

## CHAPTER III EXPERIMENT



### 3.1 Materials

The gases used in this research were hydrogen gas (99.999% purity), obtained from Praxair (Thailand) Co., Ltd., used as adsorbate and helium gas (99.99% purity), obtained from Thai Industrial Gas Co., Ltd., used as inert gas to determine manifold and sample cylinder volume of built constant volumetric isothermal adsorption apparatus.

The adsorbents used in this research were multi-walled carbon nanotubes (MWNTs) and activated carbon (AC). MWNTs was obtained from UOP LLC. These MWNTs contained MWNTs in majority with a small amount of amorphous carbon and catalyst. MWNTs were already purified by UOP from crude-MWNTs with two cycles. One cycle consists of two steps: treatment in NaOH solution at 80-90 °C under continuous stirring and then stirring again in HCl solution at room temperature. Another is the removal of amorphous carbon, which was carried out with oxidation by  $\text{KMnO}_4$ . The arising  $\text{MnO}_2$  was removed by HCl solution. The efficiency of purification was 94%, which was visually determined on the basis of TEM images and from the weight loss upon removal of catalyst. The outer and inner diameter of MWNTs that observed from 10 different TEM pictures was 18 +/- 2 nm and 6 +/- 2nm, respectively. The BET surface area of crude-MWNTs was 193  $\text{m}^2/\text{g}$ .

The activated carbon used to study potential hydrogen sorption was type BPL 4x10 obtained from Calgon Carbon Corporations. BPL 4x10 is a virgin granular activated carbon designed for uses in gas phase applications. It is bituminous coal-based product activated at high temperature in a steam atmosphere. The typical apparent density is 0.48 g/cc, and the loose-packed density, in practice, is approximately 0.42 g/cc.

### 3.2 Experimental Apparatus

The constant volumetric adsorption apparatus built and used in these measurements is composed of a gas reservoir (150 cc) and a sample cylinder (50 cc), and both are connected by high-pressure bellow valves, Swagelok (Model SS-4-UK) and diaphragm valves, Swagelok (Model SS-DSS4), with ¼ inch stainless-steel Hylok tubings and fittings. The pressure transducer used in this system was purchased from Bourdon Sedeme (Model E913) which was capable of measuring in the range of 0-1500 psig with 0.2% global error. Its output signal is a direct current, 4-20 mA, which is necessary to convert to digital signal and record the data by data logger (A/D). Data logger (Model AI200) was purchased from Wisco Co. with OD95 Microsoft Excel program support, shown in Figure 3.1., for information management. To record the real-time pressure changes, data logger was connected to computer via port com 1. The pressure gauge was also a module from Bourdon Sedeme (Model MMX5), measuring in the range of 0-1500 psig.

Evacuation the manifold and the sample cylinder were accomplished with a Vacuubrand vacuum pump, model type RZ2 and monitoring with Edwards vacuum pressure sensor (Model AGD 101L). The volumetric adsorption apparatus was wholly immersed in water container connected with digital-temperature-controlling water bath, Polyscience model 9601. The schematic apparatus was shown in Figure 3.2. and the experimental set-up and a constant volumetric isothermal adsorption apparatus were shown in Figure 3.3. and Figure 3.4., respectively.

