SEPARATION OF N-PARAFFINS FROM CYCLIC

AND BRANCHED CHAIN HYDROCARBONS

WITH MOLECULAR SIEVES

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AND BRANCHED CHAIN HYDROCARBONS

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PREFACE

The purpose of this research was to study the separation of n-paraffins from cyclic and branched chain hydrocarbons with Linde Company Molecular Sieve type 5A.

Equilibrium and dynamic capacity of the Molecular Sieves for n-paraffins were determined.

A series of experiments for separation of different n-paraffins from cyclohexane was made to investigate the influence of n-paraffin molecules on the separation characteristics. Another series of experiments for the separation of n-heptane from different nonadsorbed solvents was made to investigate the influence of different solvent material on the separation characteristics.

The studies were carried out by determining the change of composition of different cuts of the effluent taken at definite time intervals. Analysis of the various cuts was by refractive index measurements.

I wish to express my thanks and appreciation to Dr. John B. West for his guidance and constructive criticism during the course of the research work.

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CHAPTER I

INTRODUCTION

"Molecular Sieve" is the trade-name of a new series of
synthetic adsorbents developed in 1954 by Linde Company, a
division of Union Carbon and Carbide Corporation. These
adsorbent materials are synthetic zeolites, similar to many
natural clays and feldspars.

In Molecular Sieves, the atoms of sodium or calcium,
silicon, aluminum, and oxygen are arranged in a definite
crystalline pattern containing many small cavities, inter-
connected by a number of still smaller pores. The cavities
and pores of Molecular Sieves are uniform in size. Unlike
other adsorbents, Molecular Sieves have rather unusual selec-
tivity which is determined by the size and nature of the mol-
ecule that is to be adsorbed and the sieve pore size.

Molecular Sieves usually contain water molecules in the
cavities which can be driven off by heating. The physical
structure of the crystal does not collapse or rearrange upon
losing water. The dehydrated Molecular Sieves thus obtained
contain a network of empty cavities and pores. The cavities
in Molecular Sieves crystals have a very high affinity for
water molecules. In case no water is present, they will
accept almost any other material that can get into the cavities

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and be adsorbed on their interior surfaces. This sieving action, combined with their adsorptive capacity, is the reason for the ability of Molecular Sieves to separate materials on a highly selective basis. Table I lists a number of materials which may be or may not be adsorbed by Molecular Sieves type 4A and 5A.

Several types of Molecular Sieves with different pore diameters for each type have been developed. The smallest, type 3A, is a potassium aluminum silicate with a pore diameter of about 3 Angstroms, and can adsorb molecules whose diameter is less than 3 Angstroms. Type 4A is a sodium aluminum silicate and 5A is a calcium aluminum silicate. Type 10X and type 13X have correspondingly larger pore diameters of 10 Angstroms and 13 Angstroms respectively.

An extremely important factor is the regeneration of the Molecular Sieves to their original state, so that they can be used over and over again. This is performed by simultaneous heating and purging with a dry inert gas or by evacuation at a low pressure. With proper regeneration techniques, Molecular Sieves have undergone 15,000 adsorption and regeneration cycles in the course of some vapor phase hydrocarbon separation without loss of their high adsorptive capacity (18).

Because of the unique features of Molecular Sieves as a new adsorbent, it is desirable to make a detailed study of their adsorptive characteristics.

The purpose of this work was to study the separation characteristics of several n-paraffins in various nonadsorbed

TABLE I

ADSORPTIVE SELECTIVITY OF MOLECULAR SIEVES (34)

Adsorbed on type 4A and 5A	Adsorbed on type 5A but not 4A	Not adsorbed on either type 4A or 5A
Water	Propane and higher n-paraffins up to at least C_{14}	Iso-butane and all iso-paraffins
Carbon dioxide		
Carbon monoxide*	Butene and higher n-olefins	Iso-propanol and all iso-, secondary, and tertiary alcohols
Hydrogen sulfide		
Sulfur dioxide	n-Butanol and higher n-alcohols	Bezene and all aromatics
Ammonia	Cyclopropane	Cyclohexane and all cyclics with at least 4-membered rings
Nitrogen*, Oxygen*	"Freon" 12	
Methane*, Methanol		Carbon tetrachloride
Ethane, Ethanol		Hexachlorobutadiene
Ethylene		"Freon" 114
Acetylene		"Freon" 11
Propylene		Sulfur hexafluoride
n-Propanol		Boron trifluoride
Ethylene		Molecules larger than 5.0 Angstroms

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*Appreciable quantities of these low boiling materials are adsorbed only at temperatures below -20°F.

solvents.   Static equilibrium capacity for different n-paraffins
and the dynamic separation of the n-paraffins using a fixed bed
column were investigated.

CHAPTER II

REVIEW OF THE LITERATURE

The chemical composition and physical structure of Linde
Molecular Sieves are similar to a mineral known as chabazite
which occurs mostly in basaltic rocks, and occasionally in
gneiss, syenite, mica schist and hornblendic schist. Chabazite
is essentially a natural hydrous calcium aluminum silicate,
usually containing sodium and potassium. Dana (19) stated that
its composition is somewhat uncertain. He found that the com-
position usually corresponds to $[(Ca, Na_2)Al_2Si_4O_{12}] .6 H_2O.$
The crystal has a color from white to flesh-red, and a three
dimensional structure of silica tetrahedra with one-third of
the silicon atoms being replaced by aluminum ions. In nature,
calcium is a common positive ion for replacement. The phenom-
enon of a positive ion replacing an equivalent quantity of
another positive ion is called base exchange.

The hydrated water molecules can be removed by simulta-
neous heating and evacuation. The pore space thus formed is
capable of being filled by other molecules which can get into
the pores.

In 1916, Smith (51) analysed five samples of minerals and
classified them as chabazite.

Weigel and Steinhof (52) found that water, methyl alcohol,

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ethyl alcohol, and formic acid are adsorbed in considerable amounts by chabazite, with a quickly attained condition of equilibrium. Acetone, ether and benzene are only slightly adsorbed or not at all. McBain (38) concluded from this that the pore diameter of chabazite must be 5 Angstroms or less.

The adsorption of seventeen gases by chabazite was determined by Schmidt (48) in 1928. He found that ammonia, oxygen, argon, hydrogen, carbon monoxide, carbon dioxide, methane, and ethylene gave normal adsorption values, but that ethane, propylene, dimethylacetylene, butylene, benzene, butylalcohol, ether and hexamethylene showed smaller adsorption than expected or none at all. Ethylene is the largest molecule to give normal adsorption.

Ethane, with a diameter of 4.7 Angstroms, has difficulty in penetrating into the pores of chabazite, and the larger molecules of ether, benzene, and hexamethylene cannot penetrate at all. Schmidt found that the main pore diameter of chabazite is somewhere between 4.4 and 4.7 Angstroms. The smaller adsorption of the larger molecules occurs either on the external surfaces of the crystallites or, what is more probable, the adsorbent contains a small percentage of larger sized pores.

The phenomenon for adsorbents with very fine pores allowing smaller molecules to penetrate into their pores and shutting out the larger ones was called "persorption" by McBain (37).

Baba (2) continued the persorption experiments on chabazite using additional gases besides some of those already

mentioned. He found that extensive adsorption was obtained
with carbon dioxide, methyl alcohol, and methylamine; very
small adsorption with ethyl alcohol and ethylamine. The
dividing line was a molecular diameter of 4.4 Angstroms, that
of methylamine.

Rabinowitsch (44) investigated the adsorption phenomena
of gases on chabazite at very low temperature. He found that
at liquid air temperature and 300 - 400 mm. pressure chaba-
zite adsorbs more hydrogen than nitrogen. This means that a
considerable fraction of the pores can admit hydrogen mole-
cules but are too narrow to admit nitrogen.

Rabinowitsch and Wood (45) investigated the effect of
base exchange on the adsorptive capacity of chabazite in
1936. Sodium and potassium ions were used to replace the
calcium. They found that the replacement of calcium by
sodium ions had only slight effect on hydrogen adsorption,
but eliminated almost completely the nitrogen adsorption.
Replacement of calcium by potassium ions cut down very
strongly both the hydrogen and nitrogen adsorption.

In 1938, Barrer (3) determined the adsorption isotherm
for argon, hydrogen, nitrogen and helium in the temperature
range 62° to 384°K. It was shown that zeolites consisting of
three-dimensional networks such as chabazite can adsorb enor-
mous quantities of gases. The adsorption of argon or hydro-
gen by chabazite is equal in volume to the water vapor removed
during the dehydration of the adsorbent. Of the gases for
which the van der Waals adsorption energy was reported,

nitrogen had the largest value. Adsorption measurements for ammonia on chabazite in the temperature range $294^{\circ}K$ to $626^{\circ}K$ were also made.

Emmett and DeWitt (21) measured the adsorption of nitrogen, oxygen, hydrogen, argon, carbon dioxide and n-butane on partially dehydrated chabazite near the respective boiling points of the gases. Chabazite, when only 50% dehydrated, adsorbs no nitrogen at $-195^{\circ}C$, but will adsorb considerable hydrogen at $-195^{\circ}C$ and carbon dioxide at $-78^{\circ}C$. The amount of n-butane taken up by the chabazite dehydrated about 96 per cent was almost negligible, amounting to about 1 ml. per gram at a pressure of 200 mm. at $0^{\circ}C$.

Sorption rates and equilibrium were studied by Barrer and Ibbitson (8) in 1944 for the following gases: oxygen, ammonia, hydrogen chloride, methane, ethane, propane, n-butane, isobutane, n-pentane, isopentane, n-heptane and iso-octane. When the minerals were suitably outgassed, the sorption of helium, argon, nitrogen, oxygen, methane and ethane occurred in chabazites at very great velocity. Propane, n-butane, n-pentane and n-heptane were sorbed fairly rapidly at temperatures of $100 - 300^{\circ}C$. Hydrocarbons with side chains were totally excluded under all conditions. The sorption was reversible and could be approached from the adsorption or desorption side. Isotherms and isosteres were determined for the lattice increased in the order helium $<$ hydrogen $<$ oxygen, or argon $<$ nitrogen, or methane $<$ ethane $<$ propane $<$ n-butane.

Barrer and Robins (11) studied a sorption of oxygen,

argon, and nitrogen on chabazite at -183°C for the pure gases
and for mixtures of argon and oxygen, and argon and nitrogen.
There are mutual interference effects in mixtures. These
effects depend on the relative affinities between the gases
and the sorbents. There is no evidence of enhancement of
sorption in any single case.

Barrer and Rees (10) worked on molecular diffusion in
crystals modified by polar sorbates. The systems investi-
gated were hydrogen (at -194°C); hydrogen, oxygen, nitrogen,
argon (at -183°C) in ammonia-chabazite; and argon (at -183°C)
in propane-hydrogen-chabazite. Over a relatively narrow
range in the progressive additions of water, ammonia, and
methylamine, the diffusion coefficients of the permanent
gases or of ethane decreased by a factor of 10^3 or 10^4, so
that diffusion was very sensitive to the presence of critical
quantities of modifier. The amount of modifier that produced
a given effect upon the intracrystal diffusion coefficients
depended on its molecular structure. The larger the molecule
and the larger and wider the intracrystalline channels of the
modifier, the smaller the amount that was required. A quan-
titative treatment of diffusion in a system of isolated intra-
crystalline channels was developed based on the assumption
that each modifier molecule introduced an abnormally high
potential-energy barrier opposing diffusion.

