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# High Temperature Adsorption Studies On Solid Adsorbents

Julian Joseph Hamerski  
*University of the Pacific*

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HIGH TEMPERATURE ADSORPTION STUDIES  
ON SOLID ADSORBENTS

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A Dissertation  
Presented to  
the Faculty of the Graduate School  
University of the Pacific

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In Partial Fulfillment  
of the Requirements for the Degree  
Doctor of Philosophy

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by  
Julian Joseph Hamerski  
June 1963

This dissertation is approved for recommendation  
to the Graduate Council.

Department Chairman or Dean:

Emerson G. Cobb

Dissertation Committee:

Milton E. Diller, Chairman

Herschel J. Fung

C. W. Weaver

H. K. Zimmerman

Emerson G. Cobb

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## CHAPTER I

### INTRODUCTION

It has been found that there exist certain crystalline aluminosilicates which provide regular net-works of channels with diameters no bigger than those of molecules. Such crystals can act as sieves (thus the name "molecular sieves" now marketed by the Linde Air Products Company) and bring about a separation of molecular species by occluding small molecules while not adsorbing larger molecules or molecules with shapes that do not "fit."

The aluminosilicates were termed zeolites first by Baron Cronstedt (1) some 200 years ago. He observed that certain mineral crystals, when heated, appeared to melt and to boil at the same time. Thus, from the Greek "zeo," to boil, and "lithos," stone, Cronstedt coined the term "zeolite."

The use of zeolite (molecular sieves) has increased during the past several years. The earlier work (1930-1950) involved the study of the naturally occurring zeolites. During the last ten years the activity has been concerned with the use of synthetic crystalline zeolites in separating both gaseous and liquid components by the molecular sieve action.

In 1938, R. M. Barrer(2) undertook a study of zeolite molecular sieves. His investigations led a team of investigators at the Linde Company Division of Union Carbide Corporation, to synthesize some dozen crystalline zeolites. Some of these zeolites were analogous to the naturally occurring zeolites--chabazite, faujasite, etc.; but others were completely new compositions of matter. One of these had novel characteristics and was named Type A. The Linde Company is now in production and markets the following molecular sieves: 3A, 4A, 5A, 10X and 13X.

The purpose of this work is to study Linde Molecular Sieves Types 3A, 4A, 5A, 10X and 13X in regard to their adsorbing properties at high temperatures. The adsorptive properties of solids like molecular sieves, are conveniently studied by the use of high temperatures and allowing a pulse of adsorbate to be transported through a packed column of adsorbent by an inert carrier gas stream. A sensitive thermal conductivity cell is used to measure the concentration of the adsorbate in the effluent stream. Heats of adsorption are determined by measuring the pulse retention times at a series of temperatures.

This flow method is particularly useful for studying adsorption at high temperature conditions where static methods cannot be used because of the long contact times involved, which lead to decomposition of the adsorbates.

This work describes a gas-solid chromatographic technique for studying high temperature adsorption. The contact time of the hydrocarbon vapor (which is used) with the solid surface can be made quite short in such a flow system, thereby minimizing or even eliminating decomposition reactions.

In the first stage of this study, the work of Eberly(3) on benzene and n-hexane is repeated and compared along with the study of toluene, n-heptane, 2,2-dimethylbutane, 2,3-dimethylbutane, 2-methylpentane, 3-methylpentane, n-pentane, and 2-methylbutane on molecular sieve Type 13X. The rest of the work dealt with the above mentioned hydrocarbons as adsorbates and Type 3A, 4A, 5A and 10X as adsorbants.

## CHAPTER II

### HISTORY

The first recording of the phenomena of adsorption goes back to 1773 and the work<sup>a</sup> of C. W. Scheele and to Abbe F. Fontana (1777). Fontana found that wood charcoal possessed the capacity for the adsorption of gases. The earliest systematic experiments were carried out by T. de Saussure (1814), who employed a number of porous materials in conjunction with most of the gases known at the time. It is very probable that adsorption occurs on all surfaces, but the effects are not evident unless the adsorbing material is porous and has a very large area for a given mass. For this reason, various forms of charcoal have been extensively used in adsorption studies. Silica gel has also been employed in recent years for experimental work as well as in industrial practice.

Up to 1930 these investigations and studies that were made, were reviewed by J. W. McBain. S. Brunauer reviewed physical adsorption up to about 1942 and Mantell(4) reviewed adsorption as a "unit operation" of chemical engineering to

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<sup>a</sup>Much of the history was taken from C. K. Hersh's work (see reference 1) since many of the original references were not available.

1951. C. K. Hersh(1) reviewed adsorption in respect to crystalline aluminosilicates (molecular sieves) up to 1961.

It was J. W. McBain in the 1920's who noticed that the zeolites adsorbed some substances but not others, and who first spoke of zeolites as "molecular sieves," i.e., suggesting that they could be used to separate one kind of molecule from another. In 1938 R. M. Barrer undertook a lengthy study of zeolite molecular sieves. His investigations led the Linde Company to inquire whether zeolites could be used to separate atmosphere gases. By 1952 they had produced nearly a dozen types of synthetic zeolites. Some were analogous of natural crystals; others were entirely new varieties.

The work in relating chromatographic to adsorption phenomena commenced with Martin and Synge in 1941 (5), with prominent contributions from Greene and Pust in 1958 (6) and Eberly and Spencer in 1961 (7).

A sampling of the current literature (8,9,10) shows the following widely varied uses of molecular sieves; drying of gases such as air, hydrogen, natural gas, cracked gas and ethylene; drying of liquids such as benzene, alcohols, ketones, fluorocarbon refrigerants and hydrocarbons; purification and separation of gases like carbon dioxide from ethylene, carbon dioxide from annealing gas, hydrogen sulfide from natural gas; the removal of n-paraffins

from light naphthas. Recently a new and different use of molecular sieves has been introduced. They can function as carriers for a wide variety of chemical compounds. When needed, the chemical is released by heating the carrier or by displacement of the chemical with another adsorbed material, such as water.

## CHAPTER III

### STRUCTURE OF ZEOLITES

The zeolites are a family of hydrated aluminosilicates which have similar composition and properties. The mineralogist divides the silicate minerals into six rather broad classes based on the arrangement of  $\text{SiO}_4$  tetrahedra. One of these classes is known as the tectosilicates. In this class the silicate minerals are constructed around a three-dimensional framework of  $\text{SiO}_4$  tetrahedra. The oxygen atoms are shared by neighboring tetrahedra. The result of this sharing is a stable, strongly bonded structure in which the silicon to oxygen ratio is 0.50. The tectosilicate class of minerals is further subdivided into five groups or families with the Feldspar group and Zeolite family being its more important members.

The zeolite minerals are closely related in composition (see Table I), including not only the  $\text{SiO}_2$  group; but in addition, aluminum oxide,  $\text{Al}_2\text{O}_3$ , a cation, or cations, to balance the negative charge of the aluminosilicate structure, and water of hydration.

The structure of most crystals extends uniformly in all directions without leaving empty spaces on zeolites.

TABLE I

COMPOSITION OF SOME NATURAL ZEOLITES (8,11)

Mineral	Composition	Crystal Structure	Dimension A
Chabazite	$\text{CaNa}_2\text{Al}_2\text{Si}_4\text{O}_{12} \cdot 6\text{H}_2\text{O}$	Hexagonal	$a = 9.37$
Analcite	$\text{Na}_2\text{Al}_2\text{Si}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$	Cubic	$a = 13.7$
Faujasite	$\text{Na}_2\text{CaAl}_4\text{Si}_{10}\text{O}_{28} \cdot 20\text{H}_2\text{O}$	Cubic	$a = 24.65$
Stilbite	$\text{Na}_2\text{CaAl}_2\text{Si}_6\text{O}_{16} \cdot 16\text{H}_2\text{O}$	Monoclinic	
Natrolite	$\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$	Orthorhombic	$a = 18.3$
Thomsonite	$\text{NaCa}_2\text{Al}_5\text{Si}_5\text{O}_{20} \cdot 6\text{H}_2\text{O}$	Orthorhombic	$a = b = 13.0$
Heulandite	$\text{Ca}_2\text{Al}_4\text{Si}_{14}\text{O}_{36} \cdot 12\text{H}_2\text{O}$	Monoclinic	$a = 7.54$ $b = 17.97$ $c = 15.91$



However, the framework of silicon-oxygen and aluminum-oxygen tetrahedra forms a structure which is honeycombed with relatively large cavities. The shape and size of the cavities depends on the variety of zeolite. For example, in chabazite (2), which is one of the most common zeolites, six silicon and aluminum ions, with their associated oxygens, form a tight hexagon. Two of these hexagons face each other to form a flattish prism. Eight prisms linked together partially enclose a roughly football-shaped cavity whose longest diameter is about 11 angstrom units. Each cavity connects with adjacent cavities through apertures about 3.9 angstroms (A) in diameter.

The cavities are bound together in such a manner (12) that an open structure with wide channels is created. In the natural state these channels hold water. When the zeolites are heated, the water is given off readily and continuously, and not in certain amounts at definite temperatures as is usually the case. The partially dehydrated mineral can again take up an equal amount of water if exposed to water vapor, or may be filled with  $\text{NH}_3$ , mercury vapor, hydrocarbons, etc., if exposed to them. This is not true of other materials containing water; for, like gypsum, they collapse when heated, due to the fact that the water is a definite part of the structure.

The way the materials are adsorbed into the cavities

or cages has proven interesting. Barrer, et. al. (13) in their study on faujasite, found that some hydrocarbons act like liquids filling a container. He found that it took 5.4 molecules of benzene (303°K) and 4.6 molecules of toluene (313°K) to fill the faujasite cage.

As mentioned earlier, the team of chemists from the Linde Company prepared a sieve of synthetic zeolite following the theory of Winchell (11), that in zeolites the ratio  $Al_2O_3:CaO+Na_2O$  is always 1:1; that  $Al=Si:O$  ratio is always 1:2; and that in any given isomorphous part of the Zeolite Group the  $Ca+Na:O$  ratio is constant. The group, led by D. W. Breck (14,15) in 1956, announced the synthesis of 14 new zeolite species and 6 of the 35 known zeolites. The most useful of these were called Type A and Type X (see Table II). These synthetic zeolites have cavities of high capacity, and apertures that can be adjusted to perform many useful separations. They also withstand temperatures as high as 700 degrees centigrade without falling apart.

A study of the crystalline structure for Type A was made by Reed and Breck (12). Broussard and Shoemaker (16) made a more extensive study on Type A as well as the crystalline structure of Type X. They developed models to explain the structure of these molecular sieves, based on the well known principle that in many aluminosilicates, both Si and Al are tetrahedrally coordinated by oxygen anions.

TABLE II

## COMPOSITION OF SOME MOLECULAR SIEVES (8)

Type	Composition	Crystal Structure	Dimension
3A	Similar to 4A, 75% of Na ion replaced by K ion	Cubic	$a = 12.32 \text{ \AA}$
4A	$0.96 \pm 0.04 \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 1.92 \pm 0.09 \text{SiO}_2 \cdot n\text{H}_2\text{O}$	Cubic	$a = 12.32 \text{ \AA}$
5A	Similar to 4A, 75% of Na ion replaced by Ca ion	Cubic	$a = 12.32 \text{ \AA}$
10X	Similar to 13X, 75% of Na ion replaced by Ca ion	Cubic	$a = 24.95 \text{ \AA}$
13X	$0.83 \pm 0.05 \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2.48 \pm 0.03 \text{SiO}_2 \cdot n\text{H}_2\text{O}$	Cubic	$a = 24.95 \text{ \AA}$

From adsorption data, it was known that channels of certain approximate size existed. For example, ethane molecules with a diameter of 4A would readily pass through the Type 4A apertures at normal temperatures, but propane molecules of 4.9A diameter would not. Adding to this information, the X-ray study, they were then able to work out the crystal system and the unit cell size. From trial assemblies of (Si, Al)  $O_4$  tetrahedra, they recognized that the primary building block for both Type A and Type X was a framework of these tetrahedra groups that closely resembles the main structural unit in the mineral sodalite, and, thus, called this building block the "sodalite unit." It contains 24 (Si, Al) ions interconnected with 36 oxygen anions. The framework of Type A sieves consist of the more symmetrical sodalite units located at the corners of the cubic unit cell. Each sodalite unit is connected to its neighbor by four bridge oxygen ions. The main adsorption cavity is a space surrounded by eight sodalite units, and entry into this cavity is by means of a channel bounded by four sodalite units (See Figure 1).

One important property of the zeolites is base or cation exchange. This exchange involves the substitution of the cation in a water solution with the cations of the zeolite structure. This ion exchange can be used to modify the molecular-sieve property of the zeolites.

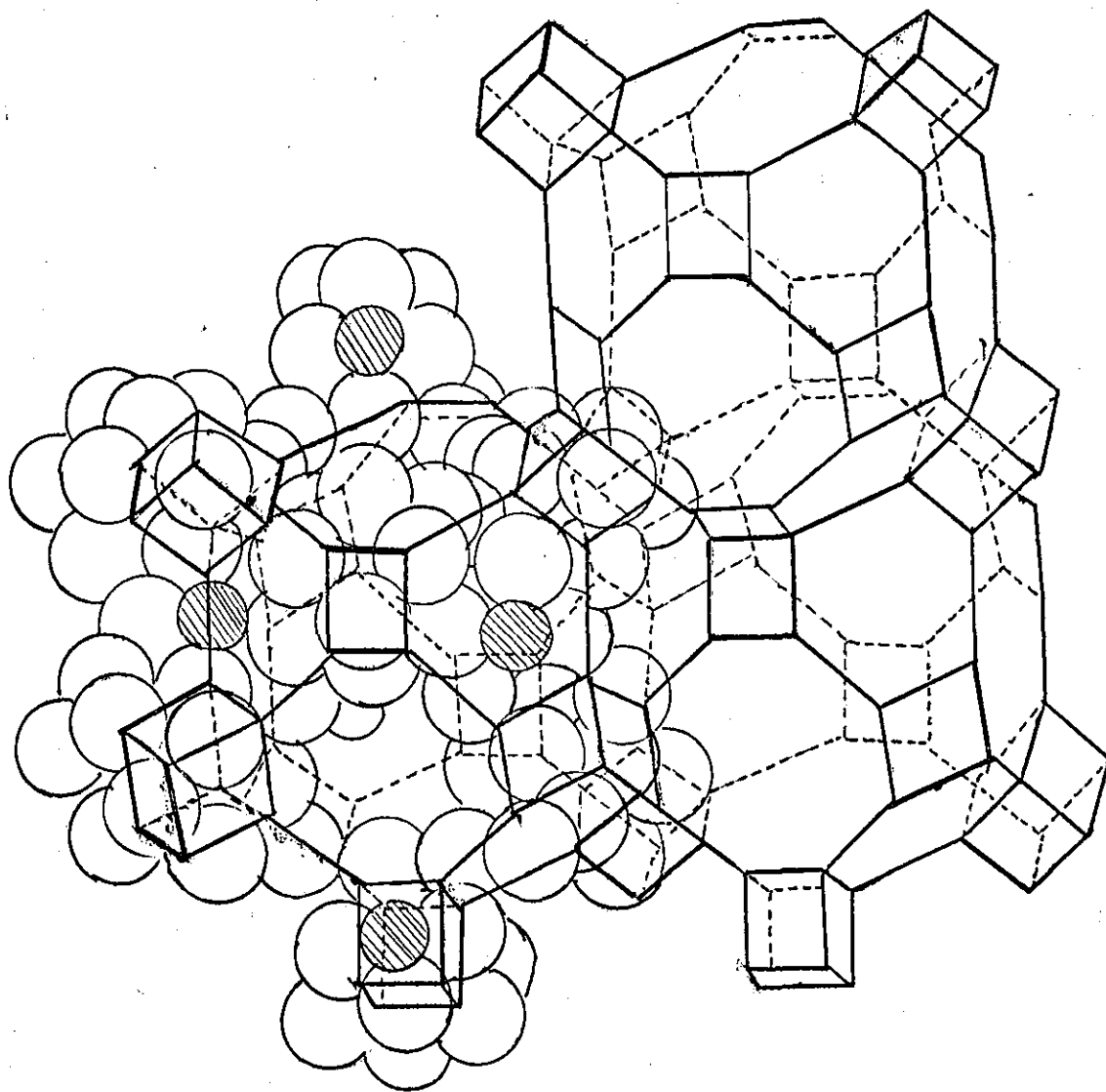


Figure 1. MOLECULAR STRUCTURE OF MOLECULAR SIEVE TYPE A.

The diagram (2) reveals the cavities which account for their peculiar properties. Si and Al ions(not shown) occupy the corners of the framework; they are surrounded by oxygen ion(the spheres). The sodium ion(small dark spheres) partially block the apertures and reduce the diameter, due to the oxygen ions.

The exchange of eight Na cations in Type 4A Molecular Sieve with four Ca ions to form the Type 5A Sieve, produces a sieve which adsorbs larger molecules than Type 4A adsorbs. The inability of the Type 4A sieve to adsorb normal paraffins might be related to plugging of the channels by four Na ions. Thus, the Type 3A, the potassium zeolite, will permit only molecules smaller than about 3A to enter the cavities and be adsorbed. Type 4A, the sodium zeolite, will permit only molecules smaller than about 4A to enter and Type 5A, the calcium zeolite, will admit molecules up to about 5A in diameter.

From the adsorption data of Type 4A molecular sieve, an adsorption volume for water of  $833 \text{ \AA}^3$  per unit cell was calculated by Breck (12). From the structure each unit cell has a  $775 \text{ \AA}^3$  cavity entered by 8-membered oxygen rings and  $157 \text{ \AA}^3$  cavity entered by 6-membered oxygen rings. Thus, the large cavity is the main adsorbing part of the sieve with an effective pore diameter of  $11.4 \text{ \AA}$  separated by circular openings  $4.2 \text{ \AA}$  in diameter. Removal of crystal water leaves mutually connected intracrystalline voids amounting to 45 vol-% of the zeolite.

In the structure of the framework of Type 13X sieve, the sodalite units are again used as the primary building block. Here the sodalite units are "distorted," i.e., the sodalite units are placed in tetrahedral coordination in

the same manner as are carbon atoms in the diamond structure. Each sodalite unit is connected to its neighbor by six bridge oxygen ions. The adsorption cavity is a space surrounded by 10 sodalite units. The channels to these cavities are bounded by six sodalite units.

The Type X sieve has been found to be chemically different from, but structurally similar to the mineral faujasite (11,12). The adsorption measurements indicate that the effective pore diameter is 10 to 13A. The void volume is 51 vol-% of the zeolite and all adsorption takes place in the crystalline voids. Because of the large pore size this zeolite readily adsorbs almost all substances of appreciable vapor pressure. However, an adsorptive selectivity is exhibited for polar molecules, and, in fact, selectivity may occur for molecules with negligible dipole moment due to other more subtle molecular characteristics.