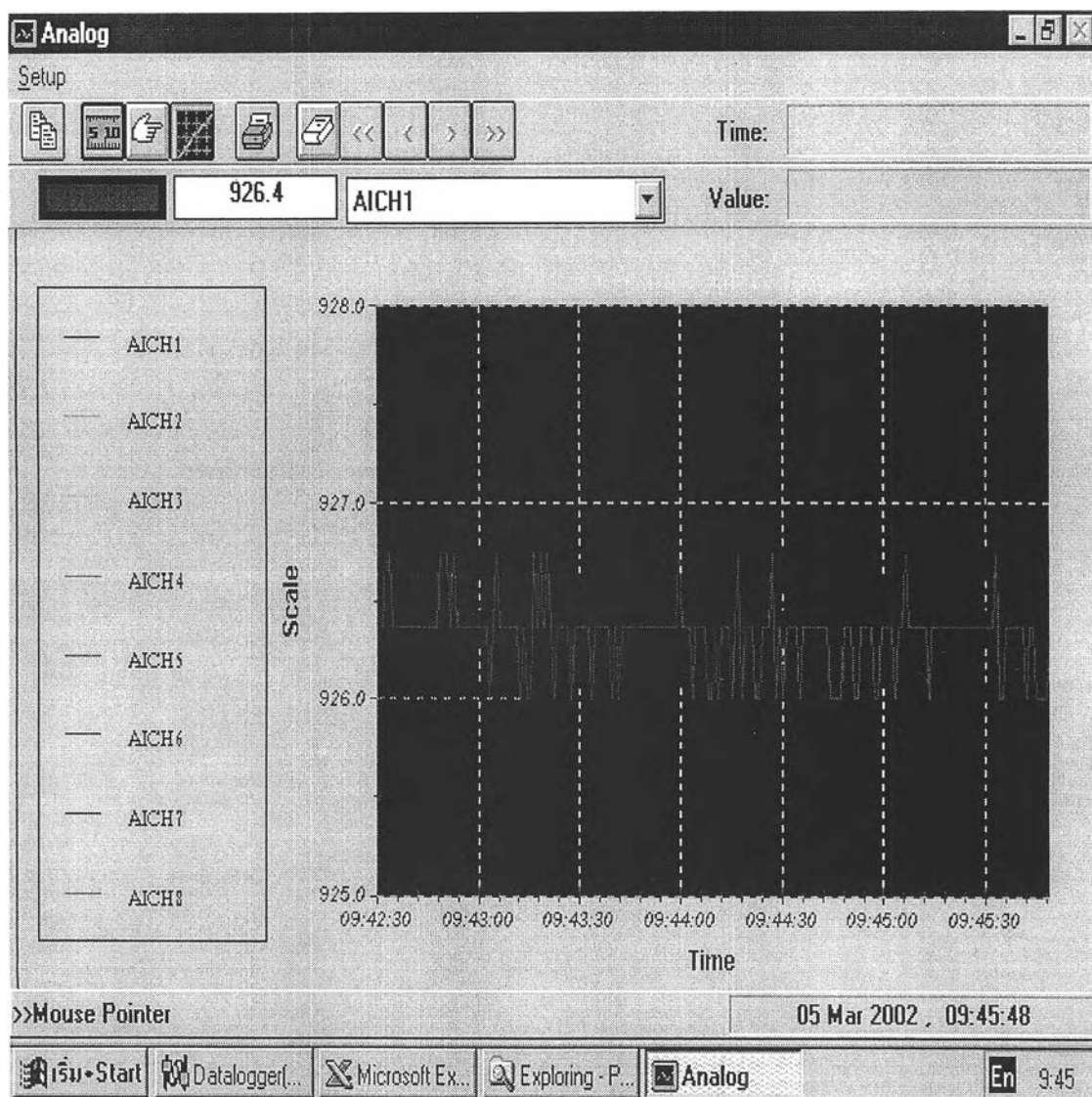
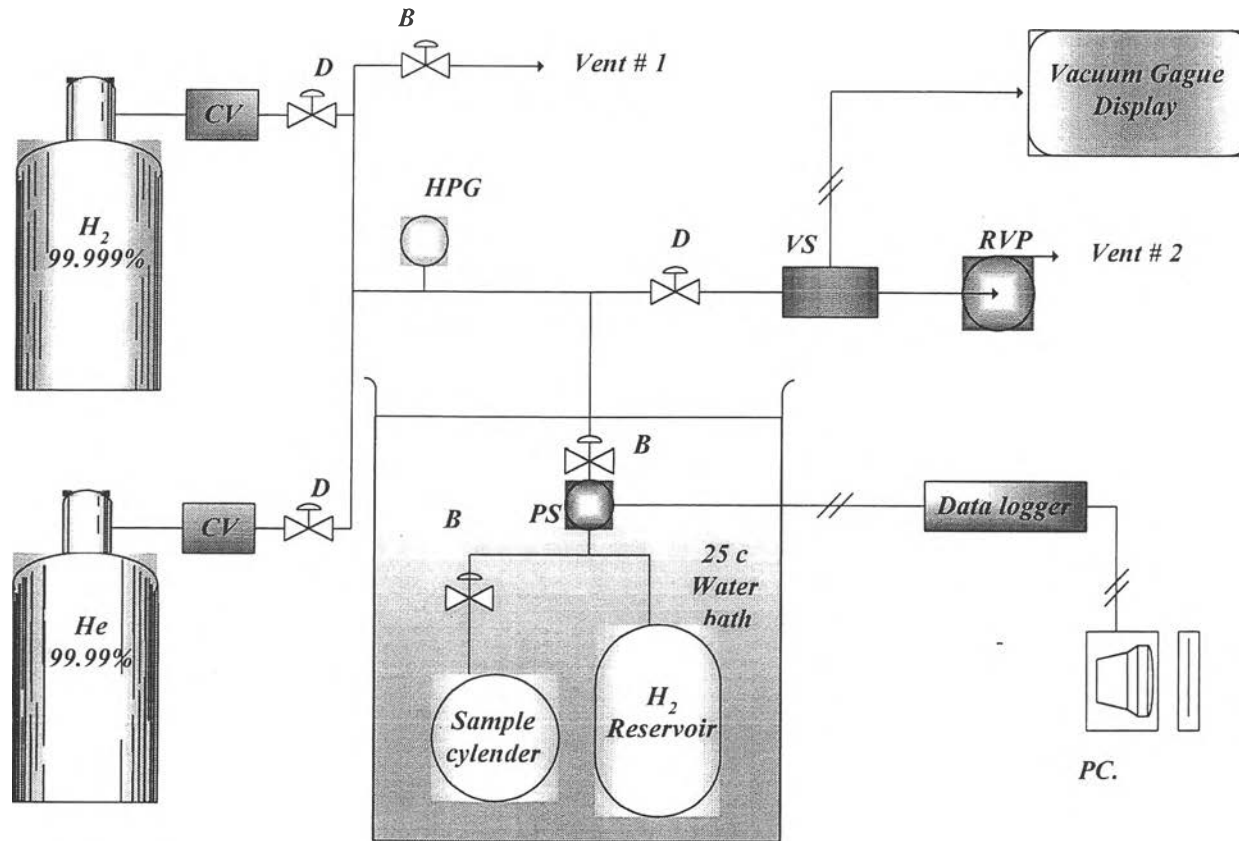