Barrer and Rees (9) also studied the polar sorbates as
modifiers of zeolitic crystals. Systematic additions of polar
molecules (ammonia, water, methylamine) to chabazite had a

profound effect on the subsequent occlusion of nonpolar gases
(hydrogen, oxygen, nitrogen, argon, and ethane). In ammonia-
chabazite the saturation sorption of argon, hydrogen, nitrogen
and oxygen at -183°C and of ethane at -78°C, decreased at first
nearly linearly with amount of ammonia up to a narrow critical
range of interstitial ammonia concentrations. Thereafter, the
amount of permanent gases sorbed fell away sharply and ap-
proached zero asymptotically. As sorption temperatures were
increased for argon to -78°C and 20°C, this critical region
disappeared. Sorption corresponded either to an interstitial
fluid or to cluster formation about intracrystalline sites in
such a manner that the maximum number of molecules in the
cluster varied with the size of the sorbate molecules. Iso-
therms for one type of cluster formation were derived.

In 1954, Barrer (5) stated that chabazite takes up slowly
the n-paraffins propane to n-heptane and rapidly methane, ethane,
and molecules with smaller dimensions. The minimum diameter of
the channel is about 4.0 Angstroms. It can be used for the
separation of the lower n-paraffins from isoparaffins, aromatics
and naphthenes. Most of the simpler methane derivatives are
rapidly occluded, those of ethane slowly, so they can be sep-
arated. Temperature has an important effect on the relative
separation; the separation can also be modified by treatment
of the chabazite with small amounts of water, ammonia, etc.,
or by treatment with solutions containing ammonium and var-
ious metallic ions. Hydrogen-chabazite has a larger pore
size and occludes propane very rapidly.

The sorptive properties required by the crystal structure
of chabazite from theoretical considerations and compared with
known experimental properties were studied by Kington and Laing
(25) in 1955. A set of large channels proceed through the
crystal parallel to the axis of three-fold symmetry, all
other channels being smaller and ineffective for sorption of
argon and molecules of similar size. The six membered sil-
icate ring provided a position of maximum potential energy,
i.e., a "squeeze point," for all sorbate molecules larger
than argon. The sorptive properties of the chabazite struc-
ture proposed by Wyart (53) were: 1. Hydrogen, oxygen, helium,
nitrogen, neon and water readily sorbed; 2. Argon was a
borderline case, showing a small or negligible activation
energy for sorption, activation energy less than desorption
energy; 3. Methane in the freely rotating state requires
an activation energy of 7 to 14 kcal/mole; 4. Molecules
larger than methane require an activation energy greater than
14 kcal/mole; 5. The sorptive properties for argon and mol-
ecules of similar size are those of a system of parallel
nonconnecting channels and not those of an interconnected
network. The use of sorbate molecules that pass into the
lattice with an activation energy must result in pore diam-
eters greater than the equilibrium diameter and thus greater
than the values required by the X-ray data.

The development of Linde Molecular Sieves has been con-
ducted since the late 1940's. In late 1954, Linde Company
announced Molecular Sieves as their new product in the field

of selective adsorption.

Illustrated bulletins (30, 31, 32, 33, 34) were published by Linde describing some of the properties and applications of Molecular Sieves.

Four experiments on liquid hydrocarbon separation were reported in Linde's work (32). They are separation of n-tetradecane from benzene, separation of n-heptane and methyl-cyclohexane, purification of isopentane, and removal of unknown impurities from n-dodecane and isosafrole.

In 1956, Breck et. al. (14) of the Linde Company reported a study of the properties and crystal structure of synthetic zeolite, type A. The new zeolite is represented by the formula: $Na_{12} \left[(AlO_2)_{12} (SiO_2)_{12}\right]$ .27 H_2O. The structure is cubic, and is characterized by a three-dimensional network consisting of cavities 11.4 Angstroms in diameter separated by circular openings 4.2 Angstroms in diameter. Removal of the crystal water leaves a stable crystalline solid containing mutually connected intracrystalline voids amounting to 45 volume per cent of the zeolite. A high capacity adsorbent is produced which readily occludes molecules of certain size and shape but excludes others. Sodium ions, accessible to the intracrystalline voids or pores, undergo cation exchange readily in aqueous solution. Replacement of sodium ions by calcium ions effectively enlarges the pore openings so straight chain hydrocarbons are readily adsorbed but branched chain hydrocarbons are excluded.

Experimental work included chemical analysis, physical

properties, X-ray diffraction, electron diffraction, infrared absorption spectra, thermal stability, decomposition products, ion-exchange reaction and adsorption studies.

The molecular sieve character of the type A zeolite is evident from the experiment. At -196°C, the type A zeolites adsorb oxygen but not nitrogen, and at room temperature ethane and ethylene oxide but not propane or cyclopropane. The adsorption of propylene (5.0 Angstroms) but not propane (4.9 Angstroms) shows that the zeolite is more selective for unsaturated hydrocarbons. The calcium-exchanged type A zeolite adsorbs larger molecules such as cyclopropane, and normal hydrocarbons up to n-tetradecane but not benzene or isobutane.

Ziegenhain (55) investigated the effect of varying liquid velocity and charge stock composition to an adsorption column under controlled conditions. Two synthetic mixtures of 5.0 weight per cent and 10.0 weight per cent n-heptane in toluene were prepared. As the liquid charge velocity through the column was increased, the yield of n-heptane free product was decreased for a given charge mixture. As the concentration of n-heptane in the charge stock was increased, the yield of n-heptane free product was lower.

The removal of straight chain hydrocarbon from specific refinery streams was also carried out and the increase in octane number of the product was determined.

In 1957, Schwartz and Brasseaux (49) studied the separation of n-heptane, n-octane, n-nonane and n-decane from

nonadsorbed hydrocarbon solvent and olefin free petroleum distillates by Molecular Sieve adsorption. A series of eight synthetic hydrocarbon mixtures was tested. The first three were 70 volume per cent, 50 volume per cent and 30 volume per cent of n-heptane in methylcyclohexane mixture. The frontal analysis technique was used in all cases and eluate fractions were collected by gravity flow without the use of pressure or vacuum. The refractive indices of all eluate portions were determined at 25.0°C. The n-paraffin content of the fraction was computed by a refractometric method which should only be applied to distillates of known boiling point range and free of olefins and water. The results of varying the n-heptane concentration confirm those obtained by Ziegenhain (55). Increase in charge rate and concentration of n-heptane in the charge stock gave less n-heptane free product.

The results for 50 volume per cent of n-heptane in methyl-cyclohexane, 2,2,4-trimethylpentane and toluene showed an inflection point in the frontal analysis curve which could not be easily explained. Four other mixtures were analyzed to determine the cause of the inflection point obtained. This inflection point was found due to the sorption of a small amount of one of the aromatic constituents of the feed.

Two distillate blends from an East Texas Crude were analyzed to determine the elution curves which were similar to that of the previous one. These tests indicated that a n-paraffin free fraction can be obtained from distillate mixtures. Batch tests of n-paraffin and nonadsorbed solvent

(n-heptane in 3-methylheptane, n-heptane in methylcyclohexane, n-heptane in toluene, n-octane in toluene and n-decane in 2,2,4-trimethylpentane) also indicated that n-heptane, n-octane and n-decane were preferentially sorbed from the mixtures.

Nelson, Grimes and Heinrich (41) investigated the sorption of n-paraffins and n-olefins in petroleum distillates as an analytical technique. The total weight per cent of n-paraffins and n-olefins was obtained by measuring the weight of sorption tube before and after adsorption. n-Paraffins were determined by analyzing the product obtained by acid treatment of the distillate, and the n-olefins were obtained as the difference between the two analyses.

CHAPTER III

MATERIALS AND EQUIPMENT

Materials

Linde type 5A Molecular Sieve was used in all the experimental work. Properties of this type of Molecular Sieve are presented in the following table.

TABLE II

PHYSICAL AND CHEMICAL PROPERTIES OF LINDE MOLECULAR SIEVE TYPE 5A (33)

Particle size	-	Pellets of 1/16 in. diameter
Bulk density	-	43 lb. per cu. ft.
Particle density	-	1.1 grams per cc.
Heat of water adsorption	-	1800 B.t.u. per lb. water
Specific heat at 40°C at 250°C	- -	0.19 0.24
Alklinity in water	-	pH 9 to 10.5

Pure grade n-pentane, n-hexane, n-heptane and n-octane obtained from Phillips Petroleum Company were used in all experiments as adsorbate.

Solvents used were technical grade cyclohexane and iso-propylbenzene, and pure grade isooctane, methylcyclohexane and ethylbenzene.

Typical properties of all materials are presented in Appendix A.

Equipment

The equipment used for the separation was that developed by Ziegenhain except for modification of the feed system. A diagram of the equipment is shown in Figure 1.

Charge stock to the column was fed by gravity from a charge bottle three and one-half feet above the outlet of adsorption column. The fluid head was sufficient to obtain steady flow at flow rates of 0.5 to 30 ml./min.

The flow rate was measured by a rotameter made by Fisher & Porter Company.

A 2.5 cm. I.d. Pyrex glass tube, 4 feet long with ball joint connections on each side was used as adsorption column. Six inches below the top of the adsorption column, a side glass tube was installed for liquid outlet.

A 20 mesh stainless steel gauze was used to support the sieves. It was held in place by indentations two inches from the bottom of the adsorption column.

An iron-constantan thermocouple (number 30 B. & S. gauge) made by the Leeds and Northrup Company was used to measure the reactivation temperature in the column. A 2 mm. I.d. Pyrex tube extending 20 inches into the middle of the adsorption column served as a thermal well for the thermocouple.

The column was thoroughly wrapped with two 6 foot sections of Briskeat flexible electric heating tape. The maximum
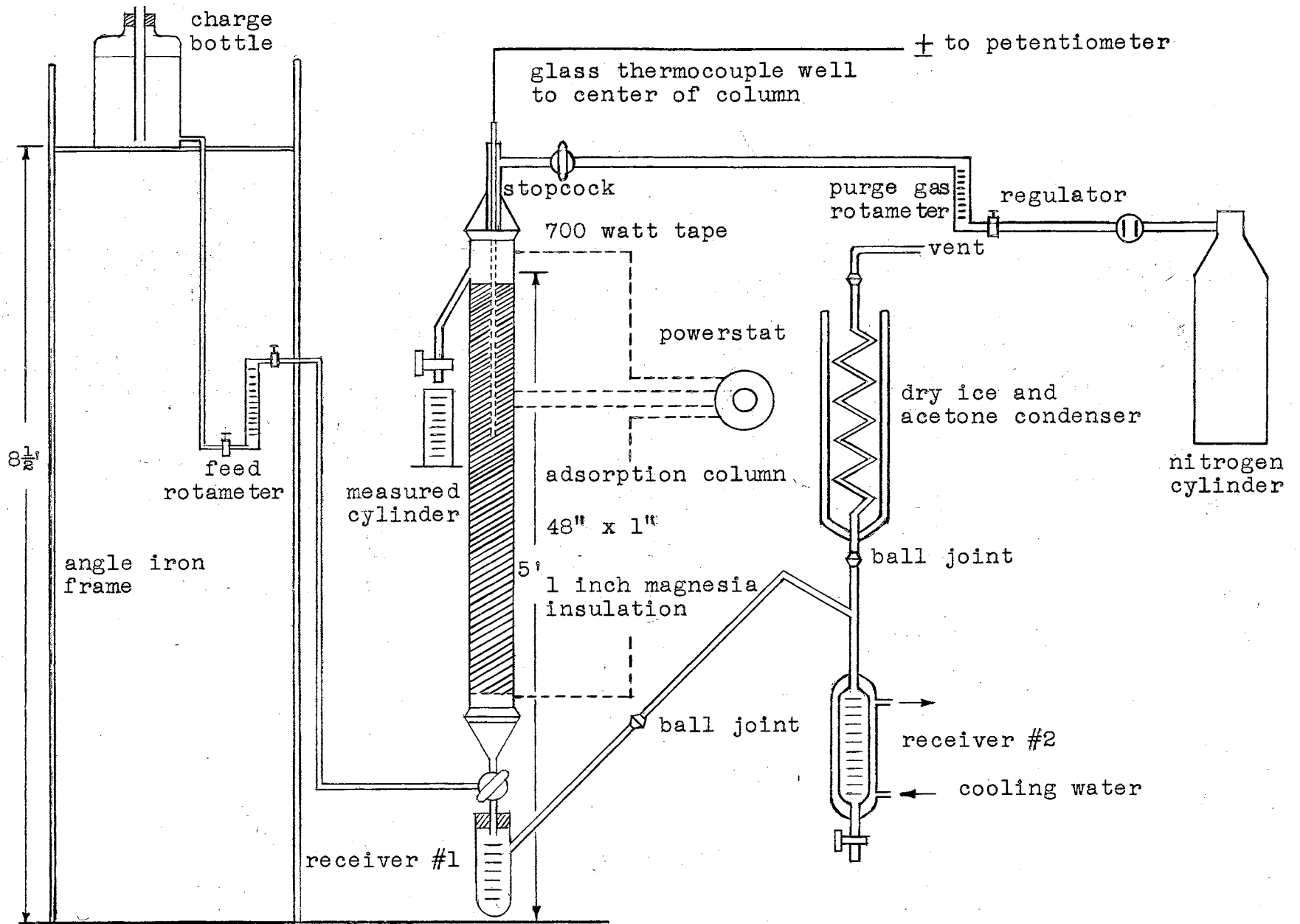
Figure 1 Schematic Diagram of Equipment

rating of each tape was 700 watts and the maximum heat output of 1400 watts was delivered when they were connected in parallel.

