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**GAS CHROMATOGRAPHIC
STUDY OF HYDROGEN AND HYDROCARBON
ADSORPTION ON PLATINUM/ALUMINA CATALYST**

by

Z. SERMIN GÖNENC

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ABSTRACT

The irreversible and the reversible adsorption of hydrogen on commercial 0.3%wt Pt/ Al_2O_3 reforming catalyst has been studied in a gas-solid chromatograph in the temperature range 74-233°C and 96-237°C respectively. The reversible adsorption of two naphthenes (cyclohexane and methylcyclohexane) and of two aromatics (benzene and toluene) on the same catalyst have also been investigated between 190-236°C. Adsorption isotherms were constructed at several temperatures for all the adsorbates studied. The elution (or the pulse) technique was used in all the experiments. From the adsorption isotherms, heats of adsorption were calculated using constant surface coverage values at different temperatures.

It was found that some hydrogen is adsorbed irreversibly within the temperature range considered and that the reversible adsorption of hydrogen is an activated process with an average heat of adsorption of 0.87 kcal/gmol (3.69 kJ/kmol). The reversible adsorptions of cyclohexane, methylcyclohexane, benzene and toluene are also activated processes with average heats of adsorption of 7.48 kcal/gmol (31.30 kJ/kmol), 7.45 kcal/gmol (31.17 kJ/kmol), 13.11 kcal/gmol (54.85 kJ/kmol) and 13.90 kcal/gmol (58.16 kJ/kmol) respectively.

Ö Z E T

Hidrojenin endüstriyel %0.3 Pt/Al₂O₃ reformlama katalizörü üzerindeki tersinmez ve tersinir adsorplanması, 74-233°C ve 96-237°C sıcaklık aralıklarında ve gaz-katı kromatografisi yöntemiyle incelenmiştir. Ayrıca, sikloheksan ve metilsikloheksan ile benzen ve toluenin aynı katalizör üzerinde tersinir adsorplanmaları 190-236°C sıcaklık aralığında ölçülmüştür. Kullanılan maddelerin çeşitli sıcaklıklarda eşsıcaklık eğrileri elde edilmiş olup, bütün deneylerde darbe tekniği kullanılmıştır. Elde edilen eşsıcaklık eğrilerinden, sabit yüzey derişim değerleri kullanılarak ortalama adsorplanma ısıları hesaplanmıştır.

Kullanılan sıcaklık aralığında bir miktar hidrojenin tersinmez olarak adsorplandığı, tersinir hidrojen adsorplanmasının ise aktivasyon gerektiren bir süreç olup, ortalama adsorplanma ısısının 0.87 kcal/gmol (3.69 kJ/kmol) olduğu saptanmıştır. Sikloheksan, metilsikloheksan, benzen ve toluenin tersinir adsorplanmalarına ilişkin ortalama adsorplanma ısıları da, sırasıyla, 7.48 kcal/gmol (31.30 kJ/kmol), 7.45 kcal/gmol (31.17 kJ/kmol), 13.11 kcal/gmol (54.85 kJ/kmol) ve 13.90 kcal/gmol (58.16 kJ/kmol) olarak bulunmuştur.

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LIST OF SYMBOLS

A	area under the elution peak (mm^2)
A^*	area under the elution peak corresponding to reversible adsorption (mm^2)
c	gas phase concentration of the sample ($\text{gmol sample/cm}^3 \text{ gas}$)
C	integration constant for Eq. (3.11)
$c(t)$	ordinate of the chromatographic peak corresponding to time t (cm)
E_p	correction for partial pressure (mm/mmHg)
F_c	volumetric carrier gas flowrate corrected to column temperature and according to the pressure drop in the column (cm^3/min)
F_D	volumetric carrier gas flowrate in the detector (cm^3/min)
F_f	volumetric carrier gas flowrate at the room temperature (cm^3/min)
$f'(c)$	derivative of the adsorption isotherm
n	number of moles of sample injected (gmol)
N	amount of adsorbed substance (gmol/g)
p	partial pressure of the adsorbate (mmHg)
P_f	pressure factor calculated from Eq. (3.3)
p_i	pressure at the inlet of the column
p_o	pressure at the outlet of the column
Q_{ads}	heat of adsorption (kcal/gmol)
R	gas constant ($\text{cm}^3 \text{ mmHg/gmol } ^\circ\text{K}$)
t	time (sec)
t_c	time corresponding to any concentration at the near of the peak

t_{MS}	total retention time of the sample (sec)
t_o	retention time of the inert gas (sec)
t_R	retention time of the sample on the catalyst (sec)
T_c	column temperature ($^{\circ}\text{C}$ or $^{\circ}\text{K}$)
T_D	detector temperature ($^{\circ}\text{C}$ or $^{\circ}\text{K}$)
T_f	room temperature ($^{\circ}\text{C}$ or $^{\circ}\text{K}$)
v	chart speed
V	volume of sample injected (μl)
V_g	specific retention volume (cm^3/g)
V_{MS}	total retention volume in the column (cm^3)
V_o	retention volume in the gas phase (cm^3)
V_R, V_R^P	retention volume on the surface (cm^3)
V_R^{Tc}	
w_k	weight of catalyst (g)
x	amount of irreversibly adsorbed hydrogen (cm^3)
μ_1	first absolute moment of the chromatographic peak (min)

I. INTRODUCTION

Heterogeneous catalytic reactions play a basic role in the modern chemical industry. Adsorption is a necessary preliminary stage in all catalytic reactions. Since supported metal catalysts have very wide industrial usage, adsorption studies on such catalysts have recently become of considerable interest.

Gas chromatography, conventionally an analytical method, is recently being rather widely used to determine physicochemical and kinetic parameters of catalytic systems (Hopfe and Marx, 1972). This method also provides a simple and rapid way to investigate the properties of the catalyst (Chaudhary and Doraiswamy, 1971).

In the present study, (i) the irreversible adsorption of hydrogen, (ii) the nature of reversible adsorption of hydrogen, and (iii) the reversible adsorption of some hydrocarbons such as cyclohexane, methylcyclohexane, benzene and toluene over commercial 0.3 wt% Pt/Al₂O₃ reforming catalyst were investigated by direct gas-chromatography. Heats of adsorption were also determined from the adsorption isotherms obtained. Using the data on the heats of adsorption, nature of adsorption of hydrogen and hydrocarbons may be estimated. The experimental

evidence obtained and the parameters determined in this study may be useful in mathematical formulations and the related reactor design.

Chapter II of the thesis contains general information about Pt/Al₂O₃ reforming catalyst, adsorption in catalysis, and a description of the gas-chromatographic method. Chapter III gives an account on the specific chromatographic methods and the methods of calculation which have been used in the present study. The experimental studies carried out are presented in Chapter IV and results are discussed in Chapter V. Conclusions and recommendations for future work are given in Chapter VI.

II. CATALYSIS, ADSORPTION AND GAS CHROMATOGRAPHY

When a gas phase is brought into contact with a solid phase, the molecules of the gas phase accumulate on the solid surface, this phenomenon is called adsorption. Heterogeneous catalysis necessitates the attachment of the reactant on the solid surface.

2.1 ADSORPTION IN CATALYSIS

When the gas-phase reactant is brought into contact with the solid catalyst, the concentration of the gas phase is higher at interface than in the bulk, because surface atoms are subjected to perpendicular forces and they possess an unsaturation. The degree of this surface unsaturation varies but one can distinguish between two types of adsorption: physical adsorption and chemisorption.

The surfaces of many substances are inert in the sense that the valency requirements of their atoms may be thought to be satisfied by bonding with adjacent atoms. On those surfaces adsorption takes place through physical attraction. This type of adsorption is called physical or van der Waals adsorption and it is similar to the condensation of a

vapor on the surface of its own liquid. If the surface is more unsaturated, however, the valency requirements of the surface atoms may not be fully satisfied by physical bonding with nearby atoms. In adsorption the surface forms a chemical bond with the adjacent phase. This type of adsorption is called chemisorption, and it is similar to a chemical reaction where electron transfers take place between adsorbent and adsorbate (Hayward and Trapnell, 1964).

Physical adsorption and chemisorption are different in some aspects, through the determination of which one can distinguish between the two types of adsorption:

- i) Heat of physical adsorption is usually low, 2 to 6 kcal mole⁻¹, whereas heat of chemisorption is larger than 20 kcal mole⁻¹ (Thomas and Thomas, 1967).
- ii) Physical adsorption is rapid, because it does not need activation, chemisorption on the other hand requires activation. Activation energy of desorption is in the order of a few kcal mole⁻¹ for physical adsorption, whereas for chemisorption activation energy of desorption is also about 20 kcal mole⁻¹ (Thomas and Thomas, 1967).
- iii) A third aspect is the temperature of adsorption. Physical adsorption takes place around the boiling point of the adsorbate at the operative pressure. Chemisorption is associated with much stronger forces and is capable of occurring at temperatures well above the boiling point of the adsorbate at the operative pressure (Hayward and Trapnell, 1964).

- iv) Physical adsorption is not specific and occurs in multilayers on the surface. Chemisorption being like a chemical reaction confined to the surface of solids is specific and occurs in a monolayer.

2.2 CONVENTIONAL EXPERIMENTAL WORK ON ADSORPTION

Several conventional experimental techniques used either to determine the properties of the adsorbent or to examine the adsorption phenomena have been reported in literature (Hayward and Trapnell, 1964; Ponec, Knor and Cerny, 1974).

Experimental methods designed to examine the adsorption phenomena are as follows:

- i) The amount of gas adsorbed can be determined by the volumetric method, the gravimetric method, the radioactive tracer technique and effect of thermal transpiration (Hayward and Trapnell, 1964; Ponec, Knor and Cerny, 1974).
- ii) Heats of adsorption can be measured calorimetrically or they can be calculated from the slope of an isostere plotted in the semilogarithmic coordinates $\ln p$ vs $1/T$, where p is the equilibrium pressure, T is the temperature, for a constant adsorbed amount, provided that this heat does not depend on the temperature in the range studied (Ponec, Knor and Cerny, 1974).
- iii) The activation energy of desorption can be determined from measurements of the desorption rate as a function of temperature

on heating the adsorbent. The measurement can be carried out in a static volumetric apparatus or in a flow system (Ponec, Knor and Cerny, 1974).

The adsorption experiments carried out to determine the properties of the solid adsorbate are:

- i) Methods developed to study changes in the electrical and magnetic properties of solids during adsorption (Ponec, Knor and Cerny, 1974).
- ii) Determination of the particle size of adsorbent by sieve classification, microscopy, sedimentation and motion of the particles in the stream of carrier and their diffraction of electromagnetic radiation (Ponec, Knor and Cerny, 1974).
- iii) Determination of the porosity of the adsorbate by density measurement, mercury porosimetry, electron microscopy and x-ray diffraction (Ponec, Knor and Cerny, 1974).
- iv) Determination of surface area of the adsorbate, acidity and basicity of surfaces and pore size distribution in the solid for studying the structure and texture of solids (Hayward and Trapnell, 1964).

2.3 GAS CHROMATOGRAPHIC METHOD IN RELATION TO ADSORPTION

Direct gas chromatography is a recent method which is used to examine adsorption phenomena and properties of the adsorbent. The system in this application of gas-solid chromatography is the

chromatographic column itself which is packed with the adsorbent. When an input of adsorbate is introduced into the carrier gas stream, the system then consists of the adsorbent with the adsorbate, and the concentration of the output adsorbate is detected and recorded at column outlet. Not only the change of the inlet concentration of the adsorbate gives a time dependent output signal but also the change of other parameters of the system, for example the flowrate of the carrier gas or the temperature of the adsorbent. So in general, the gas-solid chromatographic method is any measurement made in a chromatographic apparatus where with a change of a parameter of the system a disturbance of the stationary phase is created, which results in a time-dependent outlet concentration. Knowing the input and the output, through system analysis, the kinetics and the equilibrium characteristics of adsorption processes are examined (Hopfe and Marx, 1972).

Gas chromatography can also be used in the study of catalysis. Catalyst deactivation, effects of external electric field on the catalyst, magnetic field and irradiation on active sites, surface acidity and acid strength distribution, total number of active sites, effective diffusivity, pore structure and pore size distribution, surface area of the catalyst can be determined by gas chromatography. From energetics of adsorption (heats and activation energies of adsorption) nature of adsorption can be determined. Applications of gas chromatography in catalysis have been reviewed by Choudhary and Doraiswamy (1971). General methods of physicochemical measurement are presented by Conder (1968).

Adsorption studies are carried out either by temperature programmed adsorption-desorption chromatography (Cvetanovic and Amenomiya, 1967)

or by isothermal chromatography (Conder, 1968; Choudhary and Doraiswamy, 1971). The latter method is used in the present study. Here, properties of the system are estimated by using measurable chromatographic parameters such as retention time, retention volume, band width and shape, and behavior of the chromatographic peak. Experimental and calculation procedures based on the measurement of these parameters are discussed in the following Chapter.

2.4 Pt/Al₂O₃ REFORMING CATALYST

Platinum reforming of naphtha is the reforming process having the widest current use. In this process naphthas are converted to products of higher octane number.

The typical feedstock to the catalytic reformer is heavy straight-run gasolines and naphthas. These are C₅-C₁₀ hydrocarbons including paraffins, olefins naphthenes and aromatics (Gary and Handwerk, 1975).

The desirable reactions in a reformer to produce aromatics and isoparaffins are as follows:

- i) Olefins are saturated to form paraffins
- ii) Paraffins are isomerized and some are converted to naphthenes
- iii) The naphthenes are dehydrogenated to aromatics.

Pt/Al₂O₃ is a dual function catalyst which has dehydrogenation sites on Pt and isomerization sites on the alumina. These two functions can operate completely independently. Most of the platinum reforming processes of petrochemicals are production of motor fuel. A few reformers

are also operated to produce benzene, toluene and xylenes. The main difference of platinum reforming from ordinary reforming is the fractionation of the feed into a narrow boiling range to facilitate later separation of the aromatic hydrocarbons from the paraffins. During the reaction the catalytic activity of the catalysts decreases. Regeneration is done with recirculating flue gas containing about 0.5-1.0% O_2 .

Pt/ Al_2O_3 catalysts have 0.3-1.0% Pt well dispersed on acidic alumina. Cl^- , F^- or both may be added to the alumina to get the desired acidity (Thomas, 1970).

In this study the gas phase (adsorbate) is hydrogen or hydrocarbon vapor, while the solid catalyst (adsorbent) is a 0.3%wt Pt/ Al_2O_3 commercial catalyst.

III. GAS CHROMATOGRAPHIC STUDY ON ADSORPTION OF HYDROGEN AND SOME HYDROCARBONS ON SUPPORTED CATALYSTS

Gas chromatographic data can generally be obtained by four important procedures: elution chromatography, frontal analysis, the combined frontal-elution method and the displacement technique (Choudhary and Doraiswamy, 1971). Since the technique used in the present study is elution chromatography, procedures related to this particular technique are discussed in this Chapter.

In the elution technique, a discrete sample of material is introduced into the carrier gas stream. During passage through the column, a given component is distributed in a constant ratio between the gas and the immobile phase. This ratio is governed by a fundamental physical quantity, the partition coefficient. If the various partition coefficients differ sufficiently, each component of a mixture emerges from the column as a separate peak. At fixed conditions of temperature and flow rate, the time of emergence of a peak is characteristic of the system. The repeated distribution of material between phases leads to a more or less Gaussian concentration profile along the column for each component,

and this gives rise to the familiar elution chromatogram comprising a set of bell-shaped peaks (Choudhary and Doraiswamy, 1971). As mentioned in Section 2.3, these peaks are characterized by two sets of parameters, namely

- i) retention time and retention volume and
- ii) shape and behavior of the chromatographic peak.

Retention Time and Retention Volume

In chromatographic systems, all measurements are taken as time values or they may be associated with a time value. Retention time values are defined as shown in Figure 3.1.

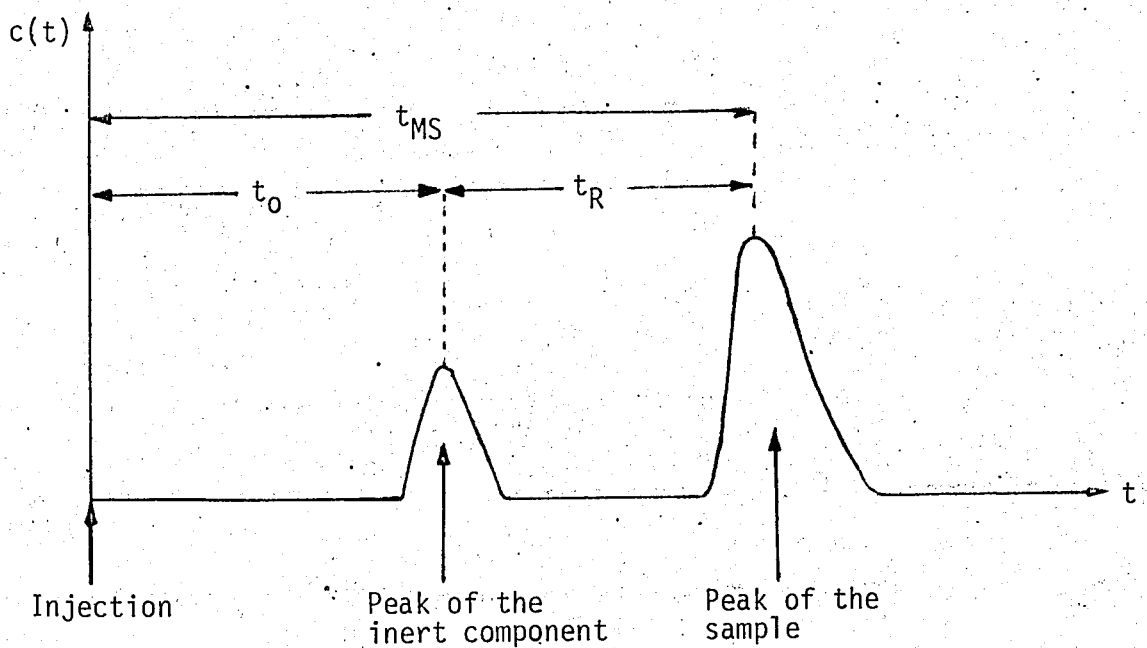


Figure 3.1 - Schematic presentation of a sample chromatogram.

The total retention time of the sample t_{MS} is defined as the time interval between sample injection and sample detection at the outlet of the column. The total retention time consists of two distinct values: the time spent in the gas phase as the sample traverses the column from one end to the other, t_0 , and the time spent on the surface of the catalyst, (t_R) . Hence the following relation exists

$$t_R = t_{MS} - t_0 \quad (3.1)$$

Here t_0 is invariant with any gas, if the column conditions are not altered, but t_R is specific for each gas.

If the carrier gas flowrate is held constant, a similar relation for retention volume can be derived:

$$F_f t_R = F_f (t_{MS} - t_0) \quad (3.2)$$

where F_f is the flowrate measured at room temperature (cm^3/min) at the outlet of the column, or

$$V_R = V_{MS} - V_0 \quad (3.2.a)$$

where the retention volume V_R may be defined as the volume of gas required to move a zone of given concentration on the boundary inlet to outlet of the column.

Normally, the measured flowrate is greater than the flowrate at any other point in the column, hence the measured retention volume obtained by multiplying the observed retention time by the outlet flowrate is greater than the true retention volume. In order to correct for this, the form of the velocity gradient must be known, and this in

turn depends on the form of the pressure gradient. An average column pressure factor, P_f , is calculated as follows (Conder, 1968; Littlewood, 1972; Beler, 1981):

$$P_f = \frac{3}{2} \frac{(p_i/p_o)^2 - 1}{(p_i/p_o)^3 - 1} \quad (3.3)$$

where p_i and p_o are pressures at the inlet and outlet of the column respectively, and V_R is corrected as:

$$V_R^p = V_R P_f \quad (3.2.b)$$

The flowrate of the carrier gas is also measured at room temperature, but during its passage through the column, the carrier gas acquires the temperature of the column. The retention volume is further corrected for column temperature:

$$V_R^{pT_c} = V_R^p \frac{T_c}{T_f} \quad (3.2.c)$$

Since the retention volume is also dependent on the amount of catalyst, it is reported per unit weight of catalyst:

$$V_g = \frac{V_R^{pT_c}}{w_k} \quad (3.2.d)$$

where V_g is the specific retention volume and w_k is the weight of the catalyst in g. In summary V_g (cm^3/g) is given as:

$$V_g = F_c (t_{MS} - t_o) / w_k \quad (3.4)$$

$$F_c = F_f \frac{T_c}{T_f} \frac{3}{2} \left[\frac{(p_i/p_o)^2 - 1}{(p_i/p_o)^3 - 1} \right] \quad (3.4.a)$$

The Chromatographic Peak

The chromatographic peak is in fact a concentration profile, $c(t)$ vs t , corresponding to the band of adsorbate moving through the column. The first absolute moment of the chromatographic peak corresponds to the centroid of the area under the chromatographic elution curve and it is a measure of the pulse retention. The first absolute moment is given by the following equation:

$$\mu_1 = \frac{\int_0^{\infty} t c(t) dt}{\int_0^{\infty} c(t) dt} \quad (3.5)$$

where $c(t)$ is the ordinate of the chromatographic peak at time t (Grubner, 1968; Hopfe and Marx, 1972; Choudhary and Srinivasan, 1978).

Adsorption Isotherm

The adsorption isotherm is the relation between the partial pressure of the adsorbate in the gas and the concentration of the adsorbate on the solid surface at equilibrium conditions and constant temperature (Smith, 1981). Adsorption isotherms may be obtained from the shape of the diffuse near boundary of an elution peak (Cremer and Huber, 1961; Huber and Kenlemans, 1962). At any point along the abscissa, t , the height of the chromatographic peak, $c(t)$, may be related to the partial pressure of adsorbate as (Cremer and Huber, 1961):

$$p = \frac{c(t)}{E_p} \quad (3.6)$$

where $c(t)$ is in mm, and E_p is calculated from:

$$E_p = \frac{AF_D}{vnRT_D} \quad (3.7)$$

where A is the area of the chromatographic peak in mm^2 , v is the chart speed in mm/sec , n is the number of moles of sample injected in gmol , R is the gas constant ($6.24 \times 10^4 \text{ cm}^3 \text{mmHg/gmol}^\circ\text{K}$), T_D is the temperature of the detector in $^\circ\text{K}$, F_D is the volumetric flowrate of the carrier gas in cm^3/sec and is defined as:

$$F_D = F_f \frac{T_D}{T_f} \quad (3.8)$$

where F_f is the carrier gas flowrate at the room temperature in cm^3/sec , T_f is the room temperature in $^\circ\text{K}$. Equation (3.7) becomes:

$$p = \frac{c(t)}{AF_f/vnRT_f} \quad (3.6.a)$$

The isotherm is obtained by integrating V_g/RT_c vs p curve. The retention volume V_g is calculated as (Cremer and Huber, 1961):

$$V_R = (t_c - t_o)F_c/w_k \quad (3.9)$$

where F_c is the volumetric carrier gas flowrate in cm^3/sec corrected for the pressure drop across the column and to the temperature T_c as in Equation (3.4.a), t_o is the retention time of the inert gas in sec,

w_k is the weight of the catalyst in g, t_c is any time on the abscissa of the chromatographic peak, which is equal to or greater than the retention time corresponding to the maximum of the sample peak, in sec.

Figure 3.2 shows, how t_c and $c(t)$ data are obtained from a chromatographic peak, to calculate V_g and p values (Cremer and Huber, 1961).

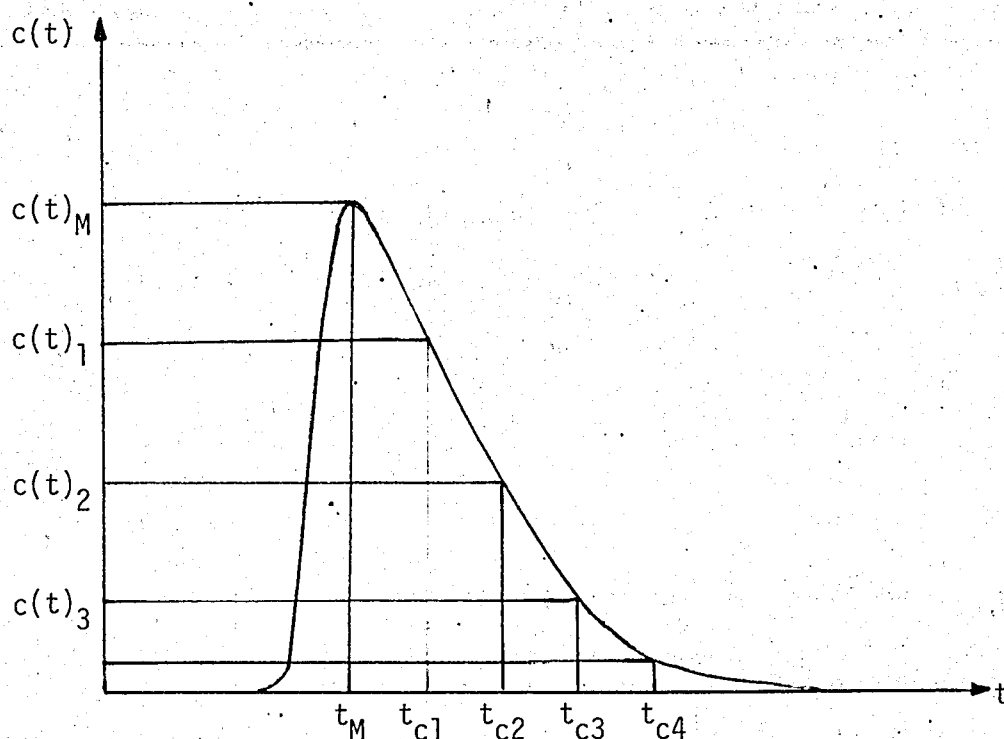


Figure 3.2 - Example of evaluation of peak to obtain t_c and $c(t)$ values.

3.1 CHROMATOGRAPHIC METHOD, EVALUATION OF CHROMATOGRAPHIC DATA AND METHOD OF CALCULATION FOR IRREVERSIBLE ADSORPTION OF HYDROGEN

In chromatographic studies of the irreversible adsorption of hydrogen, the catalyst in the column must initially be purged with the inert carrier gas at a temperature higher than the highest operating temperature, to desorb previously adsorbed hydrogen. The subsequent procedure consists mainly of repeated injections of equal-sized hydrogen samples into the nitrogen carrier gas flowing over the catalyst in the column. Sufficient time is allowed after each pulse for the desorption of the reversibly adsorbed hydrogen before injecting the next pulse. The area under the elution peak increases until saturation of the irreversible adsorption sites is completed and remains constant at this maximum value for the subsequent peaks. This maximum area is equal to the area under the elution peak of a pulse of hydrogen passing through an empty column under identical experimental conditions. The irreversible adsorption of hydrogen is determined by comparing the area under the elution peaks with the above mentioned largest area which does not correspond to irreversible but only to reversible adsorption (Gruber, 1962; Brooks and Kehrer, 1969; Hopfe and Marx, 1972; Choudhary and Srinivasan, 1978). This procedure may be repeated at various temperatures.

At all temperatures, the area of the elution peak increases with the peak number after purging; this is because of the irreversible retention of hydrogen on the catalyst. The amount of irreversibly

adsorbed hydrogen, X , is then estimated from:

$$X(\text{cm}^3) = V \sum_{n=1}^n \frac{A^* - A_n}{A^*} \quad (3.10)$$

where A^* is the area of the maximum sized peak, which is also equal to that of the peak obtained using the empty column under the same experimental conditions, A_n is the area of the n 'th peak, and V is the volume of the hydrogen pulse injected in cm^3 . Choudhary and Srinivasan (1978) have studied the irreversible adsorption of hydrogen on copper chromite using the procedure and calculations explained above. Gruber (1958), Brooks and Kehrer (1969) have also studied the irreversible adsorption of carbon monoxide on metal surfaces using the above mentioned procedure.

3.2 CHROMATOGRAPHIC METHOD, EVALUATION OF CHROMATOGRAPHIC DATA AND METHOD OF CALCULATION FOR REVERSIBLE ADSORPTION OF HYDROGEN

The reversible adsorption of hydrogen may also be studied by elution chromatography. To ensure that only reversible adsorption takes place, all irreversible adsorption sites are saturated with hydrogen by passing hydrogen over the catalyst at a temperature which is about 50°C higher than the highest operating temperature for three hours. This is followed by the desorption of reversibly adsorbed hydrogen at the operating temperature in a stream of inert carrier gas, nitrogen or helium. Then, a pulse consisting of a mixture

of the sample gas (e.g. hydrogen) and a second inert gas (e.g. argon) is introduced into the column. Two peaks should be observed after this injection, the first peak corresponding to the inert gas, which is not adsorbed at all. Hydrogen molecules are retarded in their passage over the catalyst by adsorption on the catalyst, so the second peak is that of hydrogen. The presence of two peaks indicates that one of the components in the sample mixture is being adsorbed. Since the irreversible adsorption sites have been saturated previously, the adsorption observed is certainly reversible adsorption (Choudhary and Srinivasan, 1978).

The experiment can be repeated at various temperatures. The adsorption isobar $[(t_M)_{H_2} - (t_M)_{Ar}]F_c$ vs T or $[(\mu_1)_{H_2} - (\mu_1)_{Ar}]F_c$ vs T shows whether the adsorption is activated or not. From adsorption isotherms, heats of reversible adsorption can be calculated.

3.2.1 Determination of Nature of Adsorption from Extent of Adsorption as a Function of Temperature

Nature of adsorption can be determined from chromatographic data by determining the extent of adsorption as a function of temperature. Physical adsorption generally decreases as temperature increases, while chemisorption goes through maxima as temperature increases (Smith, 1981). Choudhary and Doraiswamy (1971) have investigated how Ivanova and Zhukhovitskii (1967) have studied the adsorption of oxygen on hopcalite to determine the nature of the activated adsorption. The retention volumes of the gas samples introduced give the main information about the activated

process. The plot of $\ln V_R$ vs $1/T$, given in Figure 3.3, shows that at low temperatures, on line ab, the retention volume decreases with increasing temperature. This corresponds to molecular sorption i.e. physical adsorption. But as the temperature is increased further there is a sharp increase in retention volume, represented by the line bc and then again a decrease in retention volume with increasing temperature, represented by cd. The increase of the retention volume with increasing temperature is associated with an activated process involving chemical forces.

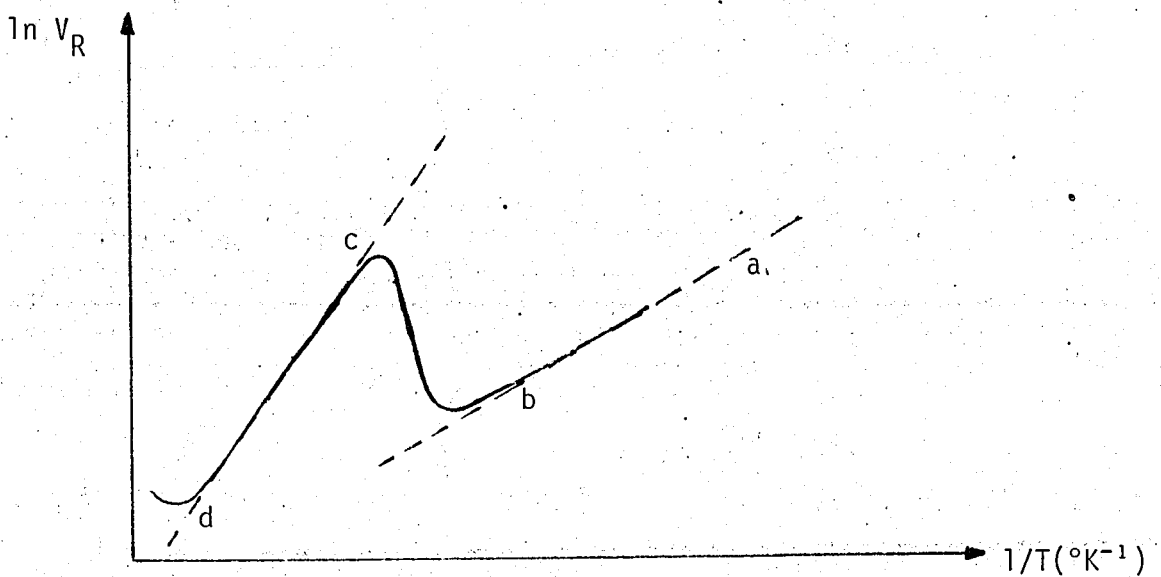


Figure 3.3 - Variation of retention volume with reciprocal temperature.