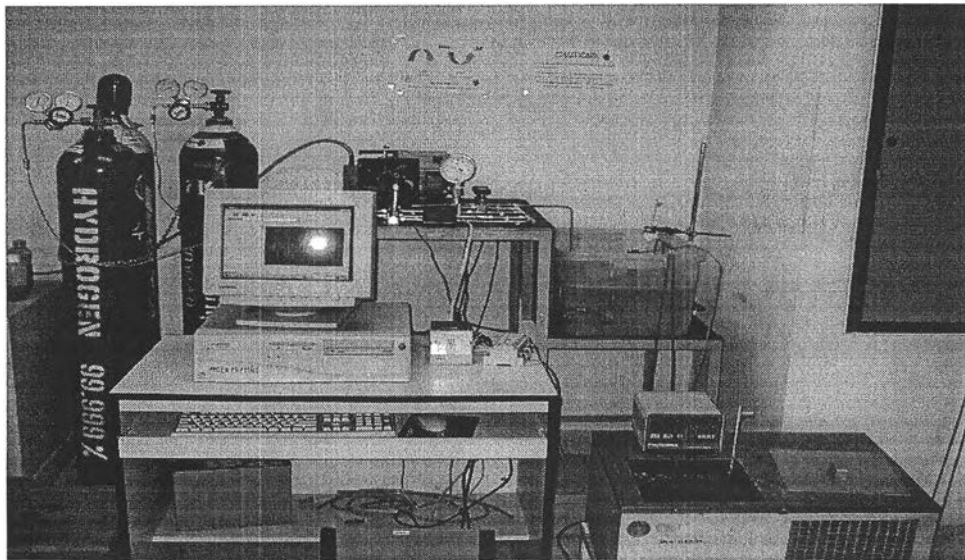