1-Inch wide fiber glass tape was used to wrap the heating tape to prevent possible slipping.

The entire system of heating elements and column was surrounded with one inch of magnesia insulation.

A 135 volt, 7 1/2 ampere output powerstat made by the Superior Electric Company was connected with the heating tape to adjust the rate of temperature increase in the column.

A total of 385.77 grams of new Linde type 5A (Lot No. 5344) Molecular Sieve was placed in the column. This was equivalent to a volume of 560 ml.

Condensate receiver #1 was a graduated 50 ml. glass tube placed directly under the column. A side-arm was designed for purging gas outlet which in turn connected with condensate receiver #2.

Condensate receiver #2 was a graduated 30 ml. buret with a water jacket. Cooling water flowed upward to reduce the amount of low boiling components vaporized.

A vacuum-jacketed condenser was built with a cooling coil about two feet long. The condenser held approximately 500 ml. of dry ice and acetone cooling mixture at a temperature of -110°F.

Stainless steel tubing was used between the liquid charge bottle and the rotameter, and also between the rotameter and

the bottom of the adsorption column.

Short sections of polyethylene tubing were used to make the connections between the glass and glass, glass and metal tubing.

The entire system was checked for leaks by evacuating and then observing the rate of pressure rise in the system with a mercury manometer. A pressure rise of 1.5 inches per hour for three hours was noted. The system was considered to be tight enough for experimental work.

Thermocouple wire was connected to a Leeds and Northrup Company double-range portable potentiometer. The potentiometer was checked before each run to insure standardization.

A cylinder of Linde high pressure nitrogen was used as purging gas required for the desorption cycle. A Hoke-Phoenix nitrogen regulator was connected to the cylinder to regulate the purging gas flow. A Fisher & Porter Company Flowrator was installed between the regulator and adsorption column to measure the amount of nitrogen gas for purging use. The Flowrator had been calibrated at flow rates of 0.6 to 30.0 liters of nitrogen per minute at room temperature $25^{\circ}C$ and atmospheric pressure.

Dow Corning silicone stopcock grease was used on all glass stopcocks. Metal spring clamps were used on each ball joint connection to insure a tight seal.

A Spencer refractometer, thermostatically controlled at $20^{\circ}C$, was used for the determination of all refractive indices. Calibration of the refractometer with standard test

sample was carried out before each series of samples was tested.

A constant temperature bath was set up for the refractometer.

An analytical balance made by Fisher Scientific Company was used in small quantity weighing. A larger one made by Eimer and Amend Laboratory Supplies was used in preparing all the synthetic mixtures. The former was checked with a set of standard weights (Class S-1) supplied by E. H. Sargent & Company. The latter was checked with a set of standard weights (Class C) supplied by Eimer and Amend Laboratory Supplies.

A Cenco Hyvac vacuum pump manufactured by Central Scientific Company was used in evacuating the whole system and removing the excess n-paraffins in determination of equilibrium sieve capacity.

CHAPTER IV

EXPERIMENTAL WORK

Linde type 5A Molecular Sieve pellets with 1/16 inch
in diameter and 3/16 inch long were used for all experi-
ments. Adsorption was carried out in liquid phase.

The experimental work was carried out in four parts.
The first part was to determine the equilibrium capacity of
n-paraffins on the sieves. The second was to study the
adsorption and desorption characteristics of n-paraffins in
a synthetic mixture of known composition. The third was to
study the adsorption and desorption characteristics of mixed
n-paraffins in a synthetic mixture of known composition. The
fourth was the purification of branched chain and cyclic
hydrocarbons.

Equilibrium Capacity for n-Paraffins

New samples of type 5A Molecular Sieve were put in a
250 ml. Erlenmyer flask. The sieves were activated to de-
sorb any materials that were possibly adsorbed on new sieves,
so that accurate equilibrium capacity could be determined.
Activation was done by evacuating the flask to absolute
pressure of 1.0 inch Hg. with simultaneous heating at 350°C
for ten hours. An impurity content of 2.43 weight per cent
was found.

Approximately 20 grams of activated sieves were placed in a 250 ml. Erlenmyer flask and the weight determined using an analytical balance.

Approximately 70 ml. of pure grade n-paraffins were added on the sieves. Adsorbed gas was vigorously released at first and the bubbling continued for about five minutes.

The temperature of the flask and contents increased slightly but was not determined.

A cork stopper was placed on the flask after the bubbling had ceased. The flask and contents were then periodically agitated by hand for forty-eight hours at an average room temperature of $68^\circ F$ to assure equilibrium point having reached.

The excess amount of n-paraffins was removed by evacuating the flask to 1.30 inch Hg. absolute pressure. For n-pentane and n-hexane, the flask and contents were removed from the vacuum line and reweighed at intervals of thirty minutes. After three hours, the weight was constant and was recorded. For n-heptane, n-octane and water, the flask and contents were reweighed at two hour intervals. After ten hours, the weight was constant and was recorded.

Separation of n-Paraffins from Cyclic and Branched Chain Hydrocarbons

The first phase of the study was the separation of n-paraffins from technical grade cyclohexane. Four synthetic mixtures with the composition and properties shown in Table III were prepared.

The new sieve bed was reactivated to remove any possible impurities contained. The bed was heated to 660°F and kept at that temperature for one hour, while purging with dry nitrogen at a rate of two liters per minute. Impurities of 1.2 ml. weighing 1.17 grams were obtained. The net weight of the sieves in column was then 384.60 grams. The recovered material had a refractive index value of 1.3330 at 20°C. This is the value reported for pure water.

TABLE III

PHYSICAL PROPERTIES OF SYNTHETIC N-PARAFFINS
IN CYCLOHEXANE MIXTURE

Run No.	Mixture	Wt.%	Vol.%	n_D^{20} Mixture
1	n-pentane cyclohexane	5.00 95.00	6.15 93.85	1.4201
2	n-hexane cyclohexane	5.00 95.00	5.87 94.29	1.4208
3	n-heptane cyclohexane	5.00 95.00	5.71 94.13	1.4212
4	n-octane cyclohexane	5.00 95.00	5.54 94.46	1.4218

A charge rate of 10 ml. per minute was maintained for all the runs which were carried out at atmospheric pressure and room temperature.

The initial and maximum bed temperatures during adsorption were recorded.

A total volume of 1,500 ml. of effluent was obtained for each run. Thirty cuts of 50 ml. of effluent for each were taken to determine the refractive index values which showed

the change of composition from n-paraffin free product to the original synthetic mixture. Outlet concentration was equal to inlet concentration in the final portions of the run.

The breakthrough point was also determined. It was defined as the point during each run when n-paraffins were appeared in the effluent. The n-paraffin content of the effluent was interpolated from the correlations presented in Figures 8 and 9 which were interpolated from the pure materials and the synthetic mixtures.

Experimental data determined on runs 1-4 are presented in Table XII. Regeneration of the sieves was carried out by first draining off the excess liquid. The liquid trapped in the void spaces was removed by slowly heating the adsorption column to a temperature of $150^\circ F$ in a period of approximately one and one-half hours. During heating, the column was purged with dry nitrogen at a rate of 2 liters per minute.

The rate of purging was reduced to 0.5 liter per minute when the bed temperature reached $150^\circ F$. The powerstat was then adjusted to give a rate of temperature increase about $5^\circ F$ per minute until the bed temperature reached $200^\circ F$.

The regeneration characteristics of the sieves were then noted for each run. No liquid was recovered in temperature range $150^\circ F$ to $300^\circ F$ for run 1, or $150^\circ F$ to $200^\circ F$ for run 2 and run 3. This intermission of liquid flowing out the column was noted. Refractive index values of the liquid recovered before and after the intermission indicated that pure n-paraffins were recovered after the intermission.

During run 4, 7.5 ml. of liquid, assumed to be n-octane because of the refractive index value, was recovered on condenser #1 in the temperature range 150°F to 200°F.

When the regeneration temperature reached 660°F, adjustment of the powerstat was made to keep the temperature constant. Purging of the sieves was continued for one hour on run 1 and run 2, one and one-half hours on run 3, and two hours on run 4 to permit the sieves to reach an equilibrium state.

The purging gas passed through condensate receiver #1, and then to the acetone and dry ice mixture condenser.

The adsorption column was then cooled to room temperature after each run. This completed one cycle.

Data on regeneration of the sieves for all the runs are presented in Table XVIII.

The second phase of this experiment was to study the separation of n-heptane from different pure or technical grade cyclic hydrocarbons. Three synthetic mixtures with the following physical properties were prepared.

TABLE IV

PHYSICAL PROPERTIES OF SYNTHETIC N-HEPTANE
IN CYCLIC HYDROCARBONS MIXTURE

Run No.	Mixture	Wt.%	Vol.%	n_D^{20} Mixture
5	n-heptane	5.00	5.41	1.4210
	methylcyclohexane	95.00	94.59	
6	n-heptane	5.00	6.32	1.4891
	ethylbenzene	95.00	93.68	
7	n-heptane	5.00	6.27	1.4839
	isopropylbenzene	95.00	93.73	

The same experimental procedure as in previous runs was followed. On regeneration, no liquid was recovered in the temperature range 150°F to 250°F for run 5. For run 6, a bed temperature of 250°F was maintained for an hour since the recovered effluent was still the synthetic mixture. Samples were taken frequently to determine the refractive index values during this period until a short intermission of liquid flowing out the bed was noted. The liquid recovered after the inter-mission was n-heptane. For run 7, the bed temperature was kept at 250°F for two hours until an intermission occured. There was no liquid recovered until the bed temperature reached 610°F.

Purging at 660°F was continued for one and one-half hours for each run.

All experimental data are presented in Appendix B.

The third phase was to study the separation of n-paraffins from pure grade isooctane. Two synthetic mixtures with the following physical properties were prepared.

TABLE V

PHYSICAL PROPERTIES OF SYNTHETIC N-PARAFFINS
IN ISOOCTANE MIXTURE

Run No.	Mixture	Wt.%	Vol.%	n_D^{20} Mixture
8	n-pentane	5.00	5.56	1.3898
	isooctane	95.00	94.44	
9	n-hexane	5.00	5.29	1.3901
	isooctane	95.00	94.71	

Experimental procedure was the same as that established during previous runs. On regeneration, no recovery was obtained

in the temperature range 150°F to 300°F for run 7, and in the range 150°F to 250°F for run 8. Purging of the sieves was continued for one hour in both cases.