On the basis of such experimental evidence, one can conclude that maxima and minima in the plot of V_R vs T show the presence of activation in the adsorption. Moreover, Choudhary and Srinivasan (1978),

suggest that, besides retention time, first absolute moments of chromatographic peaks can also be plotted against T . In fact, the authors propose that the first absolute moment data give a better indication of the presence of activated adsorption. Therefore isobar plotted is either $[(\mu_1)_{H_2} - (\mu_1)_{Ar}]F_c$ vs T_c , or $[(t_M)_{H_2} - (t_M)_{Ar}]F_c$ vs T_c , where $(\mu_1)_{H_2}$ and $(\mu_1)_{Ar}$ are first absolute moments of hydrogen and argon, $(t_M)_{H_2}$ and $(t_M)_{Ar}$ are retention times of hydrogen and argon, F_c is the carrier gas flowrate corrected for the pressure drop across the catalyst column and the column temperature T_c , as shown in Equation (3.4.a).

3.2.2 Determination of Heats of Adsorption from Adsorption Isotherms Using the Elution Technique

An additional criterion for determining the nature of adsorption is provided by the calculation of the heats of adsorption. For a dilute system one can derive the equation (Kiselev and Yashin, 1969):

$$\ln V_g = \frac{Q_{ads}}{R}(1/T_c) + C \quad (3.11)$$

where V_g is the specific retention volume, calculated from the retention time at infinite dilution, Q_{ads} is the heat of adsorption, R is the gas constant, T_c is the column temperature and C is the integration constant. Equation (3.11) shows that $\ln V_g$ is a linear function of $1/T_c$ and if $\ln V_g$ is plotted against $1/T_c$, the slope gives Q_{ads}/R (Eberly, 1961; Choudhary and Menon, 1976; Önsan, 1979; Beler, 1981).

At higher surface coverages, on the other hand, heats of adsorption are calculated from adsorption isotherms. One dimensional transport

of a sample of a single component by an inert fluid carrier through a column containing stationary sorption material was treated by Huber and Keulemans (1962) and an expression relating the concentration of the sample in the effluent to the volume of carrier fluid, which has passed through the column since the injection of the sample, was derived under the following simplifying assumptions:

- i) A segment of the column containing a given amount of stationary phase also contains a volume of moving phase which is invariant with time and with position of the segment.
- ii) The temperature of the column is constant and uniform along its length.
- iii) The volume velocity of the carrier fluid, averaged over any cross section of the column, is constant.
- iv) The volume velocity of the moving phase is equal to the volume velocity of the carrier fluid.
- v) All axial transport is due to convection.
- vi) Equilibrium is maintained at all times within any cross section.

Cremer and Huber (1961) described the same chromatographic method to determine adsorption isotherms from the shape of a single elution chromatogram. From the simplified mass balance they obtained (Baumgarten, Weinstrauch and Höffkes, 1977):

$$\frac{dN}{dc} = V_g \quad (3.12)$$

where N is the amount of adsorbed substance in (gmole/g) adsorbant, c is the concentration in the gas phase (mole/cm³), and V_g is the specific retention volume based on one gram of adsorbent at the column temperature. Equation (3.12) can also be written in the form (Cremer and Huber, 1961):

$$V_g = f'(c) \quad (3.13)$$

Equation (3.13) shows the proportionality between the retention time corresponding to a given concentration (c) and the derivative of the adsorption isotherm $f'(c)$ and it is obtained from the foregoing mass balance equation.

V_g/RT_c is plotted against the partial pressure of the adsorbate, i.e. hydrogen, (p). The adsorption isotherm is obtained from a V_g/RT_c vs p plot by graphical integration (Cremer and Huber, 1961) using Simpson's Approximation. The isostere $\ln p$ vs $1/T$ is then plotted from the adsorption isotherm at constant "moles adsorbed per gram of adsorbent". The heat of adsorption, Q_{ads} , is calculated from the slope of the isostere as shown in the Clausius-Clapeyron equation:

$$\left(\frac{\partial \ln p}{\partial (1/T)} \right)_{a,N} = \frac{-Q_{ads}}{R} \quad (3.14)$$

where a is constant adsorbent surface and N is constant amount of gas adsorbed (Shen and Smith, 1968; Kiselev and Yashin, 1969; Ponec, Knor and Cerny, 1974; Baumgarten, Weinstrauch and Hoffkes, 1977; Smith, 1981).

The pulse technique may also be used to study adsorption of other adsorbate substances such as hydrocarbons (Cremer and Huber, 1961;

Baumgarten, Weinstrauch and Höffkes, 1977). A pulse of hydrocarbon is introduced into the carrier gas stream and the elution curve at outlet is recorded. A pulse of inert gas must also be introduced into the column under the same experimental conditions and its retention time recorded so that the retention of hydrocarbons on the catalyst due to adsorption may be calculated. From the elution peak of hydrocarbons, adsorption isotherms and adsorption isosteres and heats of adsorption of hydrocarbons can be calculated in the same fashion as described above.

IV. EXPERIMENTAL WORK

4.1 EXPERIMENTAL SET-UP

The experimental set-up consists of a gas chromatograph, a strip chart recorder, a data processor, a quartz thermometer, gas cylinders with sensitive regulators, a soap bubble flowmeter, a mercury manometer and a barometer. The connections of the carrier gas tank to the chromatograph are made by 1/8 inch copper tubing, the connections to the mercury manometer and discharge of hydrogen to open air are provided by polyethylene tubing. The fittings used are either stainless steel or brass. The experimental set-up is shown in Figure 4.1.

- Gas Chromatograph

The gas chromatograph, which contains the adsorption column in its oven, is Varian Aerograph Moduline Series 2800, with possibilities of flame ionization or thermal conductivity detectors and temperature programming. The specifications of the instrument are given below:

Detector: Thermal conductivity detector
4 filament tungsten-rhenium (wx)
Usage up to 400°C
Carrier gas: H_2 , He or N_2

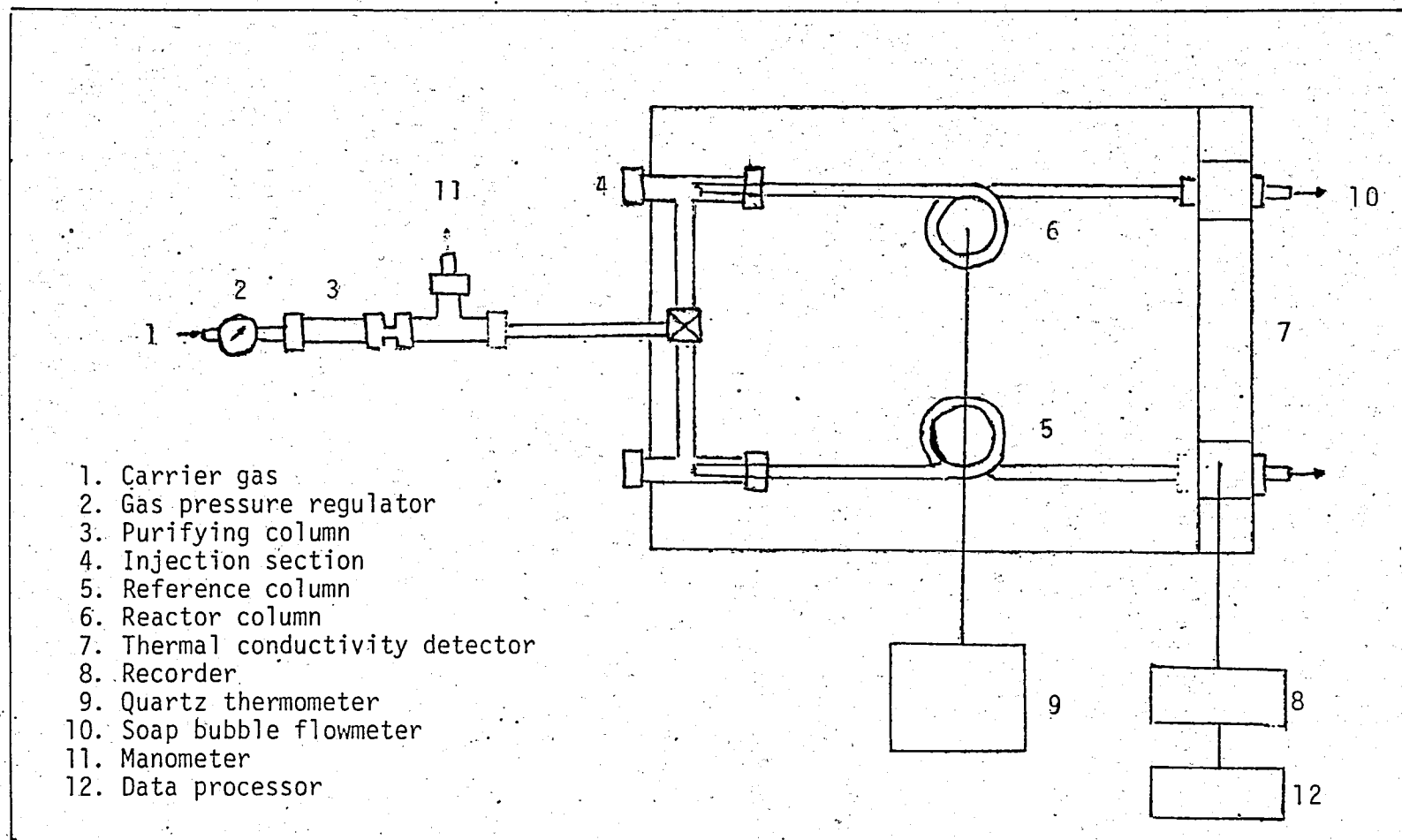


Figure 4.1 - Experimental Set-up.

Detector Control Unit: Current: 0-300 mA
 Control: % ± 0.02
 Attenuation: 1-1024

Column Oven : -100 to 400°C
 Control: $\pm 0.1^\circ\text{C}$

Injection Section : Usage up to 400°C
 Option of injection to the column
 packing or to the injection tube.

Detection Section : Usage up to 400°C
 Control: max. $\pm 0.5^\circ\text{C}$

* Specific conditions used in the present experiments:

Detector Temperature : 150°C for N₂ carrier gas
 250°C for H₂ or He carrier gas

Column Temperature : isothermal operation at 70-235°C for
 adsorption of H₂
 at 185-235°C for adsorption of hydro-
 carbons

Injector Temperatures: Same as column temperature

Detector Current : 67.5 mA for N₂ carrier gas
 125 mA for H₂ or He carrier gas

Attenuation : 2-32

- *Strip Chart Recorder*

The strip chart recorder is a Varian Aerograph recorder with the following specifications:

Full Scale Range : 1 mV-1 V

Chart Speed Range: 2-2000 cm/hr, 0.02-20 cm/min

During the experiments, the instrument operated at 1 mV full scale and a chart speed of 5-20 cm/min, depending on retention time and sample size.

- Data Processor

The data processor is a Shimadzu Data Processor Chromatopac C-R1B with the following specifications:

Range of input voltage: -5 mV to 1 mV

Recording span : 1 mV

Integration Sensitivity: 1 μ V.sec (= 1 digit of area)

For calculation of areas file No. 3 and method 41 of the data processor are used.

- Quartz Thermometer

The Hewlett Packard quartz thermometer used for measuring the column temperatures has the following specifications:

Usage : up to 250°C

Sensitivity: 0.01 to 0.0001°C

In this work a sensitivity of 0.01°C was used.

- Adsorption Column

The column was made of 1.98 mm ID stainless steel tubing. It was prepared as follows: The column was first washed with dilute HCl, distilled water, ethanol and acetone and then dried in the oven at

105-110°C by passing nitrogen through it. The industrial 0.3% Pt/Al₂O₃ granules were powdered and sieved to 0.177-0.250 mm (60-80 mesh) of particle diameter. The powdered catalyst was filled into the column by the help of mechanical vibrator and the two ends were closed by glass wool. Mechanical vibration was carried on for some time to maintain homogeneous distribution of the catalyst particles within the column (Önsan, 1979; Beler, 1981).

The column lengths and catalyst quantities used are reported in Section 4.3 for different experiments.

4.2 MATERIALS

Helium, hydrogen, nitrogen and argon gases obtained by HABAŞ A.Ş. were used in the experiments. The gas streams passed through a small trap of molecular sieve and silica gel, where they were dried. Nitrogen was passed over copper at 400°C to be purified from the trace amounts of oxygen.

The catalyst used is the industrial 0.3%wt Pt/Al₂O₃ for catalytic reforming processes.

The hydrocarbons used are cyclohexane (CH), methylcyclohexane (MCH), benzene and toluene as shown in Table 4.1.

TABLE 4.1 - Hydrocarbons Used in the Experiments

Compound	Company	Grade	Molecular Weight	Specific Gravity
CH	Merck	GPR	84.16	0.780
MCH	Flurka	GC	98.18	0.769
Benzene	Rafinex	GPR	78.11	0.879
Toluene	Atabay	GPR	92.13	0.866
(GC: Gas Chromatographic; GPR: General Purpose Reagent)				

4.3 EXPERIMENTAL METHODS

4.3.1 Experimental Method for Irreversible Adsorption of Hydrogen

The measurement of the extent of irreversible adsorption of hydrogen was performed by a pulse chromatographic procedure. Instead of helium, which is generally used as the carrier gas in similar studies, nitrogen was used as the carrier for the detection of hydrogen adsorption. The reason is the anomalous response of hydrogen in a helium carrier, when a thermal conductivity detector is used. Small quantities of hydrogen appear to have a thermal conductivity less than helium, while larger amounts produce peaks responding in both directions, so-called W peaks (David, 1974).

The catalyst column used for the determination of irreversible adsorption of hydrogen a packed length of 103 cm. The weight of 0.3% Pt/Al₂O₃ catalyst packed into the column was 2.38 grams. The column was fitted into the chromatograph oven. Hydrogen was allowed to pass over the catalyst at a flowrate of 10 cm³/min at 287°C for 24 hours for the reduction and activation of the catalyst. In order to have the same starting conditions for the catalyst surface, desorption was done for four hours at 287°C by passing nitrogen over the catalyst at about 10 cm³/min, before starting each experiment. At the end of this period, the column was cooled down to the desired operating temperature and conditioned for one hour, and the flowrate of the carrier gas was increased to about 15 cm³/min. The one cm³ sample loop was filled with hydrogen by passing hydrogen through the loop for one minute continuously.

The sample valve was brought to the "inject" position, the one cm hydrogen injected and the hydrogen peak recorded. After the hydrogen peak had reached the base line, three more minutes were allowed before the valve was brought to the "fill" position and the loop was again filled with hydrogen as described above. The areas under the peaks were calculated using the Shimadzu Data Processor. Injections were repeated until the area of the peak did not increase any more.

4.3.2 Experimental Method for Reversible Adsorption of Hydrogen

A 103 cm stainless steel column was packed with 2.71 g of 0.3%wt Pt/Al₂O₃ catalyst. The carrier gas used during the experiments was nitrogen, because of the reasons discussed in Section 4.3.1. To ensure that only reversible adsorption takes place, all irreversible adsorption sites were saturated by passing hydrogen over the catalyst for three hours at 287°C and at a flowrate of about 10 cm³/min. This was followed by the desorption of reversibly adsorbed hydrogen in a stream of nitrogen carrier gas for half an hour at the temperature at which the experiment was performed. Then, pulses consisting of argon and hydrogen (ratio of hydrogen to argon being 150 µl/850 µl, 125 µl/875 µl, 100 µl/900 µl) were introduced into the column via Hamilton syringes and the two peaks corresponding to argon and hydrogen were recorded at the detector exit.

4.3.3 Experimental Method for Reversible Adsorption of Hydrocarbons

The catalyst column used in this part was the same as the one used for reversible adsorption of hydrogen experiments described in Section 4.3.2. The carrier gas was selected so that there was no reaction in the system. In the experiments for adsorption of cyclohexane and methylcyclohexane, hydrogen was used as carrier gas so that hydrogen was in excess and therefore no dehydrogenation reaction could take place. Similarly, when benzene and toluene were injected as samples, helium was used as carrier gas to prevent hydrogenation of the samples. In all experiments, it was observed that there was no reaction taking place.

Before each experiment was started, the catalyst was treated with hydrogen at 287°C for three hours at a flowrate of 10 cm³/min in order to have the same activation level of the catalyst at each experiment. After this period the column was cooled down to the temperature at which the experiment was to be performed. Flowrate of the carrier gas, helium or hydrogen, was adjusted to about 10 cm³/min. After steady temperature and flowrate were achieved, several successive pulses of the hydrocarbon sample were injected into the catalyst bed to ensure that all irreversible sites were saturated. The peaks corresponding to reversible adsorption of hydrocarbons and peaks of inert nitrogen were recorded at the outlet of the column.

4.4 EVALUATION OF DATA

4.4.1 Evaluation of Data for the Irreversible Adsorption of Hydrogen

The area of each peak was calculated using the Shimadzu Data Processor. The areas given by the integrator are tabulated in Appendix I. The areas were plotted against the number of injections as shown in Figure 4.2 for the experiment at 73.85°C. It was observed that the peak area did not increase any further after second peak, but only fluctuated about an average value. The arithmetic average of the peaks after the first peak was calculated which was equal to A^* in Equation (3.10). The amount of irreversibly adsorbed hydrogen was calculated from:

$$x(\text{cm}^3) = V \left(\frac{A^* - A}{A^*} \right) \quad (3.10.a)$$

4.4.2 Evaluation of Retention Data for Reversible Adsorption of Hydrogen

As shown in Figure 4.3 each chromatogram consisted of two peaks, the first was that of argon and the second was the hydrogen peak. The retention time of argon, $(t_M)_{Ar}$, was found by drawing tangents through the inflection points of the leading and tailing portions of the peak and measuring the distance from the injection point to the intersection points of the tangents and then dividing by the chart speed. $(t_M)_{Ar}$ is the time required for any unadsorbed gas to pass through the void

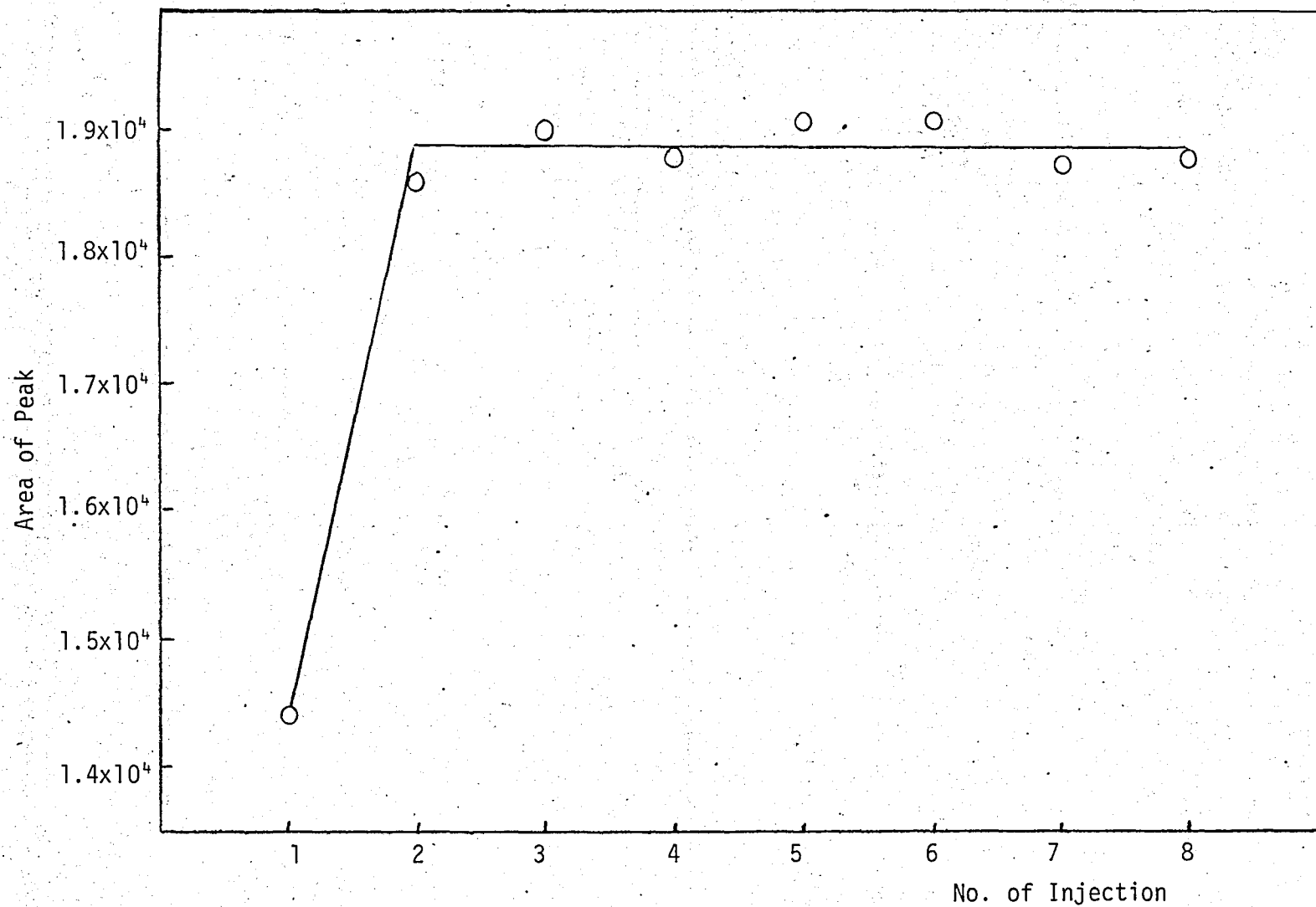


Figure 4.2 - Area of the hydrogen peak as a function of number of injection at 73.85°C.

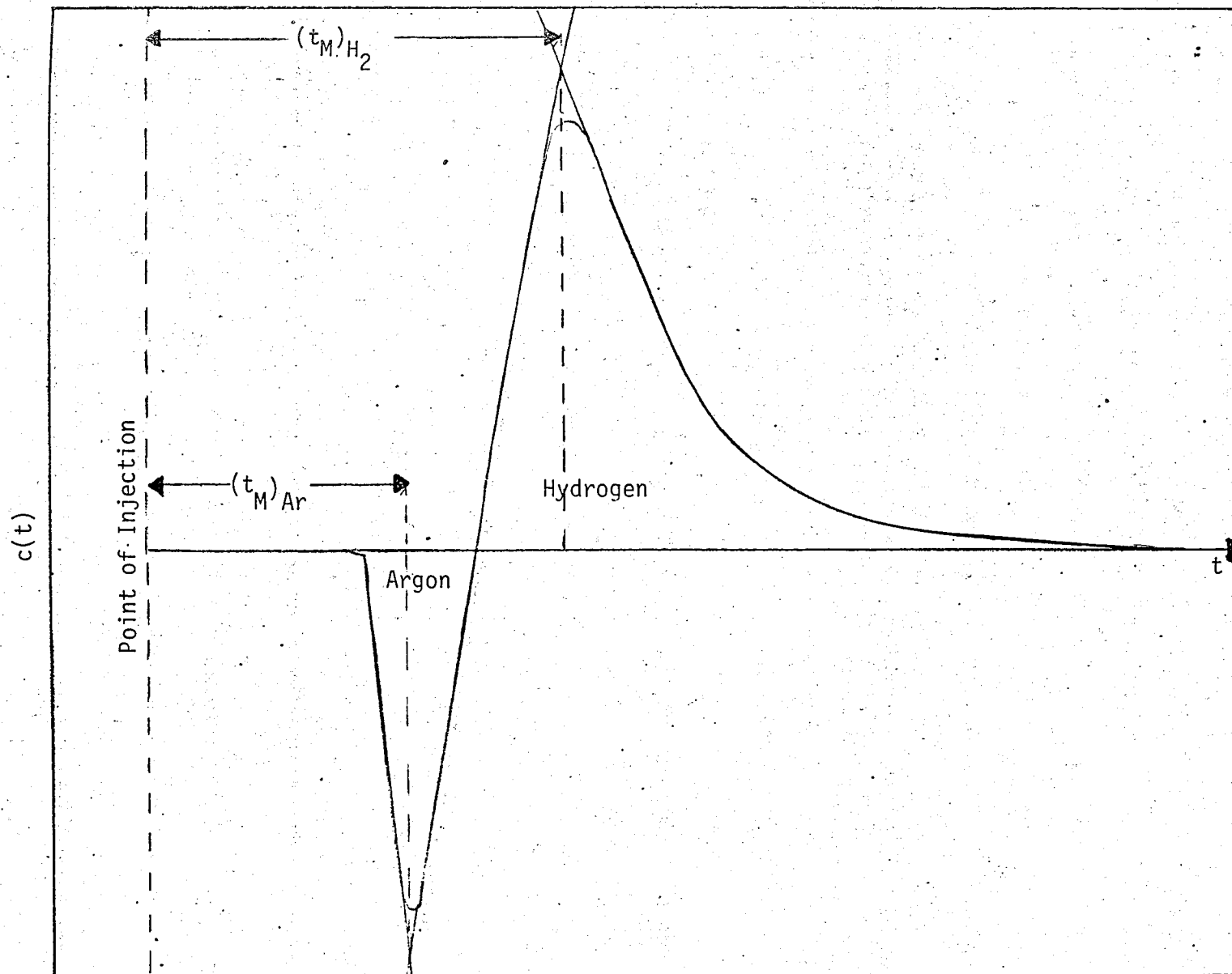


Figure 4.3 - Sample chromatogram for 125 μl hydrogen and 875 μl argon at 217.72°C.
(Attenuation = 8, Chart speed = 10 cm/min)

space of the column; in other words it is the time needed for the sample to traverse from the inlet of the column to the outlet. $(t_M)_{H_2}$ is the total time required for hydrogen to pass through the column. The difference between $(t_M)_{H_2}$ and $(t_M)_{Ar}$ gives the true retention time of hydrogen, which is the retention time due to adsorption on the surface, as given by Equation (3.1).

The first absolute moment of a peak represents the centroid of the area under the peak and was calculated from Equation (3.2). The integrals were calculated with a TI 58C desk calculator using Simpson's Approximation for discrete functions. $(\mu_1)_{Ar}$ represents the first absolute moment of argon, $(\mu_1)_{H_2}$ represents the first absolute moment of hydrogen.

The flowrate of the carrier gas was corrected for the pressure drop across the column and to the column temperature T_c as in Equation (3.4.a):

$$F_c = F_f \frac{T_f}{T_c} \frac{3}{2} \left[\frac{(p_i/p_o)^2 - 1}{(p_i/p_o)^3 - 1} \right] \quad (3.4.a)$$

where F_f is the flowrate of the carrier gas, which was measured at the outlet of the column, T_c is the column temperature, T_f is the room temperature, p_i and p_o are pressures at the inlet and outlet of the column respectively.

4.4.3 Evaluation of Data for Adsorption Isotherms and Heats of Adsorption of Hydrogen and Hydrocarbons

Adsorption Isotherms

The adsorption isotherms were obtained from a single elution chromatogram at each column temperature for each adsorbate. Specific retention volume, V_R , and partial pressure of adsorbate, p , are calculated from Equations (3.9) and (3.6) respectively. As discussed in Section 3.2.2 the adsorption isotherm was obtained by integrating the V_g/RT_c vs p curve. The integration was carried out using TI 58C desk calculator with Simpson's Approximation.

Heats of Adsorption

The resulting adsorption isotherms were moles of adsorbate adsorbed per gram of catalyst as a function of partial pressure of sample at constant values of the column temperature. A family of curves were observed for each adsorbate. Then, keeping moles adsorbed constant $\ln p$ vs $1/T$ curve was drawn for each adsorbate at different values of surface coverage. From the slope of these isosteres, heats of adsorption were calculated from Equation (3.14).

An example for the calculation of the adsorption isotherm from a chromatographic peak is shown for cyclohexane at 216.80°C and for sample size 0.4 μl (Peak No. 63 in Appendix III). The peak is drawn in Figure 5.5. Retention data for this peak are shown in Table 4.2. These data as plotted in Figure 4.4 give the derivative of the adsorption

isotherm. By integrating this curve, the adsorption isotherm is obtained (Cremer and Huber, 1961). Data for the adsorption isotherm are given in Table 4.3. The adsorption isotherm is plotted in Figure 4.5.