Figure 3.1. Display of OD 95 program

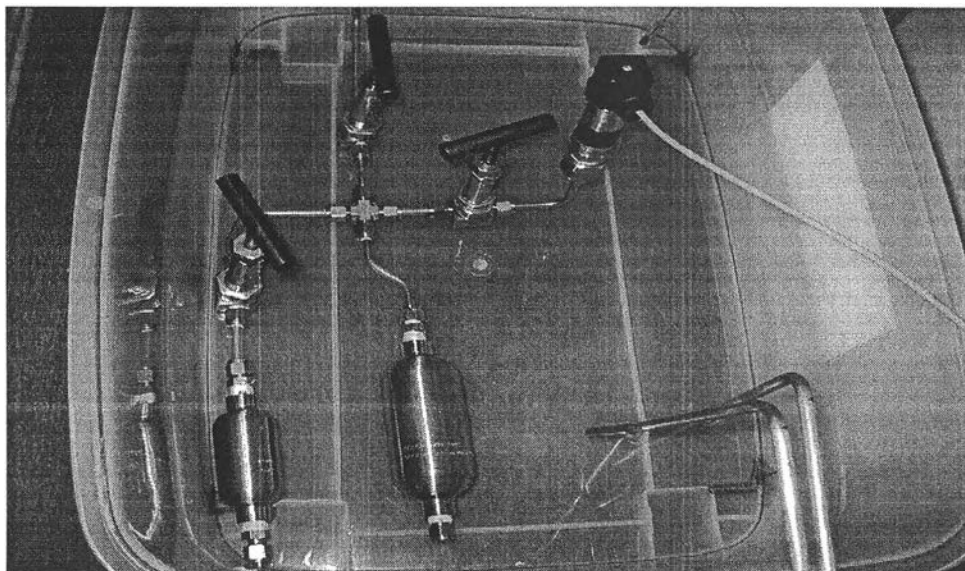


**Figure 3.2.** Schematic of the experimental apparatus

(CV = check valve, D = diaphragm valve, B = bellow valve, PS = pressure sensor, VS = vacuum sensor, HPG = high pressure gauge, RVP = rotary vacuum pump, PC = personal computer)



**Figure 3.3.** Experimental set-up



**Figure 3.4.** The constant volumetric isothermal adsorption apparatus

### 3.3 Adsorbent Characterization

#### 3.3.1 BET Surface Area

The surface areas of all adsorbents were measured by the five-point BET method using a Quantachrome Corporation Autosorb I. Before measurement, an adsorbent sample was outgassed by heating at 523 K for 4 hours under vacuum to eliminate volatile adsorbates on the surface. BET surface area were determined by measuring the quantity of gas adsorbed onto or desorbed from a solid surface at 5 equilibrium vapor pressure ( $P/P_0$ ) values (0.1115, 0.1615, 0.2115, 0.2615 and 0.3115) by the static volumetric method. The data were obtained by admitting or removing a known adsorbate gas, nitrogen, into or out of a sample cell containing the solid adsorbent maintained at a constant temperature below critical temperature of the adsorbate, that is 77 K for nitrogen.

The adsorption data were calculated using the Brunauer-Emmett-Teller (BET) equation as shown in equation 3.1 and 3.2.

$$\left[ \frac{1}{W \left( \frac{P_0}{P} - 1 \right)} \right] = \frac{1}{W_m C} + \left[ \frac{C-1}{W_m C} \right] \left[ \frac{P}{P_0} \right] \quad (3.1)$$

where  $W$  = Weight of gas adsorbed at relative pressure  $P_0$ ;

$W_m$  = Weight of adsorbate constituting a monolayer of surface coverage;

$C$  = Constant that is related to the energy of adsorption in the first adsorbed layer and magnitude of adsorbate/adsorbent interaction.

The surface area can be obtained from the following equation.

$$\text{Surface area of sample} = \frac{W_m A_{\text{nitrogen}} (6.02 \times 10^{23})}{M_{w,\text{nitrogen}}} \quad (3.2)$$

where  $A_{nitrogen}$  = Cross-sectional area of one molecule nitrogen  
 = 0.162 nm<sup>2</sup> (at 77K);  
 $M_{w,nitrogen}$  = Molecular weight of nitrogen (28)

### 3.3.2 X-ray diffractometer (XRD)

X-ray diffraction technique is a qualitative and quantitative analysis of crystallographic phase from of the adsorbent. The qualitative analysis is based on the fact that the x-ray diffraction pattern is unique for each crystallite phase. If the observed diffraction pattern of the samples can be matched to that of the reference substance, they are the same crystallite phase. For the individual substance, which has the same diffraction pattern, the intensity of crystallite indicates its content. The higher intensity, the higher content it is.