Experimental data of this series are also presented in Apprendix B.

Separation of Mixed n-Paraffins from Cyclic Hydrocarbons

A synthetic mixture of n-pentane, n-hexane and n-heptane in technical grade cyclohexane with the following physical properties was prepared.

TABLE VI

PHYSICAL PROPERTIES OF MIXED N-PARAFFINS
IN CYCLOHEXANE MIXTURE

Run No.	Mixture	Wt.%	Vol.%	n_D^{20} Mixture
10	n-pentane	1.66	2.08	1.4206
	n-hexane	1.67	1.97	
	n-heptane	1.67	1.91	
	cyclohexane	95.00	94.04	

The adsorption cycle was similar to the previous runs. No liquid was recovered on regeneration in the temperature range 150°F to 250°F.

Chromatographic analysis was utilized to determine the distribution of different n-paraffins in the effluent at different time intervals. Eight typical samples were chosen from thirty cuts. The adsorbate samples were also chromatographically analyzed to show the composition quantitatively.

Purification of Commercial Grade Methylpentane and Technical Grade Cyclohexane

Commercial grade methylpentane contains about 85% 2- and

3-methylpentane. The balance is composed principally of 2,2-dimethylbutane, 2,3-dimethylbutane, n-hexane and cyclopentane. Typical properties are presented in Table X.

A total volume of 1700 ml. was passed through the sieve bed. At definite intervals, samples were taken and refractive index values were determined. A charge rate of 24.0 ml. per minute was maintained.

Technical grade cyclohexane has a minimum purity of 95 mol per cent. Other components are mainly 2,4-dimethylpentane and 1,1-dimethylcyclopentane. A total volume of 1000 ml. was passed through the adsorption column to remove the possible straight chain hydrocarbons contained. Twenty fractions of 50 ml. for each were taken and the refractive index values were determined. Charge rate was 14 ml. per minute.

Experimental data for purification runs are presented in Table XVI and XVII.

CHAPTER V

RESULTS AND DISCUSSION

Separation characteristics of Molecular Sieves for n-paraffins from branched chain and cyclic hydrocarbons are dependent on both the adsorbate and the solvent material of a mixture. The results obtained are interpreted in the following sections.

Equilibrium Capacity of Molecular Sieves for n-Paraffins

Experimental data are presented in Table XI. The following table lists the adsorptive capacity at equilibrium.

TABLE VII

EQUILIBRIUM CAPACITY OF n-PARAFFINS
ON TYPE 5A MOLECULAR SIEVE

Adsorbate	Equilibrium Capactiy wt.%		
	Sample 1	Sample 2	
n-pentane	9.16	8.62	
n-hexane	9.94	9.60	9.71
n-heptane	12.00		11.91
n-octane	13.19		
water	19.55		

The difference between the batches varied from 0.54% for n-pentane, 0.34% for n-hexane, and 0.09% for n-heptane. This

shows a smaller deviation as the carbon number increases. The reason is probably that lower boiling n-paraffins exert greater vapor pressure at any definite temperature. Little difference in vacuum and period of evacuation causes greater deviation for lower boiling n-paraffins than for the high boiling ones.

The equilibrium capacity of Molecular Sieves as a function of the molecular weight of adsorbed n-paraffins is shown in Figure 2. This shows that the sieves have greater affinity for the higher boiling n-paraffins than the lower ones. This is similar to the result obtained by Barrer and Ibbitson (8), who found that the affinity between n-hydrocarbons and the chabazite lattices was frequently considerable and increased as the chain length increased.

Water adsorption on the sieves was also determined as 19.55 weight per cent.

Effect of Molecular Structure on the Separation of n-Paraffins from Cyclohexane

The dynamic capacity of n-pentane, n-hexane, n-heptane and n-octane from the cyclohexane mixture was also plotted vs. molecular weight as shown in Figure 2. This also shows that the sieves have greater affinity for the higher boiling n-paraffins than the lower ones. The dynamic capacity is correspondingly lower than the equilibrium capacity. The approach to equilibrium capacity is 60.2% for n-pentane, 69.5% for n-hexane, 76.8% for n-heptane, and 82.0% for n-octane. This shows that higher boiling n-paraffins were adsorbed more rapidly than the lower ones.
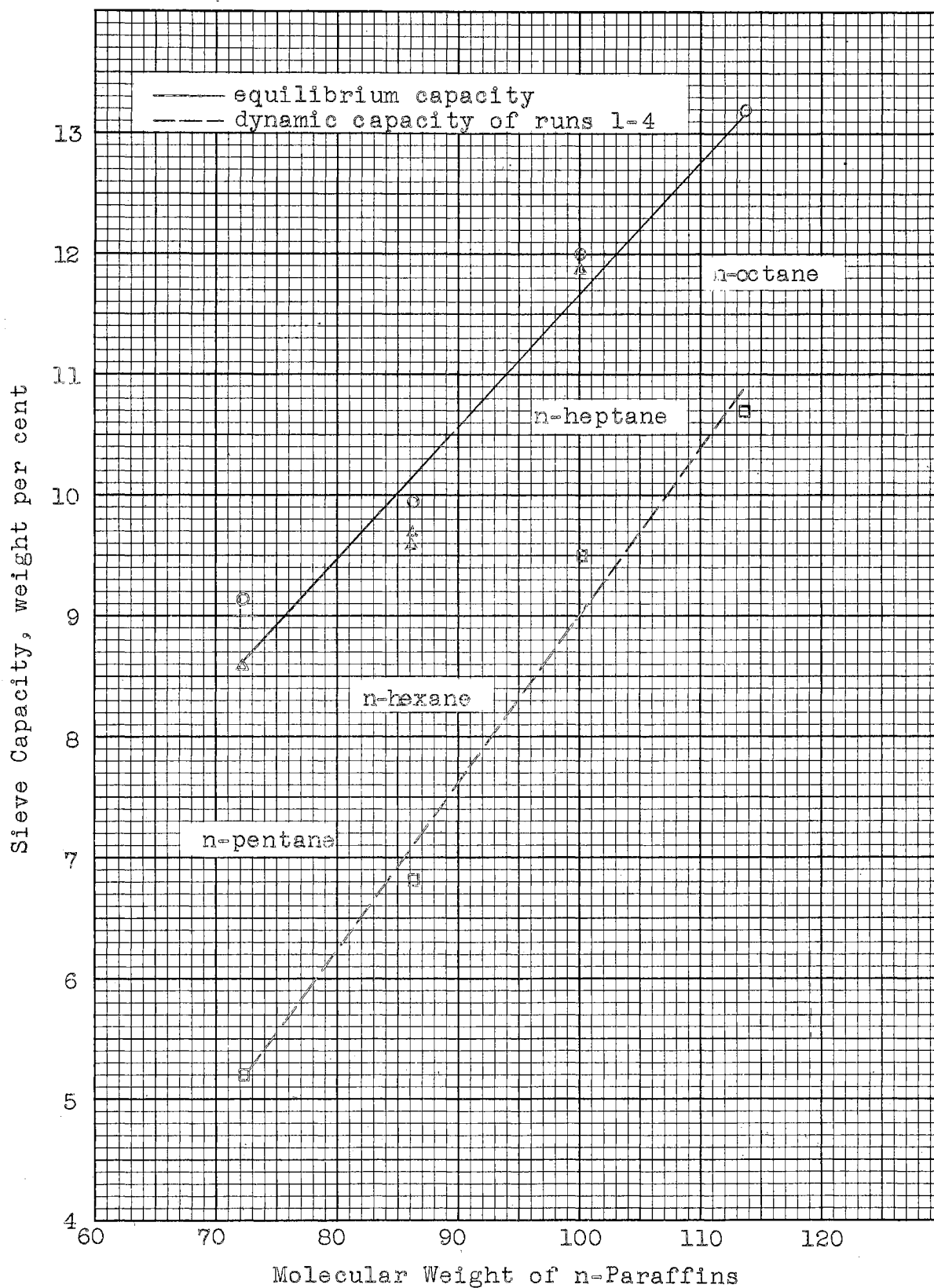
Figure 2 Equilibrium and Dynamic Capacity of n-
Paraffins vs. Molecular Weight

The curves in Figure 2 were fitted by the method of least squares. The standard error of estimate for equilibrium capacity and dynamic sieve capacity was determined to be 0.35 and 0.31 respectively.

Figure 3 shows the change of composition for different cuts of runs 1-4, and the breakthrough point of n-paraffins. Approximately 700 ml. of n-paraffins free cyclohexane recovered during the separation of n-octane from cyclohexane was noted from the Figure. Similarly, 600 ml., 700 ml., and 600 ml. of n-paraffin free cyclohexane recovered during the separation of n-heptane, n-hexane, and n-pentane from cyclohexane were also noted for the other runs. It may be seen from the figure that the rate of n-paraffin adsorption on the sieves was approximately the same for these four runs in the beginning, but that the lower boiling n-paraffins were removed more slowly as the runs progressed.

Material balances were calculated for each run. For the separation of n-heptane and n-octane from cyclohexane, the amount of n-heptane or n-octane recovered plus that remaining in the effluent was equal to the amount contained in the original mixture which passed through the column. For the separation of n-pentane and n-hexane, losses of 20 per cent of the theoretical amount of n-pentane and 8 per cent of n-hexane were noted respectively.

A study was then made to determine the losses. n-Pentane exerts approximately a ten times greater vapor pressure than n-heptane and four times that of n-hexane at a same temperature.
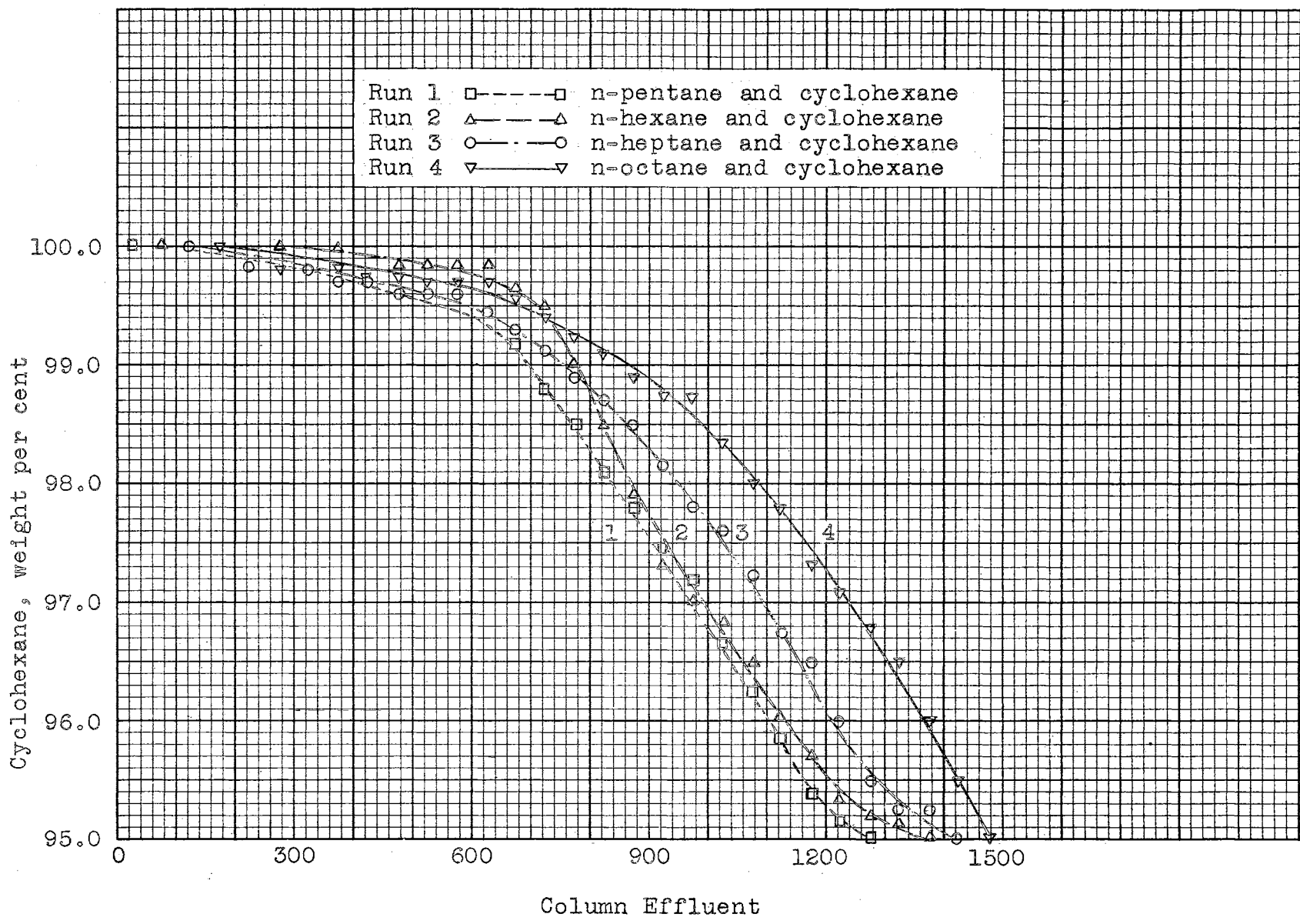
Figure 3   Separation of n-Paraffins from 5.0 Weight Per Cent
n-Paraffins in Technical Grade Cyclohexane