Type 10X, the calcium zeolite, will accept (8) molecules smaller than about 10A; Type 13X, the sodium zeolite, will admit molecules with critical diameters as large as 13A.

The entrance to the cavities of the zeolite depends not on the volume of the cavities, but on the diameter of the aperture as well as on the temperature. We may recall that atoms and molecules are not rigid bodies. The pulsations of both the aperture atoms and the incoming molecules combine to make the effective diameter of the aperture considerably

larger than its "free" diameter. The kinetic energy of the incoming molecules helps them to "shoulder their way" through the opening. Thus, it has been found, in general, that at ordinary temperatures molecules up to  $0.5\text{\AA}$  wider than the free diameter of the aperture can pass through it easily. Larger molecules enter the crystal with greater and greater difficulty. Molecules  $1\text{\AA}$  wider cannot enter at all.



## CHAPTER IV

### ADSORPTION THEORY

A certain amount of a gas or liquid is adsorbed by a solid, when the gas or liquid is exposed to a porous adsorbent. The amount of gas or liquid adsorbed, when equilibrium is established at some temperature and pressure, is a function of both the adsorbent and adsorbate. Thus, the physical structure and chemical composition of the adsorbent must be considered. Surface area, pore size, shape and distribution are all important adsorbent properties that are passed by zeolite sieves.

The temperature and pressure are also important in determining the equilibrium. In general, the higher the temperature, the less material is adsorbed; the higher the pressure, the more material will be adsorbed. Figure 2 shows the adsorption of methane on chabazite at various temperatures as a function of pressure. In general, the amount of gas or liquid adsorbed is a function of the final pressure or concentrations, and the temperature where  $\frac{x}{m}$  is,

$$\frac{x}{m} = f(p, T) \quad (1)$$

is the amount of material adsorbed per gram of adsorbent,  $p$  is the equilibrium pressure and  $T$  is the absolute

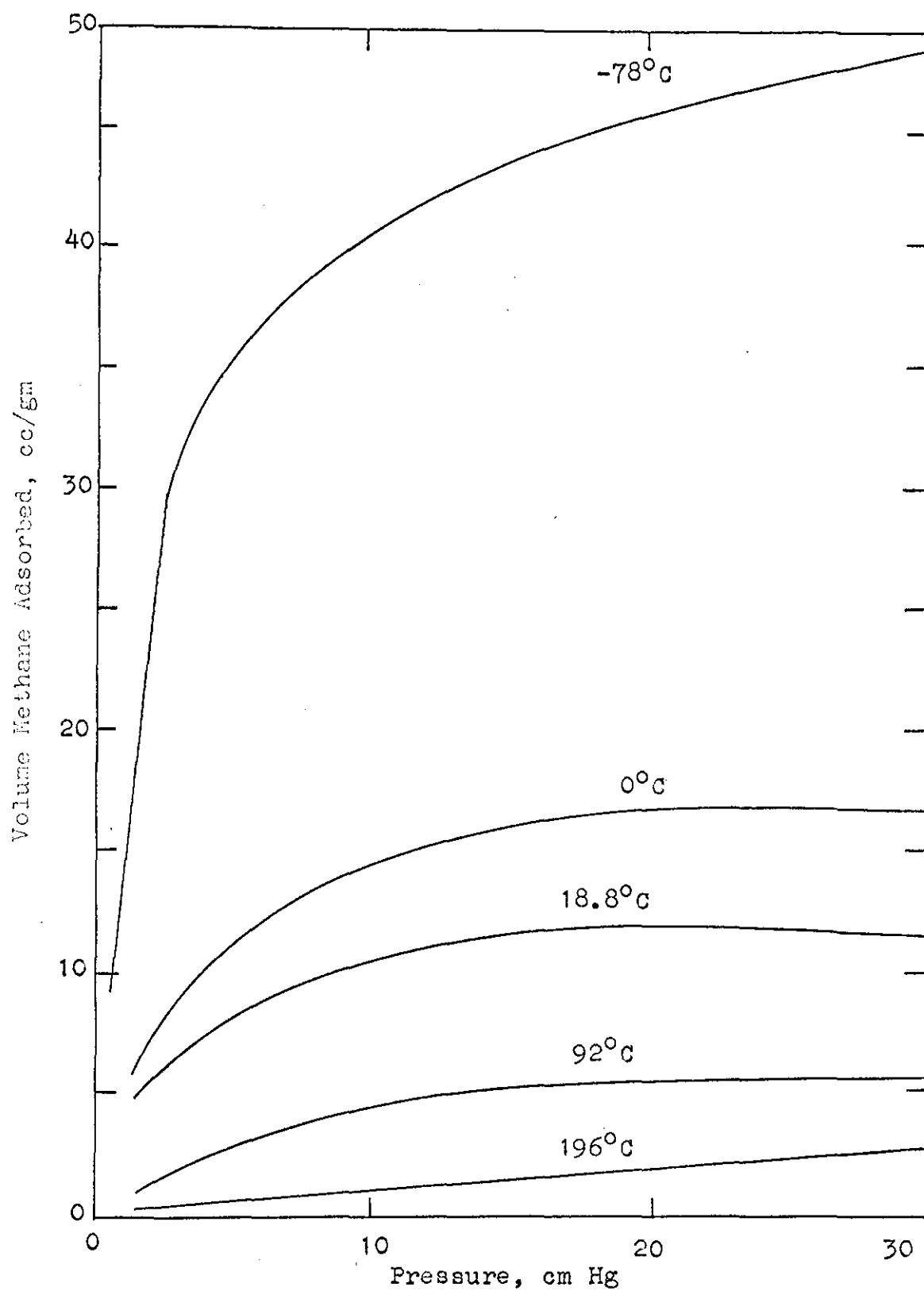


Figure 2. Typical isotherms(1). Methane on chabazite.

temperature. When the pressure of the gas is varied and the temperature is kept constant, the plot of  $\frac{x}{m}$  as a function of the pressure, is called the adsorption isotherm. Examples are shown in Figure 2.

Several observations can be made regarding the isotherms. At constant temperature, the adsorption of a gas or vapor increases with an increase in pressure. The amount of material adsorbed at equilibrium almost always decreases with an increase in temperature according to LeChatelier's principle.

By analogy with Henry's law for the solubility of

$$v = kp \quad (2)$$

gases in liquids, the amount adsorbed by a given weight of adsorbent should be proportional to the equilibrium pressure. At small concentrations the volume increases linearly with pressure. In other instances, however, Henry's law does not appear to hold even at very low pressures and concentration. As higher adsorptions are approached, the volume adsorbed becomes proportional to a power of the gas pressure smaller than unity, as expressed, where  $n$  is greater

$$v = kp^{1/n} \quad (3)$$

than 1; this is the "exponential" equation. At still higher pressures, adsorption increases only slightly with pressure,

until a region is reached where adsorption is approximately independent of the pressure; hence we get the equation

$$v = k \quad (4)$$

Isotherms having such slopes are referred to as Langmuir Isotherms, since the adsorption mechanism postulated by Langmuir leads to this type of isotherm. These isotherm curves are characterized by continually decreasing slopes, becoming practically zero in the neighborhood of the saturation pressure. Langmuir (17) proposed a theory based on the belief that adsorption was a type of chemical combination or process and that the adsorbed layer was unimolecular.

It has been found (5,7) that chromatographic data can be related to the adsorption equilibrium constant by

$$\frac{L}{t_m U_e} = \frac{1}{B'} \quad (5)$$

where

$L$  = length of packed column in cm

$t_m$  = retention time of pulse maximum in seconds

$U_e$  = superficial linear gas velocity in cm./sec.,  
i.e., velocity that would result if the  
columns were completely empty

$B'$  = adsorption equilibrium constant

=  $\frac{\text{no. of molecules adsorbed / cm}^3 \text{ of column (at equilibrium)}}{\text{no. of molecules in gas / cm}^3 \text{ of gas}}$

This derivation is based on the concept of adsorption, as first conceived by Langmuir, it was modified to describe a system exhibiting a linear adsorption isotherm, since the mathematics for a non-linear system becomes extremely formidable. Although it is recognized that most adsorptions are non-linear in nature, it is believed that the assumption of a linear isotherm will not introduce too great an error, since the concentrations normally involved in gas chromatography are so low that one is essentially only concerned with the linear portion of the isotherm. We find also that the partial pressures normally involved in gas-solid chromatography are quite small. Thus, the value of  $B'$ , as calculated from equation 5, should be expected to correspond to the limiting slope of the isotherm in the low pressure region. Eberly and Spencer in 1961 (7) have shown that this is essentially the case.

The constant  $B'$  can be treated as a thermodynamic equilibrium constant as shown by Greene and Pust (16) and Keulemans (18), i.e.,

$$B' = B e^{-\Delta H/RT} \quad (6)$$

where  $B$  = constant  
 $\Delta H$  = heat of adsorption

By making the appropriate substitution into equation 5, we get

$$\frac{t_m U_e}{L} = B e^{-\Delta H/RT} \quad (7)$$

or

$$\log t_m(\text{cor}) = C - \frac{\Delta H}{2.303R} \cdot \frac{1}{T} \quad (8)$$

Here  $t_m(\text{cor})$  represents the observed retention time corrected to 25°C and atmospheric pressure by the equation (see Appendix A for derivation) (6):

$$t_m(\text{cor}) = t_m T_c / T_f \quad (9)$$

$T_c$  = column temperature

$T_f$  = temperature of flow measuring device (25°C)

The constant  $C$  in equation 8 is a function of the entropy of adsorption, the dimension of the column, and the carrier gas flow rate. Since the material in the column has a very small expansion coefficient (estimated to be less than  $2 \times 10^{-6}$ ), the change in the dimensions of the column can be considered negligible over a range of temperatures. The change in carrier gas flow rate, as it goes through the column at different temperatures, can be considered negligible since the graphs all appear to be linear. With these factors being constant, a plot of the logarithms of the corrected retention time against the reciprocal of the absolute temperature should give a straight line with the slope being proportional to the heat of adsorption.

It is believed that the heats of adsorption obtained in this manner are average values over the range of partial

pressure involved. Since the partial pressures of the hydrocarbons in this work were of the order of 1 mm or less, the heats of adsorption should correspond to those at very low surface coverage. Working at lower temperatures, Green and Pust in 1958 (6) found good agreement between the heats of adsorption evaluated in this way and those obtained calorimetrically and isothermally.

## CHAPTER V

### EXPERIMENTAL

Introduction. The adsorptive properties of solids like the molecular sieves are conveniently studied by the use of temperatures and allowing a pulse of adsorbate to be transported through a packed column of adsorbent by an inert carrier gas stream. A sensitive thermal conductivity cell is used to measure the concentration of the adsorbate in the effluent stream. Heats of adsorption can be determined by measuring the pulse retention times at a series of temperatures. This flow method is particularly useful for studying adsorption at high temperature conditions, where static methods cannot be used because of the long contact times involved, which leads to decomposition of the adsorbates.

Emmett and his co-workers (19,20,21) were the first to report the use of a flow system in order to minimize decomposition in their study on the adsorption of hydrocarbons at high temperatures. This work describes a gas-solid chromatographic technique for studying high temperature adsorption. The contact time of the hydrocarbon vapor with the solid surface can be made quite short in such a flow system, thereby minimizing decomposition reactions. In the



first of a series of experiments, the work of Eberly (3) on benzene and n-hexane is repeated and compared along with the study of toluene, n-heptane, 2,2-dimethylbutane, 2,3-dimethylbutane, 2-methylpentane, 3-methylpentane, n-pentane, 2-methylbutane on 13X molecular sieve both in the manufactured form of 80-100 mesh and the pure powdered form.

Apparatus. The apparatus used was a Beckman GC-2 gas chromatograph. A high temperature oven was designed so that a packed column could be placed in it, and this, in turn, was attached to the Beckman GC-2 gas system. The sample was injected into the system using a capillary tube containing the sample and inserting it into a needle type injection apparatus (see Figure 3). The sample was first measured using a Hamilton Microliter Syringe and then placed into the capillary tube. The helium flow was

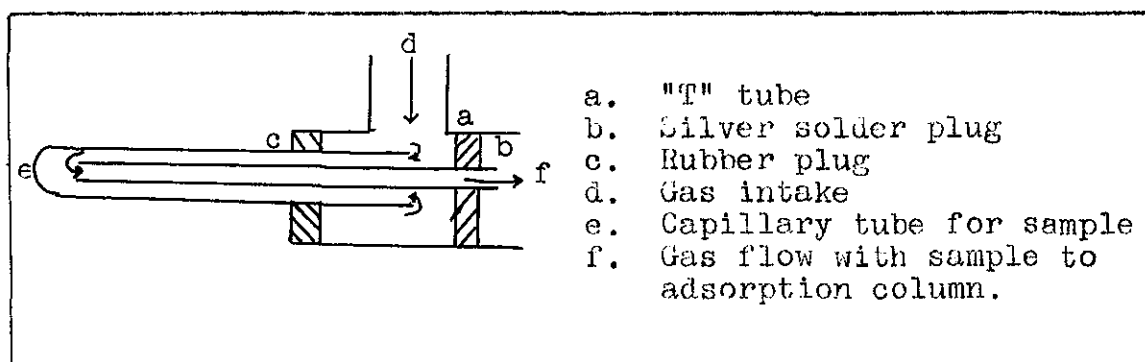


Figure 3. Sample Injection System

accurately measured by observing the movement of a soap film through a graduated buret. Since there is a slight pressure drop across the column, gas will undergo acceleration and the

velocity of sample and carrier is not constant through the column. There is also the effect of the high temperature of the column on the gas as it passes through the column. The observed retention times are corrected for these effects by equation 9, which is developed in Appendix A. The packed columns were constructed of standard  $\frac{1}{4}$ " stainless steel tubing. The adsorbents were the powdered form and the 80-100 mesh form of Linde Type Molecular Sieves. The packed columns were held at the desired temperature by means of a resistance oven, the temperature kept constant by a constant voltage transformer. Temperatures were measured using an iron-constantan thermocouple. A Sargent multi-range recorder was used to measure both the temperature and the gas chromatograph response.

Materials. The Linde Molecular Sieves Type 3A, 4A, 5A, 10X, 13X, were obtained from Linde Company in powder form and from the Matheson Coleman and Bell Company in the 80-100 mesh form. They were activated by heating to 500°C and passing He through the columns for one hour.

The benzene, toluene, n-hexane, n-pentane, n-heptane, and 2-methylbutane used in this work were chromatography grade reagents obtained from Matheson Coleman and Bell. The 2,2- and 2,3- dimethylbutane, and the 2- and 3-methylpentane were the best grade available from Matheson Coleman and Bell. All hydrocarbons were used without any further purification.

The helium carrier gas was that commercially available. No attempt was made to purify this gas further, since the purity was 99.99%.

Results. The data obtained from each Linde Type Molecular Sieve will be reported separately at various temperatures. The retention time,  $t(\text{min.})$ , values are measured by taking the time differences between the beginning of the air peak and the hydrocarbon peak (see Figure 4). It was found that the retention times measured, as described above, were more consistent and easier to measure,

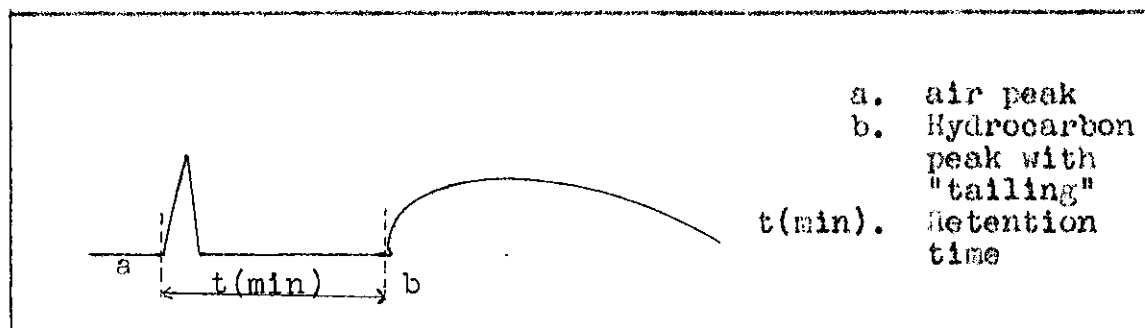


Figure 4. Measure of Retention Time

since the peaks were odd-shaped and unsymmetrical. The usual method (18) used is measuring the peak maximum or center of the zone for a symmetric curve. Since low boiling point components used in gas solid chromatography (18) give rise to asymmetric peaks, the above mentioned method gave the most consistent data.

In all runs, the volume of each sample was measured to  $3\mu\text{l}$  using a Hamilton Microliter Syringe. Since the area

under the curve is proportional to the amount of sample, the size of the base of the curve would vary with the size of the sample. Keeping the volume constant would help keep the beginning of the hydrocarbon peak constant for each different hydrocarbon.

Calibrations. An empty stainless steel column (27.2 cm long) was tested for its retention properties at room temperature (23°C). Using the less volatile, stronger adsorbing compounds, sample size 3 $\mu$ l, and with a gas flow rate of 50 ml/min, the materials (Table III) were run through the empty tube. As reported later (see page 31), benzene and toluene had their retention times measured as they

TABLE III

## RETENTION TIMES IN EMPTY STAINLESS STEEL COLUMN

Adsorbate	Retention time (min.)
toluene	0.40
benzene	0.20
n-heptane	0.15
n-hexane	approx. 0.01
2,3-dimethylbutane	0.00

passed through a column of glass wool (0.7277g). At 400°C

the retention times of 6-7 seconds for toluene and an unmeasurable time for benzene were recorded. In like manner, at 170°C there was recorded retention times of 12 seconds for benzene and approximately 30 seconds for toluene. Since the compounds with the higher volatilities have small retention times (2-4 min.) on the Molecular Sieve Columns at low temperatures, the small errors which might result due to the retention of the sample in the stainless steel tube, were not thought to be significant. In like manner, the retention times of the less volatile compounds (as toluene and benzene) are quite high in the Molecular Sieves (of order of 20 to 30 minutes or more) at lower temperatures, and likewise the resulting error due to the retention on the stainless steel tube would be small (of order 2% and less). Due to these considerations, a general practice of not using any retention times of less than half a minute was used. (This procedure was not followed on the Type 13X Sieve since this consideration was not arrived at until after its data was gathered.)

The iron-constantan thermocouple and the recording of its temperature in millivolts was checked by using the melting of ice (0°C) and the boiling of water (100°C) as check points (see Table IV). Both the 25 mv and the 50 mv range of the recorder were checked. There is about a 0.2% error on the upper level of the 25 mv range and an error of

1% on the upper level of the 50 mv range. Since the upper

TABLE IV

## THERMOCOUPLE CALIBRATION

Range	T	Conversion Chart*	Recorder
25mv	0°C	0.00mv	0.01mv
	100°C	5.28	5.27
50mv	0°C	0.00	0.02
	100°C	5.28	5.22

\*Using Iron-Constantan Thermocouple Conversion Chart-Beckman Instruction Manual 545-E.

part of the 25 mv range and the lower part of the 50 mv range are used the error will be less than 1%. Since this would be considered part of the general experimental error, no corrections were made on the data.