The Rigagu X-ray diffractometer (XRD) system equipped with RINT 2000 wide angle goniometer and a Cu Tube for generating a CuK  $\alpha$  1 radiation ( $\lambda = 1.54 \text{ \AA}$ ) was used to obtain the X-ray diffraction patterns at a generator voltage of 40 kV and a generator current of 30 mA. Nickel filter was used as the  $K_{\beta}$  filter. The goniometer parameters were divergence slit =  $1^{\circ}(2\theta)$ ; scattering slit =  $1^{\circ}(2\theta)$ ; and receiving slit = 0.3nm. The adsorbent samples were, firmly pressed on a glass slide by another glass slide. A scan speed of  $5^{\circ}(2\theta)/\text{min}$  with a scan step of  $0.02^{\circ}(2\theta)$  was used during a continuous run in the 5 to  $90^{\circ}(2\theta)$  range.

The Scherrer equation, which relates the mean crystallite diameter and the broadening of the X-ray diffraction lined per the expression, can be written as.

$$d_b = K\lambda / B_d \cos\theta \quad (3.3)$$

where  $\lambda$  = Wave length of the monochromatic X-ray diffraction,  $\text{\AA}$   
 $K$  = Scherrer constant whose value depends on the shape of the particle (assume equal to 1);  
 $B_d$  = Angular width of the peak in the terms of  $\Delta(2\theta)$ , radian  
 $\theta$  = Glancing angle, degree  
 $d_b$  = Mean crystallite diameter,  $\text{\AA}$

### 3.3.3 Transmission Electron Microscopy (TEM)

TEM images of carbon nanotubes were taken from JEM-100 SX TEM instruments from Scientific and Technology Research Equipment Center of Chulalongkorn University with magnification from 1,000 to 300,000 transmission electron microscope. TEM images were also taken from Tecnai 12 TWIN transmission electron microscope with magnification from 35 to 700,000 from FEI Company, The Netherlands. The TEM images provide unique information about the structure and diameter of the carbon nanotubes for the present research.

### 3.3.4 Raman Spectroscopy

Based on Raman spectra, diameter and chirality of CNTs have been obtained. In case of carbon nanotubes, there are three modes that are of importance, namely Radial Breathing Mode (RBM) Band, Disordered Carbon Band, and the Graphitic Band. For our study, we have performed Raman measurements on two different samples of carbon materials – multi-walled carbon nanotubes and activated carbon. Raman measurements are concerned with shifts in the frequencies of vibrations, due to changes in inter-nuclear spacing coupled with the nature of inter-atomic, inter- and intra-molecular interactions. The Raman measurements were performed with a Raman JASCO IRS-600 SZ-P single monochromator spectrophotometer equipped with a CCD (charge-couple device). The laser power used was a 514.5 nm line of an argon-ion laser. The Raman analysis has been explained by plotting the Intensity (arbitrary units) vs Wavelength ( $\text{cm}^{-1}$ ).

## 3.4 Calibration of volume spaces

The volume of the manifold ( $V_m$ ) and the sample cylinder ( $V_{sc}$ ) were determined from helium expansions at a pressure of 141 psia. The mass balance was taken over two system states. The first state was the initial state, before expansion,



where helium gas was only present in the manifold volume, and no gas was present in the outgassed cylinder. The second state, after expansion into the outgassed cylinder, where gas was being presented in both the manifold and the sample cylinder. If the mass balance is equal to zero, indicating that the system was free of leak and of adsorbed gas on an apparatus. To determine  $V_m$ , the following steps are required:

a. Material balance over manifold and the sample cylinder

$$V_m \rho_1 = (V_m + V_{sc}) \rho_2 \quad (3.5)$$

where  $V_m$  = Volume of the manifold, cc

$V_{sc}$  = Volume of the sample cylinder, cc

$\rho_1$  = Density of the gas in the manifold at pressure P1, g/cc

$\rho_2$  = Density of the gas in the manifold + sample cylinder at pressure P2,  
g/cc