For a binary mixture of n-pentane and cyclohexane, n-pentane is richer in the vapor phase and leaner in the liquid phase within a container.

The evaporation of n-pentane from the charge bottle, from the effluent sample bottles, during the measurement of refractive index, and during the period the effluent came out the column was estimated to be ninety per cent of the total loss. The loss in the effluent sample bottle was verified by noting the increase of refractive index of the synthetic mixtures at the time they were prepared and after overnight which is about the period between gathering the effluent and the refractive index analysis of the effluent sample. The increase of refractive index indicated the loss of n-pentane to vapor phase.

The loss in purging of the bed was also calculated as approximately ten per cent of the total loss. This makes an error about 0.5 weight per cent on the dynamic loading of n-pentane. An error about 0.2 weight per cent on the dynamic loading of n-hexane was also obtained.

Other losses were also investigated and were found to be comparatively small.

The breakthrough curve determined in Figure 3 for n-pentane should actually have a little lower position because of the loss of n-pentane in the effluent sample bottles. The upper part of the curve for the n-hexane separation run shows a slight inconsistancy which is probably due to the loss of n-hexane and small experimental errors due to control of the

constant temperature of the refractometer and the subsequent refractive index reading. The lower part of the four curves shows a consistent trend that the higher position of the curve indicated more n-paraffins were removed from the synthetic mixture.

Figure 4 shows the result of separation of n-heptane from various solvent materials. Separation of n-heptane from isopropylbenzene had an instantaneous breakthrough of n-heptane with a low capacity on the sieves.

Ziegenhain's work (55) on separation of n-heptane from toluene was also plotted in the Figure.

The sieve loadings, 3.1 weight per cent for separation of n-heptane from isopropylbenzene, 7.7 weight per cent from ethylbenzene and 8.2 weight per cent from toluene, were obtained respectively. The longer and branched chain on aromatic ring showed greater interference in the removal of n-heptane from the stream.

Sieve loading of 8.6 weight per cent on separation of n-heptane from methylcyclohexane and 9.5 weight per cent on that from cyclohexane indicates that methylcyclohexane had greater influence than cyclohexane.

Effect of Chain Length on the Separation of n-Paraffins from Isooctane

Figure 5 shows the separation of n-pentane and n-hexane from isooctane. n-Hexane and n-pentane had a dynamic loading of 6.6 weight per cent and 3.9 weight per cent respectively. The fact that the sieves had greater affinity for higher
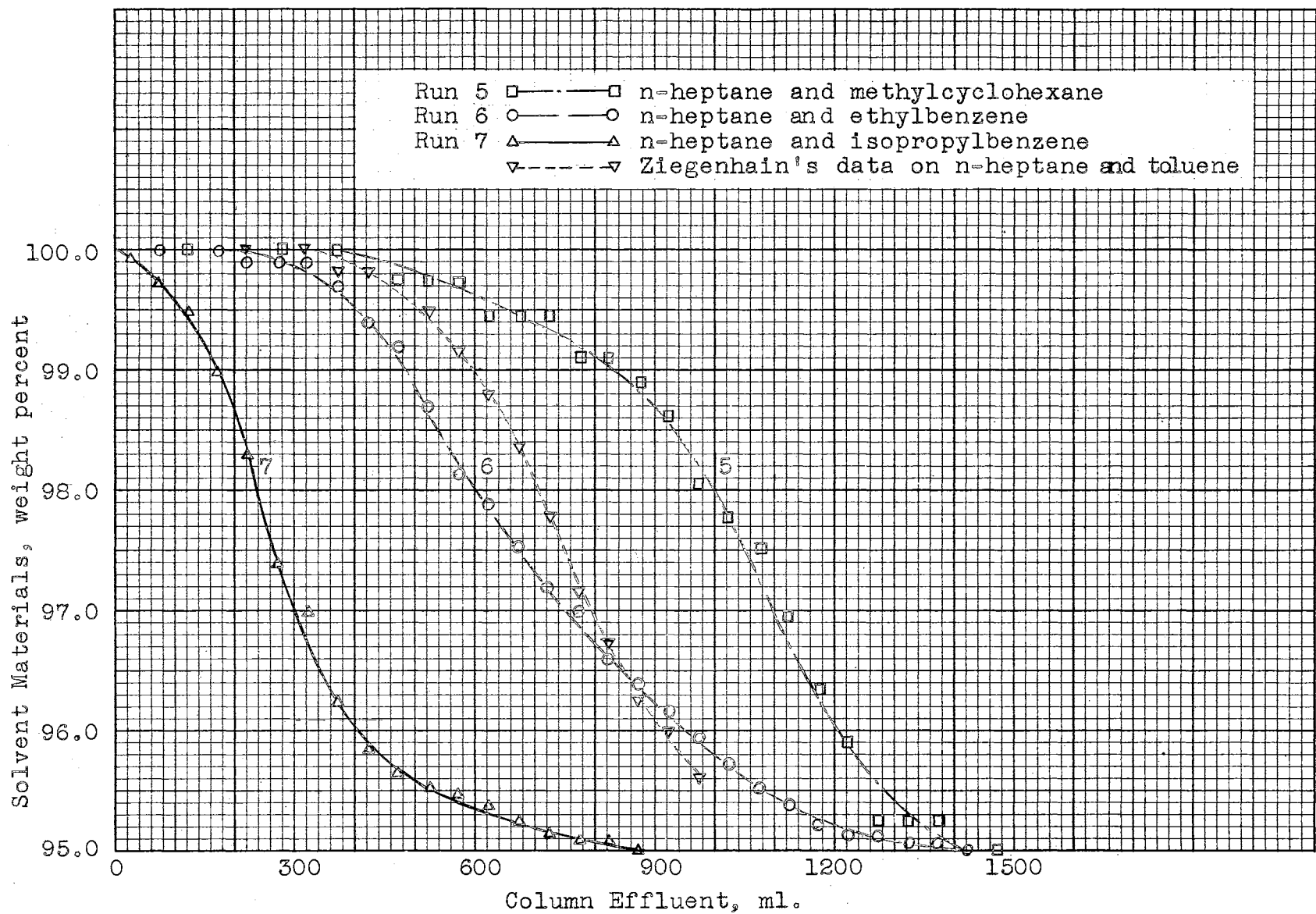
Figure 4 Separation of n-Heptane from 5.0 Weight Per Cent n-Heptane in Various Solvent Materials
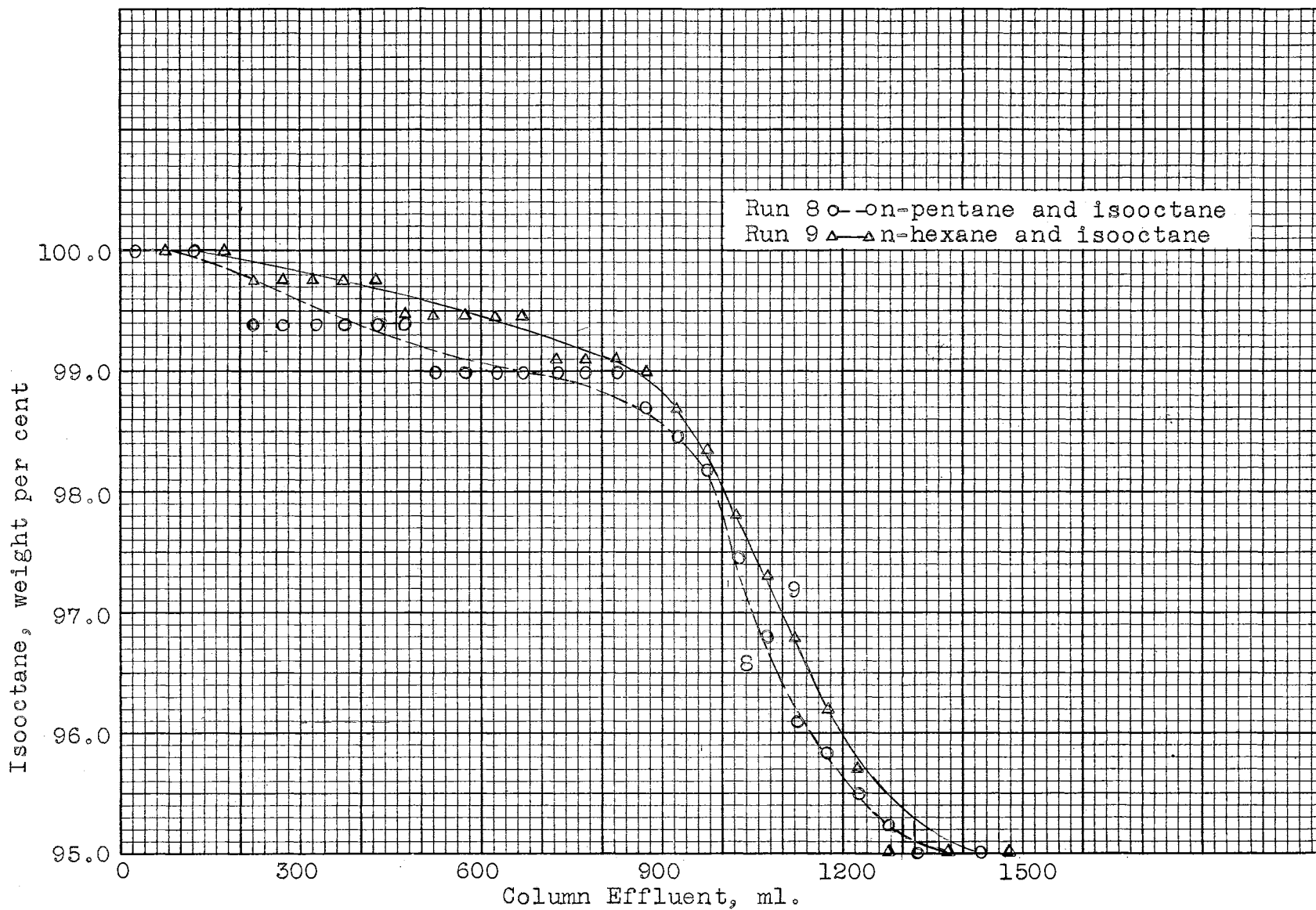
Figure 5 Separation of n-Paraffins from 5.0 Weight Per Cent n-Paraffins in Pure Grade Isooctane

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boiling n-paraffins is also verified in this series of runs.
The breakthrough curve indicates that more n-hexane was
removed than n-pentane.

