug flow volume, which represents "dead space" through which the liquid passes but in which no reaction occurs.

ii. The Response Time Modeling

The pH electrode at the reactor exit, which does not provide an instantaneous measure of the pH of the solution and whose the response time must be included in the modeling.

iii. Kinetics of adsorption of batch operation

The rate of adsorption with perfect mixing was incorporated into the model of the reactor. Also, from experimental evidence, the rate of adsorption per volume of resin based on the concept of relative volatility is

$$r = \frac{dq}{dt} = k_1 \left[\frac{q_0}{1 + \dfrac{h}{k_2 c}} - q \right] \qquad .....(28)$$

Let us consider the system having two parts of the fluidized bed (expand bed) and the clear portion which can be considered as a CSTR and a PFR, respectively. Figure 2.5 illustrates the system consisting a CSTR and a PFR in series.
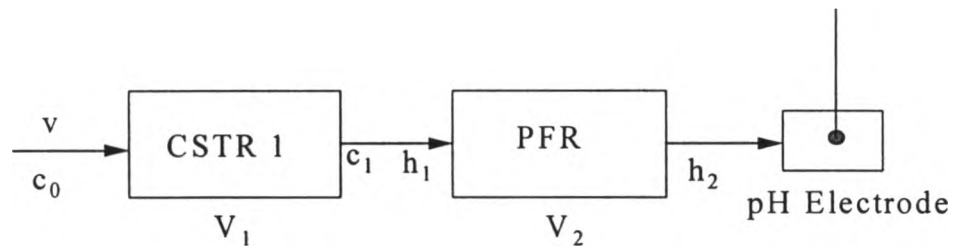
Figure 2.5 Representation of ion-exchange column as one CSTR and one PFR in series together with a pH electrode.

Na^+ balance on the CSTR

$$vc_0 - vc_1 - rV_R = V_L \frac{dc_1}{dt} \qquad \dots..(29)$$

the rate of sodium uptake by resin can be expressed as

$$r = \frac{dq}{dt} = k_1 \left[\frac{q_0}{1 + \frac{h}{k_2 c}} - q \right] \qquad \dots..(30)$$

Performing H^+ balance on the CSTR

$$-vh_1 + rV_R = V_L \frac{dh_1}{dt} \qquad \dots..(31)$$

Effect of plug flow reactor is

$$h_2(t) = h_1(t - t_r) \qquad \dots..(32)$$

Response time of pH electrode

$$\frac{dh_m}{dt} = \alpha_e\left(h_2 - h_m\right) \qquad \qquad ....(33)$$

where

$$t_r = \frac{v}{V_2}$$

h_m = H$^+$ concentration measured by pH electrode, meq/ml

h_2 = H$^+$ concentration in the solution leaving the PFR, meq/ml

h_1 = H$^+$ concentration in the solution leaving the CSTR, meq/ml

c_0 = entering of Na$^+$ concentration, meq/ml

c_1 = Na$^+$ concentration in the solution leaving the CSTR, meq/ml

v = volumetric flow rate of the solution, ml/s

V_R = volume occupied by the resin bed in the column, ml

V_L = volume occupied by the liquid bed in the column, ml

V_2 = total volume of PFR, ml

α_e = constant in the response-time model for the pH electrode

The solution of the governing equations

A numerical approximation to the solution will be used, with subscripts i and $i+1$ denoting values at the beginning and end of the time-step, Δt, respectively. To give the method the best chances of stability, it will be implicit in time, with as many quantities as possible expressed at the end of the time step. The iterate feature of Excel will be used to made all values at time-level $i+1$ consistent with one another.

Definition of constants

$$\beta = \frac{v\Delta t}{V_L} \text{ and } \gamma = \frac{V_R\Delta t}{V_L}$$

Performing a Na$^+$ balance on the CSTR yields:

$$vc_0 - vc_1^{i+1} - V_R r^{i+1} = V_L \left[\frac{c_1^{i+1} - c_1^i}{\Delta t} \right] \quad \quad .....(34)$$

then

$$c_1^{i+1} = \frac{c_1^i + \beta c_0 - \gamma r^{i+1}}{1 + \beta} \quad \quad .....(35)$$

Performing a Na$^+$ balance on the resin, gives

$$q^{i+1} = \Delta t r^{i+1} + q^i \quad \quad .....(36)$$

Performing a H$^+$ balance on the CSTR yields

$$h_1^{i+1} = \frac{h_1 + \gamma r^{i+1}}{1 + \beta} \quad \quad ....(37)$$

The rate of adsorption can be written as:

$$r^{i+1} = k_1 \left[\frac{q_0}{1 + \dfrac{h^{i+1}}{k_2 c^{i+1}}} - q^{i+1} \right] \quad \quad ....(38)$$