Errors. These following errors have been calculated (see Appendix H) for the following parameters. For the temperature an error of 0.65°C is possible in each reading. The flow rate of the helium would have an error of 0.25 ml/min for each reading which would be too small to be significant. The error for the retention time was found to be 0.036 min for each reading, which is too small to be

significant in the calculation of the heats of adsorption. In general, since these errors are considered insignificant, no correction was made on the data.

Linde Molecular Sieve Type 13X (80-100 mesh). Table V (see also Appendix B) lists the data obtained with the Linde Molecular Sieve Type 13X (80-100 mesh) at various temperatures. The weight of the adsorbent was 1.0086g including the filler (the 80-100 mesh is held together (8) with an inert clay bonding material amounting to about 20% of the total weight). The column was 9.8cm long, being contained between two small plugs of glass wool. (A column, 18.1cm in length and 0.7277g in weight, packed with glass wool, showed unmeasurably short retention times for benzene, approximately 6-7 sec. for toluene at 400°C, and approximately 12 and 30 seconds for benzene and toluene, respectively, at 170°C. Since small amounts of glass wool, in the order of 200mg or less, were used to hold the sieve in place, the resulting error in retention time due to it will be too small to be significant.) The time of vaporization of the samples in the capillary sample injection tubes varied between 2 to 8 seconds depending on the volatility of the samples.

The helium flow rate was kept at 50 ml/min. with a deviation of 1cc/min in about 2% of the runs.

The retention times, corrected in the previously

TABLE V  
CHROMATOGRAPHIC DATA ON  
LINDE MOLECULAR SIEVE TYPE 13X (80-100 MESH)

Adsorbate	T°C	$\frac{1}{T} (^{\circ}\text{K}^{-1}) \times 10^3$	Time (t min)	Log t(cor)
toluene	426	1.43	3.87	2.736
	407	1.47	5.92	2.909
	342	1.63	25.3	3.486
benzene	429	1.39	1.69	2.395
	368	1.56	6.27	1.908
	348	1.61	8.38	3.020
	316	1.70	19.9	3.373
n-heptane	428	1.428	0.77	2.032
	406	1.474	0.99	2.131
	344	1.62	2.48	2.489
	312	1.71	4.45	2.720
n-hexane	344	1.62	1.04	2.106
	312	1.71	1.50	2.246
	255	1.89	5.12	2.736
	200	2.15	18.5	3.224
2,2-dimethyl- butane	347	1.61	0.73	1.957
	315	1.70	1.30	2.188
	256	1.885	4.37	2.633
	200	2.11	16.1	3.187
	172	2.22	34.0	3.493
2,3-dimethyl- butane	347	1.61	0.86	2.031
	316	1.698	1.50	2.248
	256	1.886	4.73	2.703
	201	2.105	18.0	3.234
	173	2.22	39.4	3.549
2-methylpentane	348	1.61	0.87	2.036
	316	1.698	1.45	2.233
	257	1.888	4.68	2.698
	202	2.105	17.0	3.212
	168	2.37	44.2	3.538
3-methylpentane	348	1.61	0.86	2.032
	316	1.698	1.48	2.243
	257	1.888	5.08	2.734
	201	2.11	18.1	3.238
	170	2.26	39.0	3.531
n-pentane	297	1.78	0.80	1.964
	256	1.89	1.56	2.218
	196	2.138	5.78	2.738



described manner, were found to obey the predicted relationship and increased logarithmically with the reciprocal of the absolute temperature. The graphs of the data are shown in Figure 4a-c and the calculated heats of adsorption are given in Table VI.

TABLE VI  
HEATS OF ADSORPTION OF VARIOUS HYDROCARBONS  
ON LINDE MOLECULAR SIEVE TYPE 13X (80-100 MESH)

Adsorbate	$\Delta H$ (Kcal./mole)
toluene	19.6
benzene	14.5
n-heptane	11.1
n-hexane	9.8
2,2-dimethylbutane	10.3
2,3-dimethylbutane	10.3
2-methylpentane	11.2
3-methylpentane	11.1
n-pentane	10.1

Linde Molecular Sieve Type 13X (Powdered). Table VII (Appendix C) lists the data obtained with 0.19g of Type 13X (Powdered). The powdered form is considered to be pure zeolite. The Type 13X was placed evenly on 0.24g of glass

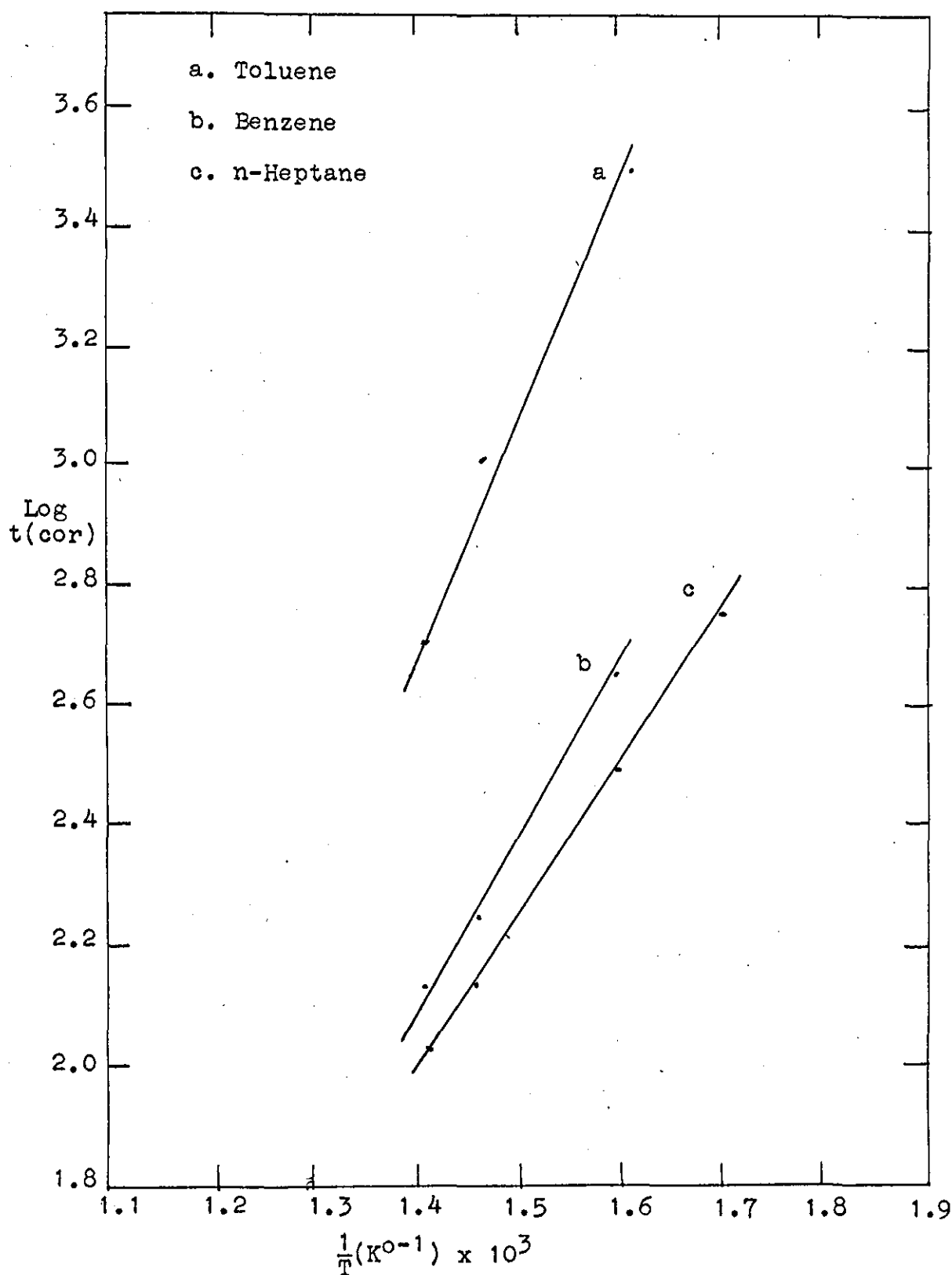


Figure 4a - Retention Times as Function of Temperature  
on Linde Molecular Sieve Type 13X(80-100 mesh)

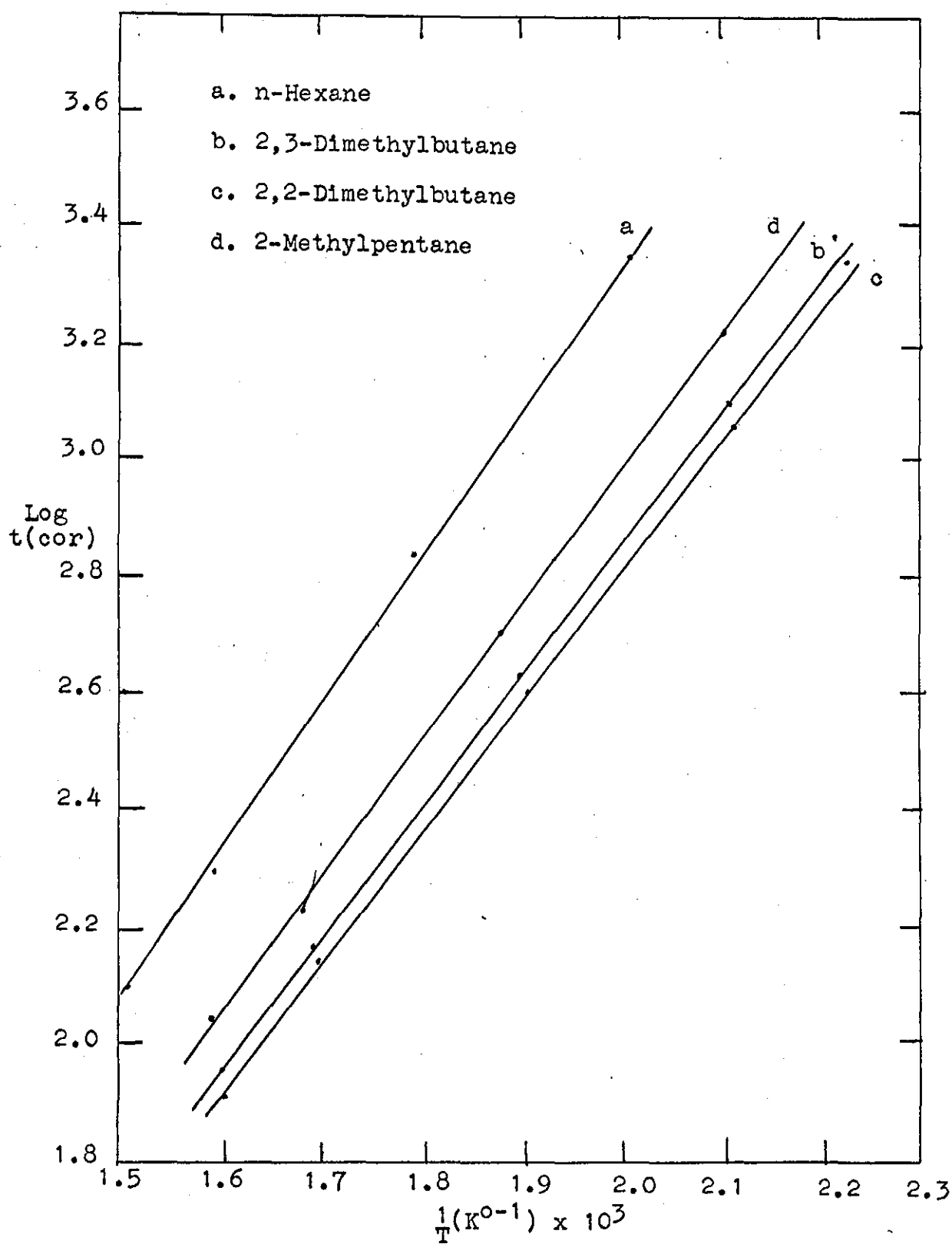


Figure 4b - Retention Times as Function of Temperature  
on Linde Molecular Sieve Type 13X(80-100 mesh)

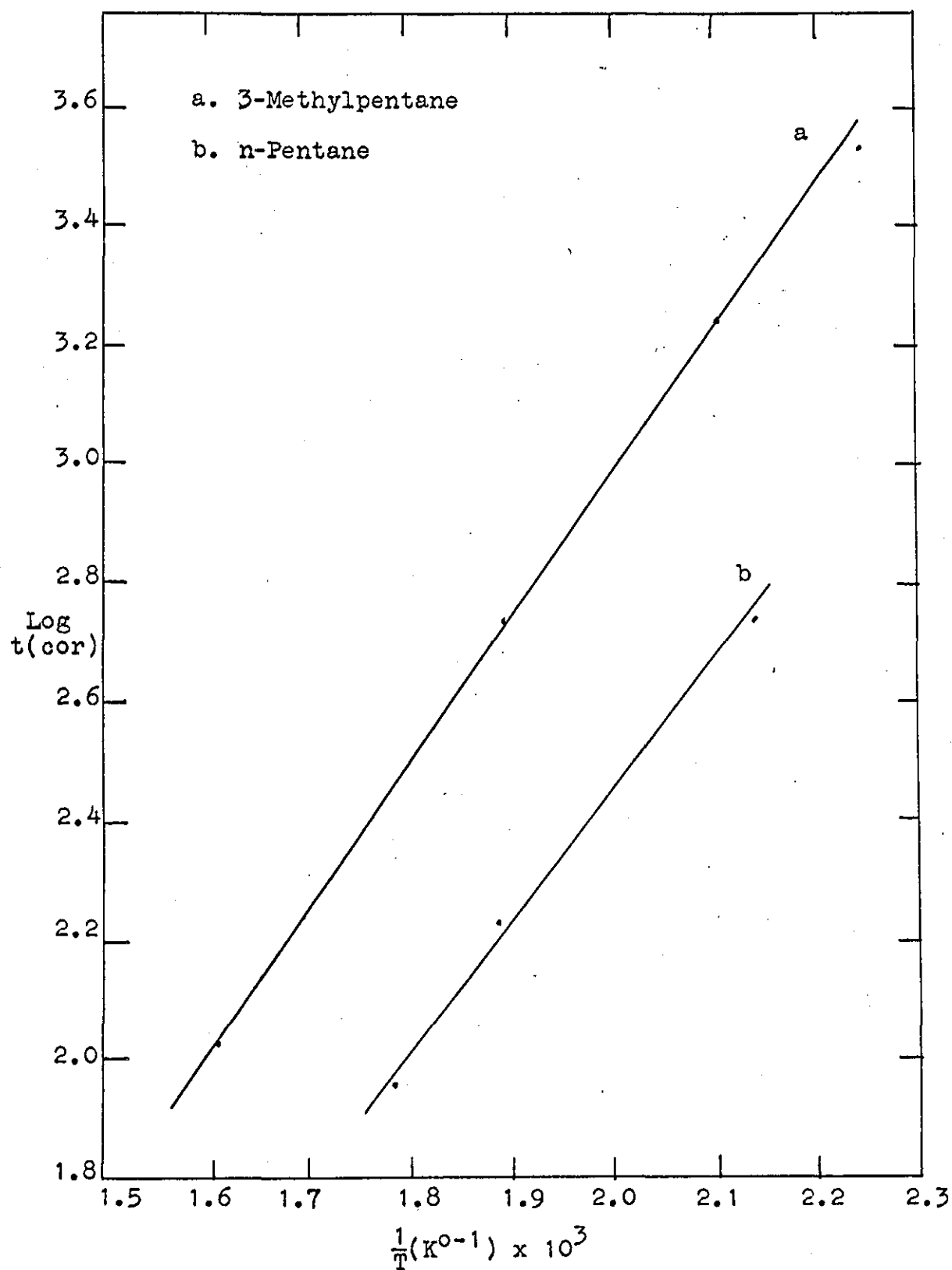


Figure 4c - Retention Times as Function of Temperature  
on Linde Molecular Sieve Type 13X(80-100 mesh)

TABLE VII  
CHROMATOGRAPHIC DATA  
FOR LINDE MOLECULAR SIEVE TYPE 13X (POWDERED)

Adsorbate	T <sup>o</sup> C	$\frac{1}{T}(\text{OK}-1)$ x 10 <sup>3</sup>	Time (t min)	Log t(cor)
toluene	469	1.345	1.55	2.364
	435	1.41	5.78	2.916
	397	1.495	12.6	3.229
benzene	431	1.42	1.74	2.392
	394	1.50	3.12	2.622
	342	1.63	13.3	3.230
	304	1.73	31.2	3.558
n-heptane	441	1.40	0.51	1.862
	431	1.42	0.78	1.990
	395	1.49	1.15	2.185
	340	1.64	3.21	2.598
	304	1.735	6.09	2.851
n-hexane	343	1.62	0.40	1.694
	306	1.725	0.74	1.936
	251	1.95	1.98	2.525
	204	2.09	7.49	2.858
2,2-dimethyl- butane	343	1.62	0.30	1.572
	305	1.73	0.55	1.807
	251	1.91	1.08	2.057
	248	1.92	1.20	2.100
	202	2.10	4.36	2.618
2,3-dimethyl- butane	343	1.62	0.34	1.625
	306	1.73	0.63	1.866
	251	1.92	1.41	2.173
	202	2.10	5.14	2.688
2-methylpentane	343	1.62	0.33	1.612
	307	1.72	0.61	1.853
	251	1.91	1.52	2.205
	202	2.10	6.71	2.808
3-methylpentane	340	1.63	0.39	1.690
	306	1.73	0.63	1.866
	251	1.92	1.62	2.233
	203	2.05	6.90	2.820
n-pentane	251	1.91	0.44	1.669
	207	2.08	1.49	2.159
	176	2.23	2.94	2.423
	154	2.34	7.11	2.786
2-methylbutane	252	1.91	0.31	1.516
	201	2.11	0.98	1.972
	169	2.26	1.14	2.004
	157	2.32	4.40	2.581

TABLE VIII  
HEATS OF ADSORPTION ON LINDE MOLECULAR SIEVE  
TYPE 13X (POWDERED)

Adsorbate	This Work	Other Work
toluene	26.4 kcal/mole	21.9 <sup>a</sup> kcal/mole
benzene	17.3	16.8 <sup>a</sup> ; 15.5 <sup>b</sup>
n-heptane	12.4	
n-hexane	11.5	10.8 <sup>b</sup>
2,2-dimethylbutane	10.5	
2,3-dimethylbutane	10.2	
2-methylpentane	11.3	
3-methylpentane	11.5	
n-pentane	11.9	
2-methylbutane	11.2	

<sup>a</sup>R. M. Barrer, F. W. Bultitude and J. W. Sutherland, Trans. Faraday Soc., 53, 1111 (1957).