Effect of Molecular Structure on the Separation of Mixed
n-Paraffins from Cyclohexane

A sieve loading of 5.6 weight per cent was obtained for
a mixture. Refractive index of condensate on receiver #1
was 1.3831 which is close to the value of n-heptane (20). Con-
densate in receiver #2 had a refractive index value 1.3760
which is close to that of n-hexane (20). Receiver #1 was at
room temperature and a greater proportion of the higher boiling
components was collected. Receiver #2 should collect more
lower boiling components which were condensed on the dry ice
and acetone condenser. Curve showing the change of composi-
tion was plotted in Figure 6.

Chromatographic analysis of eight typical samples was
not satisfactory due to the loss of lower n-paraffins from
the samples prior to analysis. Curve showing composition
change by this method was also plotted in Figure 6. The
difference between the two curves indicates the loss of n-
paraffins, especially n-pentane, from the samples for chromato-
graphic analysis. The individual distribution curve for each
n-paraffin component is not shown in the Figure.

The distribution of n-paraffin in the combined recovery
of receiver #1 and #2 was 3.1 weight per cent of n-pentane,
33.8 weight per cent of n-hexane, 62.7 weight per cent of n-
heptane and 0.4 weight per cent cyclohexane. This result of
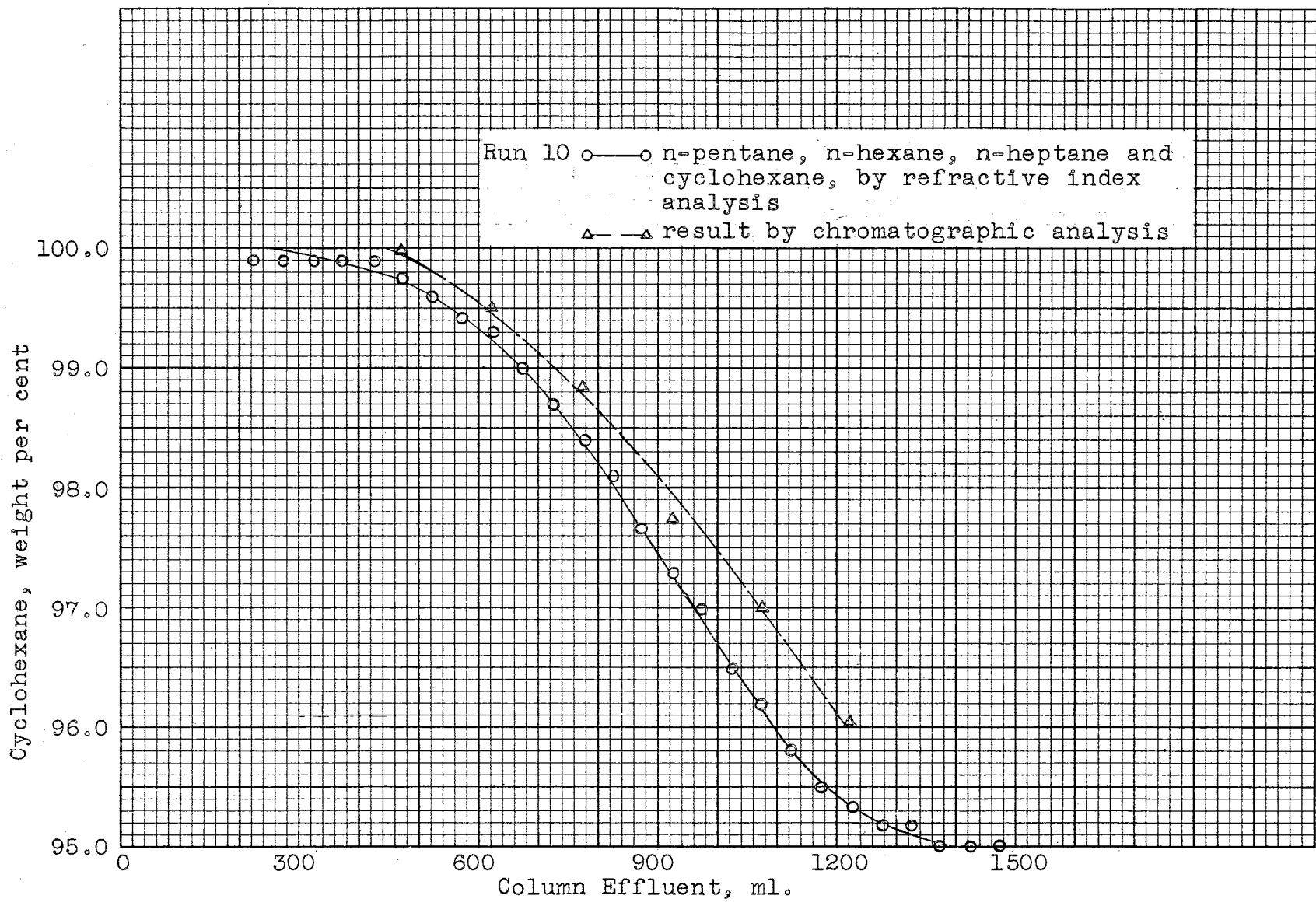
Figure 6 Separation of n-Paraffins from 5.0 Weight per Cent n-
Pentane, n-Hexane, and n-Heptane in
Technical Grade Cyclohexane

separation of mixed n-paraffins from cyclohexane shows that higher boiling n-paraffins were predominately adsorbed on the sieves. Similarly, silica gel, activated alumina, and activated carbon (34) have a tendency to adsorb the heavier and higher boiling point components of a mixture in preference to the lower boiling ones.

Regeneration

Volume of solute recovered for runs 1-4 was plotted as a function of sieve bed temperature as shown in Figure 7. It was noted that the higher boiling n-paraffins had a wider desorbing range. A combination of adsorption and desorption cycle indicated that higher boiling n-paraffins were more easily adsorbed, and the desorption started at a lower temperature compared with that required for lower boiling ones. However, longer period and higher temperature were required in attaining the equilibrium state for higher boiling n-paraffins.

From desorption data, it was noted that the molecules were so strongly held in the cavities of the sieve, that high regeneration temperature was required. n-Pentane has a boiling point of 96.9°F, and n-hexane has a boiling point of 155.8°F. No n-pentane and n-hexane were recovered at their boiling point range. Over one-half of the materials were recovered after the bed temperature reached 450°F. The vapor pressures of n-pentane and n-hexane at 450°F are approximately 50 atm and 28 atm respectively. n-Pentane and n-hexane were above or just at their critical temperatures of 386.5°F and 455°F respectively, before the reactivation of the sieve bed reached a maximum rate.
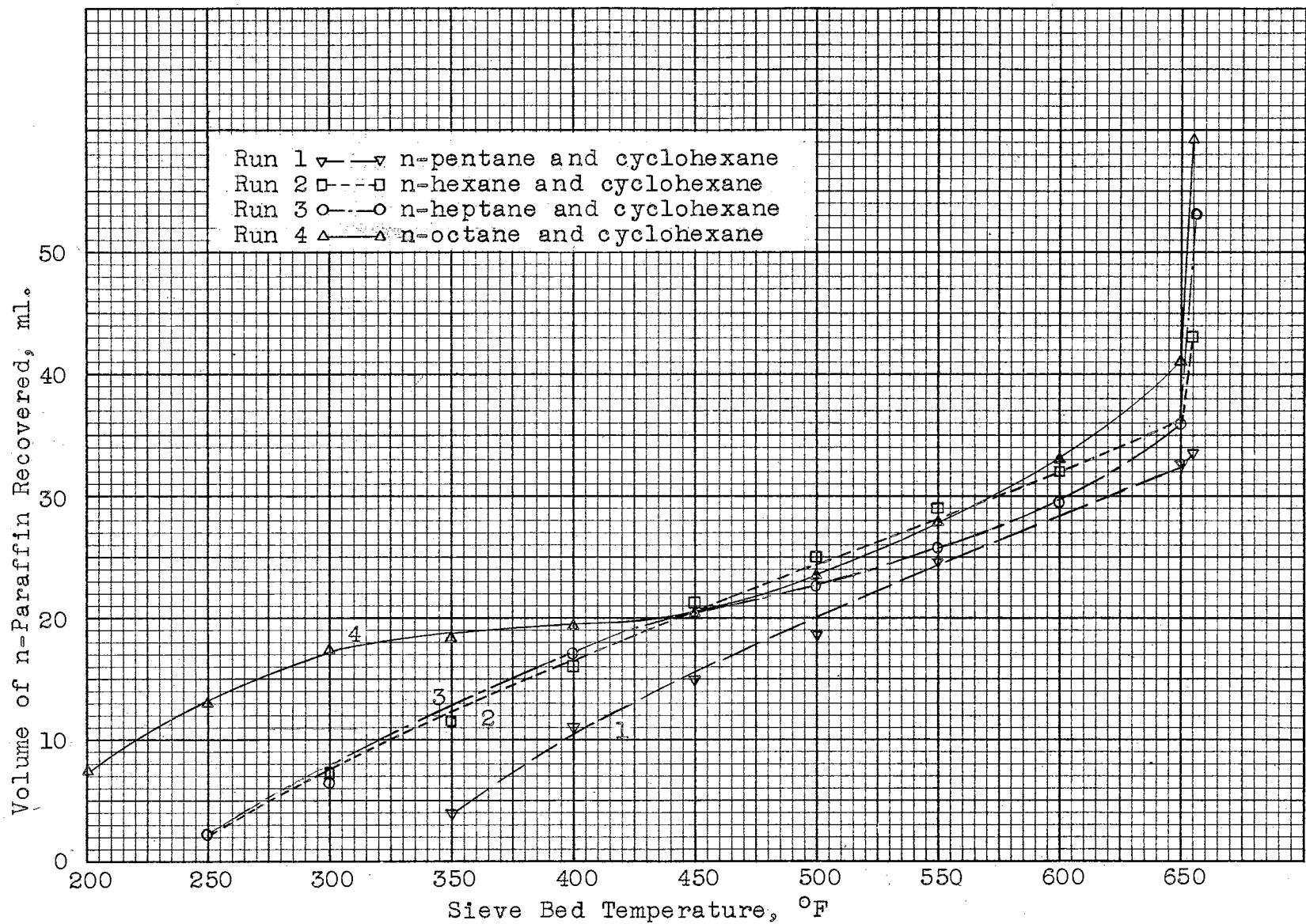
Figure 7   Volume of n-Paraffin Recovered vs. Sieve Bed Temperature for Runs 1-4

n-Heptane and n-octane have boiling points of 209.1°F and 258.2°F respectively. Over one-half the materials were recovered after the bed temperature reached 550°F. The corresponding vapor pressures are approximately 35 atm and 22 atm. n-Heptane and n-octane were above or close to their critical temperatures of 512°F and 565°F respectively, before any appreciable amount was desorbed.

The refractive indices of the recovered n-heptane and n-octane are those of the pure grade materials. Recovered n-hexane and n-pentane had refractive indices higher than that of the starting material. They were possibly contaminated by traces of the materials obtained in the range from room temperature to 150°F which were left on the container wall.

CHAPTER VI

SUMMARY AND CONCLUSIONS

Dynamic capacity of n-paraffins on the sieves varied from 3.9 weight per cent for separation of n-pentane from isooctane to 10.7 weight per cent for separation on n-octane from cyclohexane. Equilibrium capacity of n-paraffins varied from 8.8 weight per cent for n-pentane to 13.19 weight per cent for n-octane. It was found that Molecular Sieves had greater affinity for higher boiling n-paraffins in both dynamic and static conditions. Higher boiling n-paraffins were also preferentially adsorbed from a mixture of n-pentane, n-hexane and n-heptane in cyclohexane.