One mass balance equation was not enough to be solved for determining 2 parameters, volume of manifold and sample cylinder. Thus, the known volume materials were put into the sample cylinder for another mass balance equation. The material used for the known volume was 158.5438 g of 99.48 %steel kindly donated by Sahaviriya Steel Industries Public Company Limited. Knowing the density of this steel (7.7728 g/cc, generously carried out by Metallurgy and Materials Science Research Institute, Chulalongkorn University), a very precise value for its volume can be obtained.

b. Material balance over the manifold and the sample cylinder with a standard sample material with known volume,  $V_k$  (e.g. steel sheet)

$$V_m \rho_3 = (V_m + V_{sc} - V_k) \rho_4 \quad (3.6)$$

where  $V_k$  = Volume of steel that is used, g/cc

$\rho_3$  = Density of the gas in the manifold at pressure P3, g/cc

$\rho_4$  = Density of the gas, at pressure P4, in the remaining space of the manifold and the sample cylinder

Both the above equations are solved to get  $V_m$ ,

$$V_m = \frac{V_k}{\left(\frac{\rho_1}{\rho_2}\right) - \left(\frac{\rho_3}{\rho_4}\right)} \quad (3.7)$$

Hence,

$$V_{sc} = \frac{-V_k \rho_4}{\left[ \frac{\rho_2 \rho_3}{\rho_1 - \rho_2} - \frac{\rho_2 \rho_4}{\rho_1 - \rho_2} - \rho_4 \right]} \quad (3.8)$$

Experimental gas density data calculated at any pressure and temperature from Beattie-Bridgeman Equation of State (Cengel, 1994), which is accurate for density,  $\rho$  of not greater than 0.8 critical  $\rho$ , were used in measuring adsorption isotherms for all gases evaluated in this thesis.

$$P = \frac{R_u T}{v^2} \left( 1 - \frac{c}{v T^3} \right) (v + B) - \frac{A}{v^2} \quad (3.9)$$

where

$$A = A_0 \left( 1 - \frac{a}{v} \right) \quad (3.10)$$

and

$$B = B_0 \left( 1 - \frac{b}{v} \right) \quad (3.11)$$

when  $P =$  Pressure in kPa

$v =$  Specific volume in  $\text{m}^3/\text{kmol}$

$T =$  Temperature in Kelvin

$R_u = 8.314 \text{ kPa} \cdot \text{m}^3 / (\text{kmol} \cdot \text{K})$

$A_0, B_0, a, b$  and  $c$  are the five constants in the Beattie-Bridgeman Equation for gas of interest as the following;

	H <sub>2</sub> gas	He gas
$A_0$	20.0117	2.1886
$B_0$	-0.00506	0.05984
$a$	0.02096	0.01400
$b$	-0.04359	0.0
$c$	504	40

**Table3.1.** Five constants in the Beattie-Bridgeman Equation

### 3.5 Collection of data with adsorbents

After the parameters  $V_m$  and  $V_{sc}$  have been determined, it is ready to proceed to perform H<sub>2</sub> adsorption studies. It is crucial that the pressure transducer must be calibrated for each adsorption run. Atmospheric pressure, 14.7 psia can be used as a reference pressure to set the zero span on the transducer to vacuum or set it to 14.7 psig. After this step, The adsorbent was first placed in the sample cylinders and being outgassed at 0.01 Torr for at least 14 hours. the manifold was initially pressurized with the H<sub>2</sub> gas at 140 psia. Hence, the valves on both sides of manifold were closed. The manifold pressure was then allowed to reach the equilibrium,

before the pressure was recorded. Usually, this step took about 5-10 minutes. This was done to ensure that the manifold did not leak. The gas was consequently expanded into the sample cylinder by opening valves, which was initially under vacuum, containing the adsorbent. After the pressure equilibrated in the manifold and sample cylinder, the final pressure was then recorded. This process required 5-30 minutes to reach equilibrium time. The pressures were recorded every 10 seconds until the pressure in the manifold and the sample cylinder became constant. In order to check variations of equilibrium pressures, pressurizing the system with the adsorbent for about 6 hours was conducted to check the variability of equilibrium pressure. The background leaks and standard deviation of data were taken into account in the analysis of the hydrogen sorption results.