<sup>b</sup>P. E. Eberly, Jr., J. Phy. Chem., 65, 68 (1961).

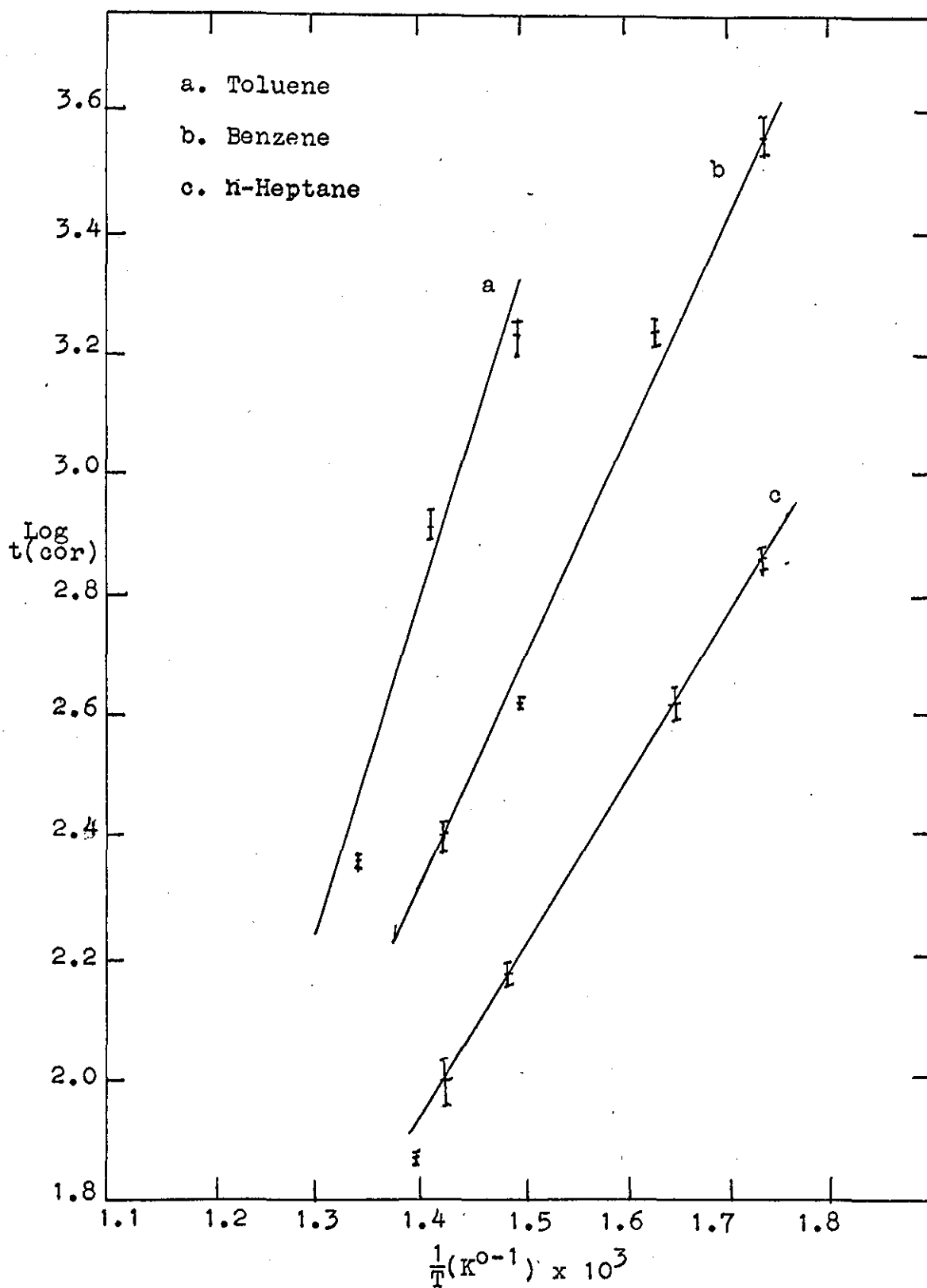


Figure 5a - Retention Times as Function of Temperature  
on Linde Molecular Sieve Type 13X(Powdered)

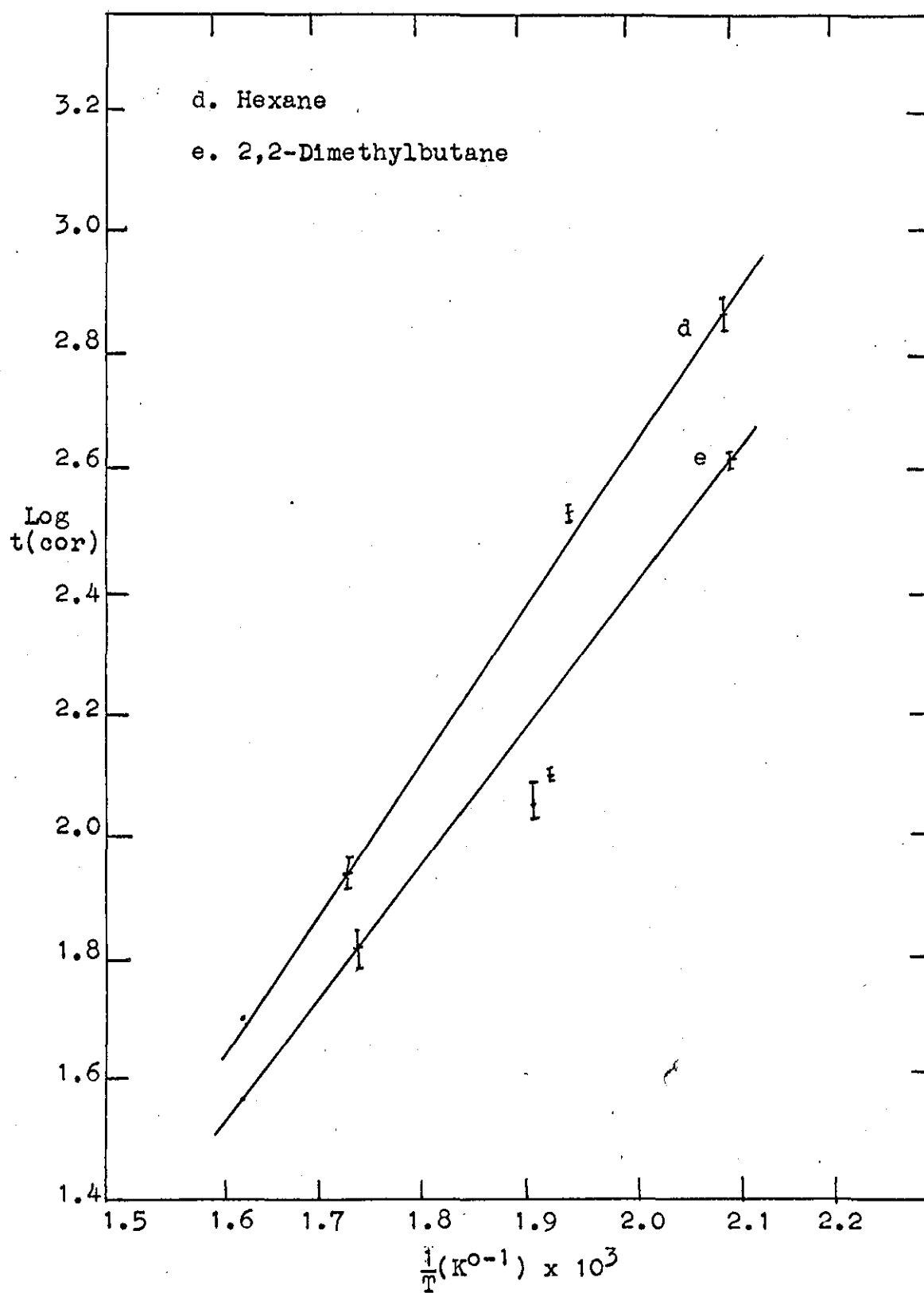


Figure 5b - Retention Times as Function of Temperature  
on Linde Molecular Sieve Type 13X(Powdered)



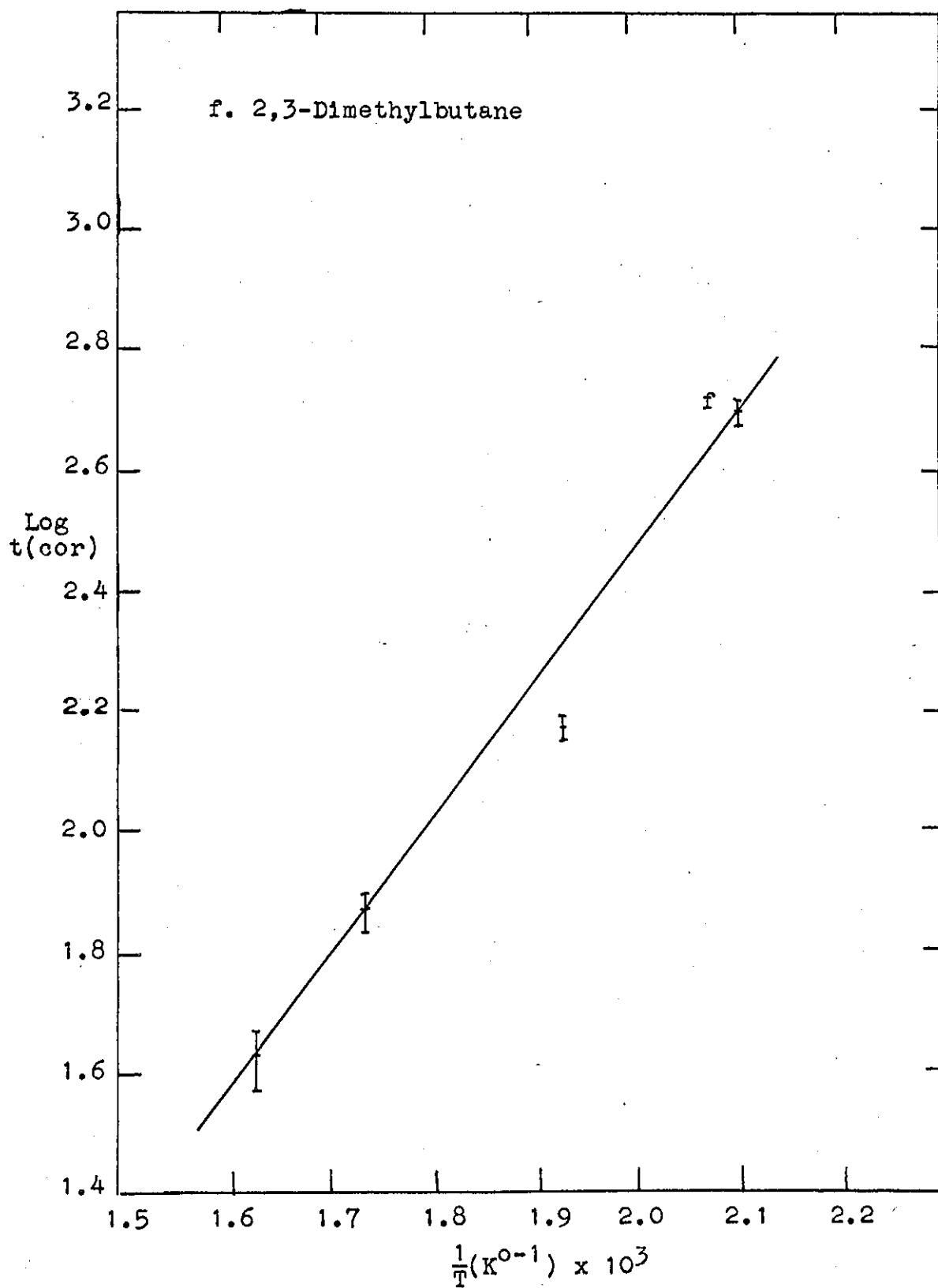


Figure 5c - Retention Times as Function of Temperature  
on Linde Molecular Sieve Type 13X(Powdered)

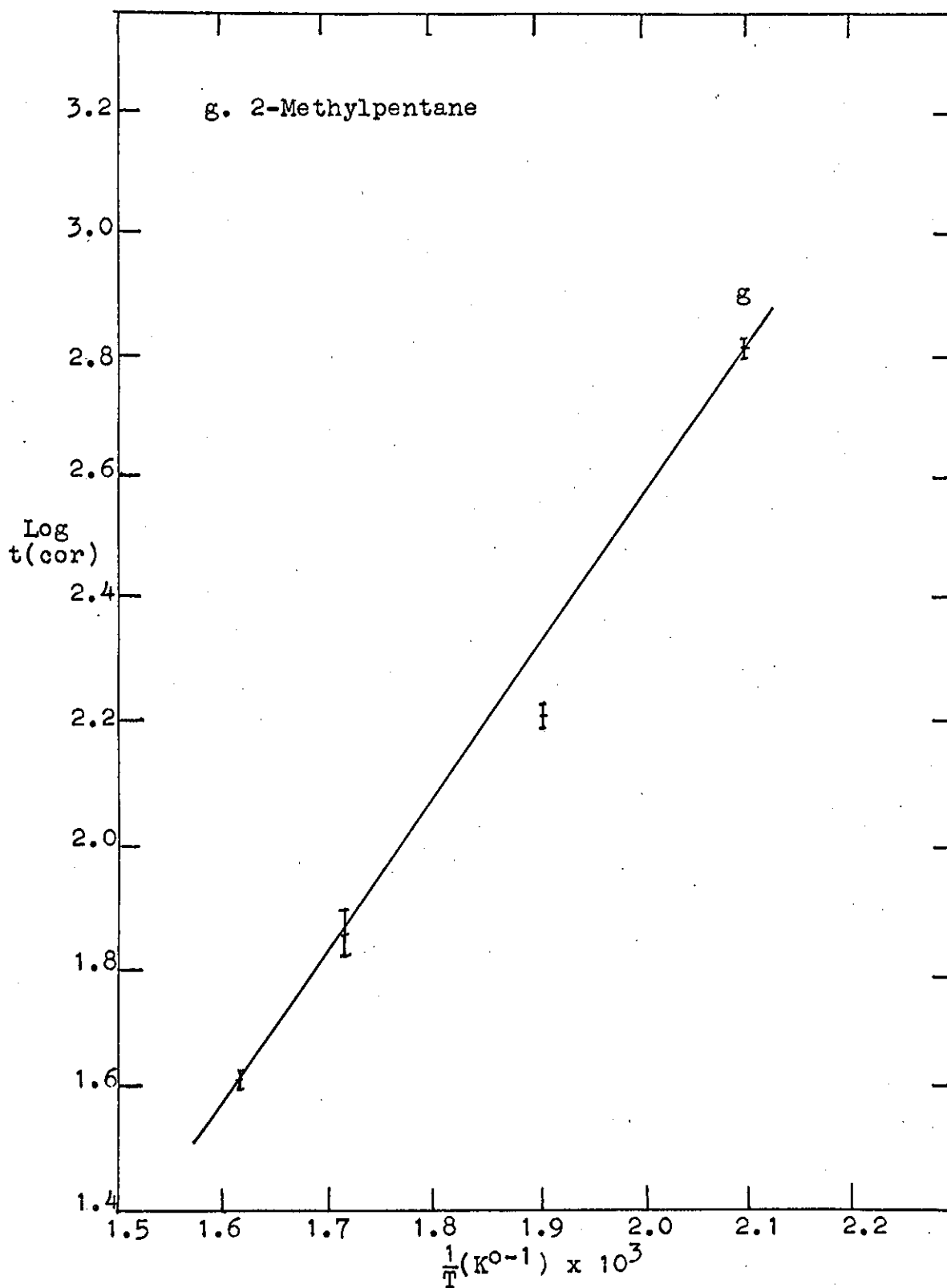


Figure 5d - Retention Times as Function of Temperature  
on Linde Molecular Sieve Type 13X(Powdered)

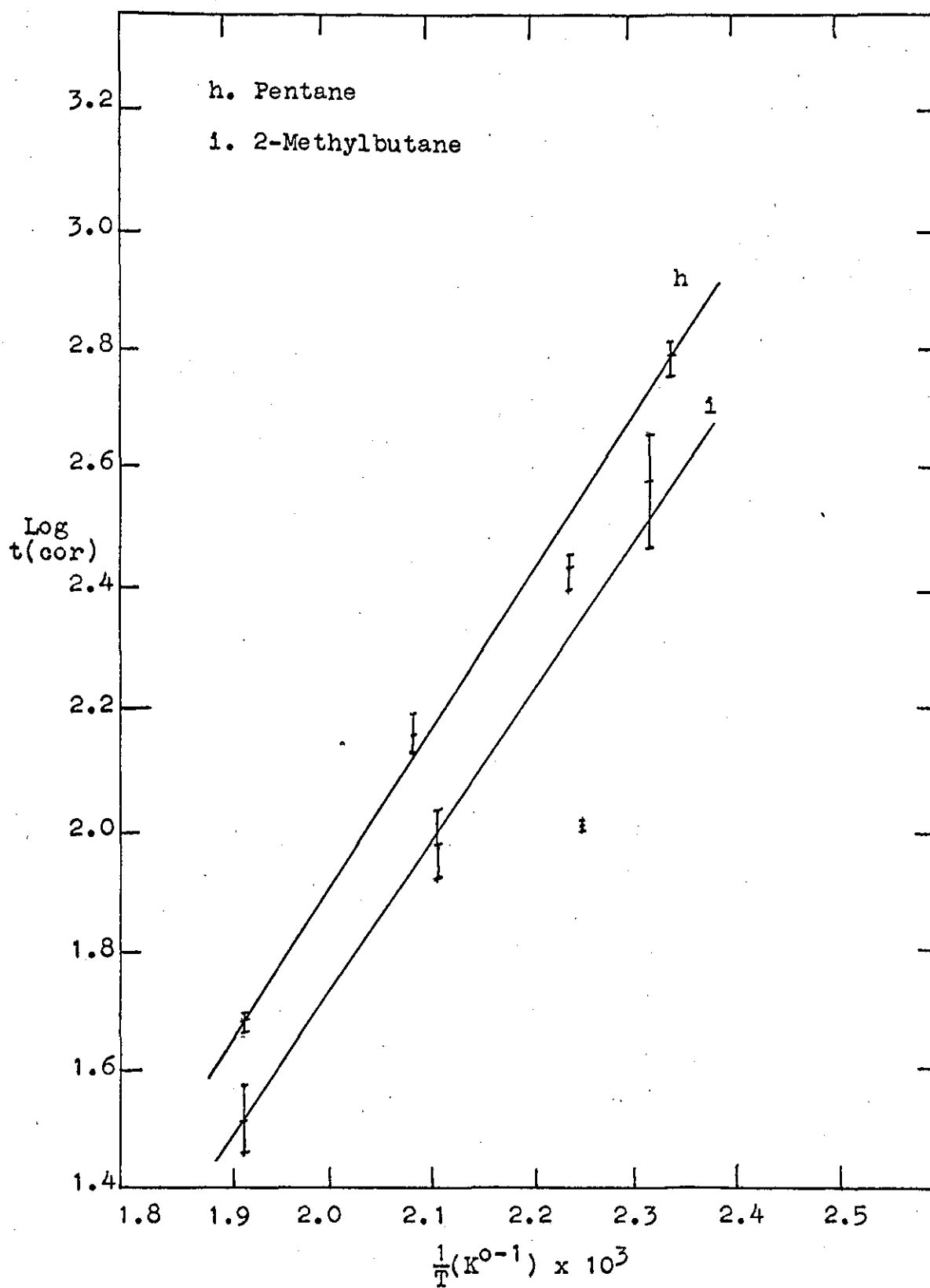


Figure 5e - Retention Times as Function of Temperature  
on Linde Molecular Sieve Type 13X(Powdered)