TABLE 4.2 - Retention Time - Height Data for Cyclohexane
 $T_c = 216.80^\circ\text{C}$ $V_{CH} = 0.4 \mu\text{l}$

$t_c(\text{cm})$	$t_c(\text{sec})$	$c(t)(\text{mm})$	$(V_g/RT_c) \times 10^{-7}$ (gmol/g mmHg)	$p(\text{mm Hg})$
19.7	59.1	117.0	1.08	31.6
20.2	60.6	109.5	1.12	29.6
20.7	62.1	96.0	1.16	25.9
21.2	63.6	81.0	1.20	21.9
21.7	65.1	66.0	1.24	17.6
22.2	66.6	51.5	1.29	13.9
22.7	68.1	39.0	1.33	10.5
23.2	69.6	29.5	1.37	8.0
23.7	71.1	21.5	1.41	5.8
24.2	72.6	16.0	1.44	4.3
24.7	74.1	11.5	1.49	3.1
25.2	75.6	8.0	1.53	2.2
25.7	77.1	5.5	1.57	1.5
26.2	78.6	4.0	1.61	1.1
26.7	80.1	3.0	1.65	0.8
27.2	81.6	2.0	1.69	0.5
27.7	83.1	2.0	1.73	0.5
28.2	84.6	1.5	1.77	0.4
28.7	86.1	1.0	1.81	0.3
29.2	87.6	1.0	1.85	0.3
29.7	89.1	0.7	1.90	0.2
30.2	90.6	0.5	1.94	0.1
30.7	92.1	0.0	1.98	0.0

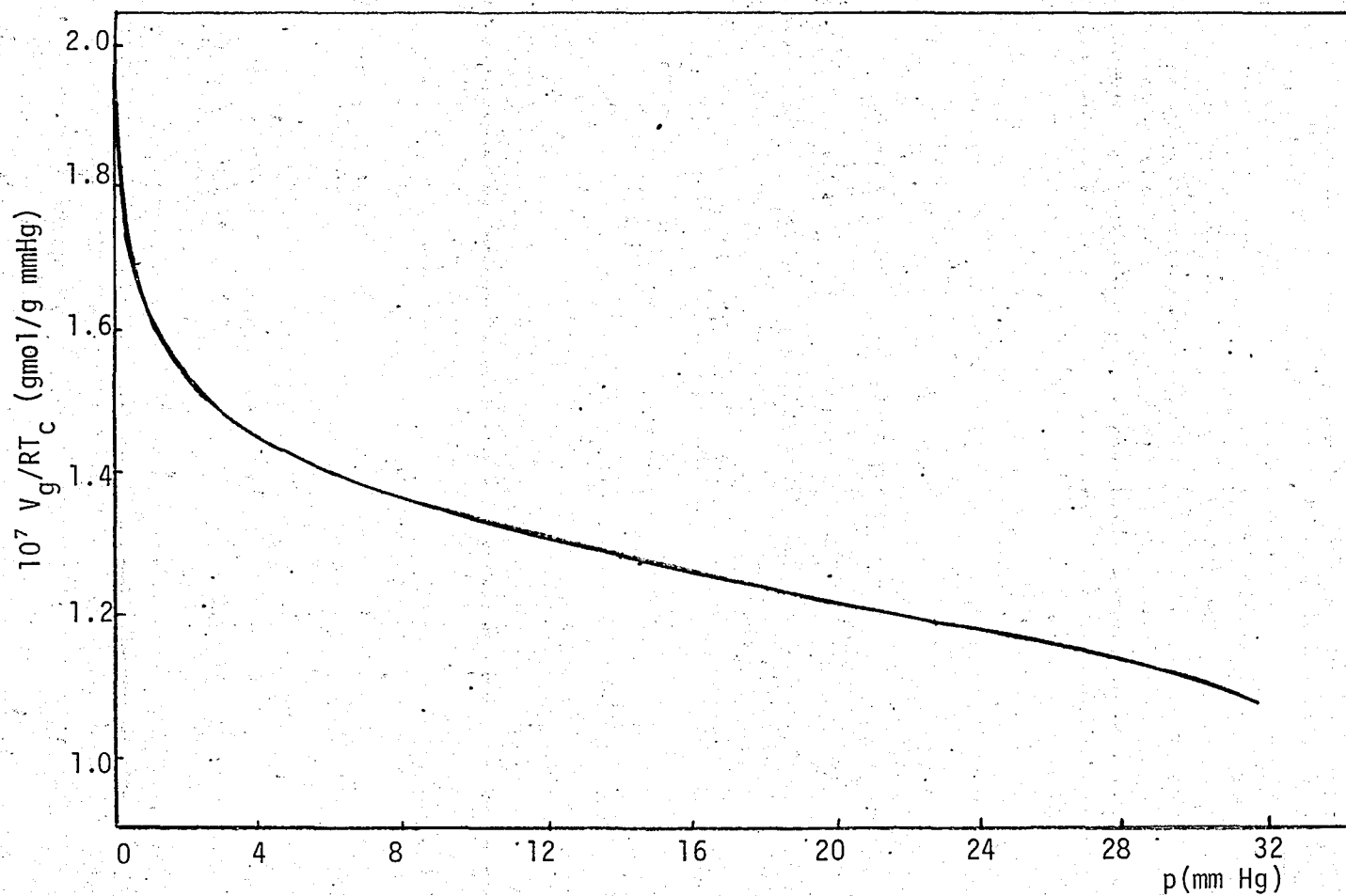


Figure 4.4 - Derivative of the adsorption isotherm of Cyclohexane.
($T = 216.80^\circ\text{C}$, $V_{\text{CH}} = 0.4 \mu\text{l}$)

TABLE 4.3 - Adsorption Isotherm for Cyclohexane
 $T_c = 216.80^\circ\text{C}$ $V_{CH} = 0.4 \mu\text{l}$

p(mm Hg)	$(V_R/RT_c) \times 10^7$ (gmol/g mmHg)	(gmol adsorbed/g catalyst) $\times 10^7$
0	1.98	0
1	1.62	
2	1.54	
3	1.48	
4	1.46	
5	1.43	
6	1.40	9.16
8	1.37	
10	1.34	
12	1.31	
14	1.29	19.87
16	1.26	
18	1.24	
20	1.22	
22	1.20	29.79
24	1.18	
26	1.16	
28	1.14	
30	1.11	39.05

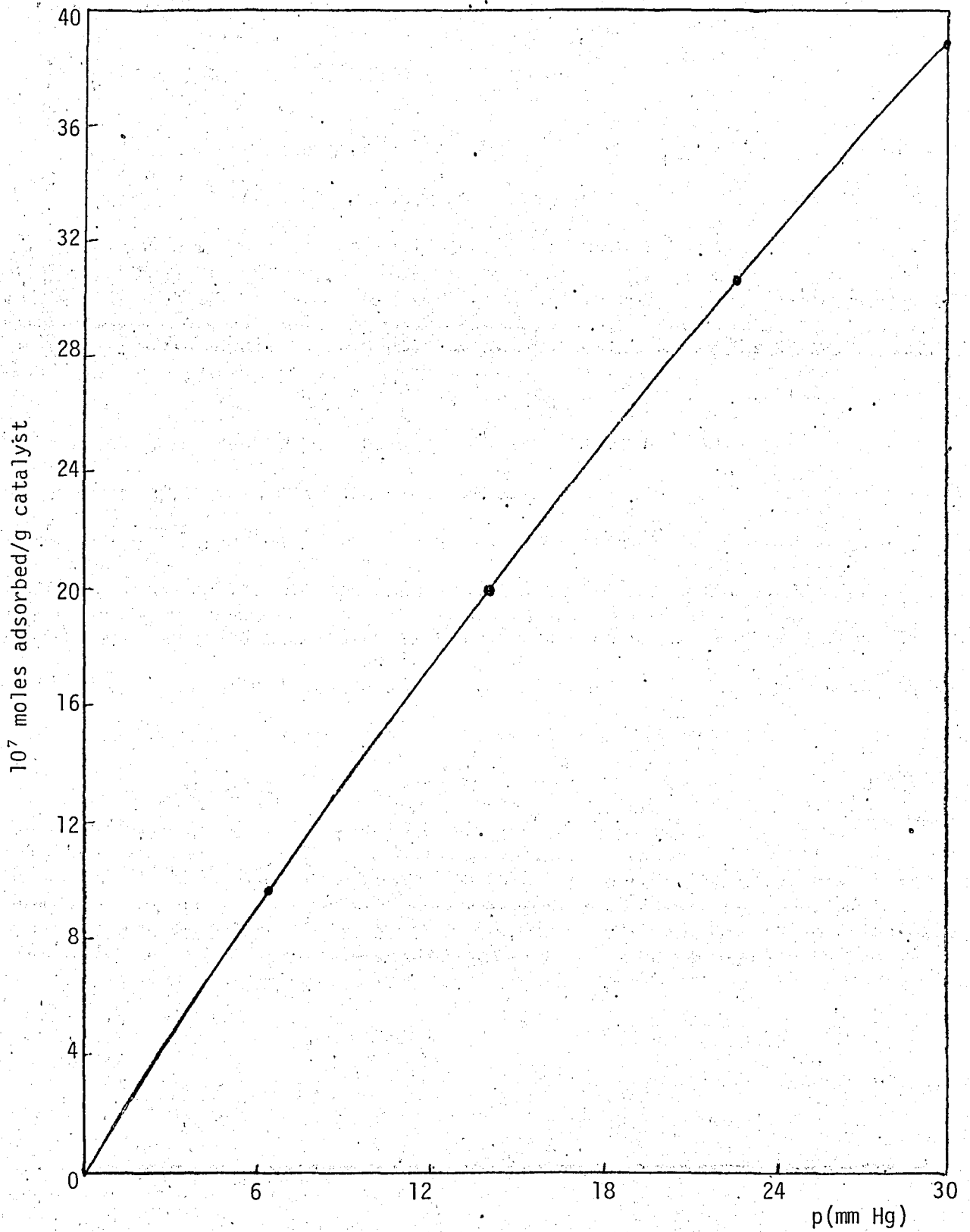


Figure 4.5 - Adsorption isotherms for cyclohexane.
($T_c = 216.80^\circ\text{C}$, $V_{CH} = 0.4 \mu\ell$)

4.5 DISCUSSION OF EXPERIMENTAL CONDITIONS

In the experiments described, the adsorption parameters of hydrogen and four different hydrocarbons were studied in the absence of chemical reaction, in order to avoid complications which may arise from interference and overlapping of reactant and product peaks. The carrier gas and the experimental conditions were chosen such that no reaction took place. The absence of chemical reaction was verified by the single chromatographic peak obtained in each case; no extra peaks corresponding to reaction products having different retention times were observed.

In the determination of the irreversible adsorption of hydrogen, the amount of hydrogen sample injected is important. The amount of test gas injected must be in excess of what could be adsorbed by the catalyst surface. The hydrogen sample injected was one cm^3 . A large excess of hydrogen has the advantage of allowing equilibrium in a short contact time. The hydrogen injections were made using a sample valve with a calibrated loop to ensure injection of exactly the same volume each time.

In direct chromatographic studies, precise temperature control is also essential. For reliable results, fluctuations must be within the range of $\pm 0.1^\circ\text{C}$ (Conder, 1968). In the present study, the column temperature was continuously measured by a quartz thermometer to the hundredths of a Centigrade degree. The column temperature was held constant at $\pm 0.05^\circ\text{C}$ in majority of the runs, but at no time did the fluctuations reach $\pm 0.1^\circ\text{C}$.

Another important parameter in such studies is the flowrate of the carrier gas, which must be carefully controlled, so that it remains constant during each experiment. The constant carrier gas stream was obtained

through sensitive pressure regulators. The flowrate was chosen slow enough to provide sufficient contact between the catalyst surface and the sample.

At such low flowrates, to avoid diffusion the catalyst particles were used in sufficiently powdered form. Diffusion could be neglected in constructing the isotherms because of the small (60-80 mesh) size particles.

V. RESULTS AND DISCUSSION

In the present work, the irreversible and the reversible adsorption of hydrogen on a commercial 0.3%wt Pt/Al₂O₃ catalyst was studied at 74-233°C using elution chromatography. The reversible adsorption of two naphthenes (cyclohexane and methylcyclohexane) and two aromatic hydrocarbons (benzene and toluene) on the same catalyst was also studied using the same technique at 190-235°C. Adsorption isotherms and isosteres were constructed both for hydrogen and for the hydrocarbons used. These isosteres were subsequently used to calculate the heats of adsorption for the adsorbates in question. The pulse technique was used in all the experiments, and information was obtained from the retention data or the shape of the single elution peak. The results obtained are tabulated and discussed in different sections of this Chapter while the bulk of the experimental data may be found in the Appendices cited.

5.1 IRREVERSIBLE ADSORPTION OF HYDROGEN ON 0.3% wt Pt/Al₂O₃

The amount of hydrogen which is irreversibly adsorbed has been calculated using the method explained in Section 4.3.1 and Equation (3.10.a). The results obtained are tabulated in Table 5.1, and Figure 5.1

shows the variation of amount of irreversibly adsorbed hydrogen with temperature in the temperature range of 74°C to 233°C. As it can be seen on Figure 5.1, the amount of irreversibly adsorbed hydrogen increases from 0.233 cm³ to 0.277 cm³ as the temperature is increased from 74°C to 136°C. After that maximum, the amount of irreversibly adsorbed hydrogen decreases to 0.245 cm³ at 165°C. Following this temperature, however, a rapid increase is observed within the next 10-20°C interval, after which a rather steady value is reached as the temperature is increased upto 233°C, except a slight decrease at 196°C. At the highest temperature considered, a maximum of 0.319 cm³ hydrogen is adsorbed irreversibly. On the basis of these results, it may be concluded that there is 0.233 ml to 0.319 ml of hydrogen which is adsorbed irreversibly on Pt/Al₂O₃ in this temperature range, if a 2.38 g-catalyst bed is cleaned sufficiently before each experiment so that all irreversible adsorption sites are unoccupied when the run is started. Corresponding data are presented in Appendix I.

Choudhary and Srinivasan (1978) have similarly observed in their study on the adsorption of hydrogen on copper chromite at 30-350°C that the amount of hydrogen adsorbed irreversibly goes through a minimum at about 100°C and then reaches a maximum value around 200°C.

TABLE 5.1 - Amount of Irreversibly Adsorbed Hydrogen on Pt/Al₂O₃

T_c (°C)	Area of the first peak	Average area of the second peak	Amount of irreversibly adsorbed hydrogen (ml)
73.85	1.44×10^4	1.89×10^4	0.237
95.77	1.37×10^4	1.78×10^4	0.233
116.77	1.35×10^4	1.80×10^4	0.251
135.55	1.21×10^4	1.67×10^4	0.277
156.33	1.20×10^4	1.61×10^4	0.253
164.92	1.36×10^4	1.80×10^4	0.245
175.16	1.18×10^4	1.69×10^4	0.300
184.62	1.07×10^4	1.56×10^4	0.314
195.60	1.10×10^4	1.57×10^4	0.299
205.49	1.10×10^4	1.62×10^4	0.317
214.98	1.07×10^4	1.57×10^4	0.318
232.71	1.02×10^4	1.50×10^4	0.319

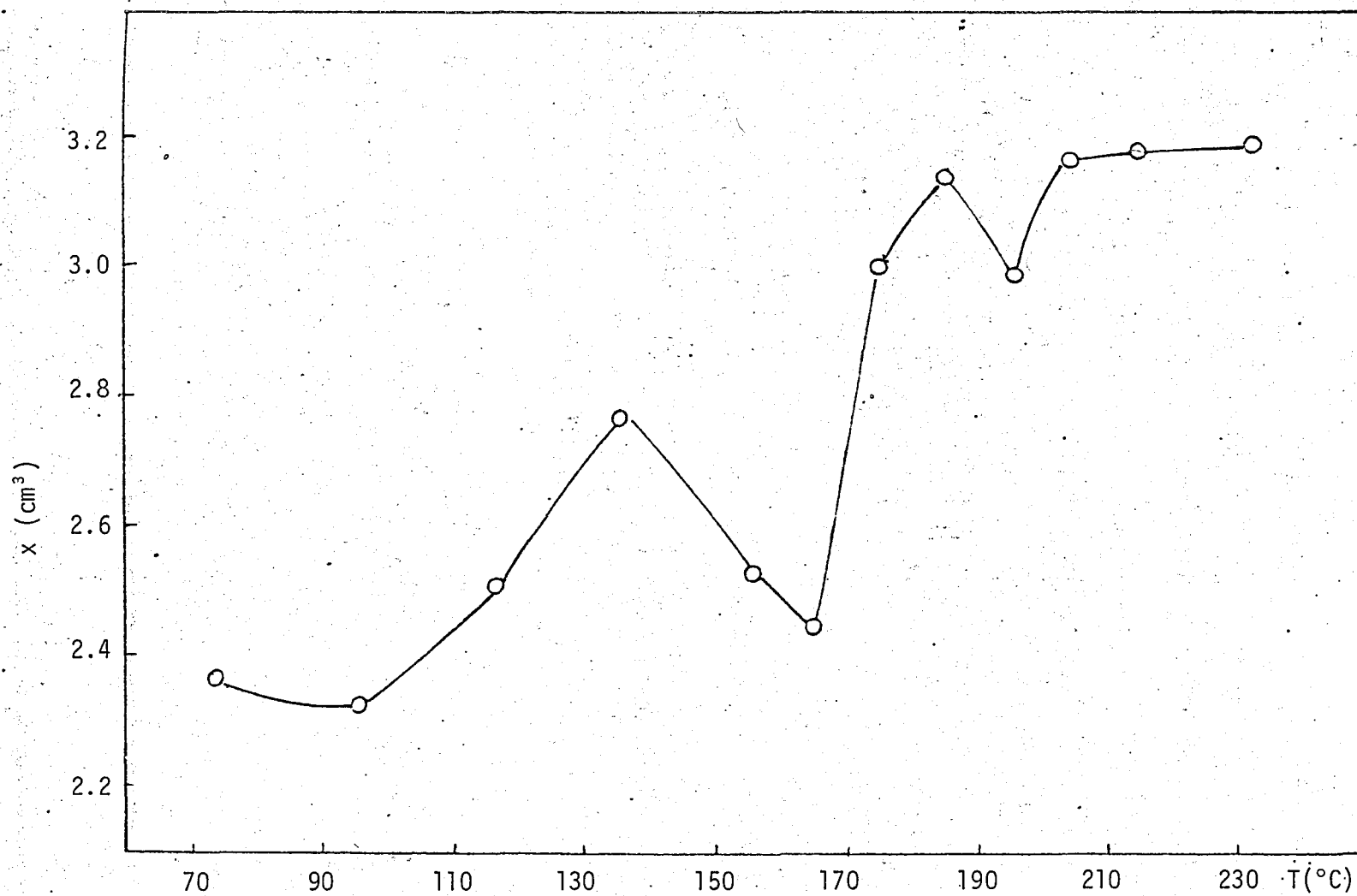


Figure 5.1 - Amount of irreversibly adsorbed hydrogen (x) as a function of temperature.

5.2 REVERSIBLE RETENTION OF HYDROGEN ON 0.3%wt Pt/Al₂O₃

As has been discussed in Section 3.2.1, the nature of reversible adsorption may be determined from the variation of retention volume, or carrier gas flowrate multiplied by the first absolute moment of the peak, with temperature. In the present experiments, the volume of hydrogen injected was also varied by varying the Argon/Hydrogen ratio at constant sample volume. For three different volumes of hydrogen sample injected, retention volumes and carrier gas flowrate times the first absolute moment of the peak show the same variation with changing temperature. All curves have their maximum around 165-175°C and their minimum at 196°C. This sharp decrease can be observed regardless of the volume of hydrogen injected. After 195°C, the curves rise as temperature increases up to 236°C. The presence of a maximum and a minimum shows that there is activation in the adsorption process within the temperature range concerned (Choudhary and Srinivasan, 1978). Retention data are given in Tables 5.2 and 5.3. These retention data are also plotted in Figure 5.2 for two sample compositions or two hydrogen volumes. The related data are presented in Appendix II.

TABLE 5.2 - Retention Data for Reversible Adsorption of Hydrogen

Peak No.	T _c (°C)	V _{Ar} (μℓ)	V _{H₂} (μℓ)	F _c (cm ³ /min)	F _c [(t _M) _{H₂} -(t _M) _{Ar}] (cm ³)	F _c [(μ ₁) _{H₂} -(μ ₁) _A] (cm ³)
1	95.74	900	100	8.82	1.76	3.67
2	95.74	900	100	8.82	2.29	3.86
3	95.74	900	100	8.82	1.94	3.45
4	116.16	900	100	8.89	2.13	3.88
5	116.16	900	100	8.89	1.78	4.12
6	116.16	900	100	8.89	2.22	4.22
7	116.16	875	125	8.89	1.51	3.91
8	116.16	875	125	8.89	2.31	4.39
9	116.16	875	125	8.89	2.31	4.43
10	116.16	875	125	8.89	2.27	3.97
11	136.19	875	125	10.08	2.21	4.56
12	136.19	875	125	10.08	2.26	4.45
13	136.19	850	150	10.08	2.21	4.26
14	136.26	850	150	9.65	2.37	4.25
15	136.26	850	150	9.65	2.41	3.93
16	136.26	850	150	9.65	2.27	4.39
17	158.36	850	150	9.95	2.24	4.57
18	158.36	850	150	9.95	2.19	4.44
19	158.36	850	150	9.95	2.19	4.32
20	158.36	850	150	9.95	2.19	4.23
21	158.36	850	150	9.95	2.19	4.50
22	158.51	900	100	10.34	2.69	4.46

TABLE 5.2 - Continued.

Peak No.	T _c (°C)	V _{Ar} (μl)	V _{H2} (μl)	F _c (cm ³ /min)	F _c [(t _M) _{H2} -(t _M) _{Ar}] (cm ³)	F _c [(μ ₁) _{H2} -(μ ₁) _{Ar}] (cm ³)
23	158.51	850	150	10.34	2.48	4.47
24	158.51	850	150	10.34	2.48	4.34
25	178.43	850	150	9.89	2.23	4.68
26	178.43	850	150	9.89	2.27	4.25
27	178.43	850	150	9.89	2.32	4.43
28	178.43	850	150	9.89	2.37	4.46
29	177.87	900	100	10.48	2.73	4.67
30	177.87	900	100	10.48	2.94	4.77
31	177.87	900	100	10.48	2.94	4.61
32	177.87	875	125	10.48	2.52	5.00
33	177.87	875	125	10.48	2.52	5.13
34	177.87	850	150	10.48	2.36	4.46
35	196.38	900	100	10.79	2.32	4.29
36	196.38	875	125	10.79	2.27	3.94
37	196.38	875	125	10.79	2.16	3.96
38	196.38	850	150	10.79	2.27	4.00
39	196.38	850	150	10.79	2.27	3.89
40	217.33	850	150	11.20	2.69	4.32
41	217.33	850	150	11.20	2.58	4.88
42	217.33	850	150	11.20	2.58	4.66
43	217.72	900	100	11.11	2.95	4.37
44	217.72	900	100	11.11	2.95	4.94

TABLE 5.2 - Continued.

Peak No.	T _c (°C)	V _{Ar} (μl)	V _{H2} (μl)	F _c (cm ³ /min)	F _c [(t _M) _{H2} -(t _M) _{Ar}] (cm ³)	F _c [(μ ₁) _{H2} -(μ ₁) (cm ³)
45	217.72	875	125	11.11	2.78	4.25
46	217.72	875	125	11.11	2.78	4.18
47	235.63	850	150	11.43	2.57	4.56
48	235.63	850	150	11.43	2.63	4.53
49	236.53	900	100	11.46	2.87	5.38
50	236.53	900	100	11.46	2.87	5.02
51	236.53	900	100	11.46	2.92	5.09
52	236.53	875	125	11.46	2.87	4.49
53	236.53	875	125	11.46	2.75	4.49
54	236.53	850	150	11.46	2.69	4.41
55	236.53	850	150	11.46	2.58	4.57

TABLE 5.3 - Average Retention Volumes and First Moments of Reversible Adsorption of Hydrogen

T_c (°C)	V_{Ar} ($\mu\ell$)	V_{H_2} ($\mu\ell$)	$F_c[(t_M)_{H_2} - (t_M)_{Ar}]$ (cm^3)	$F_c[(\mu_1)_{H_2} - (\mu_1)_{Ar}]$ (cm^3)
95.74	900	100	2.00	3.66
116.16	900	100	2.04	4.07
116.16	875	125	2.10	4.18
136.19	875	125	2.24	4.51
136.19	850	150	2.21	4.26
136.26	850	150	2.35	4.19
158.36	850	150	2.20	4.41
158.51	900	100	2.69	4.46
158.51	850	150	2.48	4.41
178.43	850	150	2.30	4.46
177.87	900	100	2.87	4.68
177.87	875	125	2.52	5.07
177.87	850	150	2.36	4.46
196.38	900	100	2.32	4.29
196.38	875	125	2.22	3.95
196.38	850	150	2.27	3.95
217.33	850	150	2.58	4.77
217.72	900	100	2.95	4.66
217.72	875	125	2.78	4.22
235.63	850	150	2.60	4.55
236.53	900	100	2.89	5.16
236.53	875	125	2.81	4.49
236.53	850	150	2.64	4.49

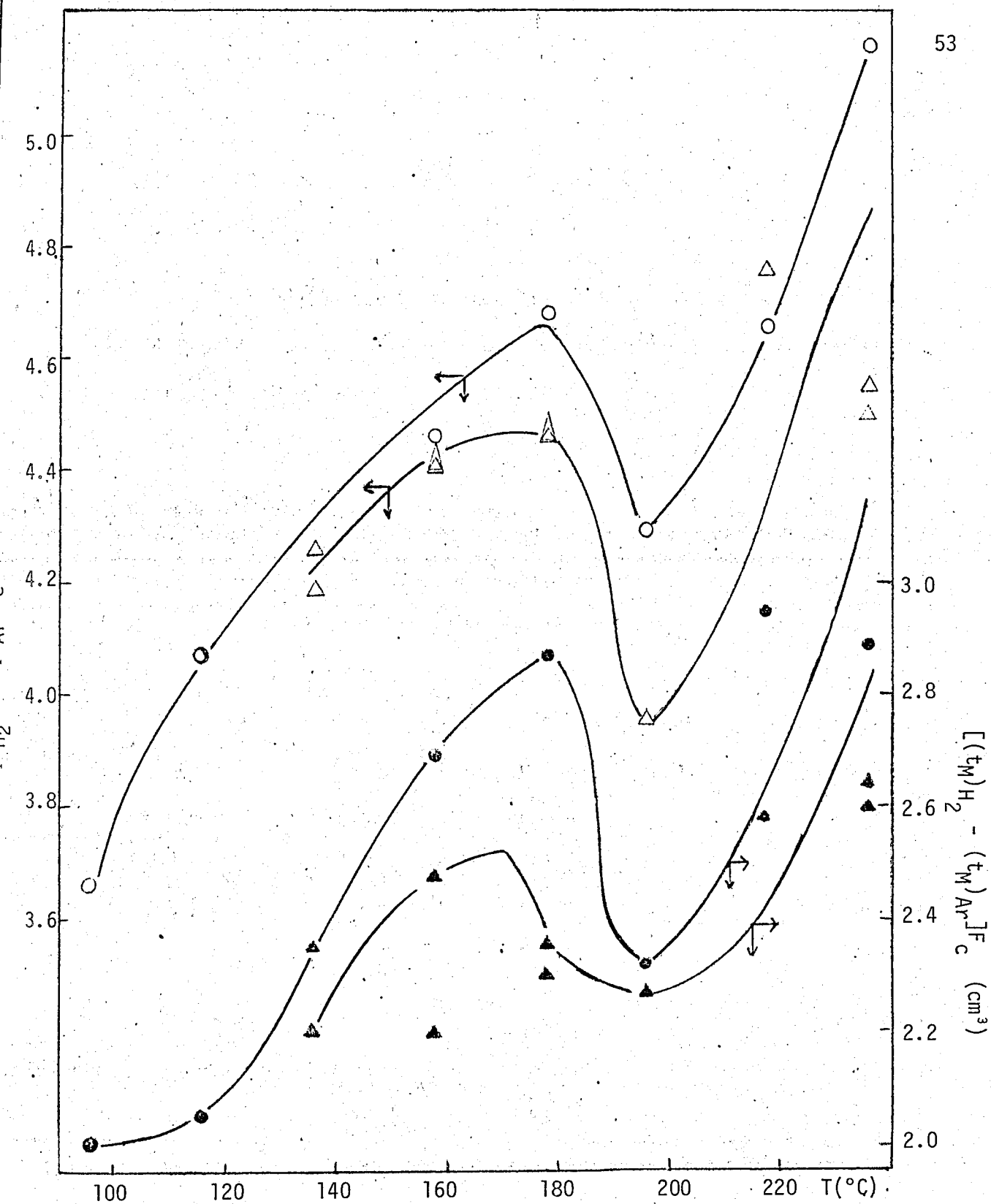


Figure 5.2 - Reversible retention of hydrogen.

Δ 100 μl Hydrogen/900 μl Argon

$\circ$ 150 μl Hydrogen/900 μl Argon

$\blacktriangle$ 100 μl Hydrogen/900 μl Argon

$\bullet$ 150 μl Hydrogen/900 μl Argon

5.3 ADSORPTION ISOTHERMS AND THE HEAT OF ADSORPTION FOR HYDROGEN

Adsorption isotherms for hydrogen are evaluated as described in Section 4.4.3. Data on the chromatographic peaks evaluated are tabulated in Appendix III. Adsorption isotherm data are presented in Table 5.4 and plotted in Figure 5.3. The anomaly at 196°C which was pointed out in relation to Figure 5.1 and Figure 5.2 is again observed in the adsorption isotherms of Figure 5.3. The isosteres are obtained from these isotherms for constant values of "moles adsorbed", namely for 12×10^{-7} , 15×10^{-7} , 18×10^{-7} gmole/g catalyst. The data used for constructing the isosteres are presented in Table 5.5 and are plotted in Figure 5.4. From the slope of these isosteres, heats of adsorption are calculated at constant surface coverage, assuming that heat of adsorption in the temperature range of 136°C to 236°C is constant at an average value. The slope of the isostere is calculated using the method of least squares. The heats of adsorption are tabulated in Table 5.6.

TABLE 5.4 - Adsorption Isotherms for Hydrogen (Sample composition = 150 μLH_2 /850 μLAr)

Partial Pressure p(mm Hg)	Moles of Hydrogen Adsorbed per Gram of Catalyst					
	136.26°C Peak No.14	158.36°C Peak No.19	177.87°C Peak No.34	196.38°C Peak No.38	217.33°K Peak No.42	236.53°C Peak No.55
0	0	0	0	0	0	0
2	4.00×10^{-7}	4.18×10^{-7}	3.93×10^{-7}	3.60×10^{-7}	3.78×10^{-7}	3.71×10^{-7}
4	6.34×10^{-7}	6.32×10^{-7}	6.19×10^{-7}	5.58×10^{-7}	5.87×10^{-7}	5.63×10^{-7}
6	8.15×10^{-7}	8.00×10^{-7}	7.64×10^{-7}	7.15×10^{-7}	7.53×10^{-7}	7.17×10^{-7}
10	11.08×10^{-7}	10.81×10^{-7}	10.54×10^{-7}	9.76×10^{-7}	10.26×10^{-7}	9.74×10^{-7}
14	13.53×10^{-7}	13.17×10^{-7}	12.99×10^{-7}	12.01×10^{-7}	12.58×10^{-7}	11.91×10^{-7}
22	17.69×10^{-7}	17.17×10^{-7}	17.15×10^{-7}	15.73×10^{-7}	16.44×10^{-7}	15.59×10^{-7}
30	20.97×10^{-7}		20.41×10^{-7}	18.74×10^{-7}	19.56×10^{-7}	18.44×10^{-7}

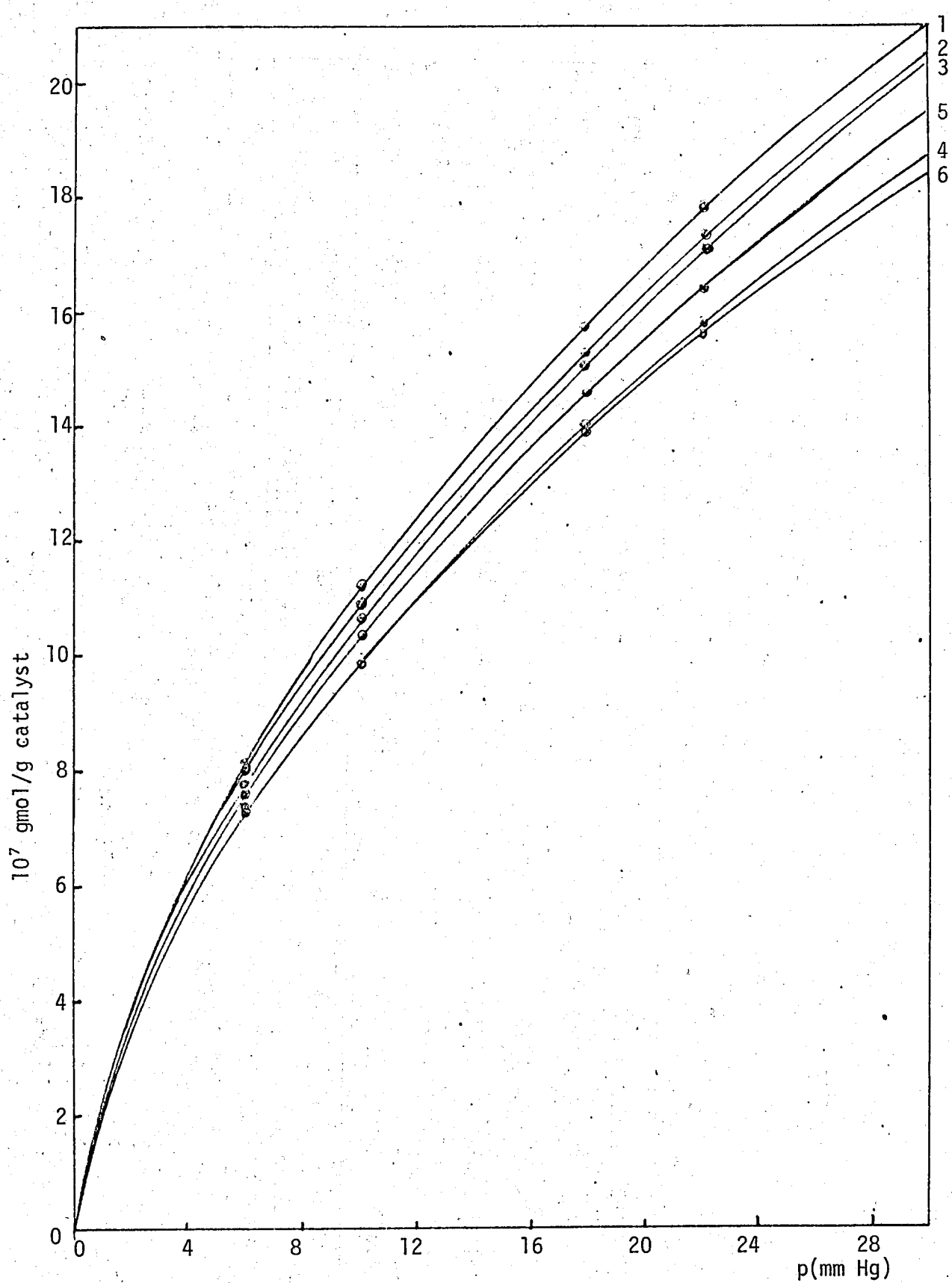


Figure 5.3 - Adsorption isotherm for hydrogen.