Separation of n-heptane from various solvents (toluene, ethylbenzene, cyclohexane and methylcyclohexane) showed that longer and branched chain on the cyclic ring of the solvents had greater interference for n-heptane separation. The lower dynamic sieve capacities were correspondingly obtained.

As a consequence of this work, further studies might include the following phases.

1. The effect of adsorption temperature and liquid charge pressure on the rate of adsorption.

2. Separation and regeneration characteristics of unsaturated and branched chain hydrocarbons.

3. Separation characteristics of straight chain hydro-
carbons in vapor phase.

4. Separation characteristics of multicomponent mixtures
containing unsaturated or both saturated and unsaturated hydro-
carbons.

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APPENDIX A

PROPERTIES OF MATERIALS USED AND REFRACTIVE

INDEX OF SYNTHETIC MIXTURES

TABLE VIII

TYPICAL PROPERTIES OF PURE
GRADE n-PARAFFINS (42)

	n-Pentane	n-Hexane	n-Heptane	n-Octane
Freezing point, °F	-201.7	-139.9	-131.3	-70.4
Boiling point, °F	96.9	155.8	209.1	258.2
Sp. gr. at 60/60F	0.631	0.665	0.689	0.706
at 20/4C	0.626	0.660	0.684	0.703
API gr. at 60°F	92.8	81.60	74.0	68.8
Vapor pressure At 70°F, psia	8.7	2.46	-	-
At 100°F, psia	15.7	4.96	1.62	0.65
At 130°F, psia	26.3	9.16	-	-
n_D at 20°C	1.3575	1.3749	1.3876	1.3974
Literature value (20)	1.35748	1.37486	1.38764	1.39743
Flash point, °F	-56.6	-10	42	72
Color, Saybolt	+30	+30	+30	+30
Sulfur content, wt. %	<0.005	-	-	-
Acidity	Not acid	Not acid	Not acid	Not acid
Nonvolatile matter	None	None	None	None

Pure grade - 99 mol per cent minimum purity.

TABLE IX

TYPICAL PROPERTIES OF PURE GRADE BRANCHED
AND CYCLIC HYDROCARBONS (42)

	Ethylbenzene	Methyl-cyclohexane	Isooctane
Freezing point, °F	-139.3	-196.2	-161.0
Boiling point, °F	277.1	213.7	210.6
Sp. gr. at 60/60F	0.872	0.773	0.696
at 20/4C	0.867	0.770	0.692
API gr. at 60°F	30.8	51.6	71.8
Vapor pressure At 70°F, psia	0.15	-	0.8
At 100°F, psia	0.37	1.65	1.7
At 130°F, psia	0.85	-	3.3
n_D at 20°C	1.4959	1.4228	1.3912
Literature value (20)	1.49594	1.42312	1.39145
Flash point, °F	71.6	22	40
Color, Saybolt	+30	+30	+30
Sulfur content, wt. %	-	-	<0.01
Acidity	Not acid	Not acid	Not acid
Nonvolatile matter	None	None	None

Pure grade - 99 mol per cent minimum purity.

TABLE X

TYPICAL PROPERTIES OF TECHNICAL GRADE AND
COMMERCIAL GRADE HYDROCARBONS (42)

	Cyclohexane (tech. grade)	Isopropylbenzene (tech. grade)	Methylpentane (comm. grade)
Freezing point, °F	139.6	-141.4	-
Boiling point, °F	177.4	306.3	-
Sp. gr. at 60/60F	0.774	0.866	0.664
at 20/4C	-	-	-
API gr. at 60°F	50.7	31.9	81.5
Vapor pressure At 70°F, psia	-	0.07	-
At 100°F, psia	3.20	0.20	6.5
At 130°F, psia	-	0.47	-
n_D at 20°C	1.4238	1.4906	1.3748
Literature value (20)	1.42623	1.49146	-
Flash point, °F	< 40	115	< -20
Color, Saybolt	+30	+30	+30
Sulfur content, wt. %	0.0029	-	0.014
Acidity	Not acid	Not acid	Not acid
Nonvolatile matter	None	None	None