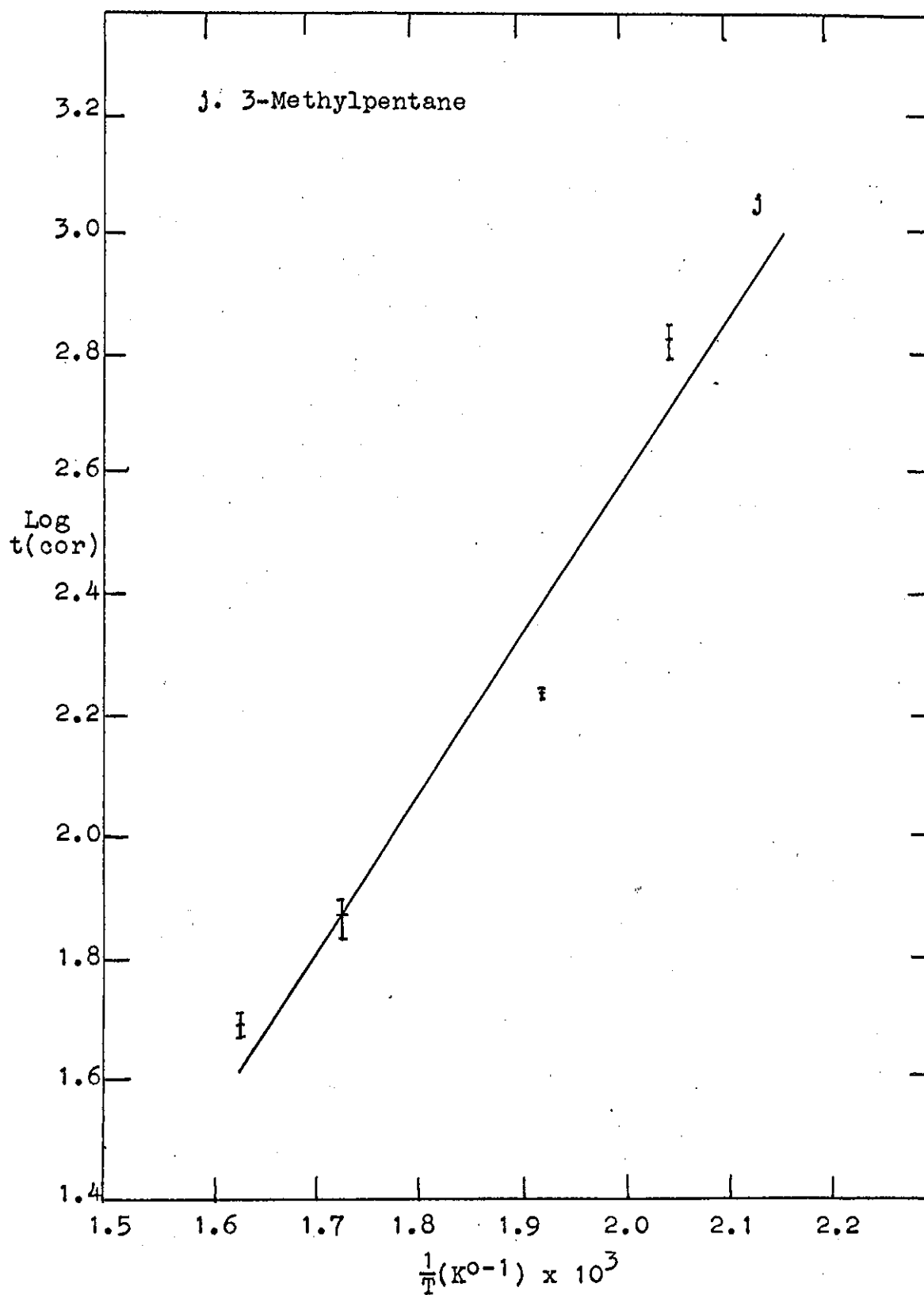


Figure 5f - Retention Times as Function of Temperature on Linde Molecular Sieve Type 13X(Powdered)

wool, making a column of 5.6cm in length. Without packing in this manner, the Type 13X (Powdered) packed too closely to let gas through.

Since some of the low volatile hydrocarbons took a long time to clean off the columns even with high gas flow rate, the temperature of the column was raised after each run to about 500°C to shorten the clean-off time. There was some fear that the sieve might have been changed, as during a couple of the later "clean offs," the temperature went over 700°C. This is a hazard since the zeolites are reported (12) to convert to amorphous material at 800°C. This might account for some of the samples producing poor straight lines.

The corrected retention times vs. absolute temperature are shown in Figure 5a-f. The calculated heats of adsorption are given in Table VIII.

Linde Molecular Sieve Type 3A (Powdered). The column was made up from 0.25 grams of Linde Type Molecular Sieve 3A (Powdered) and 0.32 grams of glass wool to hold it in place. This gave a column length of 7.1cm. The retention times at room temperature (23°C) were very close to that found for the empty tubes (see Table IX and III.)

It is therefore concluded that there is no significant retention time for this group of compounds on the Type 3A Sieve. The size of the sample used was 3 $\mu$ l and the gas

TABLE IX  
RETENTION TIMES  
ON LINDE MOLECULAR SIEVE TYPE 3A (POWDERED) AT 23°C

Compound	Time (min)
3 methylbutane	0.00
n-pentane	0.00
2,2-dimethylbutane	0.00
2-methylpentane	0.00
n-hexane	0.06
n-heptane	0.24
benzene	0.15
toluene	0.45

flow rate of helium was 50 ml/min. It was noticed that the range of time for n-heptane and benzene, i.e., smaller to larger value, in Type X Sieve is reversed in the Type A Sieve. This effect was believed to be due to their different boiling points, i.e., benzene with a lower boiling point condenses later than n-heptane.

Linde Molecular Sieve Type 4A (80-100 Mesh) This column was packed with 1.009g of the (80-100 mesh) Linde Type Molecular Sieve 4A, which gave a column length of 8.62cm. The 3 $\mu$ l samples of the various hydrocarbons were run at several different temperatures using a gas flow rate of 50ml/min. The retention times for the compounds tested

were all less than one-half minute for temperatures above 200°C. (see data Appendix D.) At room temperature (23°C) the less volatile compounds showed a significant adsorption (see Table X). The retention times of toluene, benzene and

TABLE X  
CHROMATOGRAPHIC DATA  
ON LINDE MOLECULAR SIEVE TYPE 4A (80-100 MESH)

T°C	Toluene	Benzene	n-Heptane
463	0.28 min	0.02 min	0.15 min
402	0.31		0.14
345	0.34	0.10	0.15
316	0.36	0.10	0.18
199	0.56	0.16	0.20
166	0.46	0.15	
143	0.45	0.14	
103	0.68	0.20	
	1.28(69°C)	0.37(62°C)	0.41(70°C)
	3.73(34°C)	0.70(36°C)	1.00(38°C)
23	9.30	2.48	3.68

n-heptane are quite high in comparison to the rest. n-Heptane's value is again in reverse order when compared to benzene. This adsorption may be due to regular surface adsorption and differences in boiling points. The retention

time above 200°C for benzene and n-heptane appear to be constant as can be seen in the graphs of Figure 6.

Linde Molecular Sieve Type 5A (80-100 Mesh). The column for the Linde Molecular Sieve Type 5A (80-100 mesh) was 9.9cm long when packed with 1.030 grams of sieve. The compounds that gave usable retention times were n-heptane, n-hexane and n-pentane. Toluene and benzene gave almost constant retention times over the range of 445°C to 170°C. At room temperature (23°C) the retention times for toluene and benzene were higher than at the previous temperature (see Table XI). Thus, some kind of adsorption is present.

TABLE XI  
SOME RETENTION TIMES  
ON LINDE MOLECULAR SIEVE TYPE 5A (80-100 MESH)

Toluene		Benzene	
445°C	0.45 min	442°C	0.15 min
397	0.44	397	0.13
346	0.44	341	0.14
392	0.45	296	0.16
168	0.54	181	0.14
RT(23)	1.18	RT(23)	0.50

The amount of sample retained by the sieve was roughly measured by running the sample at room temperature, then



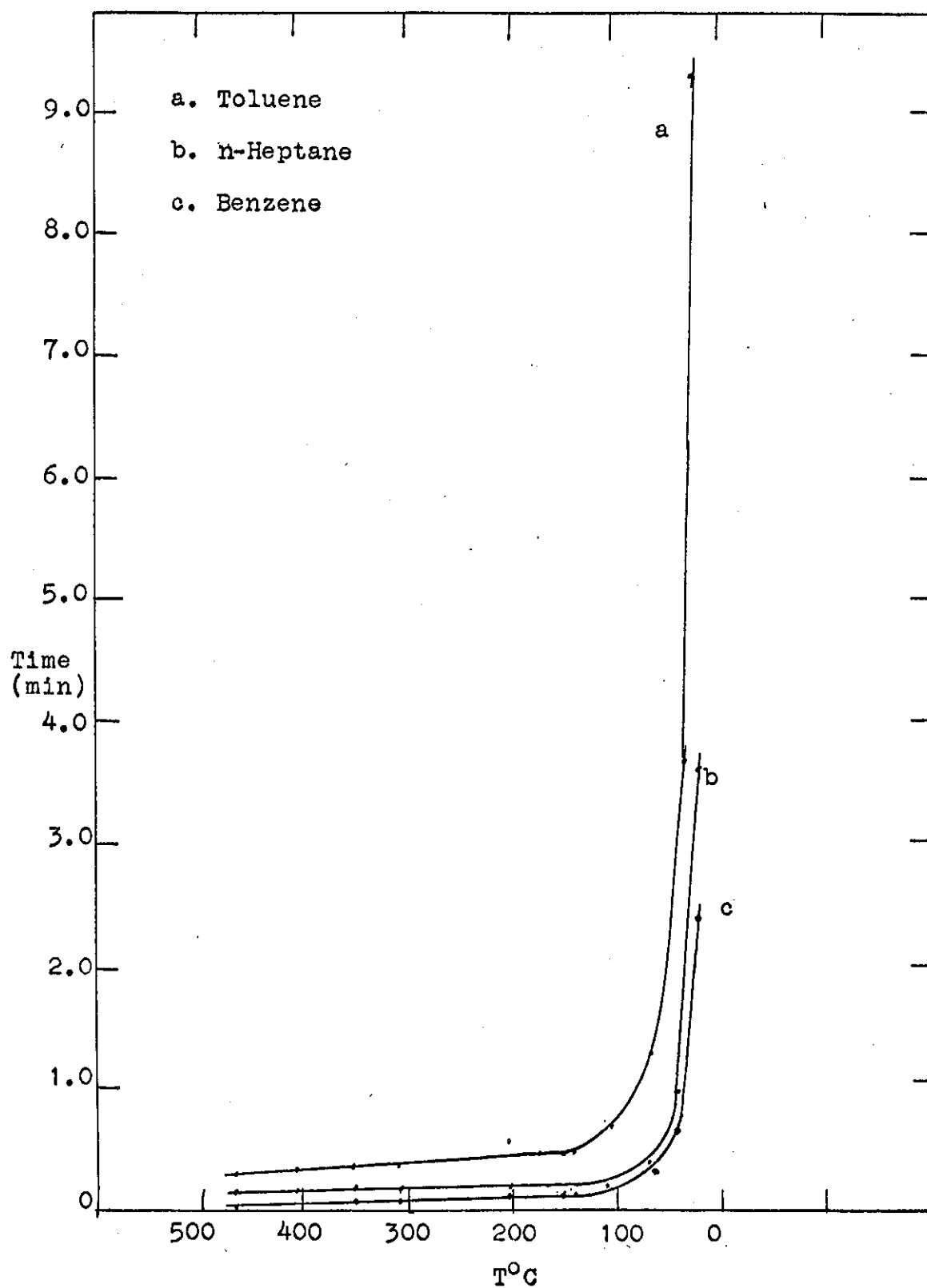


Figure 6. Retention Time vs. Temperature  $^{\circ}\text{C}$  on Linde Molecular Sieve Type 4A(80-100 mesh)

turning off the gas flow, raising the temperature to 300°C, and again resuming the gas flow. Since the concentration of the sample is proportional to the area under the graph plotted by the recorder, the amount that was recorded after resuming the gas flow was compared to that amount first recorded (to get retention time at room temperature). About 50 to 60% of the sample was observed as being retained on the sieve. This is considered to be mainly surface adsorption as in the case of the Linde Type Molecular Sieve 4A.

Table XII (Appendix E) shows the data of n-heptane, n-hexane and n-pentane on the Linde Type Molecular Sieve 5A and Figure 7 shows the graphs of this data. The calculated heats of adsorption from the corrected data using the methods described previously are shown in Table XIV.

TABLE XII  
CHROMATOGRAPHIC DATA  
OF LINDE MOLECULAR SIEVE TYPE 5A (80-100 MESH)

Adsorbate	T°C	$\frac{1}{T} (^{\circ}\text{K}^{-1}) \times 10^3$	Time (t min)	Log t(cor)
n-heptane	443	1.40	0.70	2.004
	389	1.51	1.61	2.332
	340	1.63	5.19	2.806
	301	1.74	11.5	3.124
n-hexane	390	1.51	0.64	1.934
	339	1.635	1.67	2.314
	303	1.75	3.41	2.593
	249	1.92	12.8	3.128
n-pentane	305	1.73	0.74	1.935
	247	1.92	2.79	2.465
	193	2.14	12.0	3.049

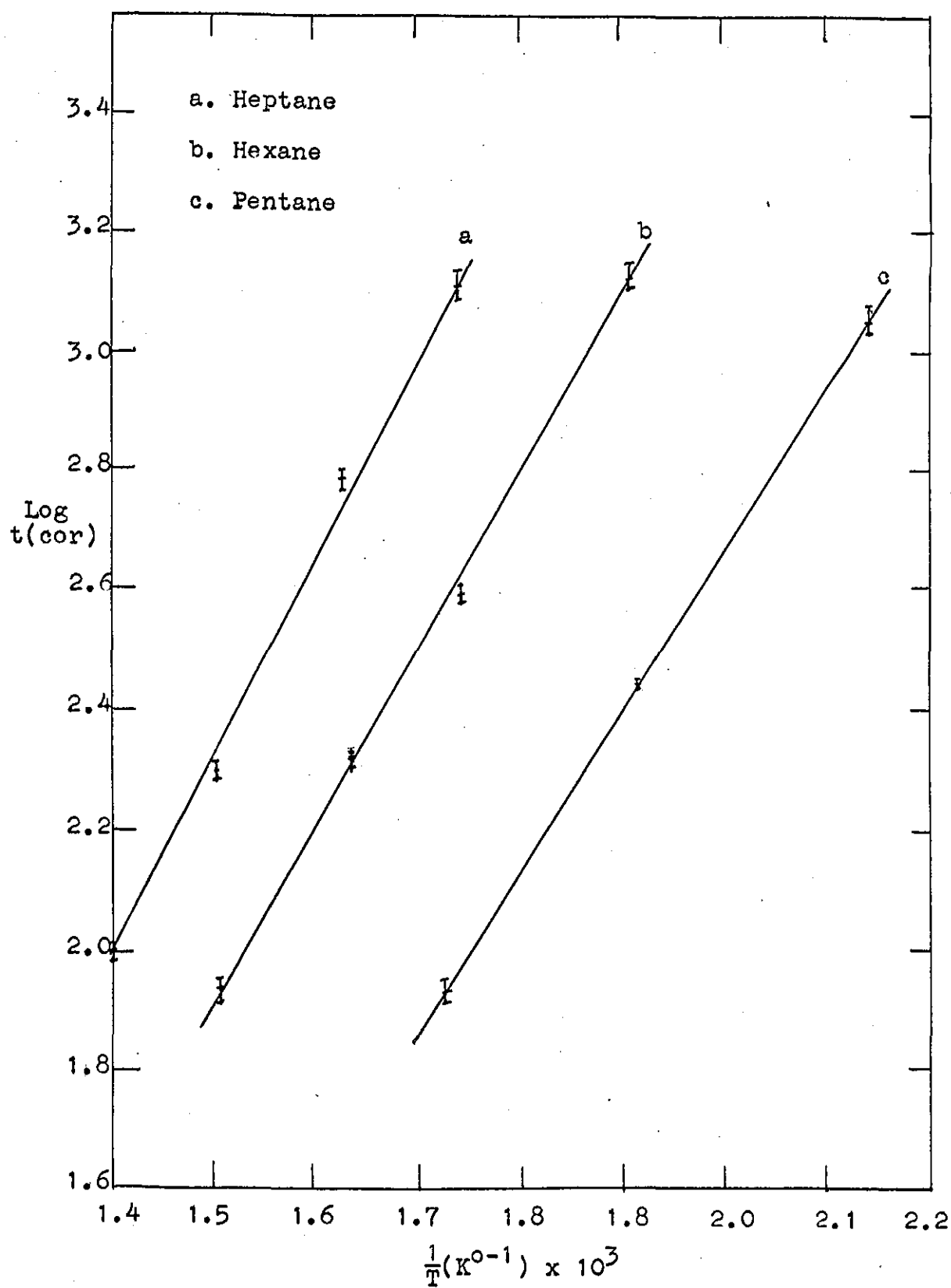


Figure 7. Retention Times as a Function of Temperature on Linde Molecular Sieve Type 5A(80-100 mesh)

Linde Molecular Sieve Type 5A (Powdered). A chromatographic column of 7.35cm long was made by using 0.24 grams of Linde Molecular Sieve Type 5A (Powdered) packed in glass wool (0.33g). As in the case of the Type 5A (80-100 mesh), the only compounds giving usable retention times were n-heptane, n-hexane and n-pentane. Table XIII (Appendix F) gives the chromatographic data for the Linde Molecular Sieve Type 5A (Powdered) and the graphs of this data are shown in Figure 8. The heats of adsorption are shown in Table XIV.