- | | |
|-------------|-------------|
| 1. 136.26°C | 4. 196.38°C |
| 2. 158.36°C | 5. 217.33°C |
| 3. 177.87°C | 6. 236.53°C |

TABLE 5.5 - Adsorption Isotheres for Hydrogen

Peak No.	T (°C)	T (°K)	1/Tx10 ³ (°K ⁻¹)	(At 12x10 ⁻⁷ gmol/g cat)		(At 15x10 ⁻⁷ gmol/g cat)		(At 18x10 ⁻⁷ gmol/g cat)	
				p(mm Hg)	ln p	p(mm Hg)	ln p	p(mm Hg)	ln p
14	136.26	409.41	2.443	11.4	2.434	16.6	2.809	22.6	3.118
19	158.36	431.51	2.317	11.9	2.477	17.5	2.862	23.7	3.165
34	177.87	451.02	2.217	12.4	2.518	17.9	2.885	24.2	3.186
38	196.38	469.53	2.130	13.7	2.617	20.1	3.001	27.9	3.329
42	217.33	490.48	2.039	12.8	2.549	18.7	2.929	25.7	3.246
55	236.53	509.68	1.962	14.2	2.653	20.6	3.025	28.7	3.357

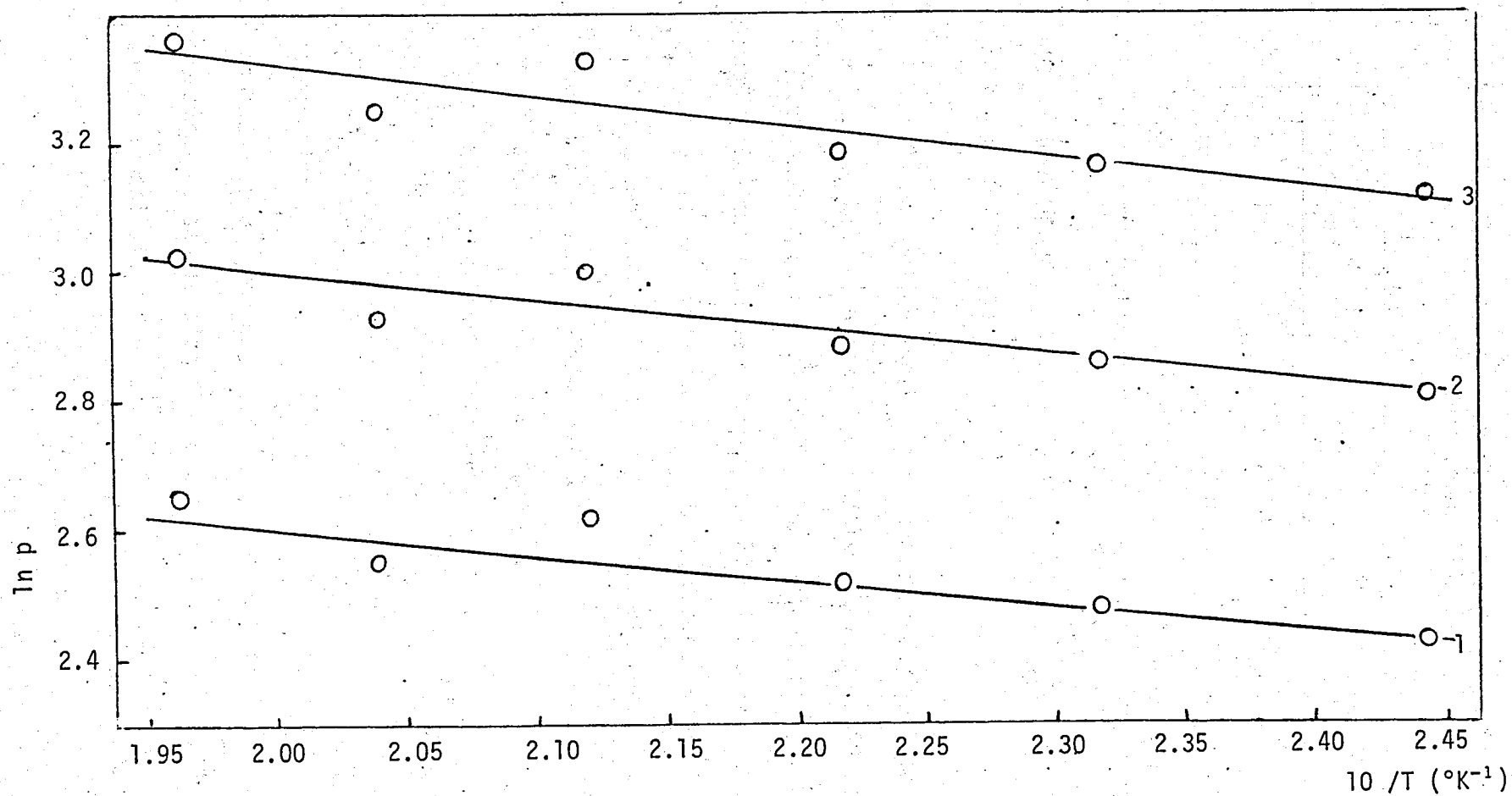


Figure 5.4 - Adsorption isosteres for hydrogen.

1. At 12×10^{-7} gmol/g cat
2. At 15×10^{-7} gmol/g cat
3. At 18×10^{-7} gmol/g cat.

TABLE 5.6 - Heats of Adsorption of Hydrogen in the Temperature Range 136.26-236.53°C

Moles adsorbed per gram of catalyst.	Q_{ads} (kcal/gmol)	Q_{ads} (J/gmol)
12×10^{-7}	0.84	3.51
15×10^{-7}	0.83	3.47
18×10^{-7}	0.94	3.93

5.4 ADSORPTION ISOTHERMS AND HEATS OF ADSORPTION OF HYDROCARBONS

The adsorption isotherms of cyclohexane, methylcyclohexane, benzene and toluene over 0.3%wt Pt/Al₂O₃ have been investigated for the temperature range 190-236°C. For cyclohexane, the influence of sample size has also been determined. Figure 5.5 illustrates the effect of sample size of cyclohexane at 216.80°C pictorially. As sample size increases the fronts of the curves become steeper. The procedure by which $c(t)$ vs t data are obtained for constructing adsorption isotherms from these curves is also indicated on Figure 5.5 for one of the cyclohexane peaks. The adsorption isotherms of cyclohexane at 216.80°C for different sample sizes is shown on Figure 5.6. This study has shown that there is only a slight change in the adsorption isotherms when sample size is changed under the experimental conditions used. Moles adsorbed per gram of catalyst increases slightly only at high partial pressures as sample size is increased, while most of the isotherms generally coincide with each other. After showing that the effect

of sample size is not significant, for cyclohexane and for the other hydrocarbons studied, adsorption isotherms at different temperatures were investigated using single sample size. The sample sizes used for cyclohexane and methylcyclohexane were chosen large, in order to reach higher partial pressures of the adsorbate. The sample sizes used for benzene and toluene were chosen small to avoid too much tailing of the peaks obtained. Sample chromatograms of methylcyclohexane, benzene and toluene are reproduced in Appendix V.

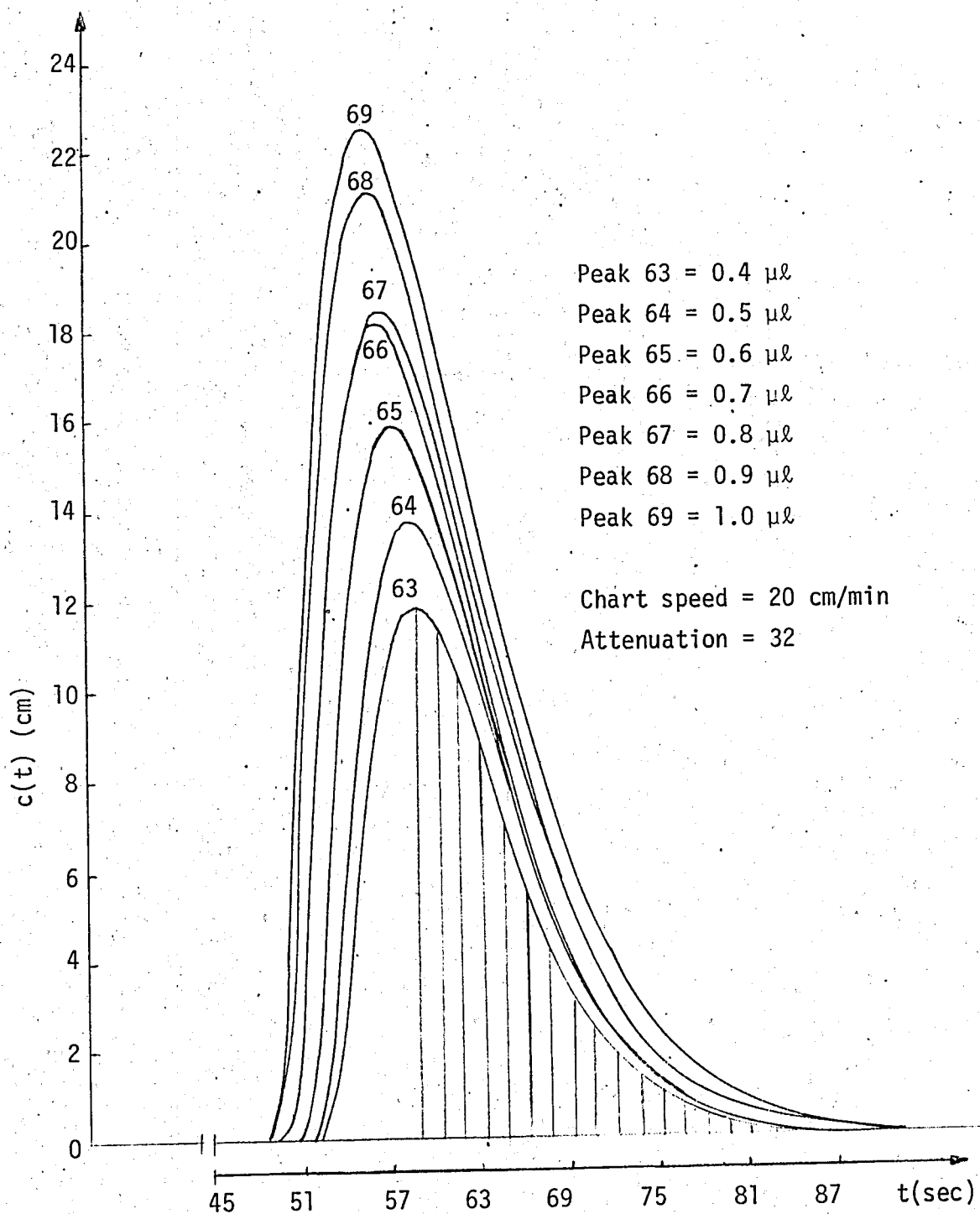


Figure 5.5 - Effect of sample size on peak shape.
(cyclohexane; $T = 216.80^\circ\text{C}$)

TABLE 5.7 - Adsorption Isotherms for Cyclohexane at 216.80°C

p(mm Hg)	Moles of Cyclohexane Adsorbed per gram of Catalyst								
	$V_{CH}=0.2\mu\ell$	$V_{CH}=0.3\mu\ell$	$V_{CH}=0.4\mu\ell$	$V_{CH}=0.5\mu\ell$	$V_{CH}=0.6\mu\ell$	$V_{CH}=0.7\mu\ell$	$V_{CH}=0.8\mu\ell$	$V_{CH}=0.9\mu\ell$	$V_{CH}=1.0\mu\ell$
0	0	0	0	0	0	0	0	0	0
6	9.13×10^{-7}	8.87×10^{-7}	9.16×10^{-7}	9.33×10^{-7}	9.24×10^{-7}	9.40×10^{-7}	9.71×10^{-7}	9.74×10^{-7}	9.97×10^{-7}
14	19.49×10^{-7}	19.23×10^{-7}	19.87×10^{-7}	20.18×10^{-7}	20.26×10^{-7}	20.41×10^{-7}	21.01×10^{-7}	21.04×10^{-7}	21.54×10^{-7}
22	-	28.63×10^{-7}	29.79×10^{-7}	30.34×10^{-7}	30.43×10^{-7}	30.73×10^{-7}	31.56×10^{-7}	31.58×10^{-7}	32.79×10^{-7}
30	-	-	39.05×10^{-7}	39.92×10^{-7}	40.10×10^{-7}	40.55×10^{-7}	41.59×10^{-7}	41.61×10^{-7}	42.49×10^{-7}
38	-	-	-	48.90×10^{-7}	49.31×10^{-7}	49.95×10^{-7}	51.15×10^{-7}	51.17×10^{-7}	52.22×10^{-7}
46	-	-	-	-	-	58.89×10^{-7}	60.33×10^{-7}	60.36×10^{-7}	61.55×10^{-7}
54	-	-	-	-	-	-	69.05×10^{-7}	69.09×10^{-7}	70.49×10^{-7}
62	-	-	-	-	-	-	-	-	79.02×10^{-7}

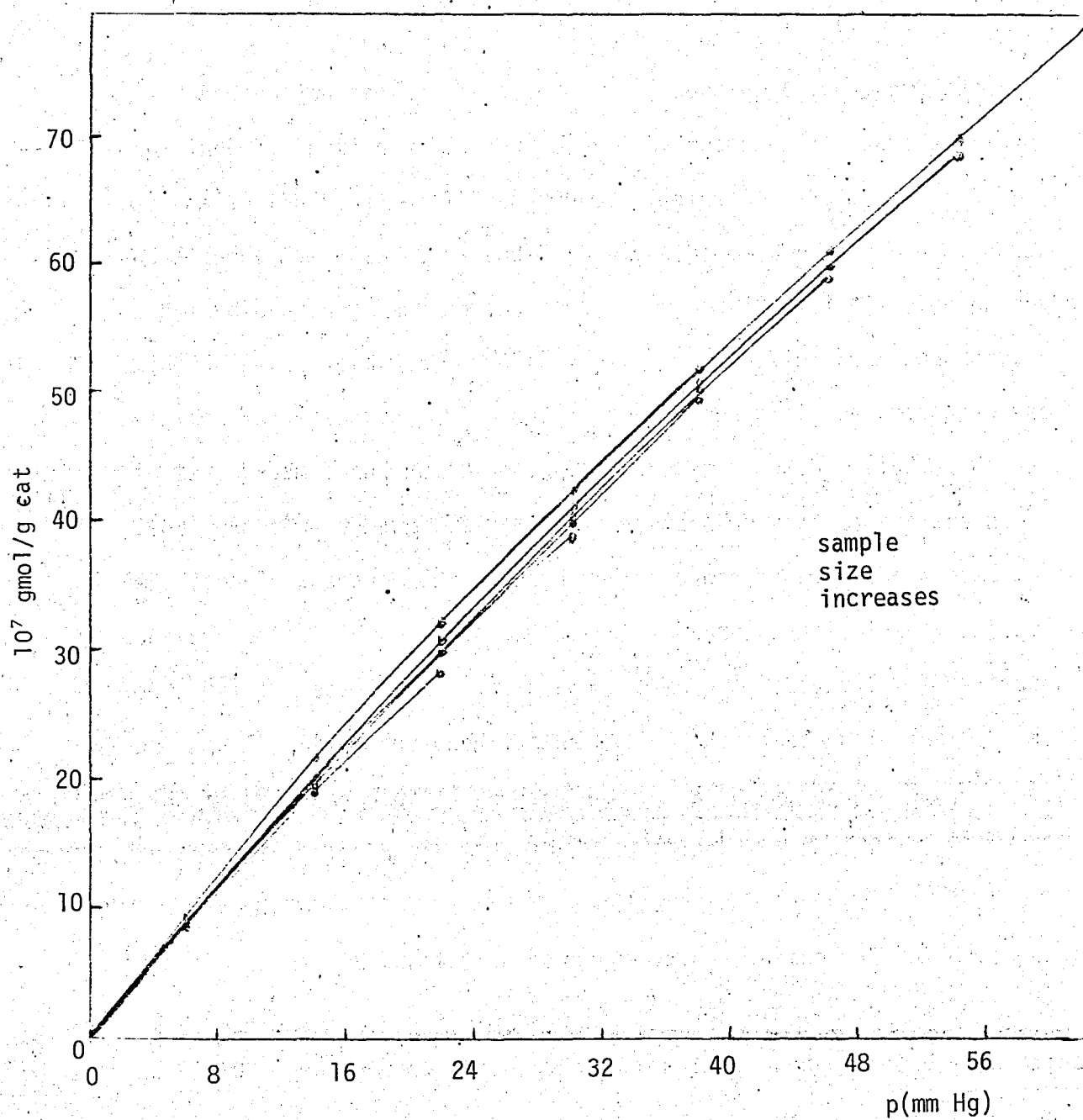


Figure 5.6 - Adsorption isotherms of cyclohexane at 216.80°C for different sample sizes.

Adsorption isotherms are plotted according to the procedure explained in Section 4.4.3 for several hydrocarbons at several temperatures in the range of 185 to 235°C. Tables 5.8, 5.10, 5.12, 5.14 and Figures 5.7, 5.9, 5.11 and 5.13 give the isotherms for cyclohexane, methylcyclohexane, benzene and toluene respectively. All elution peaks being unsymmetrical with a sharp front and a tailing rear boundary, resulted in isotherms, which curve towards the pressure axis as investigated by James and Phillips (1954), Cremer and Huber (1961), Conder (1968), Hopfe and Marx (1972). This curvature of isotherms are not very clearly observed for benzene and toluene, because the isotherms are constructed for low partial pressures of benzene and toluene, and at such low partial pressures the isotherms are much less curved. The isosteres obtained from the mentioned isotherms are tabulated in Tables 5.9, 5.11, 5.13 and 5.15 and plotted in Figures 5.8, 5.10, 5.12, and 5.14 for cyclohexane, methylcyclohexane, benzene and toluene respectively.

From Figure 5.8, it can be concluded that the heats of adsorption of cyclohexane are constant at average values in the 190-236°C temperature range at all surface coverages. For surface coverages of 10×10^{-7} gmol/g cat and 20×10^{-7} gmol/g cat, the data are less scattered compared with higher surface coverages. The slopes of the isosteres were calculated using method of least squares and the heats of adsorption obtained at different values of the surface coverage are tabulated in Table 5.16. The heats of adsorption obtained for cyclohexane from adsorption isotherms are found to be higher than the values obtained in previous studies on the same catalyst (Onsan, 1979; Beler, 1981), which were calculated using infinite retention time data.

For methylcyclohexane, the isosteres of Figure 5.10 and the heats of adsorption calculated at different surface coverages as shown in Table 5.16 cover the temperature range between 187-239°C. Within this temperature range, the heat of adsorption values obtained are constant at average values. Again, these values are also somewhat higher than the values obtained in previous studies using infinite retention time data (Onsan, 1979; Beler, 1981). Moreover they are quite close to the heats of adsorption obtained for cyclohexane.

Heats of adsorption of benzene and toluene over $\text{Pt/Al}_2\text{O}_3$ are found to be constant at average values in the temperature ranges 190-235°C and 196-235°C respectively and are given in Table 5.16. The heats of adsorption of these aromatics are higher than those of the cyclic compounds studied, and it has been reported in the literature that the heats of adsorption for aromatics increase with increasing carbon number (Choudhary and Menon, 1976).

TABLE 5.8 - Adsorption Isotherms for Cyclohexane

Partial Pressure p(mm Hg)	Moles of Cyclohexane Adsorbed per gram of Catalyst					
	189.73°C Peak No.70	200.05°C Peak No.71	209.20°C Peak No.72	216.80°C Peak No.67	228.50°C Peak No.73	236.34°C Peak No.74
0	0	0	0	0	0	0
6	15.44×10^{-7}	12.60×10^{-7}	11.60×10^{-7}	9.71×10^{-7}	8.37×10^{-7}	7.88×10^{-7}
14	33.84×10^{-7}	27.67×10^{-7}	25.40×10^{-7}	21.01×10^{-7}	18.16×10^{-7}	17.13×10^{-7}
22	51.28×10^{-7}	41.76×10^{-7}	38.30×10^{-7}	31.56×10^{-7}	27.31×10^{-7}	25.82×10^{-7}
30	67.72×10^{-7}	55.05×10^{-7}	50.54×10^{-7}	41.59×10^{-7}	36.01×10^{-7}	34.10×10^{-7}
38	83.40×10^{-7}	67.66×10^{-7}	62.16×10^{-7}	51.15×10^{-7}	44.26×10^{-7}	41.94×10^{-7}
46	-	-	73.19×10^{-7}	60.33×10^{-7}	52.04×10^{-7}	49.36×10^{-7}
54	-	-	-	69.06×10^{-7}	-	56.49×10^{-7}

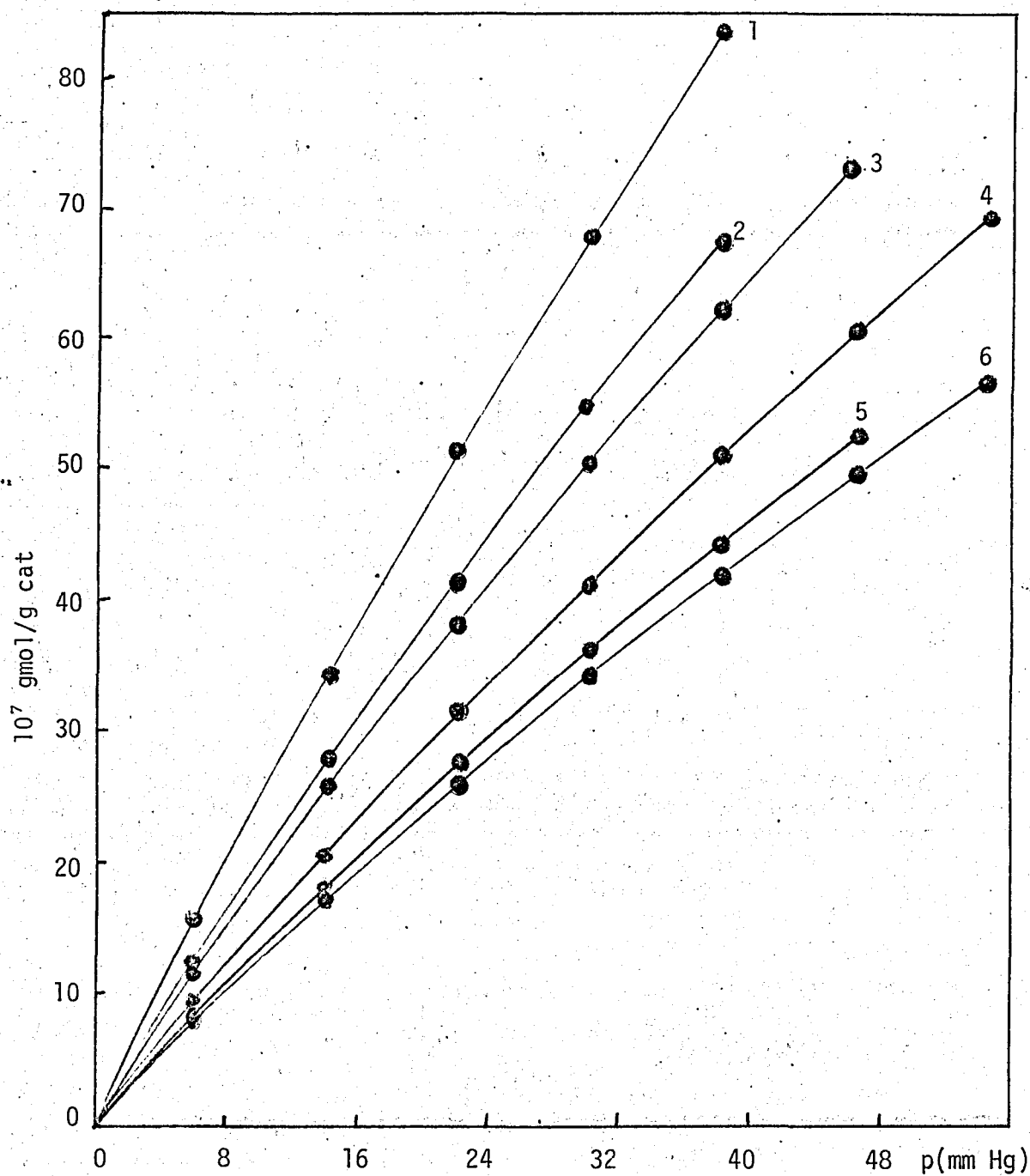


Figure 5.7 - Adsorption isotherms for cyclohexane.

1. 189.73°C
2. 200.05°C
3. 209.20°C
4. 216.80°C
5. 228.50°C
6. 236.34°C

TABLE 5.9 - Adsorption Isotherms for Cyclohexane

Peak No.	T(°C)	$10^3/T(^{\circ}\text{K}^{-1})$	(At $10 \times 10^{-7} \text{gmol/g cat}$)		(At $20 \times 10^{-7} \text{gmol/g cat}$)		(At $30 \times 10^{-7} \text{gmol/g cat}$)		(At $40 \times 10^{-7} \text{gmol/g cat}$)		(At $50 \times 10^{-7} \text{gmol/g cat}$)	
			p(mm Hg)	ln p	p(mm Hg)	ln p	p(mm Hg)	ln p	p(mm Hg)	ln p	p(mm Hg)	ln p
70	189.73	2.160	4.0	1.386	8.3	2.116	13.0	2.565	17.5	2.862	22.1	3.096
71	200.05	2.113	4.9	1.589	9.9	2.293	15.4	2.734	21.4	3.063	27.2	3.303
72	209.20	2.073	5.5	1.705	11.3	2.425	17.2	2.845	23.6	3.161	30.0	3.401
67	216.80	2.041	6.1	1.808	13.1	2.573	20.9	3.040	29.2	3.374	37.6	3.635
73	228.50	1.993	7.3	1.988	15.8	2.760	24.7	3.207	34.0	3.526	44.0	3.784
74	236.34	1.962	8.3	2.116	17.3	2.851	26.4	3.273	36.2	3.589	47.2	3.854

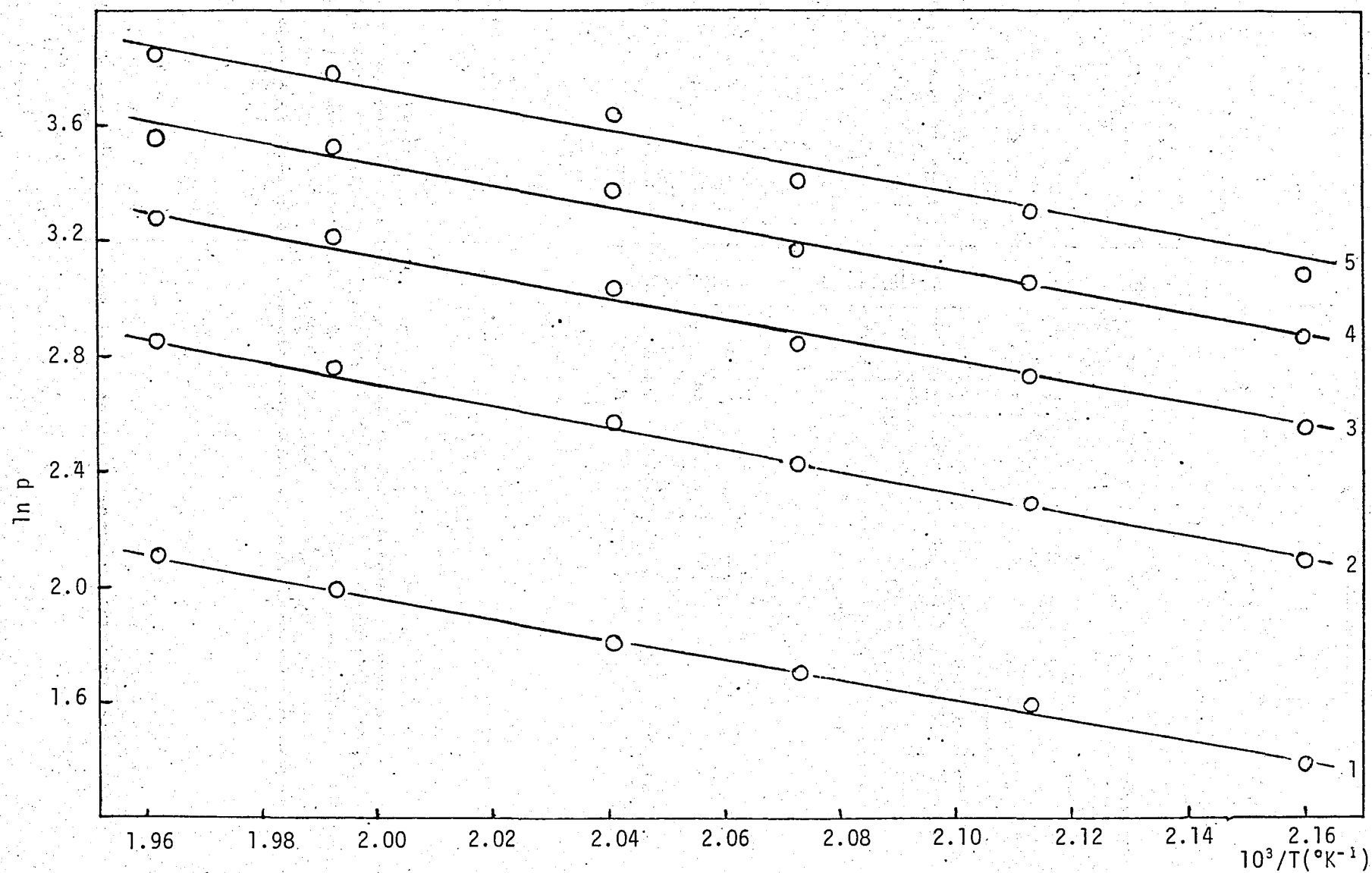


Figure 5.8 - Adsorption isosteres for cyclohexane.

- | | |
|--------------------------------------|--------------------------------------|
| 1. At 10×10^{-7} gmol/g cat | 4. At 40×10^{-7} gmol/g cat |
| 2. At 20×10^{-7} gmol/g cat | 5. At 50×10^{-7} gmol/g cat |
| 3. At 30×10^{-7} gmol/g cat | |

TABLE 5.10 - Adsorption Isotherms for Methylcyclohexane

Partial Pressure p(mm Hg)	Moles of Methylcyclohexane Adsorbed per gram of Catalyst					
	186.92°C Peak No. 75	191.65°C Peak No. 76	196.73°C Peak No. 77	199.43°C Peak No. 78	206.57°C Peak No. 79	208.22°C Peak No. 80
0	0	0	0	0	0	0
4	20.06×10^{-7}	17.85×10^{-7}	17.29×10^{-7}	16.17×10^{-7}	14.49×10^{-7}	14.04×10^{-7}
8	37.78×10^{-7}	33.65×10^{-7}	32.52×10^{-7}	30.39×10^{-7}	27.24×10^{-7}	26.53×10^{-7}
16	70.14×10^{-7}	62.69×10^{-7}	60.53×10^{-7}	56.58×10^{-7}	50.68×10^{-7}	49.50×10^{-7}
24	-	89.37×10^{-7}	86.21×10^{-7}	80.76×10^{-7}	72.32×10^{-7}	70.85×10^{-7}
28	-	-	-	-	82.55×10^{-7}	80.97×10^{-7}

TABLE 5.10 - Continued.