Let us consider the effect of plug flow reactor to be

$$h_2(t) = h_1(t - t_r) \quad \quad ....(39)$$

The response time of pH electrode can be obtained as

$$h_m^{i+1} = \frac{\alpha_e \Delta t h_2^{i+1}}{1 + \alpha \Delta t} \quad \quad .....(40)$$

2.4 Data Acquisition with Labtech Notebook

Because the Labtech Notebook software has played such an important part in the execution of this research, a brief description of this software and its operation is given here. Labtech Notebook (produced by Laboratory Technologies Corporation, Wilmington, MA) has the ability to perform data

acquisition and process control, to display process variables, to send data to files according to various menu selected forms. and to select the sample frequency and desired run time from a menu. Its output files can also be readily converted into files compatible with Excel, which is easier for spreadsheet calculations.

Labtech Notebook has a number of built-in utilities, including calculated blocks, which allow to us perform a calculation on acquired data in a real time. It can perform a complex mathematical equation, and blocks can be linked together. In a typical experiment (see Figure 2.6), the electrical analog signals from the sensors (2 pH electrodes), first pass through a signal conditioning (Wiring Terminal Board; PCLD-8115) which converts all signals to a standard 1-5 volts range. A data acquisition card (High-performance DAS card, PCL-818HG), typically handling 16 input channels, then performs an analog to digital conversion so that the signal can then be processed by the PC computer which is driven by Labtech Notebook software. The build-time and the blocks setting are indicated in Figure 4.12 and Table A1 in Appendix A. The sampling rate of collected data at 0.1 Hz is ideal.

The output from Labtech Notebook can be displayed in various forms, including

1. Graphical information displayed on the computer monitor, typically showing how one or more variables change with time.
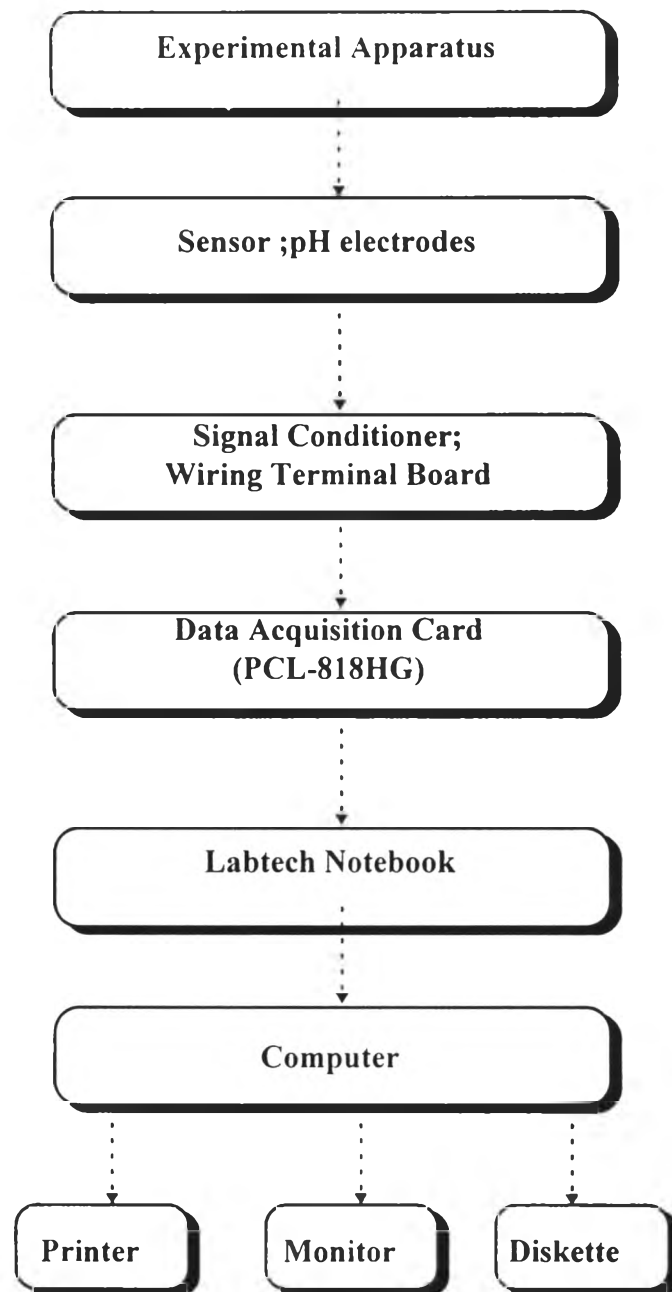
2. Digital information sent to file.

Figure 2.6 Communication between the experiment and the computer.