TABLE XIII  
CHROMATOGRAPHIC DATA  
ON LINDE MOLECULAR SIEVE TYPE 5A (POWDERED)

Adsorbate	TOC	$\frac{1}{T}(\text{OK}^{-1}) \times 10^3$	Time (t min)	Log t(cor)
n-heptane	397	1.49	0.80	2.032
	337	1.64	2.61	2.507
	300	1.745	6.24	2.857
	249	1.92	25.8	3.433
n-hexane	337	1.64	0.87	2.029
	300	1.74	1.96	2.356
	245	1.92	6.63	2.841
	222	2.02	14.4	3.159
n-pentane	300	1.74	0.59	1.833
	278	1.81	0.82	1.960
	241	1.94	1.69	2.244
	198	2.13	5.21	2.694

Linde Molecular Sieve Type 10X (Powdered). This chromatographic column was packed with 0.24 grams of the Linde Molecular Sieve Type 10X and 0.257 grams of glass wool,

TABLE XIV  
HEATS OF ADSORPTION  
ON LINDE MOLECULAR SIEVE TYPE 5A (80-100 MESH) AND (POWDERED)

Adsorbate	80-100 Mesh	Powdered Form
n-heptane	15.4 Kcal/mole	15.0 Kcal/mole
n-hexane	13.2	13.6
n-pentane	12.5	10.6

giving a column length of 5.20cm. Several different temperatures were used at a gas flow rate of 50 ml/min. The sample size used was  $3\mu\text{l}$ . The retention times are shown with their corresponding temperatures in Table XV (Appendix G). The graphs of this data are shown in Figure 9(a-d). The calculated heats of adsorption are shown in Table XVI.

The data for the 2-methylbutane does not follow a straight line as well as the other data. This is true for the other sieves as well as the Type 10X and can be observed by the larger deviations of its points on its graphs. Some of the error may be due to the difficulty in measuring out equal  $3\mu\text{l}$  samples. It is a very volatile material and results in having some of its vapor being present in the syringe. Thus, when measuring out the sample, this vapor caused an error in sample size which produced an error in retention time.

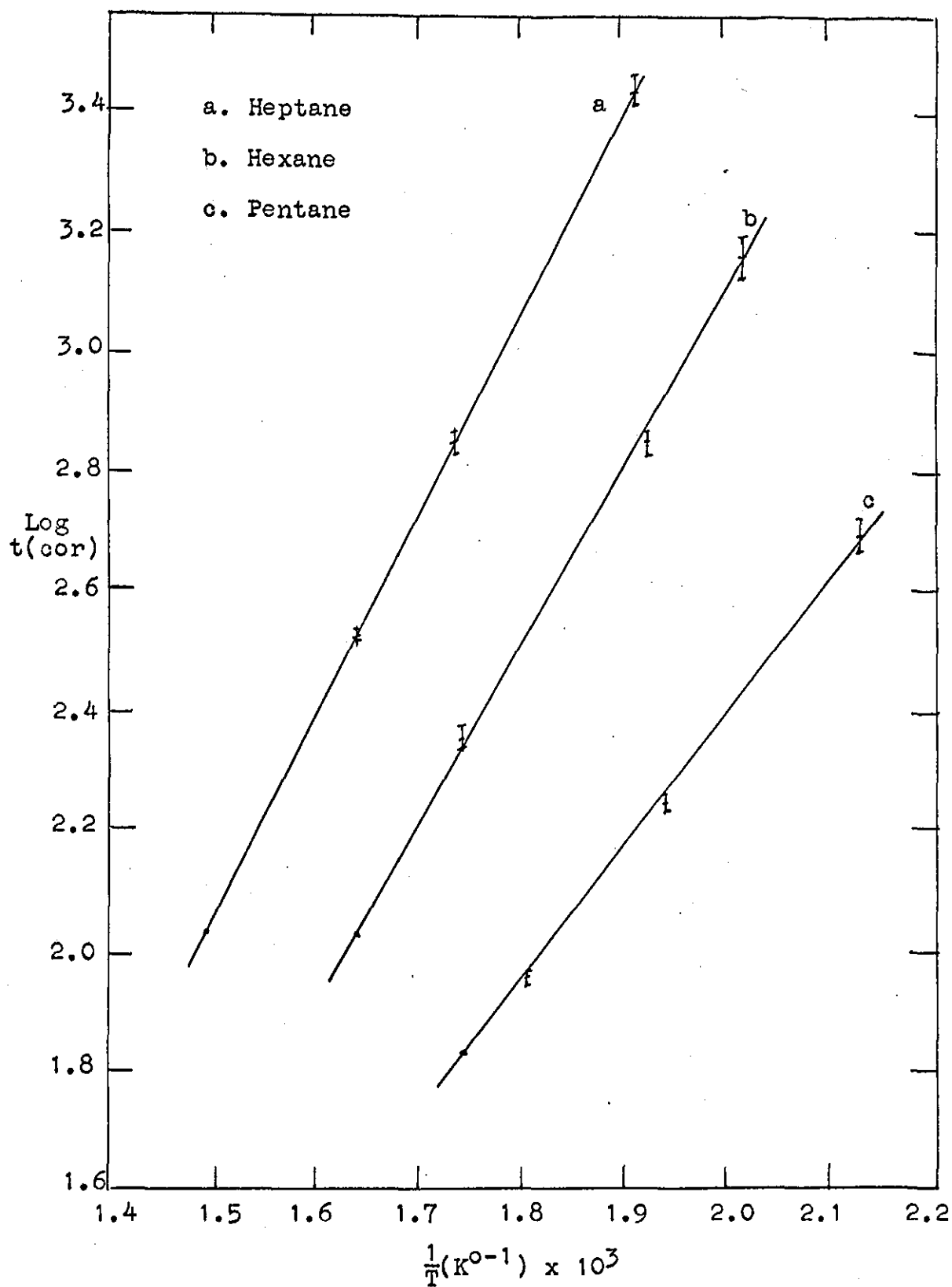


Figure 8. Retention Times as a Function of Temperature on Linde Molecular Sieve Type 5A(Powdered).

TABLE XV

## CHROMATOGRAPHIC DATA

ON LINDE MOLECULAR SIEVE TYPE 10X (POWDERED)

Adsorbate	TOC	$\frac{1}{T}(^{\circ}K^{-1})$ $\times 10^3$	Time (t min)	Log t(cor)
toluene	462	1.36	1.66	2.390
	418	1.445	3.93	2.728
	396	1.495	6.44	2.938
	350	1.61	21.2	3.424
benzene	461	1.362	0.46	1.833
	418	1.45	0.98	2.140
	397	1.49	1.46	2.297
	350	1.61	4.05	2.706
n-heptane	345	1.62	0.94	2.068
	289	1.78	2.39	2.431
	271	1.835	3.49	2.582
	253	1.91	5.13	2.735
n-hexane	293	1.77	0.73	1.920
	273	1.83	1.01	2.046
	253	1.90	1.41	2.176
	203	2.10	4.43	2.628
2,2-dimethyl- butane	269	1.84	0.74	1.909
	250	1.91	1.05	2.046
	197	2.13	3.30	2.494
2,3-dimethyl- butane	268	1.85	0.93	1.997
	250	1.91	1.35	2.152
	197	2.125	4.55	2.633
2-methyl- pentane	269	1.85	1.01	2.147
	250	1.91	1.44	2.181
	197	2.12	4.88	2.665
3-methyl- pentane	269	1.845	0.99	2.034
	250	1.91	1.44	2.181
	195	2.13	5.37	2.706
n-pentane	247	1.92	0.44	1.664
	215	2.135	0.85	2.038
	195	2.04	1.16	1.922
	178	2.22	2.02	2.263
2-methyl- butane	214	2.13	0.72	2.012
	195	2.055	1.09	1.848
	180	2.21	1.24	2.024
	159	2.31	2.47	2.328

TABLE XVI

HEATS OF ADSORPTION  
ON LINDE MOLECULAR SIEVE 10X (POWDERED)

Adsorbate	(Kcal/mole) Heats of Adsorption
toluene	19.3
benzene	16.4
n-heptane	10.4
n-hexane	9.2
2,2-dimethylbutane	9.4
2,3-dimethylbutane	9.6
2-methylpentane	10.5
3-methylpentane	11.0
n-pentane	9.2
2-methylbutane	9.2



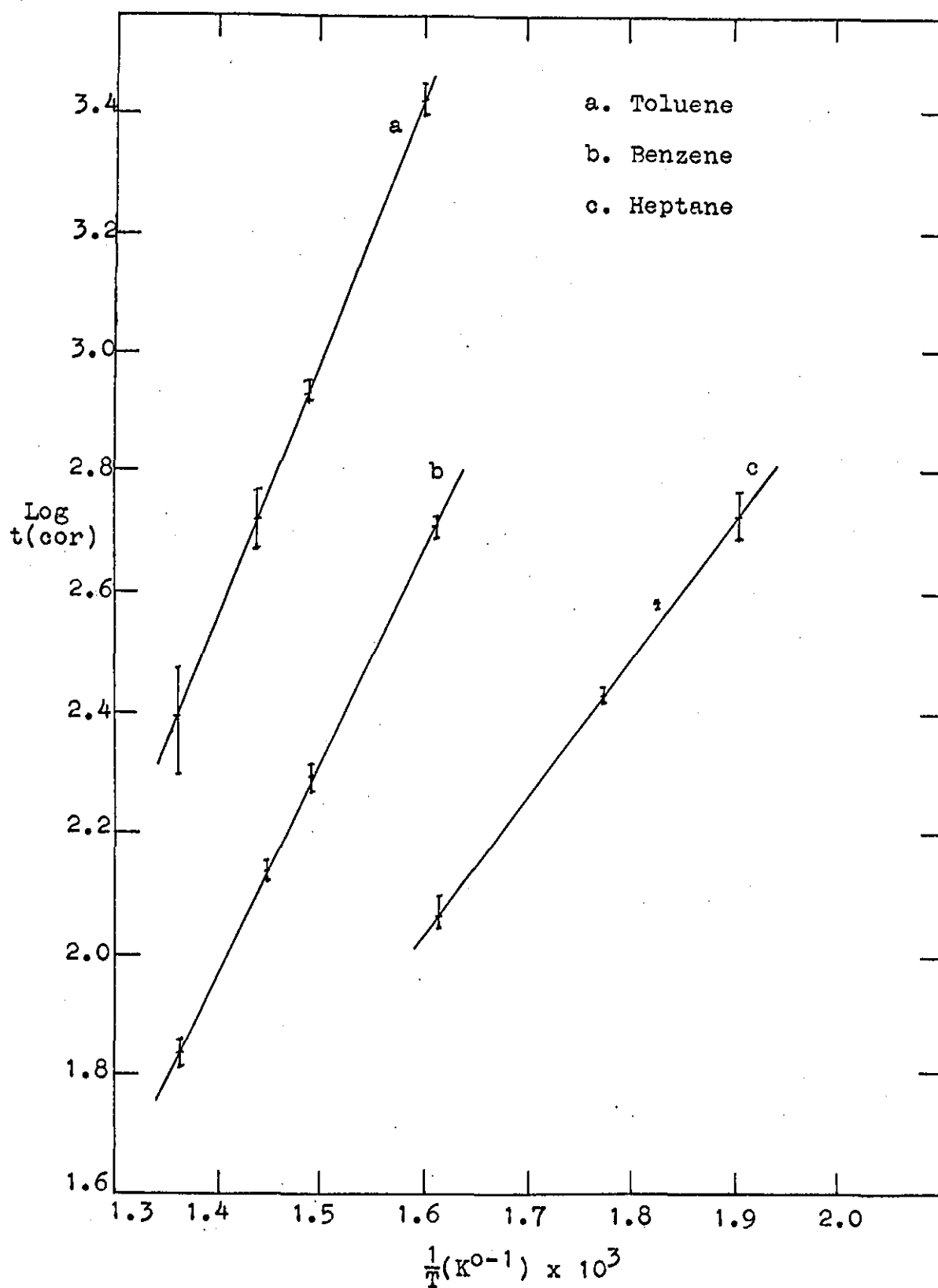


Figure 9a - Retention Time as a Function of Temperature on Linde Molecular Sieve Type 10X(Powdered).

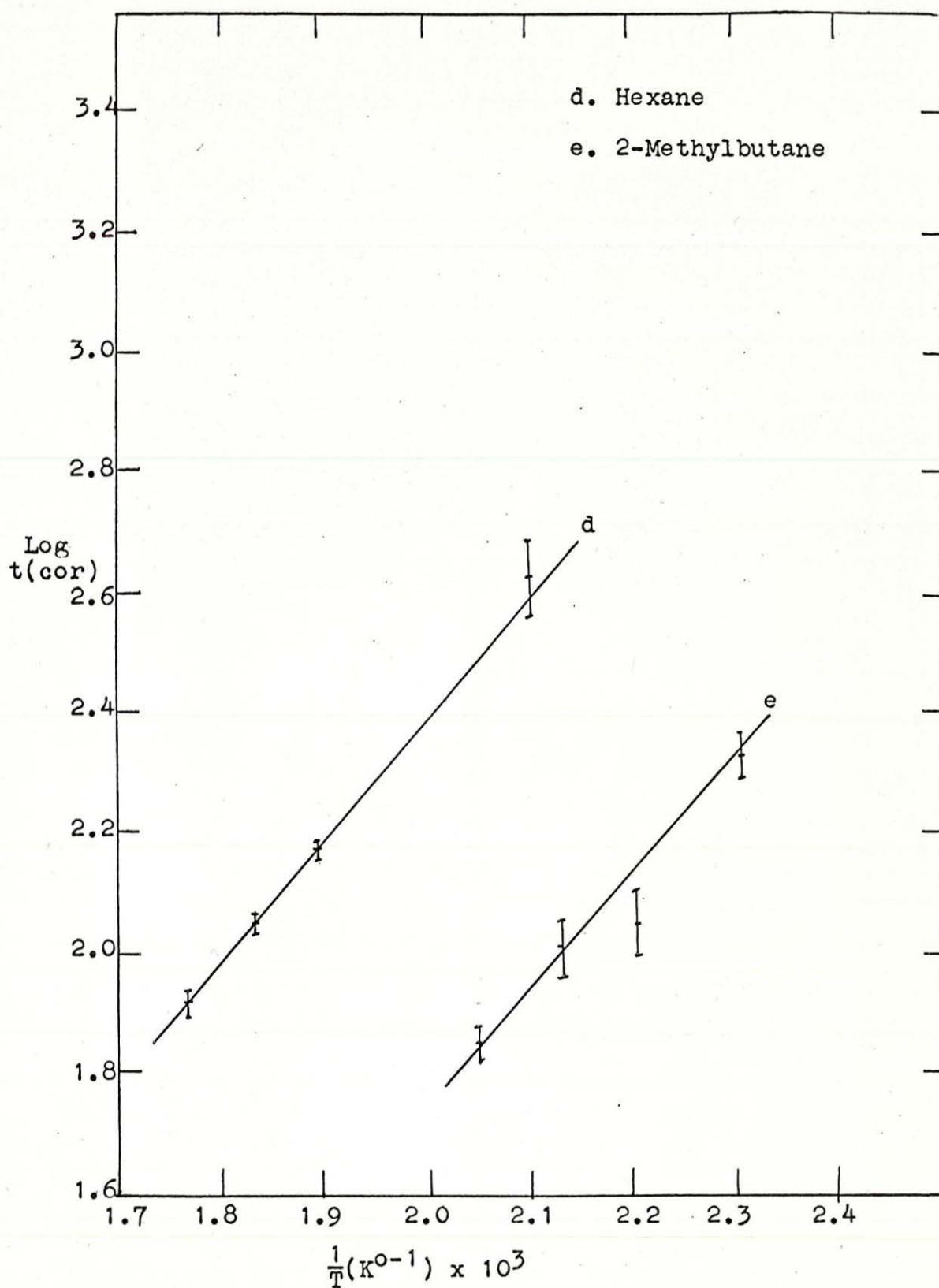


Figure 9b - Retention Time as a Function of Temperature on Linde Molecular Sieve Type 10X(Powdered).

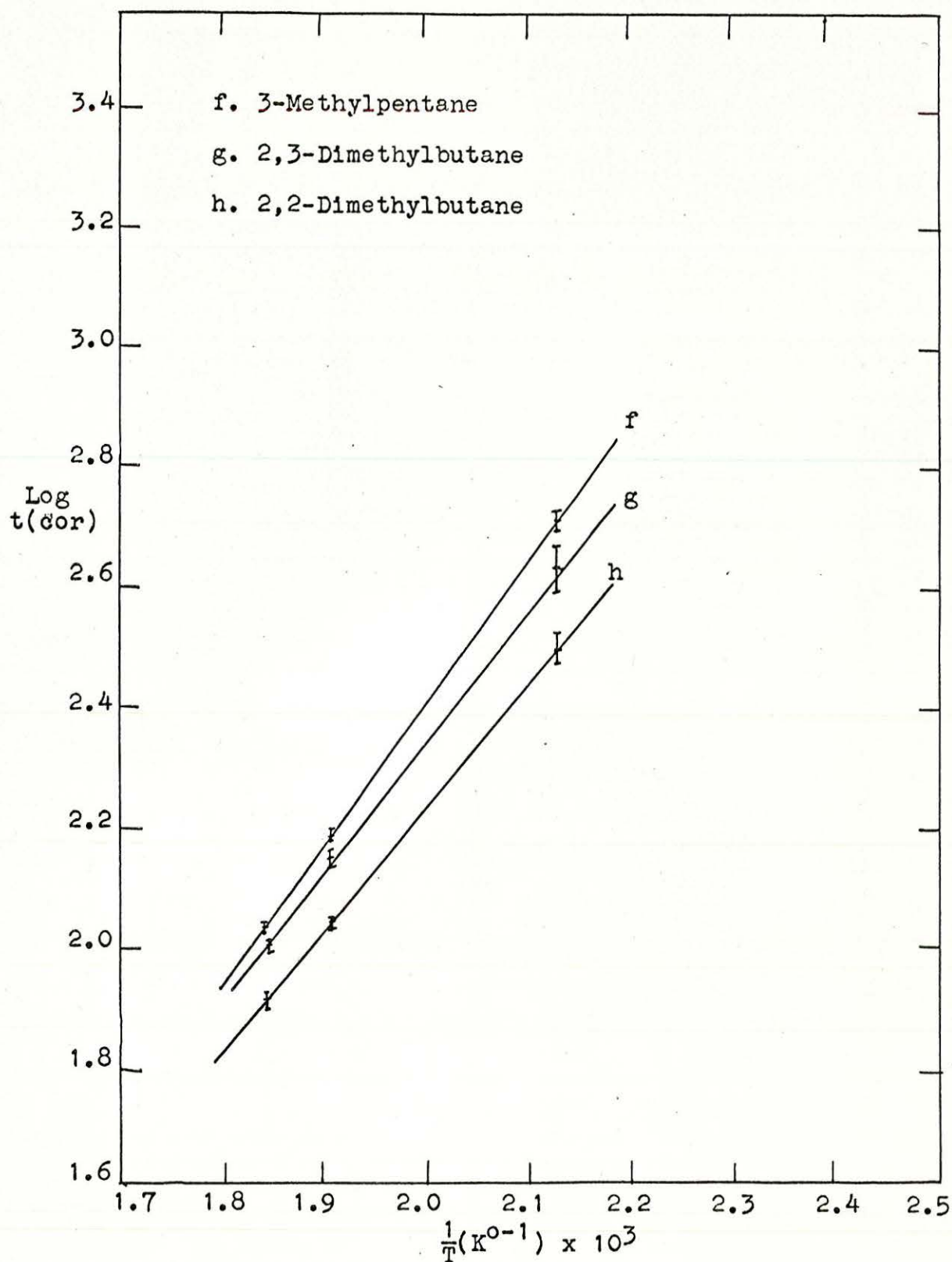


Figure 9c - Retention Times as Function of Temperature on Linde Molecular Sieve Type 10X(Powdered).