Partial Pressure p(mm Hg)	Moles of Methylcyclohexane Adsorbed per gram of Catalyst					
	216.99°C Peak No. 81	218.01°C Peak No. 82	226.84°C Peak No. 83	227.73°C Peak No. 84	236.78°C Peak No. 85	238.54°C Peak No. 86
0	0	0	0	0	0	0
4	12.28×10^{-7}	11.87×10^{-7}	10.75×10^{-7}	10.57×10^{-7}	9.71×10^{-7}	9.65×10^{-7}
8	23.02×10^{-7}	22.37×10^{-7}	20.19×10^{-7}	19.78×10^{-7}	18.28×10^{-7}	18.07×10^{-7}
16	43.01×10^{-7}	41.87×10^{-7}	37.71×10^{-7}	36.95×10^{-7}	34.12×10^{-7}	33.80×10^{-7}
24	61.65×10^{-7}	60.03×10^{-7}	54.13×10^{-7}	52.96×10^{-7}	49.05×10^{-7}	48.59×10^{-7}
32	79.10×10^{-7}	77.17×10^{-7}	69.98×10^{-7}	68.06×10^{-7}	63.27×10^{-7}	62.57×10^{-7}
40	-	-	-	-	76.75×10^{-7}	75.83×10^{-7}

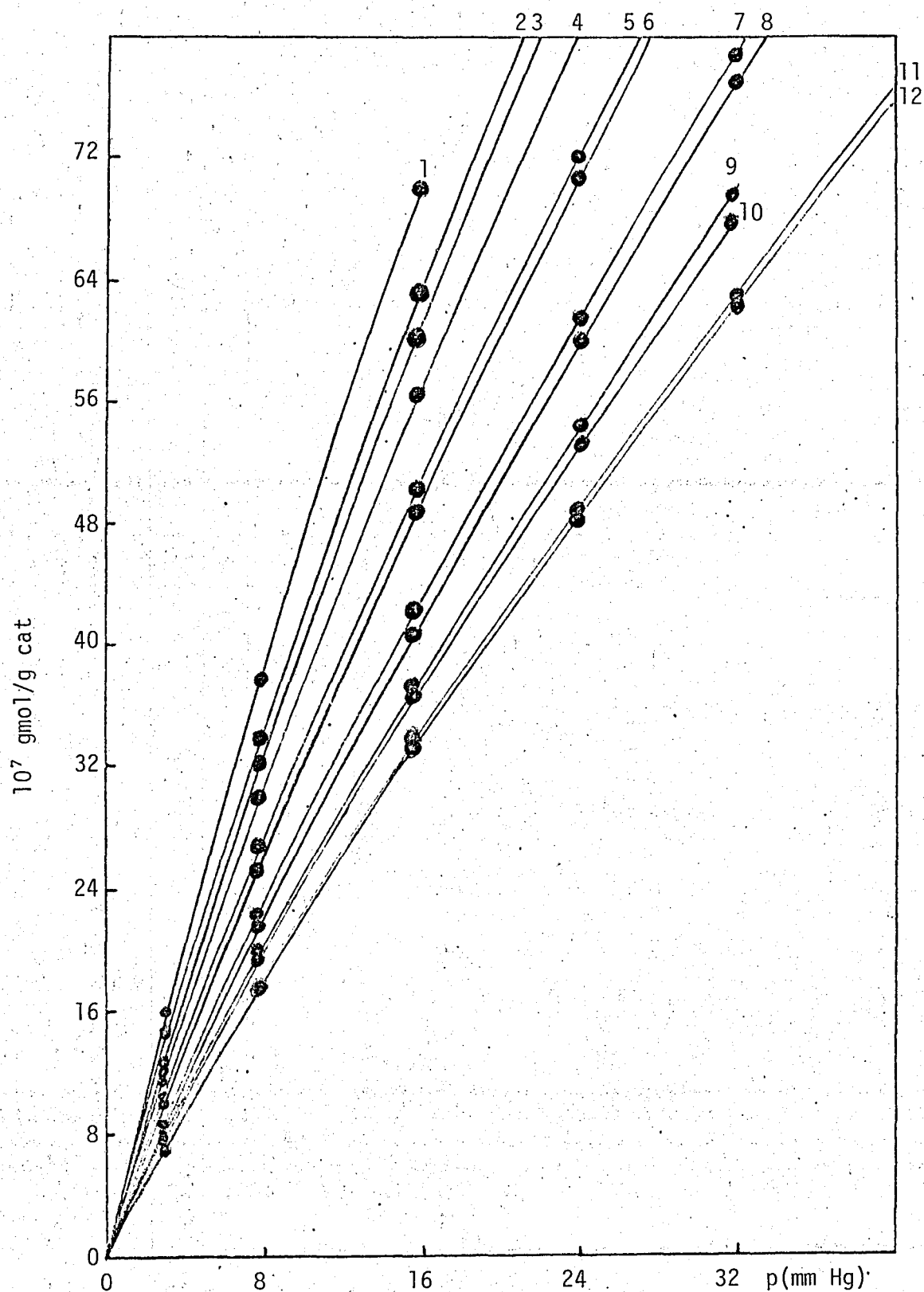


Figure 5.9 - Adsorption isotherms for methylcyclohexane.

1. 186.92°C	5. 206.57°C	9. 226.84°C
2. 191.65°C	6. 208.22°C	10. 227.73°C
3. 196.73°C	7. 216.99°C	11. 236.78°C
4. 199.43°C	8. 218.01°C	

TABLE 5.11 - Adsorption Isosteres for Methylcyclohexane.

Peak No.	T(°C)	$10^3/T(^{\circ}\text{K}^{-1})$	(At $30 \times 10^{-7} \text{ gmol/g cat}$)		(At $40 \times 10^{-7} \text{ gmol/g cat}$)		(At $50 \times 10^{-7} \text{ gmol/g cat}$)		(At $60 \times 10^{-7} \text{ gmol/g cat}$)		(At $70 \times 10^{-7} \text{ gmol/g cat}$)	
			p(mm Hg)	ln p	p(mm Hg)	ln p	p(mm Hg)	ln p	p(mm Hg)	ln p	p(mm Hg)	ln p
75	186.92	2.174	6.2	1.825	8.5	2.140	11.0	2.398	13.5	2.603	16.0	2.773
76	191.65	2.151	7.2	1.974	9.7	2.272	12.4	2.518	15.3	2.728	18.2	2.901
77	196.73	2.128	7.4	2.001	10.0	2.306	12.9	2.557	15.9	2.766	19.0	2.944
78	199.43	2.116	7.9	2.067	10.8	2.380	13.9	2.632	17.2	2.845	20.4	3.016
79	206.57	2.085	8.9	2.186	12.2	2.501	15.8	2.760	19.4	2.965	23.2	3.144
80	208.22	2.077	9.3	2.236	12.6	2.534	16.2	2.785	19.8	2.986	23.6	3.161
81	216.99	2.040	10.8	2.380	14.8	2.695	19.0	2.944	23.3	3.148	27.7	3.321
82	218.01	2.036	11.1	2.407	15.2	2.721	19.6	2.976	24.0	3.778	28.5	3.350
83	226.84	2.000	12.6	2.534	17.1	2.839	22.0	3.091	27.0	3.296	32.2	3.472
84	227.73	1.996	12.8	2.549	17.4	2.856	22.5	3.114	27.7	3.321	33.1	3.500
85	236.78	1.961	14.0	2.639	18.1	2.896	24.5	3.199	30.2	3.408	35.8	3.578
86	238.54	1.954	14.1	2.646	18.3	2.907	24.8	3.211	30.5	3.418	36.3	3.592

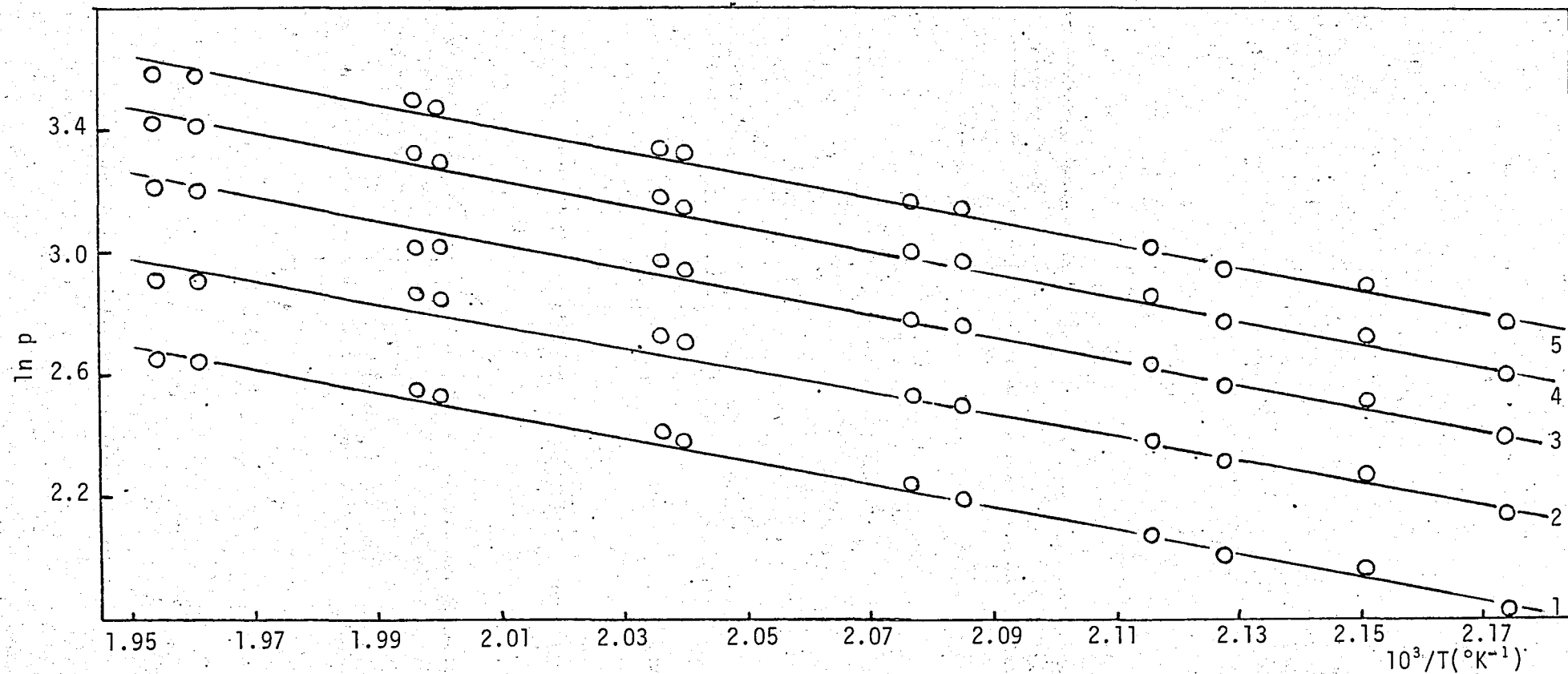


Figure 5.10 - Adsorption isosteres for methylcyclohexane.

1. At 30×10^{-7} g/mol/g cat
2. At 30×10^{-7} g/mol/g cat
3. At 50×10^{-7} g/mol/g cat
4. At 60×10^{-7} g/mol/g cat
5. At 70×10^{-7} g/mol/g cat

TABLE 5.12 - Adsorption Isotherms for Benzene

Partial Pressure p. (mm Hg)	Moles of Benzene Adsorbed per gram of Catalyst			
	190.05°C Peak No. 87	194.96°C Peak No. 88	199.62°C Peak No. 89	204.68°C Peak No. 90
0	0	0	0	0
0.3	4.20×10^{-7}	3.86×10^{-7}	3.07×10^{-7}	2.84×10^{-7}
0.7	9.22×10^{-7}	8.47×10^{-7}	6.81×10^{-7}	6.29×10^{-7}
1.1	13.94×10^{-7}	12.83×10^{-7}	10.38×10^{-7}	9.59×10^{-7}
1.5	18.48×10^{-7}	17.02×10^{-7}	13.82×10^{-7}	12.79×10^{-7}
1.9	-	-	17.16×10^{-7}	15.93×10^{-7}
2.3	-	-	-	18.98×10^{-7}

TABLE 5.12 - Continued.

Partial Pressure p(mm Hg)	Moles of Benzene Adsorbed per gram of Catalyst				
	208.91°C Peak No. 91	214.38°C Peak No. 92	222.62°C Peak No. 93	228.65°C Peak No. 94	235.32°C Peak No. 95
0	0	0	0	0	0
0.6	4.82×10^{-7}	4.16×10^{-7}	3.30×10^{-7}	2.89×10^{-7}	2.49×10^{-7}
1.4	10.52×10^{-7}	9.19×10^{-7}	7.30×10^{-7}	6.39×10^{-7}	5.49×10^{-7}
2.2	15.90×10^{-7}	13.98×10^{-7}	11.10×10^{-7}	9.78×10^{-7}	8.38×10^{-7}
3.0	-	18.62×10^{-7}	14.78×10^{-7}	13.06×10^{-7}	11.20×10^{-7}
3.8	-	-	18.36×10^{-7}	16.27×10^{-7}	13.94×10^{-7}
4.6	-	-	-	-	16.62×10^{-7}

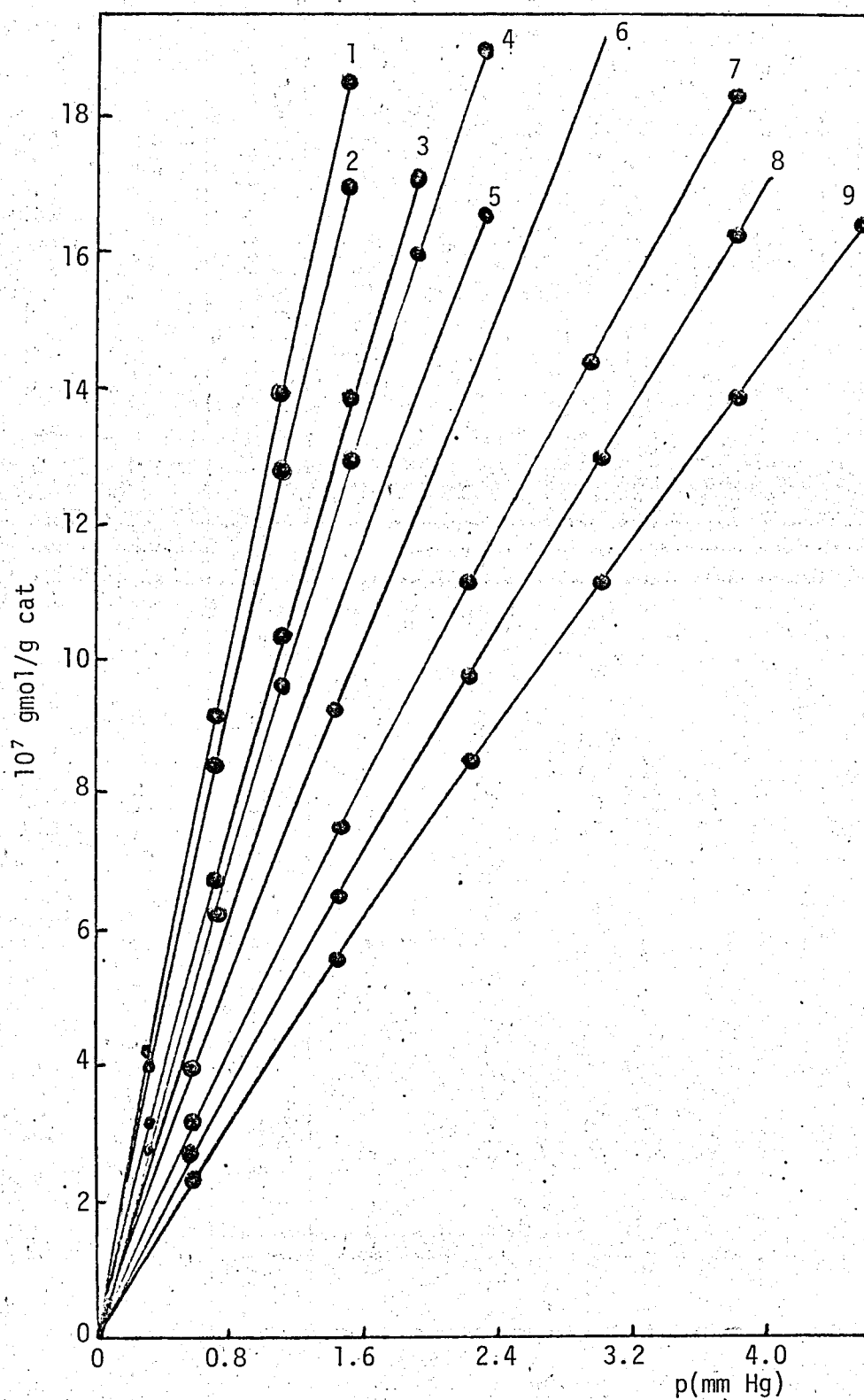


Figure 5.11 - Adsorption isotherms for benzene.

- | | |
|-------------|-------------|
| 1. 190.05°C | 6. 214.38°C |
| 2. 194.96°C | 7. 222.62°C |
| 3. 199.62°C | 8. 228.65°C |
| 4. 204.68°C | 9. 235.32°C |
| 5. 208.91°C | |

TABLE 5.13 - Adsorption Isotheres for Benzene

Peak No.	T (°C)	$10^3/T$ (°K ⁻¹)	(At 6×10^{-7} gmol/g cat) p(mmHg)	ln p	(At 10×10^{-7} gmol/g cat) p(mmHg)	ln p	(At 14×10^{-7} gmol/g cat) p(mmHg)	ln p	(At 18×10^{-7} gmol/g cat) p(mmHg)	ln p
87	190.05	2.159	0.44	-0.821	0.76	-0.274	1.10	0.095	1.46	0.378
88	194.96	2.136	0.49	-0.713	0.84	-0.174	1.21	0.191	1.60	0.470
89	199.62	2.115	0.61	-0.494	1.05	0.049	1.52	0.419	2.00	0.693
90	204.68	2.093	0.67	-0.400	1.15	0.140	1.65	0.501	2.18	0.779
91	208.91	2.074	0.77	-0.261	1.33	0.285	1.92	0.652	2.52	0.924
92	214.38	2.051	0.89	-0.117	1.53	0.425	2.20	0.788	2.89	1.061
93	222.62	2.017	1.14	0.131	1.96	0.673	2.82	1.037	3.71	1.311
94	228.65	1.993	1.31	0.270	2.25	0.811	3.24	1.176	4.25	1.447
95	235.32	1.967	1.54	0.432	2.66	0.978	3.84	1.345	5.03	1.615

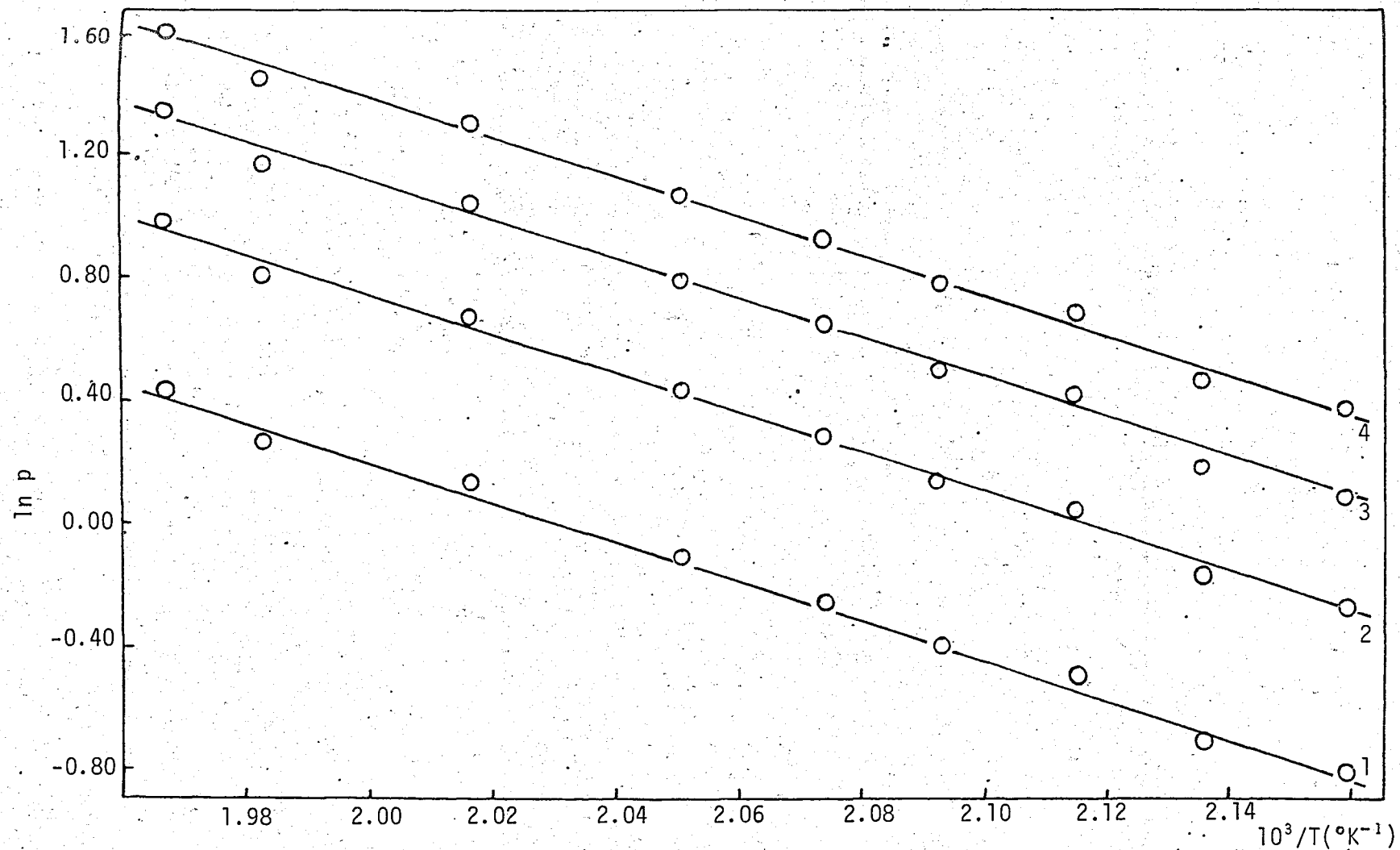


Figure 5.12 - Adsorption isosteres for benzene.

1. At 6×10^{-7} gmol/g cat
2. At 10×10^{-7} gmol/g cat
3. At 14×10^{-7} gmol/g cat
4. At 18×10^{-7} gmol/g cat

TABLE 5.14 - Adsorption Isotherms for Toluene

Partial Pressure p(mm Hg)	Moles of Toluene Adsorbed per gram of Catalyst					
	195.90°C Peak No. 96	204.32°C Peak No. 97	209.27°C Peak No. 98	215.12°C Peak No. 99	223.80°C Peak No. 100	235.35°C Peak No. 101
0	0	0	0	0	0	0
0.3	7.17×10^{-7}	6.44×10^{-7}	5.54×10^{-7}	4.69×10^{-7}	3.50×10^{-7}	2.55×10^{-7}
0.7	15.84×10^{-7}	14.04×10^{-7}	12.22×10^{-7}	10.46×10^{-7}	7.68×10^{-7}	5.67×10^{-7}
1.1	23.96×10^{-7}	21.12×10^{-7}	18.50×10^{-7}	15.94×10^{-7}	11.67×10^{-7}	8.67×10^{-7}
1.5	31.62×10^{-7}	27.80×10^{-7}	24.46×10^{-7}	21.18×10^{-7}	15.51×10^{-7}	11.59×10^{-7}
1.9	-	-	30.16×10^{-7}	-	-	14.43×10^{-7}
2.3	-	-	-	-	-	17.21×10^{-7}

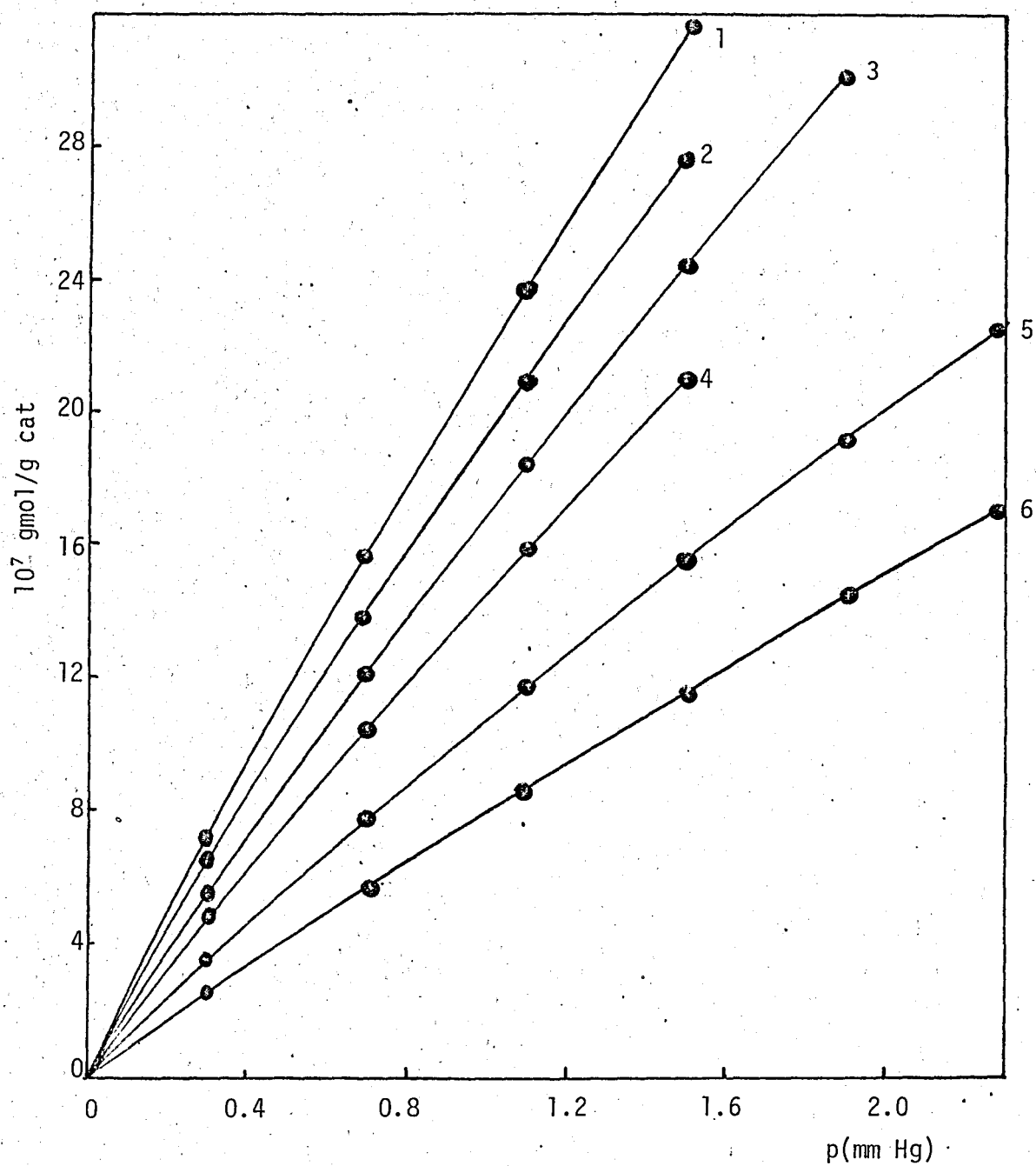


Figure 5.13 - Adsorption isotherms for toluene.

1. 195.90°C
2. 204.32°C
3. 209.27°C
4. 215.12°C
5. 223.80°C
6. 235.25°C

TABLE 5.15 - Adsorption Isotheres for Toluene

Peak No.	T (°C)	$10^3/T$ (°K ⁻¹)	(At 9×10^{-7} gmol/g cat) p(mmHg) ln p		(At 12×10^{-7} gmol/g cat) p(mmHg) ln p		(At 16×10^{-7} gmol/g cat) p(mm Hg) ln p		(At 20×10^{-7} gmol/g cat) p(mmHg) ln p	
96	195.90	2.132	0.34	-1.079	0.52	-0.654	0.71	-0.342	0.90	-0.105
97	204.32	2.094	0.36	-1.022	0.59	-0.528	0.81	-0.211	1.04	0.039
98	209.27	2.073	0.44	-0.821	0.68	-0.386	0.95	-0.051	1.19	0.174
99	215.12	2.048	0.54	-0.616	0.83	-0.186	1.13	0.122	1.42	0.351
100	223.80	2.012	0.74	-0.301	1.14	0.131	1.55	0.438	1.96	0.673
101	235.35	1.967	1.02	0.020	1.56	0.445	2.12	0.751	2.70	0.993

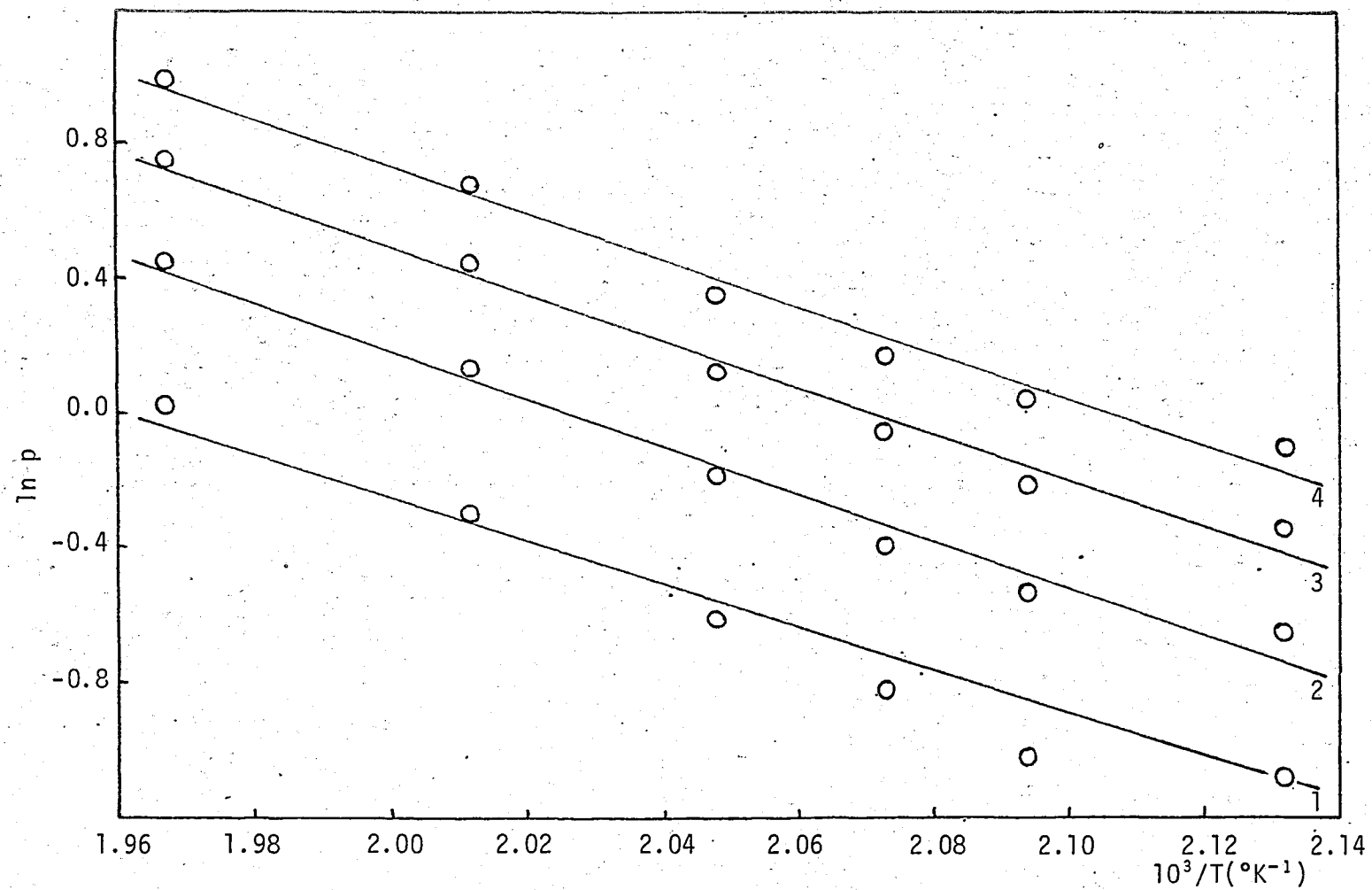


Figure 5.14 - Adsorption isosteres for toluene.

1. At 8×10^{-7} gmol/g cat
2. At 12×10^{-7} gmol/g cat
3. At 16×10^{-7} gmol/g cat
4. At 20×10^{-7} gmol/g cat

TABLE 5.16 - Heats of Adsorption of Hydrocarbons

Compound	Temperature Range (°C)	Moles adsorbed per, g catalyst	Q _{ads} (kcal/gmol)	Q _{ads} (J/gmol)
Cyclohexane	189.73-236.34	10x10 ⁻⁷	7.51	31.42
		20x10 ⁻⁷	7.12	29.79
		30x10 ⁻⁷	7.40	30.96
		40x10 ⁻⁷	7.53	31.51
		50x10 ⁻⁷	7.85	32.84
Methylcyclohexane	186.92-238.54	30x10 ⁻⁷	7.51	31.42
		40x10 ⁻⁷	7.18	30.04
		50x10 ⁻⁷	7.53	31.51
		60x10 ⁻⁷	7.52	31.46
		70x10 ⁻⁷	7.53	31.51
Benzene	190.05-235.32	6x10 ⁻⁷	13.41	54.98
		10x10 ⁻⁷	13.15	55.02
		14x10 ⁻⁷	13.12	54.89
		18x10 ⁻⁷	13.01	54.43
Toluene	195.90-235.35	8x10 ⁻⁷	14.24	59.58
		12x10 ⁻⁷	13.94	58.32
		16x10 ⁻⁷	13.78	57.66
		20x10 ⁻⁷	13.78	57.66

Cremer and Huber (1981) have calculated heats of adsorption of benzene and hexane on silica-gel, and SiO₂-Al₂O₃ using pulse technique in the temperature range of 300-550°C and they have observed that benzene is adsorbed more strongly than hexane. Similarly, Baumgarten, Weinstrauch and Höffkes (1977) have investigated adsorption isotherms of several

hydrocarbons (including cyclohexane and benzene) on γ -Alumina using the gas chromatographic method of Cremer and Huber (1961) in the temperature range of 200°C to 370°C, and their results show that the aromatics have much larger heats of adsorption than naphthenes.