The relationships governing the adsorption procedure can be derived from a mass balance around the constant volume apparatus. In practice, the manifold volume,  $V_m$ , was used to contain the adsorbate being emitted via a valve into a constant sample cylinder volume,  $V_{sc}$ . The volume of manifold plus sample cylinder was consequently the total volume of the system as the following equation;

$$V_s = V_m + V_{sc} \quad (3.12)$$

For purpose of the mass balance, the mass of the pure gas in the manifold was calculated by multiplying manifold volume,  $V_m$ , by the gas density,  $\rho$ , at that temperature and pressure. The mass in the gas phase in the cylinder with the adsorbent, was simply the gas density,  $\rho$ , multiplied by the volume of the cylinder,  $V_{sc}$ , subtract the volume occupied by the adsorbent, dead space volume,  $V_{ds}$ . This volume was the only available volume,  $V_a$ , which the gas phase molecules could occupy. The space occupied by the adsorbent is unavailable to the gas and is easily considered as dead space. The available volume,  $V_a$ , in the cylinder can then expressed as the following equation;

$$V_a = V_{sc} - V_{ds} \quad (3.13)$$

Carbon, by itself can be regarded in its graphitic form. Its density is equal to 2.25 g/cc, although in its disorder crystal state it probably is closer to 2.1g/cc (Patel, 2000). The volume occupied by MWNTs and activated carbon in the experiment were then calculated based on density of 2.20 g/cc (Park, 1999).

The mass balance was taken over two system states. If the mass balance was not equal to zero that difference was taken as the amount adsorbed.

$$(M_m)_{\text{before}} + (M_{sc})_{\text{before}} = (M_m)_{\text{after}} + (M_{sc})_{\text{after}} + M_{ad} \quad (3.14)$$

where  $M_m$  = mass of gas in manifold

$M_{sc}$  = mass of gas in the sample cylinder available volume,  $V_a$

$M_{ad}$  = mass adsorbed on the substrate, also to the total change of mass in the system,  $\Delta M$

Therefore:

$$M_{ad} = [(M_m)_{\text{before}} + (M_{sc})_{\text{before}}] - [(M_m)_{\text{after}} + (M_{sc})_{\text{after}}] \quad (3.15)$$

This equation could be rewritten in terms of the gas densities and known volumes.

$$M_{ad} = [(\rho V_m)_{\text{before}} + (\rho V_a)_{\text{before}}] - [(\rho V_m)_{\text{after}} + (\rho V_a)_{\text{after}}] \quad (3.16)$$

where  $\rho_{\text{before}}$  = Density of the gas before expansion, g/cc

$\rho_{\text{after}}$  = Density of the gas after expansion, g/cc

This procedure, method 1, was begun with initial pressure about 140 psia and repeated until the adsorbate had come to a final pressure of ~1040 psia with increment equal to 100 psia. In each increment, the system and the adsorbent were vacuumed at 0.01 Torr for at least 14 hours. For method 2, it was also begun with

same initial pressure at 140 psia and repeated until the adsorbate had come to a final pressure of ~1040 psia with the same increment, 100 psia, without outgasing in each increment. These two processes generally allowed ten equilibrium adsorption pressures to be recorded. Many more data points could be measured over this pressure range by adjusting the increment of the manifold pressure between each equilibrium step. The amount adsorbed (wt.%) was calculated as the adsorbed hydrogen mass divided by the carbon nanotubes mass.

### **3.6 Collection Data of Blank Test**

Blank test must be done to check the reliability of the set-up experimental apparatus that it was non-leak-free system or not by repeating procedure of method 1 with adding nothing into the system. If the system is not non-leak-free system, the amount of leaking gas must be taken in to account to correct the reported results.

### **3.7 Experimental-related Conditions**

The adsorption data were collected at 298 K. A water-bath was used to maintain and reach thermal equilibrium of gas in the manifold, valves and sample cylinder immersed in container connected with temperature-controlled bath with a high precision ( $\pm 0.1$  °C) temperature control set-up. A pressure transducer, as described previously, was used to record the initial and final equilibrium pressure in the manifold. The standard amount of carbon materials sample used in these experiments was about 10.0-22.0 grams, depending on the adsorbent's density.

In order to perform a new experimental run, the sample was pretreated by degassing under vacuum at about 0.01 Torr and 278 K for at least 14 hours. The use of high vacuum pressure helped in the regeneration of the substrate. The degassing procedure was carried out to remove pre-adsorbed gases.