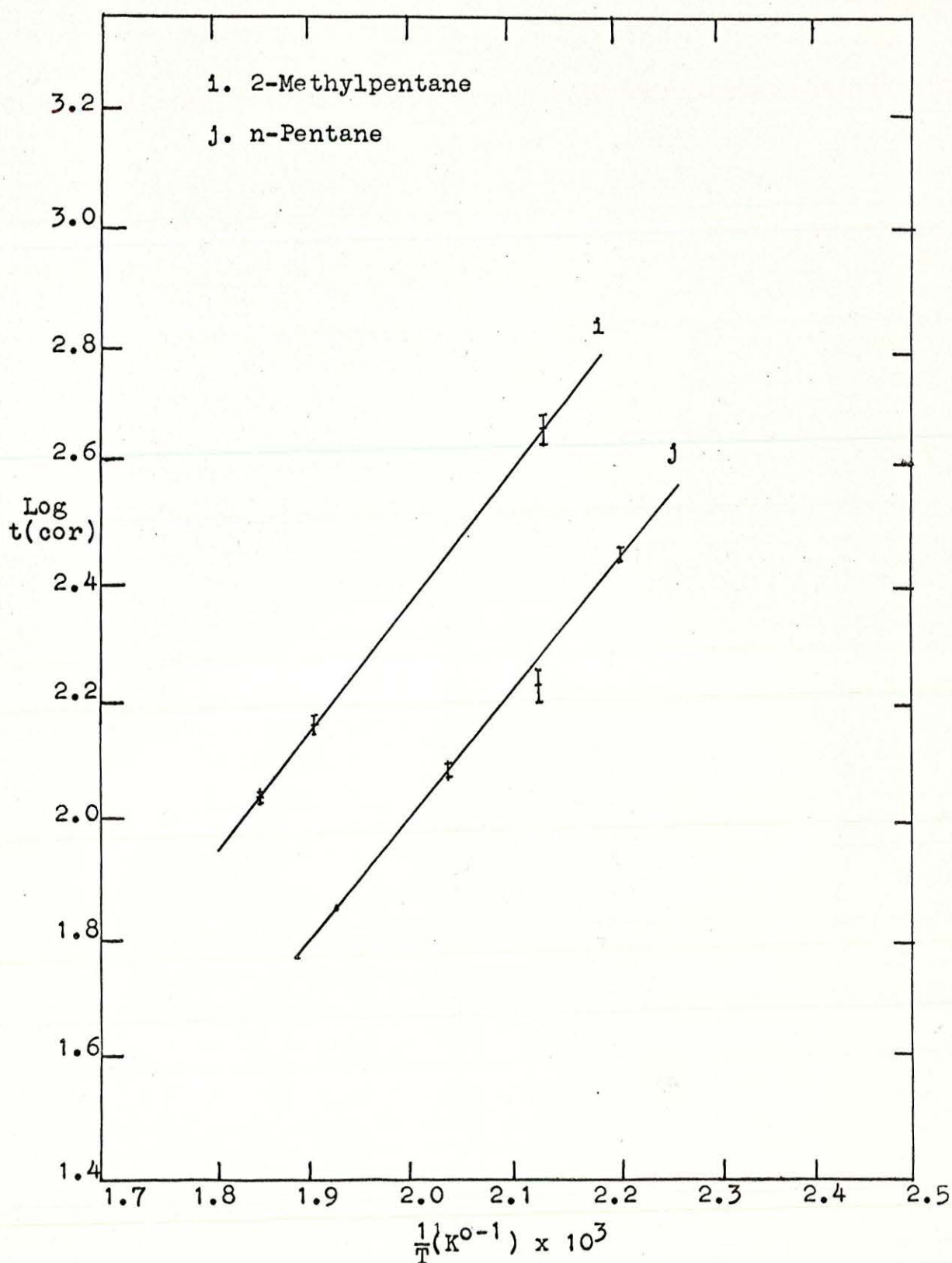


Figure 9d - Retention Times as Function of Temperature on Linde Molecular Sieve Type 10X(Powdered).

## CHAPTER VI

### DISCUSSION AND CONCLUSION

The techniques described in this work demonstrate their value for the detection of adsorption processes at high temperatures. The low contact times afforded by the flow method permit the study of adsorption without the complicating effects of decomposition frequently encountered in static systems. The dependence of the pulse retention time upon temperature permits the evaluation of the heat of adsorption. This quantity would be extremely difficult to measure at these conditions by calorimetric or isosteric methods.

In comparing the heats of adsorption of the powdered and the 80-100 mesh forms for the Type 13X and Type 5A, one finds (see Table XVII) that their values have little to poor agreement between each other. On the Type 5A, the n-heptane and n-hexane values are fairly close, but n-pentane shows a 1.9 kcal difference. On the Type 13X sieve, all the hexane isomers are very close in value, but n-hexane itself varies by 1.7 kcal. All the other compounds on Type 13X are not in good agreement. Thus, one is led to conclude that the clay binder in the 80-100 mesh sieves influences the adsorption in some cases and in others it does not. It appears that more study is required before a clearer picture can be made as to the influence of the clay binder.



TABLE XVII

COMPARING HEATS OF ADSORPTION ON LINDE MOLECULAR SIEVES

Adsorbate	Type 13X (80-100 Mesh)	Type 13X (Powdered)	Type 10X (Powdered)	Type 5A (80-100 Mesh)	Type 5A (Powdered)
toluene	19.6 kcal/mole	26.4 kcal/mole	19.3 kcal/mole		
benzene	14.5	17.3	16.4		
n-heptane	11.1	12.4	10.4	15.4	15.0
n-hexane	9.8	11.5	9.2	13.2	13.6
2,2-dimethyl- butane	10.3	10.5	9.4		
2,3-dimethyl- butane	10.3	10.2	9.6		
2-methyl- pentane	11.2	11.3	10.5		
3-methyl- pentane	11.1	11.5	11.0		
n-pentane	10.1	11.9	9.2	12.5	10.6
2-methyl- butane		11.2	9.2		

The isomers of n-hexane appear to show some order of increase in the heats of adsorption as one goes from the shorter chain of the dimethylbutane through the methylpentane to n-hexane on the Type 13X(powdered) sieve. Looking at the data on the Type 13X(80-100 mesh), one finds that the order is disrupted by n-hexane having the smallest value rather than the largest value of this group. Further, this suggested trend fails miserably on the Type 10X(powdered) where the order is opposite to that of the Type 13X(powdered). Looking at the Type 5A data, one finds the trend dramatically demonstrated by n-heptane, n-hexane and n-pentane. The longest chain molecule has by far the greatest heat of adsorption, 15 kcal, and the shortest chain molecules, the smallest heat of adsorption. Thus, there fails to be any general over-all trend for the heat of adsorption except that one finds that the aromatics have the highest heat of adsorption on the sieve where they are used.

One can postulate as to why the paraffins have a much higher heat of adsorption on the Type 5A as compared to the Type 13X sieve. The Type 5A sieve has an effective pore diameter of about 5 angstroms; whereas the Type 13X and Type 10X sieves have about twice this, i.e., about 10 to 13 angstroms. Thus, in the Type 13X and Type 10X the molecules can more freely pass through the crystal, while in the Type 5A they must wiggle through, taking more time and, thus, a higher heat of adsorption.

TABLE XVIII

## PHYSICAL DATA ON ADSORBATES\*

Adsorbate	Molecular Weight	Density	Boiling	Melting Point	Average Minimum Cross Sectional Diameter**
benzene	78.11	0.87901 <sup>20</sup>	80.099°C	5.51(5.40-0.49)°C	7.7A
toluene	92.13	0.86694 <sup>20</sup>	110.626	-95.0	7.7
n-heptane	100.20	0.68376 <sup>20</sup>	98.427	-90.5	5.3
n-hexane	86.17	0.6603 <sup>20</sup> / <sub>4</sub>	69.0	-94.3	5.3
2-methyl-pentane	86.17	0.654 <sup>20</sup> / <sub>4</sub>	60		6.2
3-methyl-pentane	86.17	0.676 <sup>20</sup> / <sub>4</sub>	64	-106.1	6.8
2,2-dimethyl-butane	86.17	0.6487 <sup>20</sup> / <sub>4</sub>	49.7	-98.2	6.5
2,3-dimethyl-butane	86.17	0.668 <sup>17</sup> / <sub>4</sub>	58.1	-135.1	6.7
n-pentane	72.15	0.626 <sup>20</sup> / <sub>4</sub>	36.2	-131.5	5.3
2-methyl-butane	72.15	0.621 <sup>19</sup> / <sub>4</sub>	28(27-31)	-160.5	6.3

\*Handbook of Chemistry and Physics (forty-second edition; Chemical Rubber Publishing Co.).

\*\*This data is a result of measurements on Fisher-Taylor-Hirschfelder Models.



From the diameters of these paraffins (see Table XVIII) one can see that there will be a tight fit for the three hydrocarbons on the Type 5A sieve, and also see that they will have plenty of room to enter the Type 10X and 13X. The diameter data also support the experimental data, in that the molecules which are about an angstrom larger in diameter than the pore diameter of the sieve, will not enter the sieves. The hydrocarbons n-heptane, n-hexane and n-pentane, being within the range, were the only molecules adsorbed by the Type 5A sieve. This diameter also supports the work on the Type 4A and 3A sieve, i.e., they are not adsorbed by the sieve.

In a study of adsorption phenomena(22), two main categories of adsorption have been established. The first case is physical in character, i.e., the association between the gas and the solid surface is physical in nature. It is known as van der Waals adsorption and is characterized by relatively small heats of adsorption, viz., about 5 kcal per mole, or less, which are of the same order as heats of vaporization.

The second type of adsorption is chemical in character and is called chemisorption since it involves forces of a chemical nature. These forces may be present even at high temperatures. The fact that the forces are similar to those concerned in chemical combination is indicated by the heats of adsorption, which are of the order of 20 to 100 kcal, per mole. The bonds formed between the material of the surface and the adsorbed gas are thus as strong as those existing

in stable stoichiometric compounds.

When we consider the heat of adsorption on the zeolites, we find values between that of van der Waals adsorption and chemisorption, i.e., 5 to 20 kcal. per mole. We, thus, appear to have adsorption of an intermediate character.

J. W. McBain (22) suggested the term persorption. One might be able to speculate as to the type of adsorption if one knew whether or not the time necessary for the molecule to get through the zeolite was due to a chemical bond being formed or just the physical feat of trying to get through all the cavities. A hint to this answer may be given by the high heats of adsorption of the aromatics. Some kind of bond might form between the benzene  $\pi$  electrons and the atoms of the zeolite. One could speculate further and suggest that part of the heat of adsorption may be due to the physical feat of diffusion of the molecules through the long channels in the crystals, since the heat of adsorption is determined from retention times.

It appears that van der Waals adsorption is evident on Type 4A sieve (see Figure 6 and Table X) for benzene, toluene and n-heptane. The retention times remain fairly constant for temperatures above 150°C, then go up very rapidly below 150°C. Since the size of the molecules are greater than the pore diameter of the zeolite, surface adsorption could be the phenomenon in action. Yet with the temperatures being so close to the boiling points of the compounds in question, another explanation might be continuous redistillation of the



compounds on the sieve. A more detailed study of the temperature area below room temperature may give a better picture of the phenomenon taking place.

A practical use of some of this data may be had by reference to the retention times. For example, on Type 10X sieve at 250°C, 2,2-dimethylbutane has a retention time of 1.05 minutes and 2,3-dimethylbutane has a time of 1.35. A half minute gives a fair amount of time for physical separation. Better yet, at 196°C on the same sieve, the 2,2-isomer has a retention time of 3.30 minutes and the 2,3-isomer has a time of 4.55, thus, a minute difference. This might be considered a better temperature for separation, but one must remember that there is "tailing" on the sieves and, thus, an optimum time and temperature could be worked out. The same could be worked out on Type 13X sieve with a five minute difference at 173°C, but again, "tailing" at this temperature is very bad and a better time-temperature combination would have to be determined.

A difference in the 2-methylpentane and 3-methylpentane isomers can be seen on both Type 13X and Type 10X sieves below 200°C. Above this temperature they tend to have the same retention times. Tailing would probably prevent any real good separation. By reducing the tailing effect possibly a method could be worked out for separating these two hexane isomers.

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## APPENDIX A

Derivation of the equation used for correcting the retention time. (6)

The full correction equation is:

$$V_m^0 = t_m F' \frac{T_c}{T_f} \frac{2/3 \left( \frac{P_i}{P_o} \right)^3 - 1}{\left( \frac{P_i}{P_o} \right)^2 - 1}$$

where

$V_m^0$  = limiting retention volume

$t_m$  = retention time

$P_i$  = column inlet pressure

$P_o$  = column outlet pressure,  $F'$  measured at  $P_o = 1$

$T_c$  = column temperature

$T_f$  = temperature of flow measuring device, 23°

$F'$  = flow rate of carrier gas

Division of the above equation by  $F'$ , which was always 60cm<sup>3</sup> per minute at  $P_o = 1$  atm., yields the retention time which would have been observed at zero pressure drop across the column. The term  $T_c/T_f$  permits the retention time of the carrier gas, derived from columns at different temperatures, to be corrected to a standard "dwell" time at 23°C. The

corrected retention are then those which would have been observed had the linear velocity of carrier at any temperature been that of 23°C.

The magnitudes of  $P_i$  and  $P_o$ , and the temperature coefficient of  $P_i/P_o$  were such that over the temperature intervals investigated, the parenthesized denominator of the above equation involved a correction to  $T_h T_c / T_f$  of less than 1.5%, and such was essentially independent of temperature. Thus, for our work, retention times, as defined by  $t_m T_c / T_f$  are used.

## APPENDIX B

## CHROMATOGRAPHIC DATA ON LINDE MOLECULAR SIEVE (80-100 MESH) TYPE 13X

Adsorbate	Temperature °C      °K	$\frac{1}{T} (^{\circ}\text{K}^{-1})$ $\times 10^3$	Time (t min)	t(sec)	t(cor)	Log t(cor)
toluene	426 - 700	1.43	3.87	232.2	545	2.736
	407 - 680	1.47	5.92	355.2	810	2.909
	342 - 615	1.63	25.3	518.3	3130	3.486
benzene	429 - 722	1.39	1.69	102.3	248	2.395
	368 - 642	1.56	6.27	376.2	810	2.908
	348 - 621	1.61	8.38	502.8	1046	3.020
	316 - 589	1.70	19.9	1194	2360	3.373
n-heptane	428 - 701	1.428	0.77	45.8	108	2.032
	406 - 679	1.474	0.99	59.4	135	2.131
	344 - 618	1.62	2.48	148.7	308	2.489
	312 - 585	1.71	4.45	267.0	524	2.720
n-hexane	344 - 617	1.62	1.04	61.8	128	2.106
	312 - 585	1.71	1.50	89.7	176	2.246
	255 - 528	1.89	5.12	307	544	2.736
	200 - 473	2.15	18.5	1110	1670	3.224
2,2-dimethyl- butane	347 - 620	1.61	0.73	43.5	90.6	1.957
	315 - 588	1.70	1.30	78.0	154	2.188
	256 - 530	1.885	4.37	265	471	2.633
	200 - 474	2.11	16.1	968	1540	3.187
	172 - 446	2.22	34.0	2084	3110	3.493
(continued)						



## APPENDIX B

(continued)

Adsorbate	Temperature °C      °K	$\frac{1}{T} (^{\circ}\text{K}-1) \times 10^3$	Time (t min)	t(sec)	t(cor)	Log t(cor)
2,3-dimethyl butane	347 - 620	1.61	0.86	51.6	107	2.031
	316 - 589	1.698	1.50	89.7	177	2.248
	256 - 528	1.886	4.73	284	504	2.703
	201 - 474	2.105	18.0	1068	1715	3.234
	173 - 446	2.22	39.4	2363	3538	3.549
2-methyl- pentane	348 - 621	1.61	0.87	52.2	107	2.036
	316 - 589	1.698	1.45	86.7	171	2.233
	257 - 530	1.888	4.68	281	499	2.698
	202 - 475	2.105	17.0	1023	1630	3.212
	168 - 441	2.37	44.2	2640	3460	3.538
3-methyl- pentane	348 - 621	1.61	0.86	51.6	107	2.032
	316 - 589	1.698	1.48	88.5	175	2.243
	257 - 530	1.888	5.08	305	543	2.734
	201 - 474	2.11	18.1	1090	1730	3.238
	170 - 443	2.26	39.0	2340	3400	3.531
n-pentane	297 - 571	1.78	0.80	48.0	92.0	1.964
	256 - 529	1.89	1.56	93.3	165	2.218
	196 - 469	2.138	5.78	347	546	2.738