Choudhary and Menon (1976), Önsan (1979), Beler (1981) have obtained heats of adsorption for the same hydrocarbons on $\text{Pt}/\text{Al}_2\text{O}_3$ using chromatographic methods. Choudhary and Menon (1976) have used small sample sizes ($0.1\ \mu\text{l}$ – $0.5\ \mu\text{l}$) and retention time data, estimating the heats of adsorption from the slopes of linear plots of $\ln V_R$ versus $1/T_c$; while Önsan (1979) and Beler (1981) have used the same estimation technique using infinite retention volumes. The heats of adsorption obtained by the different chromatographic methods mentioned are compared with the average results obtained in the present work in Table 5.17.

TABLE 5.17 - Comparison of Heats of Adsorption on $\text{Pt}/\text{Al}_2\text{O}_3$

Compound	Present Study 0.3%Pt- Al_2O_3 187–235°C	Belér (1981) 0.3%Pt/ Al_2O_3 185–235°C	Önsan (1979) 0.3%Pt/ Al_2O_3 195–240°C	Choudhary and Menon (1976) 0.6%Pt/ Al_2O_3 185–380°C
Cyclohexane	7.48*(31.30)**	4.68*(19.58)**	5.11*(21.38)**	-
Methycyclo- hexane	7.45*(31.17)**	4.93*(17.99)**	5.53*(23.14)**	-
Benzene	13.11*(54.85)**	-	10.58*(44.27)**	11.2*(46.86)**
Toluene	13.90*(58.16)**	-	11.65*(48.74)**	14.4*(60.25)**

* in kcal/gmol

** in J/gmol

As was mentioned in Chapter II, it may be possible to draw conclusions about the nature of the adsorbed state on the basis of several criteria, among which heats of adsorption and the temperature range involved are probably the most important. Physical adsorption is generally expected to occur only at temperatures close to the boiling point of the adsorbate and to involve heats of adsorption not greater than the heats of condensation. Chemisorption, on the other hand, occurs at higher temperatures with much higher heats of adsorption.

The boiling points and corresponding heats of vaporization of hydrogen and the hydrocarbons studied are listed together with the temperature range involved in the adsorption studies and the average heats of adsorption measured within this range in Table 5.18, from which one can obtain supporting evidence for the presence of chemisorption of hydrogen and hydrocarbons. This has also been demonstrated by the reversible adsorption studies of the foregoing sections. The heats of condensation were extrapolated to the operating temperatures using the Watson Equation (Reid, et.al., 1977):

$$(\Delta H_V)_2 = (\Delta H_V)_1 \left(\frac{1 - T_{r2}}{1 - T_{r1}} \right)^{0.38}$$

where ΔH_{V1} is the heats of vaporization at the boiling point and T_{r1} is the reduced temperature at the boiling point. This equation could be used for hydrocarbons. For hydrogen T_r is much larger than one and this equation is not valid for hydrogen.

TABLE 5.18 - Comparison of Heats of Adsorption and Heats of Condensation

Sample	T_b (°C)*	$(\Delta H_v)_{T_b}^*$ (kcal/gmol)	$(-\Delta H_v)_{T_b}^b$ (J/gmol)	$(-\Delta H_v)_T$ (kcal/gmol)	$(-\Delta H_v)_T$ (J/gmol)	Adsorption T(°C)	Q_{ads} (kcal/gmol)	Q_{ads} (J/gmol)
Cyclohexane	80.75	7.16	29.96	5.29(190°C)	22.13	190-236	7.48	31.30
Methylcyclohexane	100.95	7.44	31.13	5.71(200°C)	21.63	187-239	7.45	31.17
Benzene	80.15	7.35	30.75	5.34(200°C)	22.34	190-235	13.11	54.85
Toluene	110.65	7.93	33.18	6.08(215°C)	25.44	196-235	13.90	58.16
Hydrogen	-252.75	0.22	0.92			136-237	0.87	3.64

*from Reid, et.al. 1977

VI. CONCLUSIONS AND RECOMMENDATIONS

The conclusions that can be drawn from the literature survey and experimental studies are summarized below, together with the recommendations for further work at relevant points:

1. 0.233-0.319 cm³ of hydrogen is adsorbed irreversibly on 2.38 g of 0.3%wt Pt/Al₂O₃ within the temperature range 74-233°C. This amount can be determined from the areas of successive elution peaks.
2. The presence of a minimum and a maximum in the plot of retention volume versus temperature (or the first moment of a peak multiplied by carrier flowrate versus temperature) indicates that the reversible adsorption of hydrogen between 96-237°C is an activated process.
3. Elution peaks with tailing rear boundaries result in adsorption isotherms that are convex to the pressure axis (abscissa, in this case).
4. Adsorption isotherms may easily be obtained at different temperatures using elution peaks that are, in fact, $c(t)$ versus t profiles.

5. The heats of adsorption calculated using adsorption isotherms of hydrogen at different temperatures and constant surface coverage values are found to be constant at an average value of 0.87 kcal/gmol (3.69 kJ/kmol) within the temperature range 136-237°C.
6. The adsorption isosteres constructed from the adsorption isotherms of cyclohexane yield an average heat of adsorption of 7.48 kcal/gmol (31.30 kJ/kmol) between 190-236°C.
7. Similarly, the average heat of adsorption of methylcyclohexane between 187-239°C is 7.45 kcal/gmol (31.17 kJ/kmol); the average heat of adsorption of benzene between 190-235°C is 13.11 kcal/gmol (54.85 kJ/kmol) and that of toluene between 196-235°C is 13.90 kcal/gmol (58.16 kJ/kmol).
8. The heats of adsorption of the hydrocarbons are found to be larger than the corresponding heats of vaporization at the operating temperatures, which supports the conclusion that chemisorption is observed in each case.
9. The average heats of adsorption of the two aromatic compounds are larger than those of the two naphthenes used, which is in agreement with the statements in the literature.
10. In the case of hydrogen adsorption, a larger number of experiments with smaller temperature intervals are necessary, in the range 185-200°C to elucidate the nature of irreversible and reversible adsorption processes observed in the present study.

11. Other chromatographic techniques such as frontal analysis and temperature-programmed adsorption-desorption need to be used within the temperature range studied in order to verify the results obtained in the present work.

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APPENDICES

APPENDIX - I

TABLE A.1 - Peak Number - Area of the Peak Data for Irreversible Adsorption of Hydrogen

$T_c = 73.85^\circ\text{C}$		$T_c = 95.77^\circ\text{C}$		$T_c = 116.77^\circ\text{C}$	
Peak No.	Area	Peak No.	Area	Peak No.	Area
1	1.44×10^4	1	1.37×10^4	1	1.35×10^4
2	1.86×10^4	2	1.80×10^4	2	1.79×10^4
3	1.90×10^4	3	1.81×10^4	3	1.81×10^4
4	1.88×10^4	4	1.80×10^4	4	1.84×10^4
5	1.91×10^4	5	1.78×10^4	5	1.80×10^4
6	1.91×10^4	6	1.78×10^4	6	1.84×10^4
7	1.88×10^4	7	1.77×10^4	7	1.75×10^4
8	1.88×10^4	8	1.75×10^4	8	1.78×10^4
$T_c = 135.55^\circ\text{C}$		$T_c = 156.33^\circ\text{C}$		$T_c = 164.92^\circ\text{C}$	
Peak No.	Area	Peak No.	Area	Peak No.	Area
1	1.21×10^4	1	1.20×10^4	1	1.36×10^4
2	1.65×10^4	2	1.64×10^4	2	1.82×10^4
3	1.69×10^4	3	1.64×10^4	3	1.81×10^4
4	1.69×10^4	4	1.61×10^4	4	1.79×10^4
5	1.69×10^4	5	1.61×10^4	5	1.80×10^4
6	1.65×10^4	6	1.60×10^4	6	1.82×10^4
7	1.67×10^4	7	1.56×10^4	7	1.81×10^4
8	1.67×10^4	8	1.59×10^4	8	1.76×10^4

TABLE A.1 - Continued.

$T_c = 175.16^\circ\text{C}$		$T_c = 184.62^\circ\text{C}$		$T_c = 195.60^\circ\text{C}$	
Peak No.	Area	Peak No.	Area	Peak No.	Area
1	1.18×10^4	1	1.07×10^4	1	1.10×10^4
2	1.72×10^4	2	1.55×10^4	2	1.54×10^4
3	1.71×10^4	3	1.55×10^4	3	1.58×10^4
4	1.69×10^4	4	1.55×10^4	4	1.56×10^4
5	1.61×10^4	5	1.59×10^4	5	1.57×10^4
6	1.70×10^4	6	1.55×10^4	6	1.59×10^4
7	1.67×10^4	7	1.57×10^4	7	1.57×10^4
8	1.71×10^4	8	1.56×10^4	8	1.58×10^4
$T_c = 205.49^\circ\text{C}$		$T_c = 214.98^\circ\text{C}$		$T_c = 232.71^\circ\text{C}$	
Peak No.	Area	Peak No.	Area	Peak No.	Area
1	1.11×10^4	1	1.07×10^4	1	1.02×10^4
2	1.61×10^4	2	1.57×10^4	2	1.50×10^4
3	1.63×10^4	3	1.58×10^4	3	1.51×10^4
4	1.65×10^4	4	1.57×10^4	4	1.51×10^4
5	1.62×10^4	5	1.59×10^4	5	1.48×10^4
6	1.63×10^4	6	1.57×10^4	6	1.51×10^4
7	1.61×10^4	7	1.55×10^4	7	1.50×10^4
8	1.61×10^4	8	1.56×10^4	8	1.48×10^4

APPENDIX - II

TABLE A.2 - Retention Data for Reversible Adsorption of Hydrogen

Peak No.	T _c (°C)	T _f (°C)	F _f (cm ³ /min)	P _i (mm Hg)	P _o (mm Hg)	V _{Ar} (μℓ)	V _{H₂} (μℓ)	(t _M) _{Ar} (min)	(t _M) _{H₂} (min)	(μ ₁) _{Ar} (min)	(μ ₁) _{H₂} (min)
1	95.74	20.40	9.71	1281.5	751.5	900	100	0.61	0.81	0.591	1.008
2	95.74	20.40	9.71	1281.5	751.5	900	100	0.56	0.82	0.573	1.010
3	95.74	20.40	9.71	1281.5	751.5	900	100	0.61	0.83	0.594	0.986
4	116.16	21.10	9.84	1297.5	751.5	900	100	0.54	0.78	0.560	0.996
5	116.16	21.10	0.84	1297.5	751.5	900	100	0.55	0.75	0.539	1.003
6	116.16	21.10	9.84	1297.5	751.5	900	100	0.55	0.80	0.561	1.036
7	116.16	21.10	0.84	1297.5	751.5	875	125	0.55	0.72	0.524	0.965
8	116.16	21.10	9.84	1297.5	751.5	875	125	0.49	0.75	0.484	0.978
9	116.16	21.10	0.84	1297.5	751.5	875	125	0.50	0.76	0.503	1.002
10	116.16	21.10	9.84	1297.5	751.5	875	125	0.52	0.77	0.531	0.978
11	136.19	22.10	10.08	1337.2	755.2	875	125	0.48	0.70	0.477	0.940
12	136.19	22.10	10.08	1337.2	755.2	875	125	0.47	0.70	0.465	0.918
13	136.19	22.10	10.08	1337.2	755.2	850	150	0.45	0.68	0.434	0.867
14	136.26	22.50	9.65	1325.0	755.0	850	150	0.47	0.72	0.466	0.915
15	136.26	22.50	9.65	1325.0	755.0	850	150	0.48	0.73	0.465	0.881
16	136.26	22.50	9.65	1325.0	755.0	850	150	0.48	0.72	0.483	0.947

TABLE A.2 - Continued.

Peak No.	T _c (°C)	T _f (°C)	F _f (cm ³ /min)	P _i (mm Hg)	P _o (mm Hg)	V _{Ar} (μl)	V _{H₂} (μl)	(t _M) _{Ar} (min)	(t _M) _{H₂} (min)	(μ ₁) _{Ar} (min)	(μ ₁) _{H₂} (min)
17	158.36	22.70	10.49	1487.0	755.0	850	150	0.43	0.65	0.423	0.882
18	158.36	22.70	10.49	1487.0	755.0	850	150	0.43	0.65	0.405	0.851
19	158.36	22.70	10.49	1487.0	755.0	850	150	0.43	0.65	0.420	0.854
20	158.36	22.70	10.49	1487.0	755.0	850	150	0.43	0.65	0.424	0.849
21	158.36	22.70	10.49	1487.0	755.0	850	150	0.44	0.66	0.427	0.879
22	158.51	17.65	10.17	1390.2	756.2	900	100	0.48	0.74	0.506	0.937
23	158.51	17.65	10.17	1390.2	756.2	850	150	0.45	0.69	0.448	0.881
24	158.51	17.65	10.17	1390.2	756.2	850	150	0.44	0.68	0.422	0.842
25	178.43	22.20	9.97	1491.5	755.5	850	150	0.43	0.65	0.421	0.894
26	178.43	22.20	9.97	1491.5	755.5	850	150	0.43	0.66	0.424	0.854
27	178.43	22.20	9.97	1491.5	755.5	850	150	0.44	0.67	0.433	0.880
28	178.43	22.20	9.97	1491.5	755.5	850	150	0.43	0.67	0.431	0.881
29	177.87	19.45	10.10	1422.2	756.2	900	100	0.47	0.73	0.501	0.947
30	177.87	19.45	10.10	1422.2	756.2	900	100	0.47	0.75	0.495	0.951
31	177.87	19.45	10.10	1422.2	756.2	900	100	0.46	0.74	0.494	0.934
32	177.87	19.45	10.10	1422.2	756.2	876	125	0.46	0.70	0.476	0.954
33	177.87	19.45	10.10	1422.2	756.2	875	125	0.45	0.69	0.462	0.951

TABLE A.2 - Continued.

Peak No.	T _c (°C)	T _f (°C)	F _f (cm ³ /min)	P _i (mm Hg)	P _o (mm Hg)	V _{Ar} (μℓ)	V _{H₂} (μℓ)	(t _m) _{Ar} (min)	(t _m) _{H₂} (min)	(μ ₁) _{Ar} (min)	(μ ₁) _{H₂} (min)
34	177.87	19.45	10.10	1422.7	756.2	850	150	0.44	0.66	0.439	0.865
35	196.38	20.15	10.20	1458.2	756.2	900	100	0.47	0.69	0.510	0.908
36	196.38	20.15	10.20	1458.2	756.2	875	125	0.46	0.67	0.474	0.839
37	196.38	20.15	10.20	1458.2	756.2	875	125	0.46	0.66	0.466	0.833
38	196.38	20.15	10.20	1458.2	756.2	850	150	0.41	0.62	0.409	0.780
39	196.38	20.15	10.20	1458.2	756.2	850	150	0.44	0.65	0.436	0.797
40	217.33	22.60	10.14	1443.0	757.0	850	150	0.42	0.66	0.406	0.792
41	217.33	22.60	10.14	1443.0	757.0	850	150	0.42	0.65	0.423	0.859
42	217.33	22.60	10.14	1443.0	757.0	850	150	0.41	0.64	0.411	0.826
43	217.72	21.10	10.17	1461.0	749.0	900	100	0.46	0.73	0.481	0.874
44	217.72	21.10	10.17	1461.0	749.0	900	100	0.46	0.73	0.481	0.925
45	217.72	21.10	10.17	1461.0	749.0	875	125	0.43	0.68	0.429	0.811
46	217.72	21.10	10.17	1461.0	749.0	875	125	0.42	0.67	0.417	0.793
47	235.63	21.90	10.08	1468.5	756.5	850	150	0.43	0.65	0.426	0.825
48	235.63	21.90	10.08	1468.5	756.5	850	150	0.42	0.65	0.417	0.813
49	236.53	21.90	10.51	1532.5	748.5	900	100	0.41	0.66	0.425	0.894
50	236.53	21.90	10.51	1532.5	748.5	900	100	0.43	0.68	0.451	0.889
51	236.53	21.90	10.51	1532.5	748.5	900	100	0.42	0.68	0.440	0.884

TABLE A.2 - Continued.

Peak No.	T _C (°C)	T _f (°C)	F _f (cm ³ /min)	P _i (mm Hg)	P _o (mm Hg)	V _{Ar} (μℓ)	V _{H₂} (μℓ)	(t _M) _{Ar} (min)	(t _M) _{H₂} (min)	(μ ₁) (min)	(μ ₁) (min)
52	236.53	21.90	10.51	1532.5	748.5	875	125	0.41	0.66	0.420	0.812
53	236.53	21.90	10.51	1532.5	748.5	875	125	0.41	0.65	0.412	0.804
54	236.53	21.90	10.51	1532.5	748.5	850	150	0.40	0.63	0.399	0.784
55	236.53	21.90	10.51	1532.5	748.5	850	150	0.40	0.63	0.400	0.799

APPENDIX - III

TABLE A.3.1 - Data for Adsorption Isotherms of Hydrogen

Peak No.	$T_c(^{\circ}\text{C})$	$V_{\text{H}_2} (\mu\text{l})$	$F_f(\text{cm}^3/\text{sec})$	$P_i(\text{mm Hg})$	$P_o(\text{mm Hg})$	$T_f(^{\circ}\text{C})$	$t_o(\text{sec})$	$A(\text{mm}^2)$	$v(\text{mm}/\text{sec})$
14	136.26	150	9.65	1325.0	755.0	22.50	28.2	2865.0	1.67
19	158.36	150	10.49	1487.0	755.0	22.70	25.8	4511.5	1.67
34	177.87	150	10.10	1422.7	756.2	19.45	26.1	2229.2	1.67
38	196.38	150	10.20	1458.2	756.2	20.15	24.3	3575.7	1.67
42	217.33	150	10.14	1443.0	757.0	22.60	24.6	4633.3	1.67
55	236.53	150	10.51	1532.5	748.5	21.90	24.0	3870.9	1.67

TABLE A.3.2 - Data for Adsorption Isotherms of Cyclo-hexane

Peak No.	$T_c (^{\circ}\text{C})$	$V_{\text{CH}} (\mu\text{l})$	$F_f (\text{cm}^3/\text{sec})$	$P_i (\text{mm Hg})$	$P_o (\text{mm Hg})$	$T_f (^{\circ}\text{C})$	$t_o (\text{sec})$	$A (\text{mm}^2)$	$v (\text{mm}/\text{sec})$
61	216.80	0.2	0.180	1252.5	756.5	16.65	19.2	4957.1	3.33
62	216.80	0.3	0.180	1252.5	756.5	16.65	19.2	6944.0	3.33
63	216.80	0.4	0.180	1252.5	756.5	16.65	19.2	4596.7	3.33
64	216.80	0.5	0.180	1252.5	756.5	16.65	19.2	5567.3	3.33
65	216.80	0.6	0.180	1252.5	756.5	16.65	19.2	6605.3	3.33
66	216.80	0.7	0.180	1252.5	756.5	16.65	19.2	7674.3	3.33
67	216.80	0.8	0.180	1252.5	756.5	16.65	19.2	8164.0	3.33
68	216.80	0.9	0.180	1252.5	756.5	16.65	19.2	9617.7	3.33
69	216.80	1.0	0.180	1252.5	756.5	16.65	19.2	10688.0	3.33
70	189.73	0.8	0.169	1176.0	756.0	19.35	21.0	8918.6	3.33
71	200.05	0.7	0.165	1178.5	750.5	17.40	20.7	9100.2	3.33
72	209.20	0.8	0.169	1172.5	748.5	13.70	19.7	10127.0	3.33
73	228.50	0.6	0.170	1239.2	753.2	16.20	19.5	6958.3	3.33
74	236.34	0.7	0.167	1231.5	753.5	16.90	19.8	8880.3	3.33

TABLE A.3.3 - Data for Adsorption Isotherms of Methyl-cyclo-hexane

Peak No.	$T_c(^{\circ}\text{C})$	$V_{\text{MCH}}(\mu\text{l})$	$F_f(\text{cm}^3/\text{sec})$	$P_i(\text{mm Hg})$	$P_o(\text{mm Hg})$	$T_f(^{\circ}\text{C})$	$t_o(\text{sec})$	$A(\text{mm}^2)$	$v(\text{mm}/\text{sec})$
75	186.92	0.8	0.170	1174.0	766.0	20.2	20.4	8581.3	1.67
76	191.65	0.8	0.168	1161.0	763.0	15.7	20.4	8215.3	1.67
77	196.73	0.8	0.167	1166.0	766.0	21.3	21.6	8770.7	1.67
78	199.43	0.8	0.164	1157.0	763.0	17.1	21.0	8770.0	1.67
79	206.57	0.8	0.169	1176.0	766.0	22.7	21.0	9128.0	1.67
80	208.22	0.8	0.168	1186.0	763.0	17.1	20.7	8275.0	1.67
81	216.99	0.8	0.169	1170.5	747.5	19.1	20.4	4434.0	1.67
82	218.01	0.8	0.174	1191.0	763.0	17.3	19.5	3933.0	1.67
83	226.84	0.8	0.164	1170.5	747.5	20.3	21.0	4771.0	1.67
84	227.73	0.8	0.167	1189.0	763.0	16.9	19.8	4328.0	1.67
85	236.78	0.8	0.164	1181.5	747.5	21.7	21.0	4494.3	1.67
86	238.54	0.8	0.172	1209.0	763.0	16.9	19.5	4346.3	1.67

TABLE A.3.4 - Data for Adsorption Isotherms of Benzene

Peak No.	$T_c (^{\circ}\text{C})$	$V_{\text{Ben}} (\mu\text{l})$	$F_f (\text{cm}^3/\text{sec})$	$P_i (\text{mm Hg})$	$P_o (\text{mm Hg})$	$T_f (^{\circ}\text{C})$	$t_o (\text{sec})$	$A (\text{mm}^2)$	$v (\text{mm/sec})$
87	190.05	0.1	0.163	1530.5	750.5	22.9	26.5	18971.7	1.67
88	194.96	0.1	0.163	1497.5	749.5	21.7	24.6	20025.0	1.67
89	199.62	0.1	0.168	1568.5	750.5	23.3	24.9	17996.0	1.67
90	204.68	0.1	0.170	1543.2	749.2	21.3	23.4	17169.2	1.67
91	208.91	0.1	0.166	1509.2	751.2	19.6	24.6	10522.5	1.67
92	214.38	0.1	0.163	1535.0	749.0	21.2	24.3	9722.5	1.67
93	222.62	0.1	0.160	1529.0	751.0	19.8	23.7	10592.5	1.67
94	228.65	0.1	0.169	1616.5	750.5	22.3	23.1	9548.3	1.67
95	235.32	0.1	0.169	1569.8	749.8	20.1	22.8	5320.3	1.67

TABLE A.3.5 - Data for Adsorption Isotherms of Toluene

Peak No.	$T_c (^{\circ}\text{C})$	$V_{\text{TOL}} (\mu\text{l})$	$F_f (\text{cm}^3/\text{sec})$	$P_i (\text{mm Hg})$	$P_o (\text{mm Hg})$	$T_f (^{\circ}\text{C})$	$t_o (\text{sec})$	$A (\text{mm}^2)$	$v (\text{mm}/\text{sec})$
96	195.90	0.2	0.162	1558.0	752.0	22.6	24.6	6275.8	0.333
97	204.32	0.2	0.154	1526.3	742.3	21.7	28.2	6772.1	0.333
98	209.27	0.2	0.172	1594.2	742.2	22.0	24.0	16756.3	0.833
99	215.12	0.1	0.175	1612.2	742.2	22.0	22.8	5713.8	0.833
100	223.80	0.1	0.157	1586.0	752.0	19.8	24.0	7898.3	0.833
101	235.35	0.1	0.171	1616.0	752.0	21.7	23.1	8339.2	0.833

APPENDIX - IV

TABLE A.4 - Retention Time - Height Data

For Peak No. 14

$t_c(\text{sec})$	$(V_g/RT_c) \times 10^8$ (gmol/g mmHg)	$c(t)(\text{mm})$	$p(\text{mm Hg})$
43.2	3.42	71.5	29.29
46.2	4.10	64.0	26.21
49.2	4.79	51.0	20.89
52.2	5.47	39.0	15.97
55.2	6.15	30.0	12.29
58.2	6.84	23.0	9.42
61.2	7.52	18.5	7.58
64.2	8.20	15.0	6.14
67.2	8.89	12.5	5.12
70.2	9.57	10.5	4.30
73.2	10.25	9.0	3.69
76.2	10.94	8.0	3.28
79.2	11.62	7.5	3.07
82.2	12.30	6.5	2.66
85.2	12.89	6.0	2.46
88.2	13.67	5.5	2.25
91.2	14.36	5.0	2.05
94.2	15.04	4.5	1.84
97.2	15.72	4.0	1.64
100.2	16.41	3.5	1.43
103.2	17.09	3.0	1.23
175.2	33.50	0	0

TABLE A.4 - Continued.

For Peak No. 19

t_c (sec)	$(Vg/RT_c) \times 10^8$ (gmol/g mmHg)	$c(t)$ (mm)	p (mm Hg)
39.0	3.16	117.0	28.00
42.0	3.88	106.0	25.37
45.0	4.60	85.0	20.34
48.0	3.32	64.5	15.44
51.0	6.03	48.0	11.49
54.0	6.75	36.0	8.62
57.0	7.47	28.0	6.70
60.0	8.19	22.0	5.27
63.0	8.91	18.0	4.31
66.0	9.62	15.5	3.71
69.0	10.34	13.0	3.11
72.0	11.06	11.0	2.63
75.0	11.78	10.0	2.39
78.0	12.50	9.0	2.15
81.0	13.22	7.5	1.80
84.0	13.93	7.0	1.68
87.0	14.65	6.5	1.56
90.0	15.37	6.0	1.44
93.0	16.09	5.5	1.32
96.0	16.81	5.0	1.20
99.0	17.52	4.5	1.08
102.0	18.24	4.0	0.96
105.0	18.96	4.0	0.96
108.0	19.68	4.0	0.96
111.0	20.40	3.5	0.84

TABLE A.4 - Continued.

For Peak No. 34

t_c (sec)	$(V_g/RT_c) \times 10^8$ (gmol/g mmHg)	$c(t)$ (sec)	p (mm Hg)
39.6	3.09	63.0	31.74
42.6	3.78	58.0	29.22
45.6	4.47	47.0	23.68
48.6	5.15	35.5	17.88
51.6	5.84	26.5	13.35
54.6	6.23	20.0	10.08
57.6	7.22	16.0	8.06
60.6	7.90	13.0	6.55
63.6	8.59	10.5	5.29
66.6	9.28	9.0	4.53
69.6	9.97	7.5	3.78
72.6	10.65	6.5	3.27
75.6	11.34	5.5	2.77
78.6	12.03	5.0	2.52
81.6	12.71	4.5	2.27
84.6	13.40	4.0	2.02
87.6	14.09	3.5	1.76
90.6	14.78	3.0	1.51
93.6	15.46	3.0	1.51
96.6	16.15	2.5	1.26
99.6	16.84	2.5	1.26
102.6	17.53	2.5	1.26
105.6	18.21	2.0	1.01
108.6	18.90	2.0	1.01
111.6	19.59	2.0	1.01
114.6	20.27	1.5	0
156.6	29.90	0	

TABLE A.4 - Continued.

For Peak No. 38

$t_c(\text{sec})$	$(V_g/RT_c) \times 10^8$ ($\text{g mol}^{-1}/\text{g mmHg}$)	$c(t)(\text{mm})$	$p(\text{mm Hg})$
36.9	2.85	98.0	30.49
39.9	3.53	88.0	27.38
42.9	4.21	68.5	21.31
45.9	4.89	52.0	16.18
48.9	5.57	38.0	11.82
51.9	6.25	28.0	8.71
54.9	6.93	21.5	6.69
57.9	7.61	17.0	5.29
60.9	8.29	13.5	4.20
63.9	8.97	11.5	3.58
66.9	9.65	9.5	2.96
69.9	10.32	8.5	2.65
72.9	11.00	7.5	2.33
75.9	11.68	6.5	2.02
78.9	12.36	6.0	1.87
81.9	13.04	5.5	1.71
84.9	13.72	5.0	1.56
87.9	14.40	4.5	1.40
90.9	15.08	4.0	1.25
93.9	15.76	3.5	1.09
96.9	16.44	3.0	0.93
162.9	31.38	0	0

TABLE A.4 - Continued.

For Peak No. 42

$t_c(\text{sec})$	$(V_g/RT_c) \times 10^8$ (gmol/g mmHg)	$c(t)(\text{mm})$	$p(\text{mm Hg})$
38.4	3.11	126.0	30.51
41.4	3.78	112.5	27.24
44.4	4.46	86.0	20.82
47.4	5.14	66.0	15.98
50.4	5.81	49.0	11.86
53.4	6.49	36.5	8.84
56.4	7.16	28.5	6.90
59.4	7.84	23.0	5.57
62.4	8.51	19.0	4.60
65.4	9.19	16.0	3.97
68.4	9.87	13.5	3.27
71.4	10.54	12.0	2.91
74.4	11.22	10.0	2.42
77.4	11.89	9.0	2.18
80.4	12.57	8.0	1.94
83.4	13.24	7.0	1.70
85.4	13.92	6.5	1.57
88.4	14.60	6.0	1.45
91.4	15.27	5.5	1.33
94.4	15.95	5.0	1.21
97.4	16.62	4.5	1.09
100.4	17.30	4.0	0.97
104.4	17.98	4.0	0.97
107.4	18.65	3.5	0.85
110.4	19.33	3.5	0.85
113.4	20.00	3.0	0.73
116.4	20.68	2.5	0.61
119.4	21.35	2.5	0.61
122.4	22.03	2.0	0.48
182.4	35.54	0	0

TABLE A.4 - Continued.

For Peak No. 55

$t_c(\text{sec})$	$(V_g/RT_c) \times 10^8$ (gmol/g mmHg)	$c(t)(\text{mm})$	$p(\text{mm Hg})$
37.5	2.99	105.0	28.98
39.0	3.33	101.0	27.88
42.0	3.99	83.0	22.91
45.0	4.65	64.0	17.67
48.0	5.32	45.0	12.42
51.0	5.98	34.0	9.39
54.0	6.65	25.5	7.04
57.0	7.31	20.5	5.66
60.0	7.98	16.5	4.55
63.0	8.64	13.5	3.73
66.0	9.31	11.5	3.17
69.0	9.97	10.0	2.76
72.0	10.64	8.5	2.35
75.0	11.30	8.0	2.21
78.0	11.97	7.0	1.93
81.0	12.63	6.0	1.66
84.0	13.30	5.5	1.52
87.0	13.96	5.0	1.38
90.0	14.63	4.5	1.24
93.0	15.29	4.5	1.24
96.0	15.96	4.0	1.10
99.0	16.62	3.5	0.97
102.0	17.29	3.5	0.97
105.0	17.95	3.0	0.83
165.0	31.25	0	0

TABLE A.4 - Continued.

For Peak No. 61

t_c (sec)	$(V_g/RT_c) \times 10^7$ (gmol/g mmHg)	$c(t)$ (mm)	p (mm Hg)
62.55	1.18	127.0	15.90
64.05	1.22	105.0	13.15
65.55	1.26	99.0	12.40
67.05	1.30	79.5	9.96
68.55	1.34	63.0	7.89
70.05	1.38	48.5	6.07
71.55	1.42	39.0	4.88
73.05	1.46	28.0	3.51
74.55	1.50	20.0	2.50
76.05	1.54	15.0	1.88
77.55	1.58	11.0	1.38
79.05	1.62	8.0	1.00
80.55	1.66	5.5	0.69
82.05	1.70	4.0	0.50
83.55	1.75	3.0	0.38
85.05	1.79	2.0	0.50
86.55	1.83	1.5	0.19
88.05	1.87	1.0	0.13
89.55	1.91	0.5	0.06
91.05	1.95	0.5	0.06
92.55	1.99	0	0

TABLE A.4 - Continued.

For Peak No. 62

t_c (sec)	$(V_g/RT_c) \times 10^7$ (gmol/g mmHg)	$c(t)$ (mm)	p (mm Hg)
59.1	1.08	181.0	24.27
60.6	1.12	168.0	22.53
62.1	1.16	146.0	19.58
63.6	1.20	120.0	16.09
65.1	1.24	98.0	13.14
66.6	1.29	77.0	10.33
68.1	1.33	63.0	8.45
68.6	1.37	43.0	5.77
71.1	1.41	30.0	4.02
72.6	1.45	22.0	2.95
74.1	1.49	16.0	2.15
75.6	1.53	11.0	1.48
77.1	1.57	8.0	1.07
78.6	1.61	5.5	0.74
80.1	1.65	4.0	0.54
81.6	1.69	2.5	0.34
83.1	1.73	2.0	0.27
84.6	1.77	1.5	0.20
86.1	1.81	1.0	0.13
87.6	1.85	0.5	0.07
89.1	1.90	0	0

TABLE A.4 - Continued.

For Peak No. 63

t_c (sec)	$(V_g/RT_c) \times 10^7$ (gmol/g mmHg)	$c(t)$ (mm)	p (mm Hg)
59.1	1.08	117.0	31.60
60.6	1.12	109.5	29.57
62.1	1.16	96.0	25.93
63.6	1.20	81.0	21.88
65.1	1.24	66.0	17.58
66.6	1.29	51.5	13.91
68.1	1.33	39.0	10.53
69.6	1.37	29.5	7.97
71.1	1.41	21.5	5.81
72.6	1.45	16.0	4.32
74.1	1.49	11.5	3.11
75.6	1.53	8.0	2.16
77.1	1.57	5.5	1.49
78.6	1.61	4.0	1.08
80.1	1.65	3.0	0.81
81.6	1.69	2.0	0.54
83.1	1.73	2.0	0.54
84.6	1.77	1.5	0.41
86.1	1.81	1.0	0.27
87.6	1.85	1.0	0.27
89.1	1.90	0.7	0.19
90.6	1.94	0.5	0.14
92.1	1.98	0	0

TABLE A.4 - Continued.

For Peak No. 64

t_c (sec)	$(V_g/RT_c) \times 10^7$ (gmol/g mmHg)	$c(t)$ (mm)	p (mm Hg)
58.65	1.07	136.5	38.05
60.15	1.11	128.0	35.68
61.65	1.15	112.5	31.36
63.15	1.19	98.0	27.32
64.65	1.23	80.5	22.44
66.15	1.27	64.5	17.98
67.65	1.31	48.5	13.52
69.15	1.35	38.0	10.59
70.65	1.40	27.0	7.53
72.15	1.44	21.0	5.85
73.65	1.48	15.0	4.18
75.15	1.52	11.5	3.21
76.65	1.56	8.0	2.23
78.15	1.60	5.5	1.53
79.65	1.64	4.0	1.12
81.15	1.68	3.0	0.84
82.65	1.72	2.5	0.70
84.15	1.76	2.0	0.56
85.65	1.80	1.5	0.42
87.15	1.84	1.0	0.28
88.65	1.88	0.8	0.22
90.15	1.93	0.5	0.14
91.65	1.96	0.4	0.11
93.15	2.01	0.2	0.06
94.65	2.05	0	0

TABLE A.4 - Continued.

For Peak No. 65

$t_c(\text{sec})$	$(V_g/RT_c) \times 10^7$ (gmol/g mmHg)	$c(t)(\text{mm})$	$p(\text{mm Hg})$
57.6	1.04	157.5	44.0
59.1	1.08	152.0	42.85
60.6	1.12	133.0	37.50
62.1	1.16	118.5	33.41
63.6	1.20	98.0	27.63
65.1	1.24	78.5	22.13
66.6	1.29	60.5	17.06
68.1	1.33	47.0	13.25
69.6	1.37	35.0	9.87
71.1	1.41	26.5	7.47
72.6	1.45	19.0	5.36
74.1	1.49	14.0	3.95
75.6	1.53	9.5	2.68
77.1	1.57	7.5	2.11
78.6	1.61	5.0	1.41
80.1	1.65	3.5	0.99
81.6	1.69	3.0	0.85
83.1	1.73	2.0	0.56
84.6	1.77	1.5	0.42
86.1	1.81	1.0	0.28
87.6	1.85	0.8	0.23
89.1	1.90	0.5	0.14
90.6	1.94	0	0

TABLE A.4 - Continued.

For Peak No. 66

t_c (sec)	$(V_g/RT_c) \times 10^7$ (gmol/g mmHg)	$c(t)$ (mm)	p (mm Hg)
56.85	1.02	179.5	50.82
58.35	1.06	174.0	49.26
59.85	1.10	157.5	44.59
61.35	1.14	136.0	38.50
62.85	1.18	116.0	32.84
64.35	1.22	94.5	26.75
65.85	1.27	74.0	20.95
67.35	1.31	57.5	16.28
68.85	1.34	44.5	12.60
70.35	1.39	32.5	9.20
71.85	1.43	23.5	6.65
73.35	1.47	17.5	4.95
74.85	1.51	12.5	3.54
76.35	1.55	9.0	2.54
77.85	1.59	6.0	1.70
79.35	1.63	4.5	1.27
80.85	1.67	3.5	0.99
82.35	1.71	2.5	0.71
83.85	1.75	2.0	0.57
85.35	1.79	1.5	0.43
86.85	1.83	1.0	0.28
88.35	1.88	0.5	0.14
89.85	1.92	0	0

TABLE A.4 -- Continued.

For Peak No. 67

t_c (sec)	$(V_g/RT_c) \times 10^7$ (gmol/g mmHg)	$c(t)$ (mm)	p (mm Hg)
57.0	1.03	183.5	55.81
58.5	1.07	175.0	53.22
60.0	1.11	158.0	48.05
61.5	1.15	137.0	41.67
63.0	1.19	117.0	35.58
64.5	1.23	97.5	29.65
66.0	1.27	79.0	24.03
67.5	1.31	64.0	19.47
69.0	1.35	50.0	15.21
70.5	1.39	38.0	11.56
72.0	1.43	29.0	8.82
73.5	1.47	21.5	6.54
75.0	1.51	16.0	4.87
76.5	1.55	12.0	3.65
78.0	1.59	9.5	2.89
79.5	1.64	6.5	1.98
81.0	1.68	5.0	1.52
82.5	1.72	3.5	1.06
84.0	1.76	2.5	0.76
85.5	1.80	2.0	0.61
87.0	1.84	1.5	0.46
88.5	1.88	1.2	0.37
90.0	1.92	1.0	0.30
91.5	1.96	0.5	0.15
93.0	2.00	0.3	0.09
94.5	2.04	0.2	0.06
96.0	2.08	0	0

TABLE A.4 - Continued.

For Peak No. 68

t_c (sec)	$(V_g/RT_c) \times 10^7$ (gmol/g mmHg)	$c(t)$ (mm)	p (mm Hg)
56.1	1.00	209.0	60.71
57.6	1.04	201.0	58.38
59.1	1.08	178.0	51.70
60.6	1.12	157.5	45.75
62.1	1.16	137.5	39.79
63.6	1.20	118.0	34.27
65.1	1.24	97.0	29.17
66.6	1.29	87.5	25.42
68.1	1.33	60.5	17.57
69.6	1.37	47.5	13.80
71.1	1.41	35.5	10.31
72.6	1.45	27.5	7.99
74.1	1.49	20.0	5.81
75.6	1.53	14.5	4.21
77.1	1.57	11.0	3.20
78.6	1.61	8.0	2.32
80.1	1.65	6.0	1.74
81.6	1.69	4.5	1.31
83.1	1.73	3.0	0.87
84.6	1.77	2.5	0.73
86.1	1.81	1.5	0.44
87.6	1.85	1.2	0.35
89.1	1.90	1.0	0.29
90.6	1.94	0.6	0.17
92.1	1.98	0.4	0.12
93.6	2.02	0.3	0.09
95.1	2.06	0.2	0.06
96.6	2.10	0.1	0.03
98.1	2.14	0	0

TABLE A.4 - Continued.

For Peak No. 69

$t_c(\text{sec})$	$(V_g/RT_c) \times 10^7$ (gmol/g·mmHg)	$c(t)(\text{mm})$	$p(\text{mm Hg})$
55.65	0.99	223.0	64.76
57.15	1.03	216.0	62.73
58.65	1.07	199.0	57.79
60.15	1.11	177.5	51.55
61.65	1.51	153.0	44.43
63.15	1.19	132.0	38.33
64.65	1.23	111.0	32.24
66.15	1.27	91.0	26.43
67.65	1.31	73.0	21.20
69.15	1.35	58.0	16.84
70.65	1.40	48.0	13.94
72.15	1.44	36.0	10.46
73.65	1.48	28.5	8.28
75.15	1.52	21.0	6.10
76.65	1.56	16.0	4.65
78.15	1.60	12.0	3.49
79.65	1.64	9.0	2.61
81.15	1.68	6.5	1.89
82.65	1.72	5.0	1.45
84.15	1.76	4.0	1.16
85.65	1.80	3.0	0.87
87.15	1.84	2.0	0.58
88.65	1.88	1.5	0.44
90.15	1.93	1.0	0.29
91.65	1.96	0.5	0.15
93.15	2.01	0.3	0.09
94.65	2.05	0.2	0.06
96.15	2.09	0.1	0.03
97.65	2.13	0	0

TABLE A:4 - Continued.

For Peak No. 70

$t_c(\text{sec})$	$(V_g/RT_c) \times 10^7$ (gmol/g mmHg)	$c(t)(\text{mm})$	$p(\text{mm Hg})$
89.4	1.80	142.5	42.65
90.9	1.84	139.0	41.60
92.4	1.88	132.5	39.66
93.9	1.92	123.0	36.81
95.4	1.96	113.5	33.97
96.9	2.00	104.0	31.13
98.4	2.04	92.0	27.53
99.9	2.08	84.0	25.14
101.4	2.12	74.0	22.15
102.9	2.16	64.0	19.15
104.4	2.20	55.0	16.46
105.9	2.24	47.0	14.07
107.4	2.27	39.0	11.67
108.9	2.31	34.0	10.18
110.4	2.35	28.0	8.38
111.9	2.39	23.0	6.88
113.4	2.43	19.0	5.69
114.9	2.47	15.5	4.64
116.4	2.51	12.5	3.74
117.9	2.55	9.5	2.84
119.4	2.59	7.5	2.25
120.9	2.63	6.0	1.80
122.4	2.67	4.5	1.35
123.9	2.71	3.0	0.90
125.4	2.75	2.5	0.75
126.9	2.79	2.0	0.60
128.4	2.83	1.5	0.45
129.9	2.87	1.0	0.30
131.4	2.91	0.5	0.15
132.9	2.95	0.2	0.06
134.4	2.99	0	0

TABLE A.4 - Continued.

For Peak No. 71

t_c (sec)	$(V_g/RT_c) \times 10^7$ (gmol/g mmHg)	$c(t)$ (mm)	p (mm Hg)
76.8	1.44	162.0	42.30
78.3	1.48	157.5	41.13
79.8	1.52	148.5	38.78
81.3	1.56	135.0	35.25
82.8	1.60	123.0	32.12
84.3	1.64	110.0	28.72
85.8	1.67	96.0	25.07
87.3	1.71	84.0	21.93
88.8	1.75	72.0	18.80
90.3	1.79	61.5	16.06
91.8	1.83	51.5	13.45
93.3	1.87	41.0	10.71
94.8	1.91	34.0	8.88
96.3	1.94	27.0	7.05
97.8	1.98	21.5	5.61
99.3	2.02	16.5	4.31
100.8	2.06	12.5	3.26
102.3	2.10	9.5	2.48
103.8	2.14	7.0	1.83
105.3	2.18	5.5	1.44
106.8	2.21	4.0	1.04
108.3	2.25	3.0	0.78
109.8	2.29	2.0	0.52
111.3	2.33	1.0	0.26
112.8	2.37	0.5	0.13
114.3	2.41	0.2	0.05
115.8	2.45	0	0

TABLE A.4 - Continued.

For Peak No. 72

t_c (sec)	$(V_g/RT_c) \times 10^7$ (gmol/g mmHg)	$c(t)$ (mm)	p (mm Hg)
67.35	1.27	188.0	48.60
68.85	1.31	183.0	47.30
70.35	1.36	172.0	44.46
71.85	1.40	158.0	40.84
73.35	1.44	141.0	36.45
74.85	1.48	125.0	32.31
76.35	1.52	107.5	27.79
77.85	1.56	91.0	23.52
79.35	1.60	76.5	19.77
80.85	1.64	63.0	16.28
82.35	1.68	50.5	13.05
83.85	1.72	40.5	10.47
85.35	1.76	31.5	8.14
86.85	1.80	24.0	6.20
88.35	1.84	18.0	4.65
89.85	1.88	14.0	3.62
91.35	1.92	10.0	2.59
92.85	1.96	7.5	1.94
94.35	2.00	5.5	1.42
95.85	2.04	4.0	1.03
97.35	2.08	3.0	0.78
98.85	2.12	2.0	0.52
100.35	2.16	1.5	0.39
101.85	2.20	1.0	0.26
103.35	2.24	0.5	0.13
104.85	2.28	0.2	0.05
106.35	2.32	0	0

TABLE A.4 - Continued.

For Peak No. 73

$t_c(\text{sec})$	$(V_g/RT_c) \times 10^7$ (gmol/g mmHg)	$c(t)(\text{mm})$	$p(\text{mm Hg})$
54.6	0.90	169.0	47.82
56.1	0.94	162.0	45.83
57.6	0.98	146.5	41.45
59.1	1.02	127.0	35.93
60.6	1.06	106.0	29.99
62.1	1.10	86.0	24.33
63.6	1.14	67.0	18.96
65.1	1.18	52.0	14.71
66.6	1.21	34.0	9.62
68.1	1.25	28.5	8.06
69.6	1.29	20.0	5.66
71.1	1.33	14.0	3.96
72.6	1.37	10.0	2.83
74.1	1.41	7.5	2.12
75.6	1.45	5.0	1.42
77.1	1.48	3.5	0.99
78.6	1.52	2.5	0.71
80.1	1.56	2.0	0.57
81.6	1.60	1.5	0.42
83.1	1.64	1.0	0.28
84.6	1.68	0.5	0.14
86.1	1.72	0.2	0.06
87.6	1.75	0	0

TABLE A.4 - Continued.

For Peak No. 74

t_c (sec)	$(V_g/RT_c) \times 10^7$ (gmo1/g mmHg)	$c(t)$ (mm)	p (mm Hg)
52.5	0.83	211.5	55.93
54.0	0.85	205.0	54.21
55.5	0.90	186.0	49.19
57.0	0.91	161.5	42.71
58.5	0.98	133.0	35.17
60.0	1.02	109.0	28.83
61.5	1.06	84.0	22.21
63.0	1.09	63.0	16.66
64.5	1.13	41.0	10.84
66.0	1.17	34.0	8.99
67.5	1.21	23.0	6.08
69.0	1.25	16.5	4.36
70.5	1.28	12.0	3.17
72.0	1.32	8.5	2.25
73.5	1.36	6.0	1.59
75.0	1.40	4.0	1.06
76.5	1.44	3.5	0.93
78.0	1.47	2.0	0.53
79.5	1.51	1.0	0.26
81.0	1.55	0.5	0.13
82.5	1.59	0	0

TABLE A.4 - Continued.

For Peak No. 75

t_c (sec)	$(V_g/RT_c) \times 10^7$ (gmol/g mmHg)	$c(t)$ (mm)	p (mm Hg)
153.6	3.56	172.0	22.49
156.6	3.64	166.0	21.71
159.6	3.72	150.0	19.62
162.6	3.80	136.5	17.85
165.6	3.88	120.0	15.69
168.6	3.96	106.0	13.86
171.6	4.04	91.5	11.97
174.6	4.12	81.0	10.59
177.6	4.20	70.0	9.15
180.6	4.28	60.5	7.91
183.6	4.36	52.0	6.80
186.6	4.44	44.5	5.82
189.6	4.52	38.0	4.97
192.6	4.60	32.0	4.18
195.6	4.68	27.0	3.53
198.6	4.76	22.5	2.94
201.6	4.84	18.5	2.42
204.6	4.92	15.0	1.96
207.6	5.00	12.5	1.63
210.6	5.08	10.0	1.31
213.6	5.16	8.0	1.05
216.6	5.24	6.5	0.85
219.6	5.32	5.0	0.65
222.6	5.40	4.0	0.52
225.6	5.48	3.5	0.46
228.6	5.56	2.5	0.33
231.6	5.64	2.0	0.26
234.6	5.73	1.5	0.20
237.6	5.81	1.0	0.13
240.6	5.89	0.6	0.08
243.6	5.97	0.4	0.05
246.6	6.05	0.2	0.03
249.6	6.13	0	0

TABLE A.4 - Continued.

For Peak No. 76

t_c (sec)	$(V_g/RT_c) \times 10^7$ (gmol/g mmHg)	$c(t)$ (mm)	p (mmHg)
136.8	3.14	182.0	24.77
139.8	3.22	174.0	23.68
142.8	3.30	155.5	21.16
145.8	3.38	138.0	18.78
148.8	3.46	119.0	16.20
151.8	3.54	104.5	14.22
154.8	3.62	90.0	12.25
157.8	3.70	76.0	10.34
160.8	3.78	64.0	8.71
163.8	3.87	54.0	7.35
166.8	3.95	45.0	6.12
169.8	4.03	37.0	5.04
172.8	4.11	30.5	4.15
175.8	4.19	24.0	3.27
178.8	4.27	20.0	2.72
181.8	4.35	16.0	2.18
184.8	4.43	12.5	1.70
187.8	4.51	10.0	1.36
190.8	4.59	7.5	1.02
193.8	4.67	5.5	0.75
196.8	4.75	4.5	0.61
199.8	4.84	3.5	0.48
202.8	4.92	2.5	0.34
205.8	5.00	2.0	0.27
208.8	5.08	1.5	0.20
211.8	5.16	1.0	0.14
214.8	5.24	0.5	0.07
217.8	5.32	0.2	0.03
220.8	5.40	0	0

TABLE A.4 - Continued.

For Peak No. 77

t_c (sec)	$(V_g/RT_c) \times 10^7$ (gmol/g mmHg)	$c(t)$ (mm)	p (mm Hg)
136.8	3.02	189.5	24.88
139.8	3.09	180.5	23.69
142.8	3.18	162.0	21.27
145.8	3.25	145.0	19.03
148.8	3.33	126.0	16.54
151.8	3.41	110.0	14.44
154.8	3.49	93.0	12.21
157.8	3.56	79.0	10.37
160.8	3.64	67.5	8.86
163.8	3.72	56.5	7.42
166.8	3.80	46.5	6.10
169.8	3.88	38.5	5.05
172.8	3.96	31.5	4.13
175.8	4.04	25.5	3.35
178.8	4.11	20.5	2.69
181.8	4.19	16.5	2.17
184.8	4.27	13.5	1.77
187.8	4.35	10.5	1.38
190.8	4.43	8.0	1.05
193.8	4.51	6.5	0.85
196.8	4.59	4.5	0.59
199.8	4.66	3.5	0.46
202.8	4.74	3.0	0.39
205.8	4.82	2.5	0.33
208.8	4.90	2.0	0.26
211.8	4.98	1.5	0.20
214.8	5.06	1.0	0.13
217.8	5.13	0.6	0.08
220.8	5.21	0.4	0.05
223.8	5.29	0.2	0.03
226.8	5.37	0	0

TABLE A.4 - Continued.

For Peak No. 78

$t_c(\text{sec})$	$(V_g/RT_c) \times 10^7$ (gmol/g mmHg)	$c(t)(\text{mm})$	$p(\text{mm Hg})$
127.2	2.79	204.0	26.75
130.2	2.87	191.5	25.11
133.2	2.95	174.0	22.82
136.2	3.03	151.0	19.80
139.2	3.10	129.5	16.98
142.2	3.18	111.5	14.62
145.2	3.26	93.5	12.26
148.2	3.34	78.0	10.23
157.2	3.42	65.0	8.52
154.2	3.50	53.5	7.02
157.2	3.58	43.0	5.64
160.2	3.66	35.0	4.59
163.2	3.74	28.0	3.67
166.2	3.81	22.0	2.88
169.2	3.89	17.5	2.29
172.2	3.97	13.5	1.77
175.2	4.05	10.0	1.31
178.2	4.13	8.5	1.11
181.2	4.21	6.0	0.79
184.2	4.29	5.0	0.66
187.2	4.37	4.0	0.52
190.2	4.44	3.0	0.39
193.2	4.52	2.0	0.26
196.2	4.60	1.5	0.20
199.2	4.68	1.2	0.16
202.2	4.76	1.0	0.13
205.2	4.84	0.7	0.09
208.2	4.92	0.5	0.07
211.2	5.00	0.4	0.05
214.2	5.07	0.2	0.03
217.2	5.15	0	0

TABLE A.4 - Continued.

For Peak No. 79

$t_c(\text{sec})$	$(V_g/RT_c) \times 10^7$ (gmol/g mmHg)	$c(t)(\text{mm})$	$p(\text{mm Hg})$
114.6	2.45	230.0	28.81
117.6	2.53	215.0	26.93
120.6	2.61	193.0	24.17
123.6	2.69	167.0	20.92
126.6	2.77	141.0	17.66
129.6	2.85	118.0	14.78
132.6	2.92	98.0	12.27
135.6	3.00	80.0	10.02
138.6	3.08	63.5	7.95
141.6	3.16	51.0	6.39
144.6	3.24	40.0	5.01
147.6	3.32	31.0	3.88
150.6	3.40	24.0	3.01
153.6	3.47	18.0	2.25
156.6	3.55	14.0	1.75
159.6	3.63	10.0	1.25
162.6	3.71	8.0	1.00
165.6	3.79	6.0	0.75
168.6	3.87	4.5	0.56
171.6	3.95	3.0	0.38
174.6	4.03	2.5	0.31
177.6	4.10	2.0	0.25
180.6	4.18	1.5	0.19
183.6	4.26	1.0	0.13
186.6	4.34	0.8	0.10
189.6	4.42	0.6	0.08
192.6	4.50	0.4	0.05
195.6	4.58	0.2	0.03
198.6	4.65	0.1	0.01
201.6	4.73	0	0

TABLE A.4 - Continued.

For Peak No. 80

t_c (sec)	$(V_g/RT_c) \times 10^7$ (gmol/g mmHg)	$c(t)$ (mm)	p (mm Hg)
112.2	2.42	221.0	30.06
115.2	2.49	205.0	27.88
118.2	2.57	178.0	24.21
121.2	2.65	151.0	20.54
124.2	2.73	128.0	17.41
127.2	2.81	103.5	14.08
130.2	2.89	85.0	11.56
133.2	2.97	67.0	9.11
136.2	3.05	53.5	7.28
139.2	3.13	41.0	5.58
142.2	3.21	32.0	4.35
145.2	3.29	24.0	3.26
148.2	3.37	18.0	2.45
151.2	3.45	13.0	1.77
154.2	3.52	10.0	1.36
157.2	3.60	7.5	1.02
160.2	3.68	5.5	0.75
163.2	3.76	4.0	0.54
166.2	3.84	3.0	0.41
169.2	3.92	2.5	0.34
172.2	4.00	1.5	0.20
175.2	4.08	1.3	0.17
178.2	4.16	1.0	0.14
181.2	4.24	0.8	0.11
184.2	4.32	0.6	0.08
187.2	4.40	0.4	0.05
190.2	4.47	0.2	0.03
193.2	4.55	0.1	0.01
196.2	4.63	0	0

TABLE A.4 - Continued.

For Peak No. 81

t_c (sec)	$(V_g/RT_c) \times 10^7$ (gmol/g mmHg)	$c(t)$ (mm)	p (mm Hg)
99.0	2.07	127.5	32.31
102.0	2.15	118.0	29.90
105.0	2.23	102.0	25.85
108.0	2.30	84.0	21.29
111.0	2.38	69.0	17.49
114.0	2.46	53.0	13.43
117.0	2.54	41.0	10.39
120.0	2.62	31.5	7.98
123.0	2.70	24.0	6.08
126.0	2.78	18.0	4.56
129.0	2.86	13.0	3.29
132.0	2.94	9.5	2.41
135.0	3.02	6.5	1.65
138.0	3.09	5.0	1.27
141.0	3.17	3.5	0.89
144.0	3.25	2.5	0.63
147.0	3.33	2.0	0.51
150.0	3.41	1.5	0.38
153.0	3.49	1.0	0.25
156.0	3.57	0.8	0.20
159.0	3.65	0.5	0.13
162.0	3.73	0.4	0.10
165.0	3.80	0.3	0.76
168.0	3.88	0.2	0.05
171.0	3.96	0.1	0.03
174.0	4.04	0	0

TABLE A.4 - Continued.

For Peak No. 82

t_c (sec)	$(V_g/RT_c) \times 10^7$ (gmol/g mmHg)	$c(t)$ (mm)	p (mm Hg)
93.6	2.02	123.0	34.01
96.6	2.10	111.0	30.69
99.6	2.18	93.0	25.72
102.6	2.26	75.5	20.88
105.6	2.34	59.0	16.32
108.6	2.43	45.5	12.52
111.6	2.51	34.0	9.40
114.6	2.60	24.0	6.64
117.6	2.67	18.0	4.98
120.6	2.75	12.0	3.32
123.6	2.83	8.5	2.35
126.6	2.92	6.0	1.66
129.6	3.00	4.5	1.24
132.6	3.08	3.0	0.83
135.6	3.16	2.0	0.55
138.6	3.24	1.5	0.41
141.6	3.32	1.0	0.28
144.6	3.41	0.8	0.22
147.6	3.49	0.6	0.17
150.6	3.57	0.4	0.11
153.6	3.65	0.3	0.08
156.6	3.73	0.2	0.06
159.6	3.81	0.1	0.03
162.6	3.90	0	0

TABLE A.4 - Continued.

For Peak No. 83

t_c (sec)	$(V_g/RT_c) \times 10^7$ (gmol/g mmHg)	$c(t)$ (mm)	p (mm Hg)
91.2	1.78	147.5	36.06
94.2	1.86	138.0	33.74
97.2	1.93	117.0	28.61
100.2	2.01	96.0	23.47
103.2	2.08	75.0	18.34
106.2	2.16	54.0	13.20
109.2	2.24	40.5	9.90
112.2	2.31	30.0	7.34
115.2	2.39	22.0	5.38
118.2	2.46	15.0	3.67
121.2	2.54	10.0	2.45
124.2	2.62	7.5	1.83
127.2	2.69	5.5	1.34
130.2	2.77	4.0	0.98
133.2	2.84	3.0	0.73
136.2	2.92	2.0	0.49
139.2	3.00	1.5	0.37
142.2	3.07	1.2	0.29
145.2	3.15	1.0	0.24
148.2	3.22	0.9	0.22
151.2	3.30	0.7	0.17
154.2	3.38	0.5	0.12
157.2	3.45	0.4	0.10
160.2	3.53	0.3	0.07
163.2	3.60	0.1	0.02
166.2	3.68	0	0

TABLE A.4 - Continued.

For Peak No. 84

t_c (sec)	$(V_g/RT_c) \times 10^7$ (gmol/g mmHg)	$c(t)$ (mm)	p (mm Hg)
85.8	1.73	144.0	37.73
88.8	1.80	131.0	34.33
91.8	1.88	110.0	28.82
94.8	1.96	87.0	22.80
97.8	2.04	66.5	17.43
100.8	2.12	50.5	13.23
103.8	2.20	36.5	9.56
106.8	2.28	26.0	6.81
109.8	2.35	13.5	3.54
112.8	2.43	13.0	3.41
115.8	2.51	9.5	2.49
118.8	2.59	7.0	1.83
121.8	2.67	5.0	1.31
124.8	2.75	3.5	0.92
127.8	2.82	2.5	0.66
130.8	2.90	2.0	0.52
133.8	2.98	1.5	0.39
136.8	3.06	1.0	0.26
139.8	3.14	0.8	0.21
142.8	3.22	0.6	0.16
145.8	3.30	0.4	0.10
148.8	3.37	0.3	0.08
151.8	3.45	0.2	0.05
154.8	3.53	0.1	0.03
157.8	3.61	0	0

TABLE A.4 - Continued.

For Peak No. 85

t_c (sec)	$(V_g/RT_c) \times 10^2$ (gmol/g mmHg)	$c(t)$ (mm)	p (mm Hg)
85.2	1.61	153.0	39.90
88.2	1.68	141.0	36.77
91.2	1.76	114.0	29.73
94.2	1.83	88.0	22.95
97.2	1.91	64.0	16.69
100.2	1.99	47.5	12.39
103.2	2.06	34.0	8.87
106.2	2.14	24.0	6.26
109.2	2.21	16.0	4.17
112.2	2.29	10.5	2.74
115.2	2.36	7.0	1.82
118.2	2.44	5.0	1.30
121.2	2.49	3.5	0.91
124.2	2.59	2.5	0.65
127.2	2.66	1.5	0.39
130.2	2.74	1.0	0.26
133.2	2.81	0.8	0.21
136.2	2.89	0.6	0.16
139.2	2.96	0.3	0.08
142.2	3.04	0	0

TABLE A.4 - Continued.

For Peak No. 86

t_c (sec)	$(V_g/RT_c) \times 10^7$ (gmol/g mmHg)	$c(t)$ (mm)	p (mm Hg)
78.6	1.58	158.0	39.85
81.6	1.66	145.5	36.70
84.6	1.74	113.0	28.50
87.6	1.82	89.0	22.45
90.6	1.90	62.0	15.64
93.6	1.98	43.5	10.97
96.6	2.06	29.0	7.31
99.6	2.14	20.0	5.04
102.6	2.22	12.5	3.15
105.6	2.30	9.0	2.27
108.6	2.38	6.0	1.51
111.6	2.46	4.0	1.01
114.6	2.54	3.0	0.76
117.6	2.62	2.0	0.50
120.6	2.70	1.5	0.38
123.6	2.78	1.0	0.25
126.6	2.86	0.9	0.23
129.6	2.95	0.7	0.18
132.6	3.03	0.5	0.13
135.6	3.11	0.3	0.08
138.6	3.19	0.2	0.05
141.6	3.27	0.1	0.03
144.6	3.35	0	0

TABLE A.4 - Continued.

For Peak No. 87

t_c (sec)	$(V_g/RT_c) \times 10^7$ (gmol/g mmHg)	$c(t)$ (mm)	p (mm Hg)
552.0	10.85	145.0	1.62
555.0	10.92	144.0	1.61
558.0	10.98	142.0	1.59
561.0	11.04	138.0	1.55
564.0	11.10	133.5	1.50
567.0	11.16	128.0	1.43
570.0	11.23	124.0	1.39
573.0	11.29	118.5	1.33
576.0	11.34	114.0	1.28
579.0	11.41	109.0	1.22
582.0	11.47	104.0	1.16
585.0	11.54	99.5	1.11
588.0	11.60	95.0	1.06
591.0	11.66	90.5	1.01
594.0	11.72	86.0	0.96
597.0	11.78	82.0	0.92
600.0	11.84	78.0	0.87
603.0	11.91	74.0	0.83
606.0	11.97	70.5	0.79
609.0	12.03	67.0	0.75
612.0	12.09	63.5	0.71
615.0	12.15	61.0	0.68
618.0	12.22	57.5	0.64
621.0	12.28	55.0	0.62
624.0	12.34	52.0	0.58
630.0	12.46	47.0	0.53
636.0	12.59	42.0	0.47
642.0	12.71	37.0	0.41
648.0	12.84	32.5	0.36
654.0	12.96	28.5	0.32
660.0	12.08	25.0	0.28
666.0	13.21	22.0	0.25
672.0	13.83	19.0	0.21
678.0	13.45	16.5	0.19
684.0	13.57	14.5	0.16
690.0	13.70	13.0	0.15
696.0	13.83	11.0	0.12
702.0	13.95	10.0	0.11
708.0	14.07	8.0	0.09
714.0	14.20	7.0	0.08
720.0	14.32	6.5	0.07
726.0	14.45	6.0	0.07
732.0	14.57	5.0	0.06
744.0	14.69	4.5	0.05
764.0	14.82	4.0	0.05
864.0	17.29	0	0

TABLE A.4 - Continued.