## APPENDIX C

## CHROMATOGRAPHIC DATA ON LINDE MOLECULAR SIEVE TYPE 13X (POWDERED)

Adsorbate	Temperature	$\frac{1}{T} (^{\circ}\text{K}^{-1}) \times 10^3$	Time (t min)	t(sec)	t(cor)	Log t(cor)	Range
Toluene	469 - 742	1.345	1.55 $\pm$ 0.03	93.0 $\pm$ 1.8	231.0 $\pm$ 4.4	2.364	2.356
							2.371
	435 - 708	1.41	5.78 $\pm$ 0.33	347.0 $\pm$ 20.0	824.0 $\pm$ 48.0	2.916	2.890
							2.941
	397 - 670	1.495	12.6 $\pm$ 0.90	754.0 $\pm$ 54.0	1694.0 $\pm$ 121.0	3.229	3.198
							3.256
benzene	431 - 704	1.42	1.74 $\pm$ 0.06	104.0 $\pm$ 3.6	246.0 $\pm$ 8.5	2.392	2.372
							2.406
	394 - 667	1.50	3.12 $\pm$ 0.10	187.0 $\pm$ 6.0	418.0 $\pm$ 13.0	2.622	2.608
							2.634
	342 - 615	1.63	13.3 $\pm$ 0.73	800.0 $\pm$ 44.0	1700.0 $\pm$ 91.0	3.230	3.206
							3.254
	304 - 577	1.73	31.2 $\pm$ 2.32	1868.0 $\pm$ 140.0	3620.0 $\pm$ 270.0	3.558	3.525
							3.590
n-heptane	441 - 714	1.40	0.51 $\pm$ 0.01	30.4 $\pm$ 0.6	728.0 $\pm$ 1.4	1.862	1.854
							1.870
	431 - 704	1.42	0.70 $\pm$ 0.06	41.8 $\pm$ 3.6	98.0 $\pm$ 8.5	1.990	1.952
							2.028
	395 - 668	1.49	1.15 $\pm$ 0.04	69.0 $\pm$ 2.4	153.0 $\pm$ 5.4	2.185	2.170
							2.200
	340 - 612	1.64	3.21 $\pm$ 0.16	193.0 $\pm$ 9.5	396.0 $\pm$ 19.0	2.598	2.576
							2.618
	304 - 577	1.735	6.09 $\pm$ 0.22	366.0 $\pm$ 13.0	708.0 $\pm$ 25.0	2.851	2.830
							2.865

(continued)



## APPENDIX C (continued)

Adsorbate	Temperature	$\frac{1}{T} (^{\circ}\text{K}^{-1}) \times 10^3$	Time (t min)	t(sec)	t(cor)	Log t(cor)	Range
n-hexane	343 - 616	1.62	0.40 $\pm$ 0.00	24.0 $\pm$ 0.0	49.5 $\pm$ 0.0	1.694	None
	306 - 580	1.725	0.74 $\pm$ 0.05	44.4 $\pm$ 3.0	86.4 $\pm$ 5.8	1.936	1.906
							1.964
	251 - 524	1.95	1.98 $\pm$ 0.09	119.0 $\pm$ 5.4	335.0 $\pm$ 9.5	2.525	2.512
	204 - 477	2.09	7.49 $\pm$ 0.51	450.0 $\pm$ 31.0	720.0 $\pm$ 50.0	2.858	2.537 2.826 2.886
2,2-dimethyl- butane	343 - 616	1.62	0.30 $\pm$ 0.00	18.0 $\pm$ 0.0	37.2 $\pm$ 0.0	1.572	None
	305 - 578	1.73	0.55 $\pm$ 0.03	33.0 $\pm$ 1.8	64.0 $\pm$ 3.5	1.807	1.782
							1.829
	251 - 524	1.91	1.08 $\pm$ 0.07	64.8 $\pm$ 4.2	114.0 $\pm$ 7.4	2.057	2.028
	248 - 521	1.92	1.20 $\pm$ 0.20	72.0 $\pm$ 1.2	126.0 $\pm$ 2.1	2.100	2.084 2.094 2.107
	202 - 475	2.10	4.36 $\pm$ 0.12	261.0 $\pm$ 7.2	415.0 $\pm$ 11.0	2.618	2.606 2.630
2,3-dimethyl- butane	343 - 616	1.62	0.34 $\pm$ 0.04	20.4 $\pm$ 2.4	42.2 $\pm$ 5.0	1.625	1.568
	306 - 579	1.73	0.63 $\pm$ 0.05	37.8 $\pm$ 3.0	73.5 $\pm$ 5.8	1.866	1.673 1.836 1.898
	251 - 524	1.92	1.41 $\pm$ 0.06	84.7 $\pm$ 3.6	149.0 $\pm$ 6.3	2.173	2.156
	202 - 475	2.10	5.14 $\pm$ 0.21	306.0 $\pm$ 13.0	488.0 $\pm$ 21.0	2.688	2.190 2.670 2.707

(continued)

## APPENDIX C (continued)

Adsorbate	Temperature	$\frac{1}{T} (^{\circ}\text{K}-1) \times 10^3$	Time (t min)	t(sec)	t(cor)	Log t(cor)	Range
2-methyl-pentane	343 - 615	1.62	0.33 $\pm$ 0.01	19.8 $\pm$ 0.6	41.0 $\pm$ 1.2	1.612	1.604 1.625
	307 - 580	1.72	0.61 $\pm$ 0.05	36.6 $\pm$ 3.0	71.3 $\pm$ 5.8	1.853	1.816 1.887
	251 - 524	1.91	1.52 $\pm$ 0.07	91.2 $\pm$ 4.4	160.0 $\pm$ 7.7	2.205	2.183 2.224
	202 - 475	2.10	6.71 $\pm$ 0.19	403.3 $\pm$ 11.4	643.0 $\pm$ 17.0	2.808	2.794 2.820
3-methyl-pentane	340 - 613	1.63	0.39 $\pm$ 0.01	23.8 $\pm$ 1.0	49.0 $\pm$ 2.0	1.690	1.672 1.708
	306 - 579	1.73	0.63 $\pm$ 0.05	37.8 $\pm$ 3.0	73.5 $\pm$ 5.7	1.866	1.831 1.898
	251 - 524	1.92	1.62 $\pm$ 0.03	97.3 $\pm$ 1.8	171.0 $\pm$ 3.2	2.233	2.225 2.241
	203 - 476	2.05	6.90 $\pm$ 0.36	414.0 $\pm$ 22.0	661.0 $\pm$ 35.0	2.820	2.796 2.842
n-pentane	251 - 524	1.91	0.44 $\pm$ 0.02	26.5 $\pm$ 1.0	46.7 $\pm$ 1.7	1.669	1.654 1.684
	207 - 480	2.08	1.49 $\pm$ 0.09	89.5 $\pm$ 5.4	144.0 $\pm$ 8.7	2.159	2.132 2.184
	176 - 449	2.23	2.94 $\pm$ 0.22	176.0 $\pm$ 13.0	265.0 $\pm$ 20.0	2.423	2.389 2.455
	154 - 427	2.34	7.11 $\pm$ 0.46	426.0 $\pm$ 28.0	611.0 $\pm$ 40.0	2.786	2.757 2.814

(continued)

## APPENDIX C (continued)

Adsorbate	Temperature	$\frac{1}{T} (^{\circ}\text{K}^{-1}) \times 10^3$	Time (t min)	t(sec)	t(cor)	Log t(cor)	Range
2-methyl- butane	252 - 525	1.91	0.31 $\pm$ 0.04	18.6 $\pm$ 2.4	32.8 $\pm$ 4.2	1.516	1.456 1.568
	201 - 474	2.11	0.98 $\pm$ 0.14	58.8 $\pm$ 8.3	93.6 $\pm$ 13.0	1.972	2.028 1.903
	169 - 442	2.26	1.14 $\pm$ 0.22	68.0 $\pm$ 13.0	101.0 $\pm$ 19.0	2.004	1.920 2.008
	157 - 430	2.32	4.40 $\pm$ 1.03	264.0 $\pm$ 62.0	381.0 $\pm$ 89.0	2.581	2.466 2.672



## APPENDIX D

## RETENTION TIMES ON LINDE MOLECULAR SIEVE TYPE 4A (80-100 MESH)

Adsorbate	463°C	402°C	345°C	316°C	199°C	RT(23°)
toluene	0.28 min	0.31 min	0.34 min	0.36 min	0.56 min	9.30 min
benzene	0.02		0.10	0.10	0.16	2.48
n-heptane	0.15	0.14	0.15	0.18	0.21	3.68
n-hexane	0.01		0.00	0.01	0.05	0.84
2-methyl- pentane	0.00					0.48
2,2-dimethyl- butane	0.00					0.32
n-pentane	0.00		0.00	0.00	0.00	0.24

## APPENDIX E

## CHROMATOGRAPHIC DATA ON LINDE MOLECULAR SIEVE TYPE 5A (80-100 MESH)

Adsorbate	Temperature	$\frac{1}{T} (^{\circ}\text{K}^{-1}) \times 10^3$	Time (t min)	t (sec)	t(cor)	Log t(cor)	Range
n-heptane	443 ± 716	1.40	0.70 ± 0.014	42.0 ± 0.84	101.0 ± 2.0	2.004	1.996
							2.012
	389 ± 662	1.51	1.608 ± 0.05	96.6 ± 2.7	214.0 ± 6.0	2.332	2.316
							2.343
	339 ± 613	1.63	5.19 ± 0.21	311.0 ± 12.6	640.0 ± 25.3	2.806	2.789
							2.822
	301 ± 574	1.74	11.5 ± 0.48	692.0 ± 28.8	1330.0 ± 55.5	3.124	3.105
							3.142
n-hexane	389 ± 663	1.51	0.64 ± 0.03	38.6 ± 1.6	86.0 ± 3.5	1.934	1.916
							1.952
	339 ± 612	1.635	1.67 ± 0.026	100.0 ± 1.6	206.0 ± 3.2	2.314	2.308
							2.320
	303 ± 572	1.75	3.41 ± 0.11	204.0 ± 6.6	392.0 ± 12.6	2.593	2.587
							2.607
	249 ± 522	1.92	12.78 ± 0.52	766.0 ± 31.2	1340.0 ± 54.5	3.128	3.109
							3.146
n-pentane	305 ± 578	1.73	0.74 ± 0.026	44.4 ± 1.5	86.2 ± 2.9	1.935	1.919
							1.950
	247 ± 520	1.92	2.79 ± 0.01	167.0 ± 0.6	292.0 ± 1.0	2.465	2.464
	193 ± 466	2.14	11.95 ± 0.50	717.0 ± 30.0	1120.0 ± 47.0	3.049	3.031
							3.067

## APPENDIX F

## CHROMATOGRAPHIC DATA ON LINDE MOLECULAR SIEVE TYPE 5A (POWDERED)

Adsorbate	Temperature	$\frac{1}{T} (^{\circ}\text{K}^{-1}) \times 10^3$	t(min)	t(sec)	t(cor)	Log t(cor)	Range
n-heptane	397 - 669.5	1.49	0.80 ± 0.00	48.0 ± 0.0	108.0 ± 0.0	2.032	None
	337 - 610.0	1.64	2.61 ± 0.05	157.0 ± 3.0	322.0 ± 6.1	2.507	2.500
	300 - 574.0	1.745	6.24 ± 0.25	374.0 ± 15.0	720.0 ± 29.0	2.857	2.526 2.840
	249 - 522	1.92	25.8 ± 1.68	1550.0 ± 101.0	2710.0 ± 177.0	3.433	2.874 3.403 3.461
n-hexane	337 - 610	1.64	0.87 ± 0.0	52.2 ± 0.0	107.0 ± 0.0	2.029	None
	300 - 573	1.74	1.96 ± 0.06	118.0 ± 0.0	227.0 ± 7.1	2.356	2.342
	245 - 519	1.92	6.63 ± 0.29	398.0 ± 17.4	693.0 ± 30.4	2.841	2.369 2.321
	222 - 495	2.02	14.4 ± 1.23	868.0 ± 73.8	1440.0 ± 122.0	3.159	2.859 3.120 3.194
n-pentane	300 - 573	1.74	0.59 ± 0.0	35.4 ± 0.0	68.0 ± 0.0	1.833	None
	278 - 551	1.81	0.82 ± 0.02	49.3 ± 1.0	91.2 ± 1.8	1.960	1.950
	241 - 515	1.94	1.69 ± 0.04	101.0 ± 2.4	175.0 ± 4.1	2.244	1.968 2.234
	198 - 471	2.13	5.21 ± 0.39	313.0 ± 23.4	495.0 ± 37.0	2.694	2.253 2.661 2.726



## APPENDIX G

## CHROMATOGRAPHIC DATA ON LINDE MOLECULAR SIEVE TYPE 10X (POWDERED)

Adsorbate	Temperature	$\frac{1}{T} (^{\circ}\text{K}^{-1}) \times 10^3$	t(min)	t(sec)	t(cor)	Log t(cor)	Range
toluene	462.0 - 735	1.36	1.66 ± 0.36	99.5 ± 21.6	245.0 ± 53.4	2.390	2.284 2.475
	418.0 - 691	1.445	3.93 ± 0.45	236.0 ± 28.0	547.0 ± 65.0	2.738	2.683 2.780
	396.0 - 669	1.495	6.44 ± 0.23	386.0 ± 13.8	867.0 ± 31.0	2.938	2.922 2.953
	350.0 - 623	1.61	21.22 ± 1.98	127.0 ± 119.0	2660.0 ± 249.0	3.424	3.382 3.464
benzene	461.0 - 734	1.362	0.46 ± 0.02	27.6 ± 1.2	68.0 ± 2.9	1.833	1.813 1.851
	418.0 - 691	1.45	0.98 ± 0.02	59.4 ± 1.2	138.0 ± 2.8	2.140	2.131 2.148
	397.0 - 670	1.49	1.46 ± 0.08	87.6 ± 4.8	197.0 ± 10.8	2.297	2.273 2.317
	350.0 - 623	1.61	4.05 ± 0.15	232.0 ± 9.0	507.0 ± 18.8	2.706	2.689 2.720
n-heptane	345.0 - 619	1.62	0.94 ± 0.05	56.4 ± 3.0	117.0 ± 6.2	2.068	2.042 2.090
	289.0 - 562	1.78	2.39 ± 0.06	143.0 ± 3.6	270.0 ± 6.8	2.431	2.420 2.442
	272.0 - 545	1.835	3.49 ± 0.04	209.0 ± 2.4	382.0 ± 4.4	2.582	2.576 2.387
	253.0 - 526	1.91	5.13 ± 0.42	308.0 ± 24.6	543.0 ± 43.3	2.735	2.699 2.768

(continued)

## APPENDIX G (continued)

Adsorbate	Temperature	$\frac{1}{T}(^{\circ}\text{K}^{-1}) \times 10^3$	t(min)	t(sec)	t(cor)	Log t(cor)	Range
n-hexane	293.0 - 566	1.77	0.73 $\pm$ 0.04	43.8 $\pm$ 2.4	83.2 $\pm$ 4.6	1.920	1.896 1.943
	273.0 - 547	1.83	1.01 $\pm$ 0.05	60.6 $\pm$ 3.0	111.0 $\pm$ 5.5	2.046	2.024 2.066
	253.0 - 526	1.90	1.41 $\pm$ 0.03	85.4 $\pm$ 1.8	150.0 $\pm$ 3.2	2.176	2.168 2.186
	203.0 - 476	2.10	4.43 $\pm$ 0.62	266.0 $\pm$ 37.0	425.0 $\pm$ 59.0	2.628	2.563 2.685
2,2-dimethyl- butane	269.5 - 543	1.84	0.74 $\pm$ 0.01	44.5 $\pm$ 0.6	81.0 $\pm$ 1.09	1.909	1.914 1.903
	250.0 - 523	1.91	1.05 $\pm$ 0.01	63.3 $\pm$ 0.06	111.0 $\pm$ 1.05	2.046	1.049 1.040
	197.0 - 470	2.13	3330 $\pm$ 0.19	198.0 $\pm$ 11.4	312.0 $\pm$ 18.0	2.494	2.466 2.519
2,3-dimethyl- butane	268.0 - 541	1.85	0.93 $\pm$ 0.03	55.8 $\pm$ 1.8	9.94 $\pm$ 3.3	1.997	1.982 2.011
	250.0 - 523	1.91	1.35 $\pm$ 0.03	81.0 $\pm$ 1.8	142.0 $\pm$ 3.2	2.152	2.143 2.162
	197.0 - 470	2.125	4.55 $\pm$ 0.38	272.0 $\pm$ 22.8	430.0 $\pm$ 36.0	2.633	2.596 2.638
n-pentane	247.0 - 521	1.92	0.44 $\pm$ 0.0	26.4 $\pm$ 0.0	46.2 $\pm$ 0.0	1.664	None
	195.0 - 468	2.135	1.16 $\pm$ 0.10	69.6 $\pm$ 6.0	109.0 $\pm$ 9.4	2.038	2.000 2.073
	215.0 - 488	2.04	0.85 $\pm$ 0.02	51.0 $\pm$ 1.2	83.5 $\pm$ 1.96	1.922	1.911 1.932

(continued)



## APPENDIX G (continued)

Adsorbate	Temperature	$\frac{1}{T} (^{\circ}\text{K}^{-1}) \times 10^3$	(t(min))	(t(sec))	t(cor)	Log t(cor)	Range
n-pentane (continued)	178.0 - 451	2.22	2.02 ± 0.02	122.0 ± 1.83	183.0 ± 1.83	2.263	2.258 2.267
2-methyl- pentane	269.0 - 542	1.85	1.01 ± 0.01	6.06 ± 0.6	111.0 ± 1.1	2.147	2.042 2.050
	250.0 - 523	1.91	1.44 ± 0.02	86.5 ± 1.2	152.0 ± 2.1	2.181	2.176 2.188
	197.0 - 471	2.12	4.88 ± 0.28	293.0 ± 16.8	463.0 ± 26.5	2.665	2.640 2.690
3-methyl- pentane	269.0 - 542	1.845	0.99 ± 0.01	59.4 ± 0.6	108.0 ± 1.1	2.034	2.033 2.038
	250.0 - 523	1.91	1.44 ± 0.01	86.5 ± 0.6	152.0 ± 1.05	2.181	2.179 2.184
	195.0 - 469	2.13	5.37 ± 0.20	322.0 ± 12.0	507.0 ± 18.9	2.706	2.689 2.721
2-methyl- butane	195.0 - 469	2.13	1.09 ± 0.13	65.4 ± 7.8	103.0 ± 12.3	2.012	1.959 2.062
	214.0 - 487	2.055	0.72 ± 0.05	43.2 ± 3.0	705.0 ± 4.9	1.848	1.817 1.878
	180.0 - 453	2.21	1.24 ± 0.16	74.5 ± 9.7	113.0 ± 14.8	2.024	1.992 2.106
	159.0 - 432	2.31	2.47 ± 0.23	147.0 ± 13.8	211.0 ± 19.9	2.328	2.281 2.364

# APPENDIX H

## CALCULATION OF ERRORS

Temperature. The conversion unit for changing the millivolts from the recorder to temperature is 0.055 mv/10. The chart paper on the recorder has divisions down to 0.1 mv and can be estimated down to 0.02 mv, which give an error of 0.38°C.

The thickness of the line made by the pen of the chart is 0.02 mv. thus giving an error of 0.38°C. The play in the recording pen is over 0.02 mv, an error of 0.38°C.

$$\text{Total error} = \sqrt{3(0.38)^2} = 0.65^\circ\text{C}.$$

Flow rate of helium. The error in timing using a stop watch is estimated to be 0.005 minutes. This will give an error in flow rate of 0.25 ml/min.

Retention time. The estimated error on reading the time from the graph is 0.03 minutes. The error due to the thickness of the pen is 0.02 minutes.

$$\text{Total error} = \sqrt{(0.03)^2 + (0.02)^2} = 0.036 \text{ minutes}$$