For Peak No. 88

t_c (sec)	$(V_g/RT_c) \times 10^7$ (gmo1/g mmHg)	$c(t)$ (mm)	p (mm Hg)
495.0	9.92	173.0	1.82
498.0	9.98	171.0	1.80
501.0	10.04	167.5	1.77
504.0	10.11	162.0	1.71
507.0	10.17	155.0	1.63
510.0	10.23	149.0	1.57
513.0	10.30	142.5	1.50
516.0	10.36	135.5	1.43
519.0	10.42	129.5	1.37
522.0	10.49	129.0	1.36
525.0	10.55	117.0	1.23
528.0	10.61	110.5	1.17
531.0	10.68	105.0	1.11
534.0	10.74	99.5	1.05
537.0	10.80	93.5	0.99
540.0	10.87	88.5	0.93
543.0	10.93	83.0	0.88
546.0	10.99	79.0	0.83
549.0	11.06	74.5	0.79
552.0	11.12	69.5	0.73
555.0	11.18	65.5	0.69
558.0	11.25	61.5	0.65
561.0	11.31	58.0	0.61
564.0	11.37	53.5	0.56
567.0	11.44	50.5	0.53
570.0	11.50	47.0	0.50
576.0	11.63	41.0	0.42
582.0	11.75	35.5	0.37
588.0	11.88	30.5	0.32
594.0	12.01	26.0	0.27
600.0	12.13	22.5	0.24
606.0	12.26	19.0	0.20
612.0	12.38	16.0	0.17
618.0	12.51	14.0	0.15
624.0	12.64	12.0	0.13
630.0	12.76	10.0	0.11
636.0	12.89	9.0	0.10
642.0	13.02	8.0	0.08
648.0	13.14	7.0	0.07
654.0	13.27	6.0	0.06
660.0	13.40	5.5	0.06
666.0	13.52	5.0	0.05
672.0	13.65	4.5	0.05
678.0	13.78	4.0	0.04
684.0	13.90	3.5	0.04
690.0	14.03	3.0	0.03
840.0	17.19	0	0

TABLE A.4 - Continued.

For Peak No. 89

t_c (sec)	$(V_g/RT_c) \times 10^7$ (gmol/g mmHg)	$c(t)$ (mm)	p (mm Hg)
408.0	7.98	197.0	2.26
411.0	8.05	194.0	2.23
414.0	8.11	186.0	2.13
417.0	8.17	177.5	2.04
420.0	8.23	166.5	2.91
423.0	8.30	157.0	1.80
426.0	8.36	148.0	1.70
429.0	8.42	141.0	1.62
432.0	8.48	130.0	1.49
435.0	8.55	122.5	1.41
438.0	8.61	114.0	1.31
441.0	8.67	106.0	1.22
444.0	8.73	99.0	1.14
447.0	8.80	92.5	1.06
450.0	8.86	85.0	0.98
453.0	8.92	78.0	0.90
456.0	8.98	72.0	0.83
459.0	9.05	66.0	0.76
462.0	9.11	60.0	0.69
465.0	9.17	55.0	0.63
468.0	9.23	51.0	0.59
471.0	9.30	46.0	0.53
474.0	9.36	42.0	0.48
477.0	9.42	38.0	0.44
480.0	9.48	35.0	0.40
483.0	9.55	31.0	0.36
486.0	9.61	28.0	0.32
489.0	9.67	25.5	0.29
492.0	9.73	23.0	0.26
495.0	9.80	20.5	0.24
498.0	9.86	18.5	0.21
501.0	9.92	16.5	0.19
504.0	9.98	15.0	0.17
507.0	10.05	13.5	0.16
510.0	10.11	12.0	0.14
513.0	10.17	11.0	0.13
516.0	10.23	10.0	0.12
519.0	10.30	9.0	0.10
522.0	10.36	8.0	0.09
525.0	10.42	7.0	0.08
528.0	10.48	6.5	0.08
531.0	10.55	5.5	0.06
534.0	10.61	5.0	0.06
537.0	10.67	4.8	0.06
540.0	10.73	4.5	0.05
543.0	10.80	4.0	0.05
546.0	10.86	3.5	0.04
549.0	10.92	3.0	0.03
609.0	12.17	0	0

TABLE A.4 - Continued.

For Peak No. 90

t_c (sec)	$(V_g/RT_c) \times 10^7$ (gmol/g mmHg)	$c(t)$ (mm)	p (mm Hg)
363.6	7.36	218.5	2.58
366.6	7.42	214.0	2.53
369.6	7.48	206.0	2.44
372.6	7.55	191.5	2.26
375.6	7.61	181.5	2.15
378.6	7.68	169.5	2.00
381.6	7.74	155.5	1.84
384.6	7.81	145.0	1.71
387.6	7.87	133.5	1.58
390.6	7.93	123.0	1.45
393.6	8.00	123.0	1.33
396.6	8.06	103.5	1.22
399.6	8.13	93.0	1.10
402.6	8.19	85.0	1.01
405.6	8.26	77.5	1.92
408.6	8.32	68.0	0.80
411.6	8.38	63.0	0.75
414.6	8.45	56.0	0.66
417.6	8.51	51.0	0.60
420.6	8.58	45.0	0.53
423.6	8.64	40.5	0.48
426.6	8.71	36.0	0.43
429.6	8.77	32.0	0.38
432.6	8.83	28.0	0.33
435.6	8.90	24.5	0.29
438.6	8.96	22.0	0.26
441.6	9.03	19.5	0.23
447.6	9.16	15.0	0.18
453.6	9.28	12.0	0.14
459.6	9.41	9.0	0.11
465.6	9.54	7.5	0.09
471.6	9.67	5.5	0.07
477.6	9.80	4.5	0.05
483.6	9.93	4.0	0.05
489.6	10.06	3.0	0.04
495.6	10.18	2.0	0.02
501.6	10.31	1.5	0.02
561.6	11.60	0	0

TABLE A.4 - Continued.

For Peak No. 91

t_c (sec)	$(V_g/RT_c) \times 10^7$ (gmol/g mmHg)	$c(t)$ (sec)	p (mm Hg)
319.8	6.33	143.0	2.81
322.8	6.39	140.0	2.75
325.8	6.45	133.0	2.62
328.8	6.52	124.5	2.45
331.8	6.58	114.0	2.24
334.8	6.65	105.0	2.07
337.8	6.71	96.0	1.89
340.8	6.78	88.0	1.73
343.8	6.84	78.5	1.54
346.8	6.90	71.5	1.41
349.8	6.97	65.0	1.28
352.8	7.03	59.0	1.16
355.8	7.10	52.5	1.03
358.8	7.16	47.0	0.92
361.8	7.23	42.0	0.83
364.8	7.29	37.0	0.73
367.8	7.35	33.0	0.65
370.8	7.42	29.5	0.58
373.8	7.48	25.5	0.50
379.8	7.61	20.0	0.39
385.8	7.74	15.5	0.31
391.8	7.87	12.0	0.24
397.8	8.00	9.5	0.19
403.8	8.13	7.5	0.15
409.8	8.25	6.0	0.12
415.8	8.38	5.0	0.10
421.8	8.51	4.0	0.08
427.8	8.64	3.5	0.07
433.8	8.77	3.0	0.06
523.8	10.70	0	0

TABLE A.4 - Continued.

For Peak No. 92

t_c (sec)	$(V_g/RT_c) \times 10^7$ (gmo1/g mmHg)	$c(t)$ (mm)	p (mm Hg)
291.6	5.53	155.5	3.38
294.6	5.59	151.0	3.28
297.6	5.66	141.5	3.07
300.6	5.72	130.5	2.83
303.6	5.78	119.0	2.58
306.6	5.84	108.0	2.34
309.6	5.90	97.0	2.11
312.6	5.97	87.0	1.89
315.6	6.03	77.0	1.67
318.6	6.09	69.0	1.50
321.6	6.15	62.0	1.35
324.6	6.22	54.0	1.17
327.6	6.28	47.0	1.02
330.6	6.34	41.0	0.89
333.6	6.40	35.5	0.77
336.6	6.46	30.5	0.66
339.6	6.53	26.0	0.56
342.6	6.59	22.5	0.49
345.6	6.65	19.0	0.41
348.6	6.71	16.0	0.35
351.6	6.77	13.5	0.29
354.6	6.84	11.0	0.24
357.6	6.90	10.0	0.22
360.6	6.96	8.5	0.18
366.6	7.08	6.0	0.13
372.6	7.21	4.0	0.09
378.6	7.33	3.0	0.07
384.6	7.46	2.5	0.05
390.6	7.58	2.0	0.04
396.6	7.71	1.5	0.03
444.6	8.70	0	0

TABLE A.4 - Continued.

For Peak No. 93

t_c (sec)	$(V_g/RT_c) \times 10^7$ (gmol/g mmHg)	$c(t)$ (mm)	p (mm Hg)
234.0	4.31	200.0	4.05
237.0	4.37	195.0	3.95
240.0	4.43	179.0	3.62
243.0	4.49	161.5	3.27
246.0	4.55	141.5	2.86
249.0	4.62	126.0	2.55
252.0	4.68	111.0	2.25
255.0	4.74	94.0	1.91
258.0	4.80	81.5	1.65
261.0	4.86	69.0	1.40
264.0	4.92	57.0	1.14
267.0	4.98	49.0	0.99
270.0	5.05	40.0	0.81
273.0	5.11	33.5	0.68
276.0	5.17	27.5	0.56
279.0	5.23	22.0	0.45
282.0	5.29	18.0	0.36
285.0	5.35	15.0	0.30
288.0	5.41	12.5	0.25
291.0	5.48	10.5	0.21
294.0	5.54	8.5	0.17
297.0	5.60	7.5	0.15
300.0	5.66	6.5	0.13
303.0	5.72	5.5	0.11
309.0	5.84	4.0	0.08
315.0	5.97	3.5	0.07
321.0	6.09	3.0	0.06
327.0	6.21	2.5	0.05
333.0	6.34	2.0	0.04
339.0	6.46	1.5	0.03
393.0	7.56	0	0

TABLE A.4 - Continued.

For Peak No. 94

t_c (sec)	$(V_g/RT_c) \times 10^7$ (gmol/g mmHg)	$c(t)$ (mm)	p (mm Hg)
208.2	3.81	212.0	4.53
211.2	3.87	206.5	4.41
214.2	3.94	184.0	4.93
217.2	4.00	162.5	3.47
220.2	4.06	140.0	2.99
223.2	4.12	117.0	2.50
226.2	4.18	99.0	2.12
229.2	4.24	82.0	1.75
232.0	4.31	67.0	1.43
235.2	4.37	54.0	1.15
238.2	4.43	43.0	0.92
241.2	4.49	34.0	0.73
244.2	4.55	26.0	0.56
247.2	4.62	20.5	0.44
250.2	4.68	16.0	0.34
253.2	4.74	12.0	0.26
256.2	4.80	9.5	0.20
259.2	4.86	7.5	0.16
262.2	4.92	6.0	0.13
265.2	4.99	4.5	0.10
268.2	5.05	4.0	0.09
271.2	5.11	3.5	0.08
274.2	5.17	3.0	0.06
277.2	5.23	2.5	0.05
280.2	5.30	2.0	0.04
315.0	6.01	0	0

TABLE A.4 - Continued.

For Peak No. 95

t_c (sec)	$(V_g/RT_c) \times 10^7$ (gmol/g mmHg)	$c(t)$ (mm)	p (mm Hg)
174.6	3.22	133.0	5.06
177.6	3.28	127.0	4.83
180.6	3.35	111.5	4.24
183.6	3.41	96.0	3.65
186.6	3.48	78.5	2.99
189.6	3.54	63.0	2.40
192.6	3.60	51.0	1.94
195.6	3.67	39.0	1.48
198.6	3.73	29.0	1.10
201.6	3.79	22.0	0.84
204.6	3.86	16.5	0.63
207.6	3.92	12.5	0.48
210.6	3.98	9.0	0.34
213.6	4.05	7.0	0.27
216.6	4.11	5.5	0.21
219.6	4.18	4.0	0.15
222.6	4.24	3.5	0.13
225.6	4.30	3.0	0.11
228.6	4.37	2.5	0.10
231.6	4.43	2.3	0.09
234.6	4.49	2.0	0.08
276.6	5.38	0	0

TABLE A.4 - Continued.

For Peak No. 96

t_c (sec)	$(V_g/RT_c) \times 10^6$ (gmol/g mmHg)	$c(t)$ (mm)	p (mm Hg)
939.0	1.85	130.5	1.48
954.0	1.89	124.5	1.42
969.0	1.92	114.0	1.30
984.0	1.95	103.5	1.18
999.0	1.98	93.5	1.06
1014.0	2.01	84.0	0.95
1029.0	2.04	75.0	0.85
1044.0	2.07	66.0	0.75
1059.0	2.10	59.5	0.68
1074.0	2.13	52.0	0.59
1089.0	2.16	45.0	0.51
1104.0	2.19	39.0	0.44
1119.0	2.22	34.0	0.39
1134.0	2.25	29.0	0.33
1149.0	2.28	24.0	0.27
1164.0	2.31	20.0	0.23
1179.0	2.34	16.0	0.18
1194.0	2.37	13.0	0.15
1209.0	2.40	11.0	0.13
1224.0	2.43	8.0	0.09
1239.0	2.46	6.0	0.07
1254.0	2.49	5.0	0.06
1269.0	2.52	3.0	0.03
1284.0	2.55	2.0	0.02
1299.0	2.59	1.0	0.01
1314.0	2.62	0.5	0.01
1329.0	2.65	0	0

TABLE A.4 - Continued.

For Peak No. 97

$t_c(\text{sec})$	$(V_g/RT_c) \times 10^6$ (gmol/g mmHg)	$c(t)(\text{mm})$	$p(\text{mm Hg})$
852.0	1.60	140.5	1.55
867.0	1.63	134.0	1.48
882.0	1.66	121.0	1.34
897.0	1.69	111.0	1.23
912.0	1.72	98.5	1.09
927.0	1.75	89.0	0.89
942.0	1.77	78.5	0.87
957.0	1.80	70.5	0.78
972.0	1.83	62.0	0.69
987.0	1.86	55.0	0.61
1002.0	1.89	47.0	0.52
1017.0	1.92	41.0	0.45
1032.0	1.95	35.0	0.39
1047.0	1.98	30.5	0.34
1062.0	2.01	25.5	0.28
1077.0	2.04	22.0	0.24
1092.0	2.07	18.0	0.20
1107.0	2.09	15.0	0.17
1122.0	2.12	12.5	0.14
1137.0	2.15	10.0	0.11
1152.0	2.18	8.5	0.09
1167.0	2.21	7.0	0.08
1182.0	2.24	5.5	0.06
1197.0	2.27	4.5	0.05
1212.0	2.30	4.0	0.04
1227.0	2.33	3.0	0.03
1242.0	2.36	2.5	0.03
1257.0	2.39	2.0	0.02
1272.0	2.42	1.5	0.02
1422.0	0	1.0	0

TABLE A.4 - Continued.

For Peak No. 98.

t_c (sec)	$(V_g/RT_c) \times 10^6$ (gmol/g mmHg)	$c(t)$ (mm)	p (mm Hg)
685.8	1.39	189.5	1.89
688.8	1.40	188.5	1.88
694.8	1.41	181.0	1.81
700.8	1.42	174.0	1.74
706.8	1.43	165.0	1.65
712.8	1.45	155.5	1.55
718.8	1.46	148.5	1.48
724.8	1.47	141.0	1.41
730.8	1.49	133.0	1.33
736.8	1.50	126.0	1.26
742.8	1.51	119.0	1.19
748.8	1.52	113.0	1.13
754.8	1.54	105.0	1.05
760.8	1.55	99.0	0.99
766.8	1.56	94.0	0.94
772.8	1.57	87.0	0.87
778.8	1.58	81.0	0.81
784.8	1.60	76.0	0.76
790.8	1.61	71.0	0.71
796.8	1.62	65.5	0.65
802.8	1.64	61.0	0.61
808.8	1.65	56.0	0.56
814.8	1.66	52.0	0.52
820.8	1.67	48.0	0.48
826.8	1.69	43.5	0.43
832.8	1.70	41.0	0.41
844.8	1.73	34.0	0.34
856.8	1.75	28.0	0.28
868.8	1.78	23.0	0.23
880.8	1.80	18.5	0.18
892.8	1.83	14.5	0.14
904.8	1.85	11.5	0.11
916.8	1.88	9.0	0.09
928.8	1.90	7.0	0.07
940.8	1.93	5.0	0.05
952.8	1.95	4.0	0.04
964.8	1.98	3.0	0.03
1024.8	2.10	0	0

TABLE A.4 - Continued.

For Peak No. 99

$t_c(\text{sec})$	$(V_g/RT_c) \times 10^6$ (gmol/g mmHg)	$c(t)(\text{mm})$	$p(\text{mm Hg})$
632.4	1.29	98.0	1.41
638.4	1.30	95.0	1.37
644.4	1.31	89.0	1.28
650.4	1.33	82.0	1.18
656.4	1.34	76.0	1.09
662.4	1.36	70.0	1.01
668.4	1.37	63.0	0.91
674.4	1.38	57.5	0.83
680.4	1.40	52.0	0.75
686.4	1.41	46.5	0.67
692.4	1.42	41.0	0.59
698.4	1.43	37.0	0.53
704.4	1.44	33.0	0.47
710.4	1.46	29.0	0.42
716.4	1.47	25.0	0.36
722.4	1.48	22.0	0.32
728.4	1.50	19.0	0.27
734.4	1.51	17.0	0.24
740.4	1.52	14.5	0.21
746.4	1.53	12.5	0.18
752.4	1.55	11.0	0.16
758.4	1.56	9.5	0.14
764.4	1.57	7.5	0.11
770.4	1.58	6.5	0.09
776.4	1.60	5.5	0.08
782.4	1.61	5.0	0.07
788.4	1.62	4.0	0.06
794.4	1.64	3.0	0.04
800.4	1.65	2.5	0.04
806.4	1.66	2.0	0.03
812.4	1.67	1.5	0.02
818.4	1.69	1.2	0.02
824.4	1.70	1.0	0.01
830.4	1.71	0.5	0.01
836.4	1.72	0	0

TABLE A.4 - Continued.

For Peak No. 100

t_c (sec)	$(V_g/RT_c) \times 10^6$ (gmol/g mmHg)	$c(t)$ (mm)	p (mm Hg)
492.0	0.92	149.0	1.72
498.0	0.93	142.0	1.63
504.0	0.94	132.0	1.52
510.0	0.95	117.0	1.35
516.0	0.97	106.0	1.22
522.0	0.98	95.0	1.09
528.0	0.99	84.0	0.97
534.0	1.00	73.5	0.85
540.0	1.01	65.0	0.75
546.0	1.02	57.0	0.66
552.0	1.04	48.0	0.55
558.0	1.05	42.0	0.48
564.0	1.06	36.0	0.41
570.0	1.07	31.5	0.36
576.0	1.08	26.5	0.31
582.0	1.09	23.0	0.26
588.0	1.11	19.0	0.22
594.0	1.12	16.5	0.19
600.0	1.13	14.0	0.16
606.0	1.14	12.0	0.14
612.0	1.15	11.0	0.13
618.0	1.17	9.5	0.11
624.0	1.18	8.5	0.10
630.0	1.19	7.5	0.09
636.0	1.20	7.0	0.08
642.0	1.21	6.0	0.07
648.0	1.22	5.5	0.06
654.0	1.24	5.0	0.06
660.0	1.25	4.5	0.05
666.0	1.26	4.0	0.05
672.0	1.27	3.5	0.04
678.0	1.28	3.0	0.03
684.0	1.29	2.5	0.03
690.0	1.31	2.0	0.02
696.0	1.32	1.5	0.02
702.0	1.33	1.0	0.01
708.0	1.34	0.8	0.01
744.0	1.41	0	0

TABLE A.4 - Continued.

For Peak No. 101

t_c (sec)	$(V_g/RT_c) \times 10^6$ (gmol/g mmHg)	$c(t)$ (mm)	p (mm Hg)
348.0	0.68	121.0	2.45
351.0	0.68	117.5	2.38
354.0	0.69	111.0	2.24
357.0	0.70	104.0	2.10
360.0	0.70	96.0	1.94
363.0	0.71	87.5	1.77
366.0	0.72	80.0	1.62
369.0	0.72	73.0	1.48
372.0	0.73	66.5	1.34
375.0	0.73	60.0	1.21
378.0	0.74	54.0	1.09
381.0	0.75	48.0	0.97
384.0	0.75	43.0	0.87
387.0	0.76	37.5	0.76
390.0	0.77	33.5	0.68
393.0	0.77	30.0	0.61
396.0	0.78	25.5	0.52
399.0	0.78	23.0	0.47
402.0	0.79	19.0	0.38
405.0	0.80	17.0	0.34
408.0	0.80	14.5	0.29
411.0	0.81	12.0	0.24
414.0	0.82	10.5	0.21
420.0	0.83	8.0	0.16
426.0	0.84	6.0	0.12
432.0	0.85	4.0	0.08
438.0	0.87	3.5	0.07
444.0	0.88	3.0	0.06
450.0	0.89	2.5	0.05
456.0	0.90	2.0	0.04
528.0	1.05	0	0

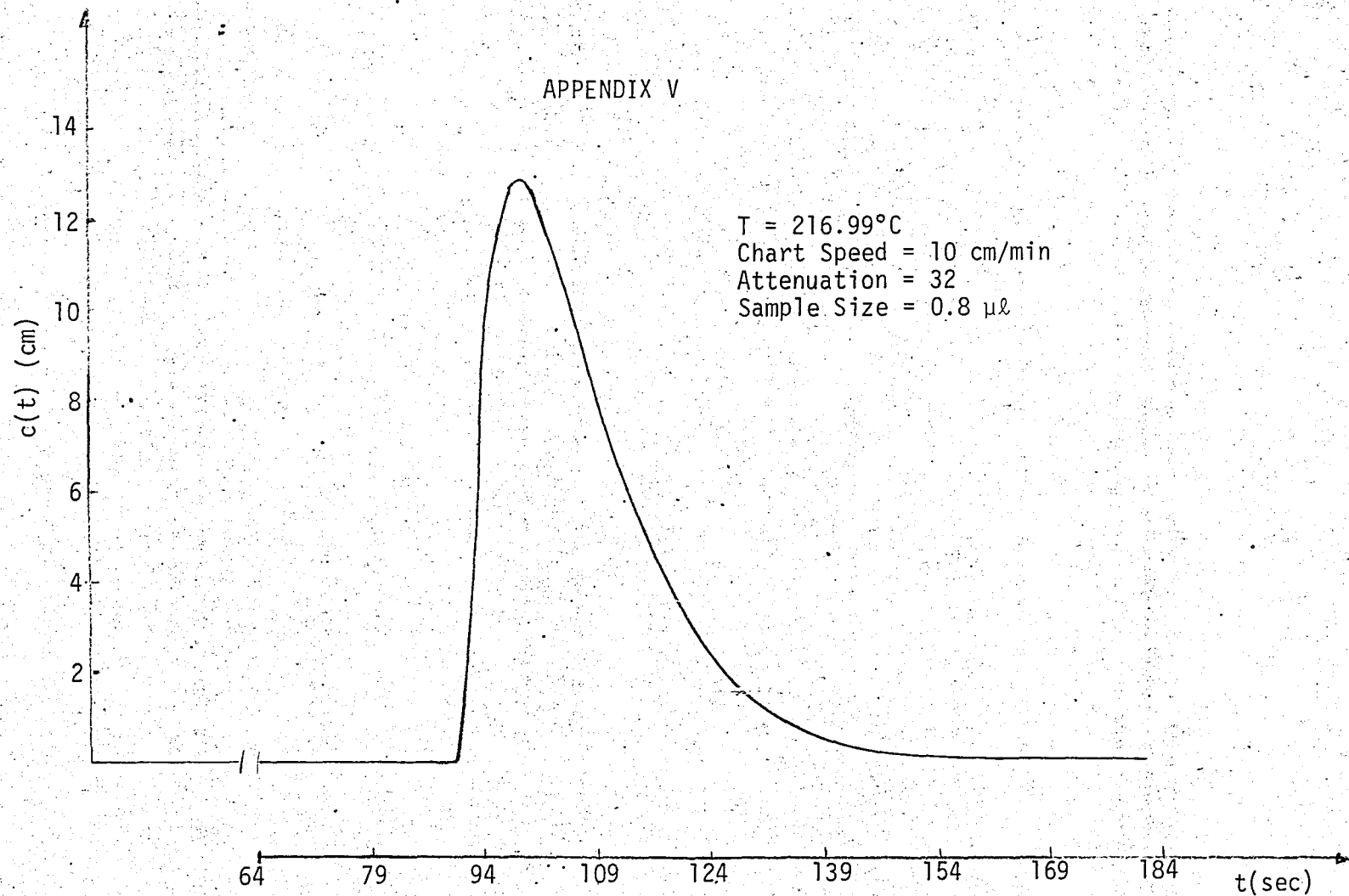


Figure A.5.1 - Sample chromatogram for methylcyclohexane.

APPENDIX V - Continued.

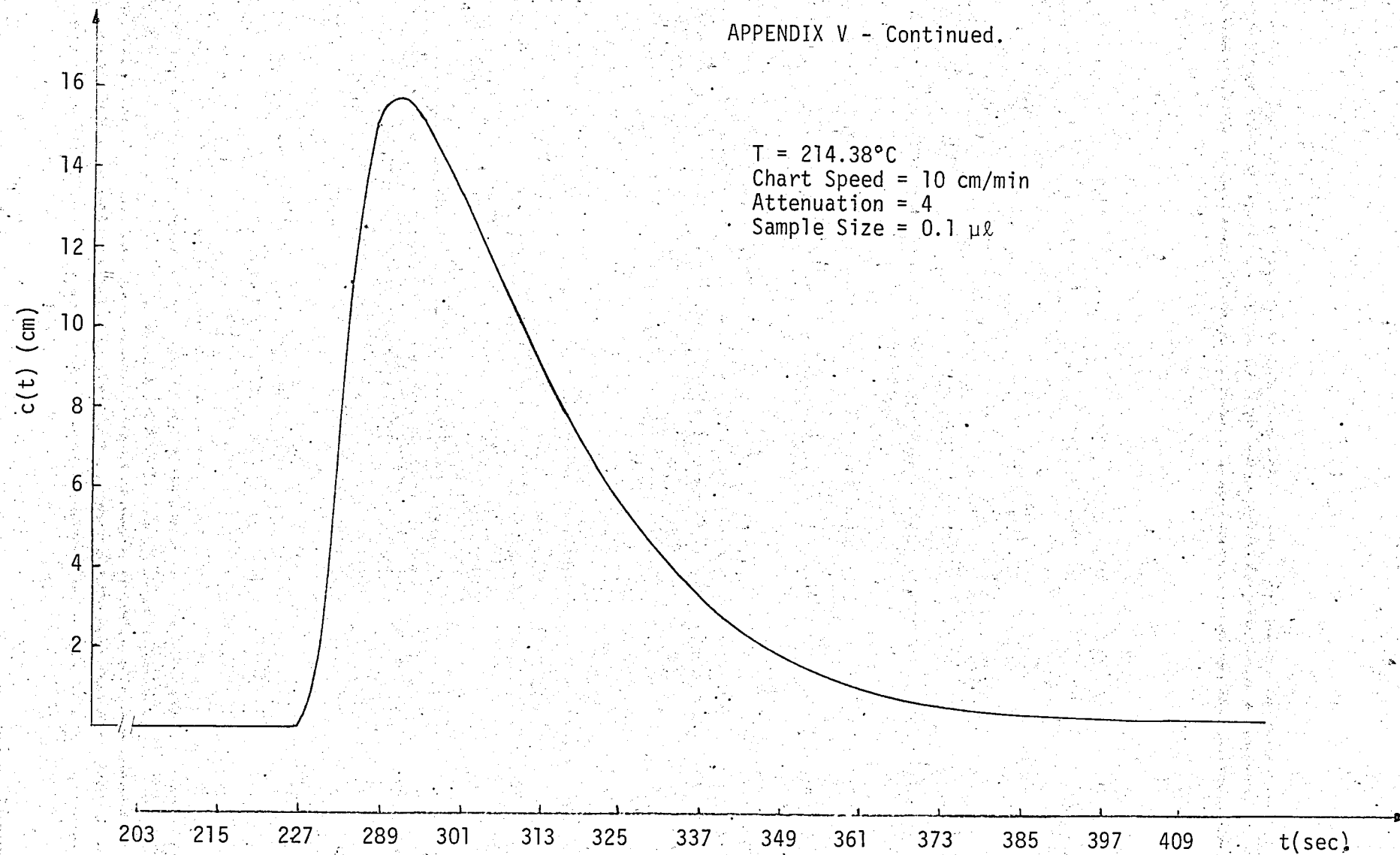


Figure A.5.2 - Sample chromatogram for benzene.

APPENDIX V - Continued.

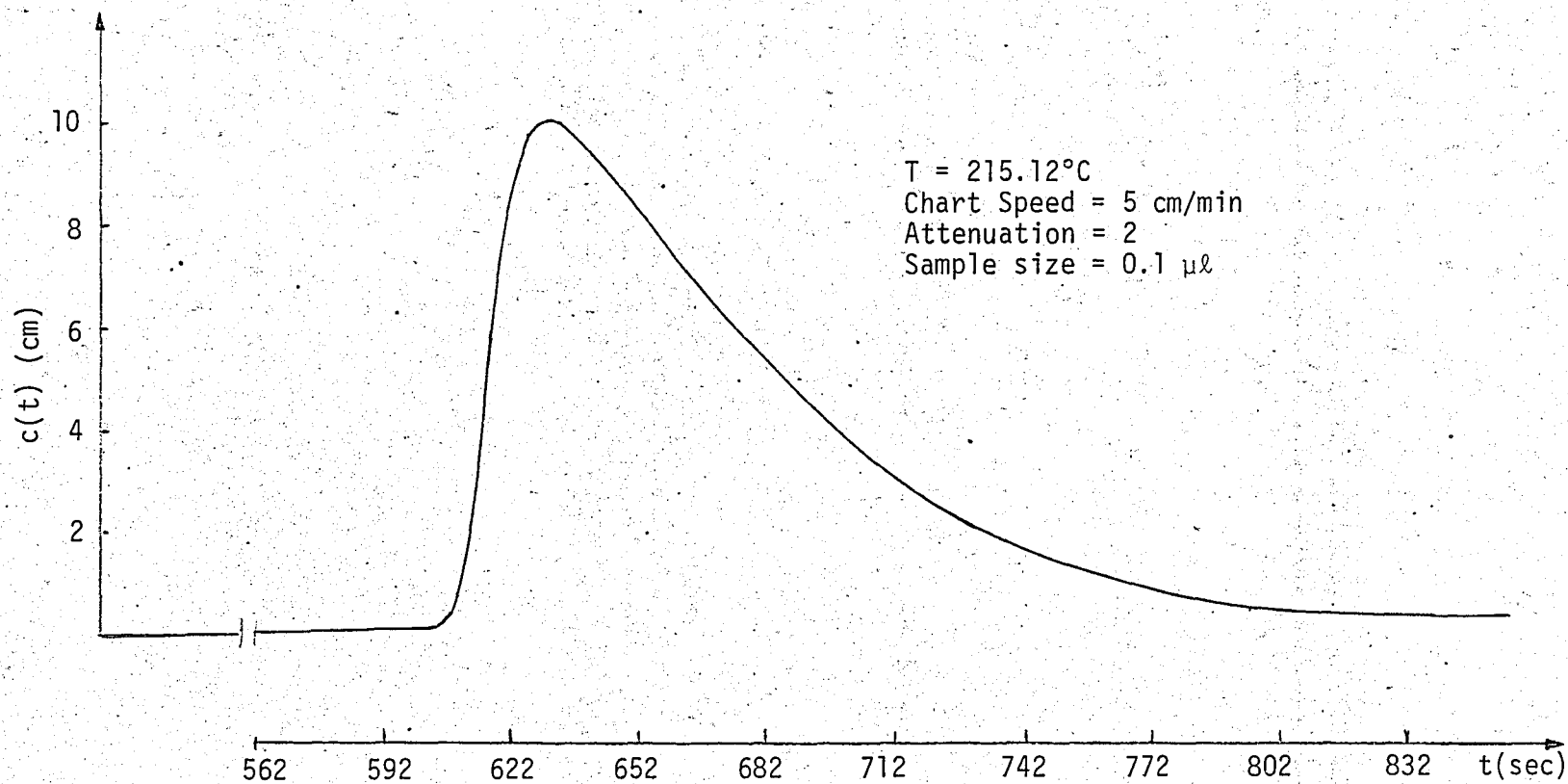


Figure A.5.3 - Sample chromatogram for toluene.