Technical grade - 95 mol per cent minimum purity

Commercial grade - about 85% 2- and 3-methylpentane
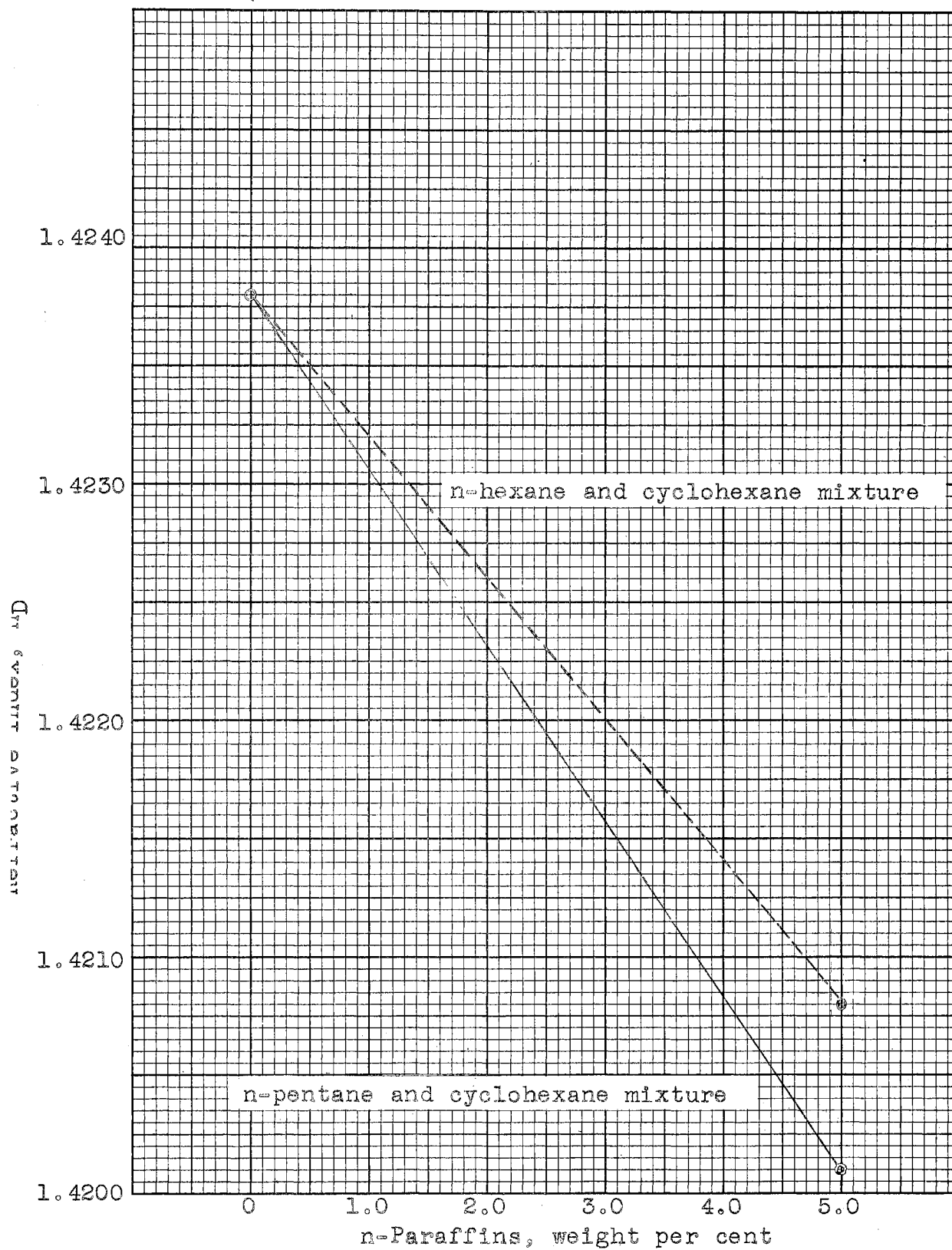
Figure 8   Refractive Index of n-Paraffins and Cyclohexane
Mixture (I)
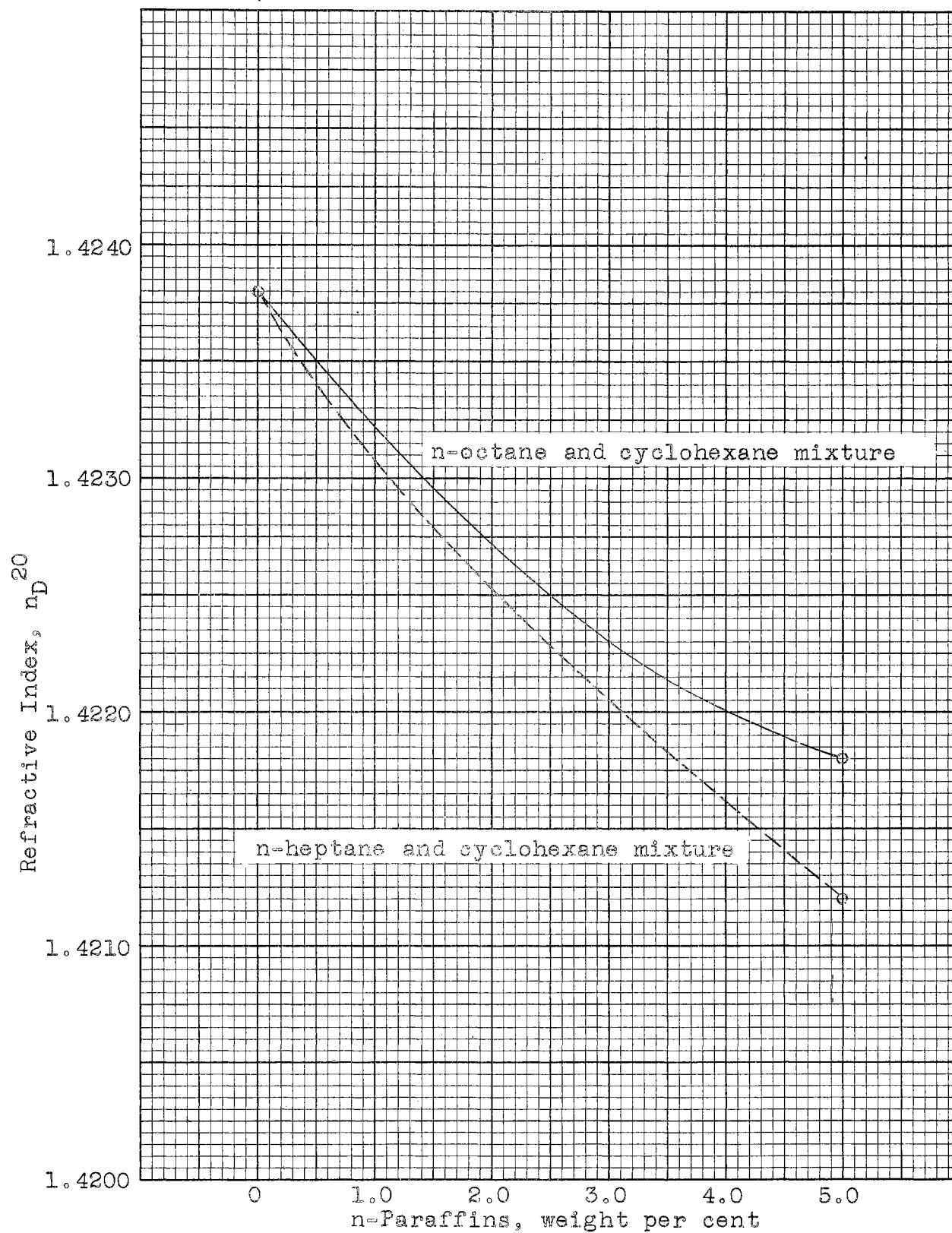
Figure 9   Refractive Index of n-Paraffins and Cyclohexane
Mixture (II)
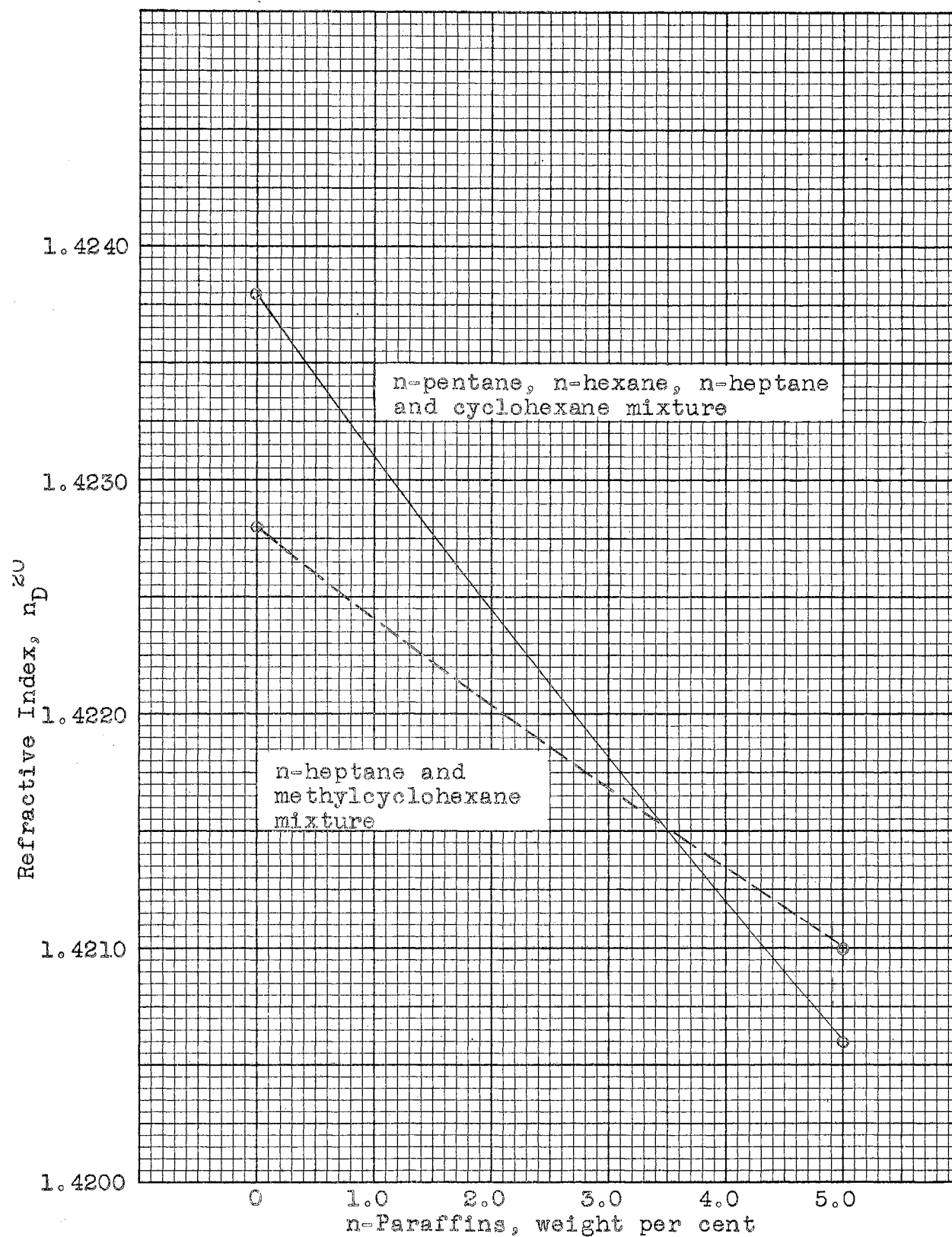
Figure 10 Refractive Index of n-Heptane and Methylcyclo-
hexane, and Mixed n-Pentane, n-Hexane,
n-Heptane and Cyclohexane Mixtures
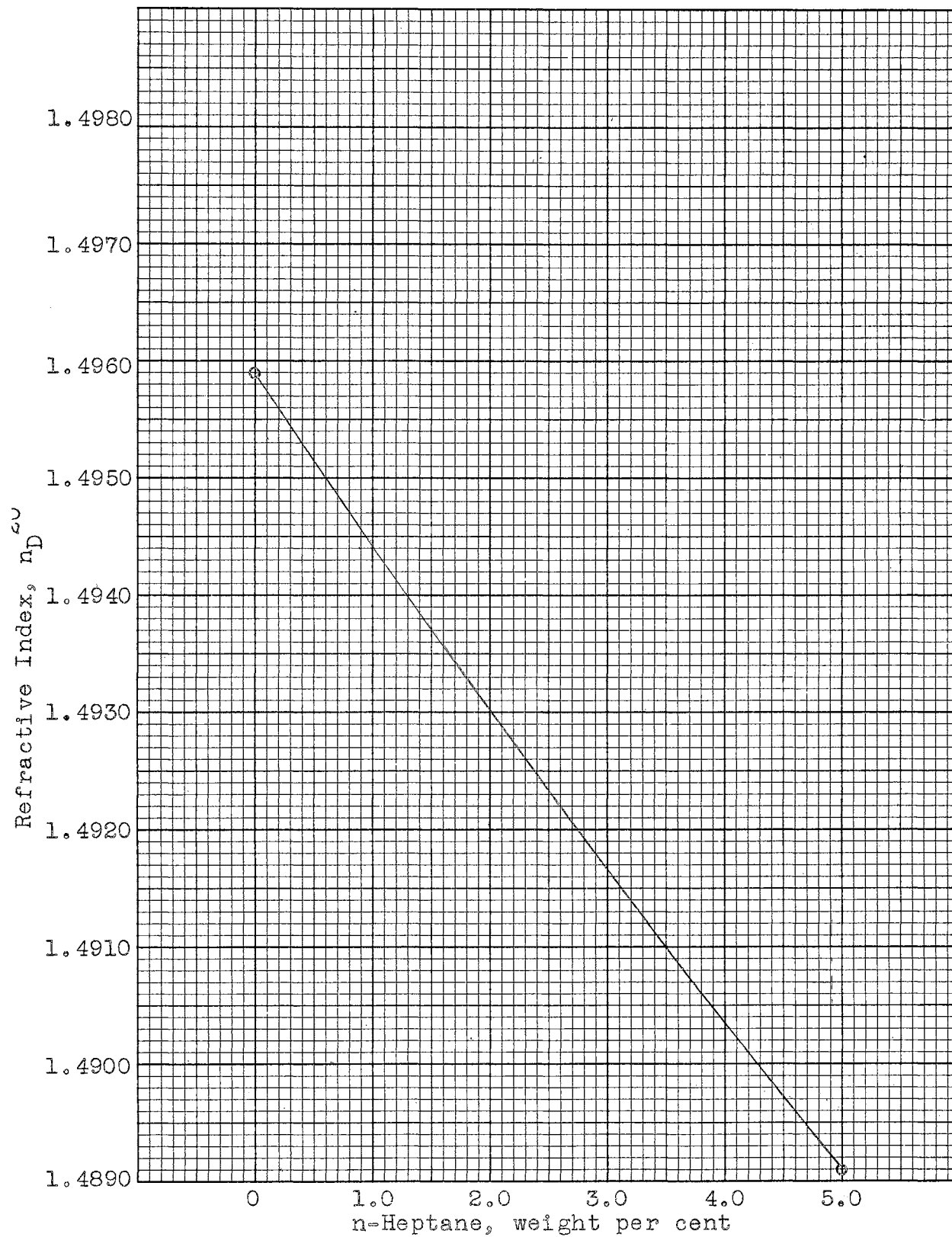
Figure 11 Refractive Index of n-Heptane and Ethylbenzene
Mixture
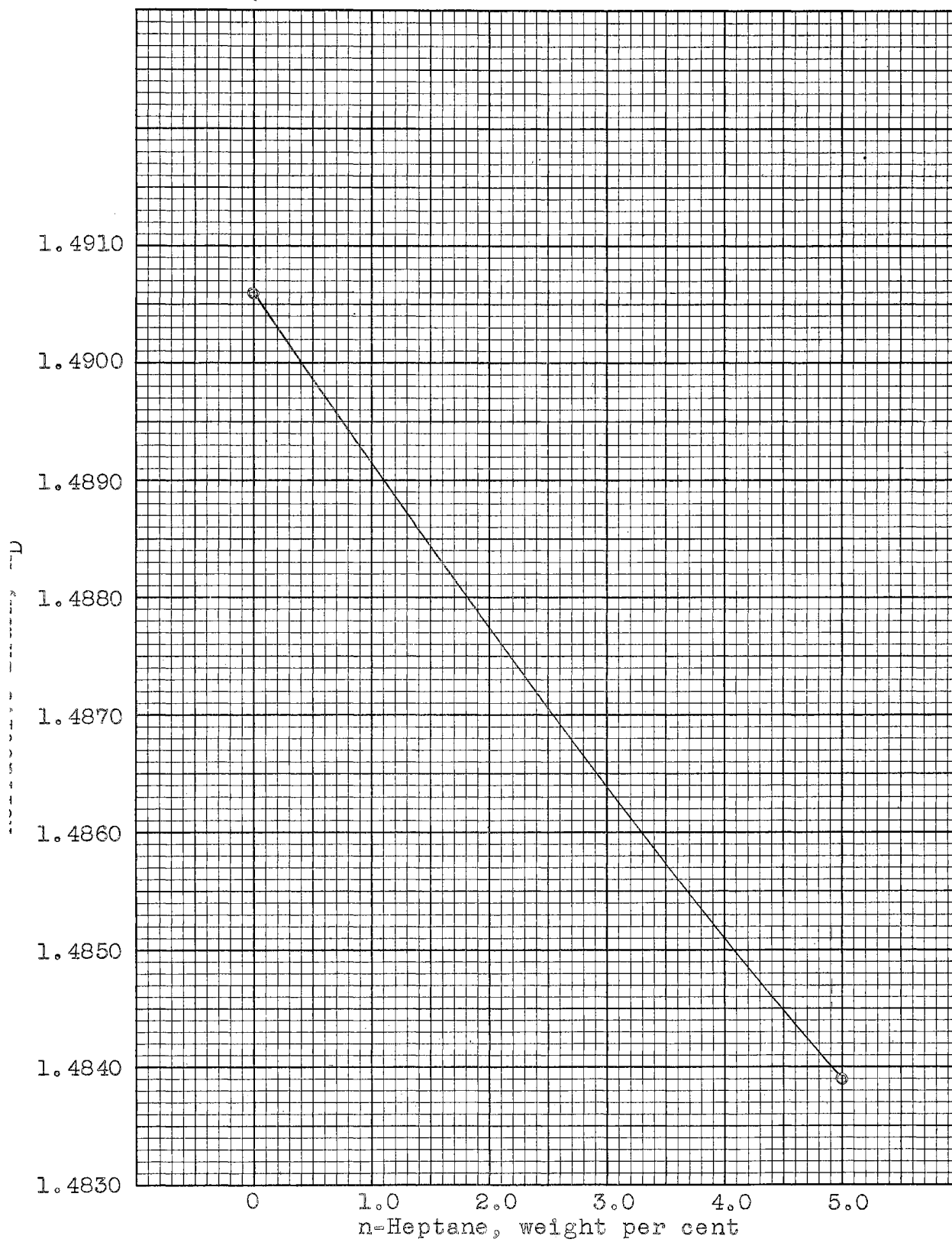
Figure 12 Refractive Index of n-Heptane and Isopropyl-
benzene Mixture
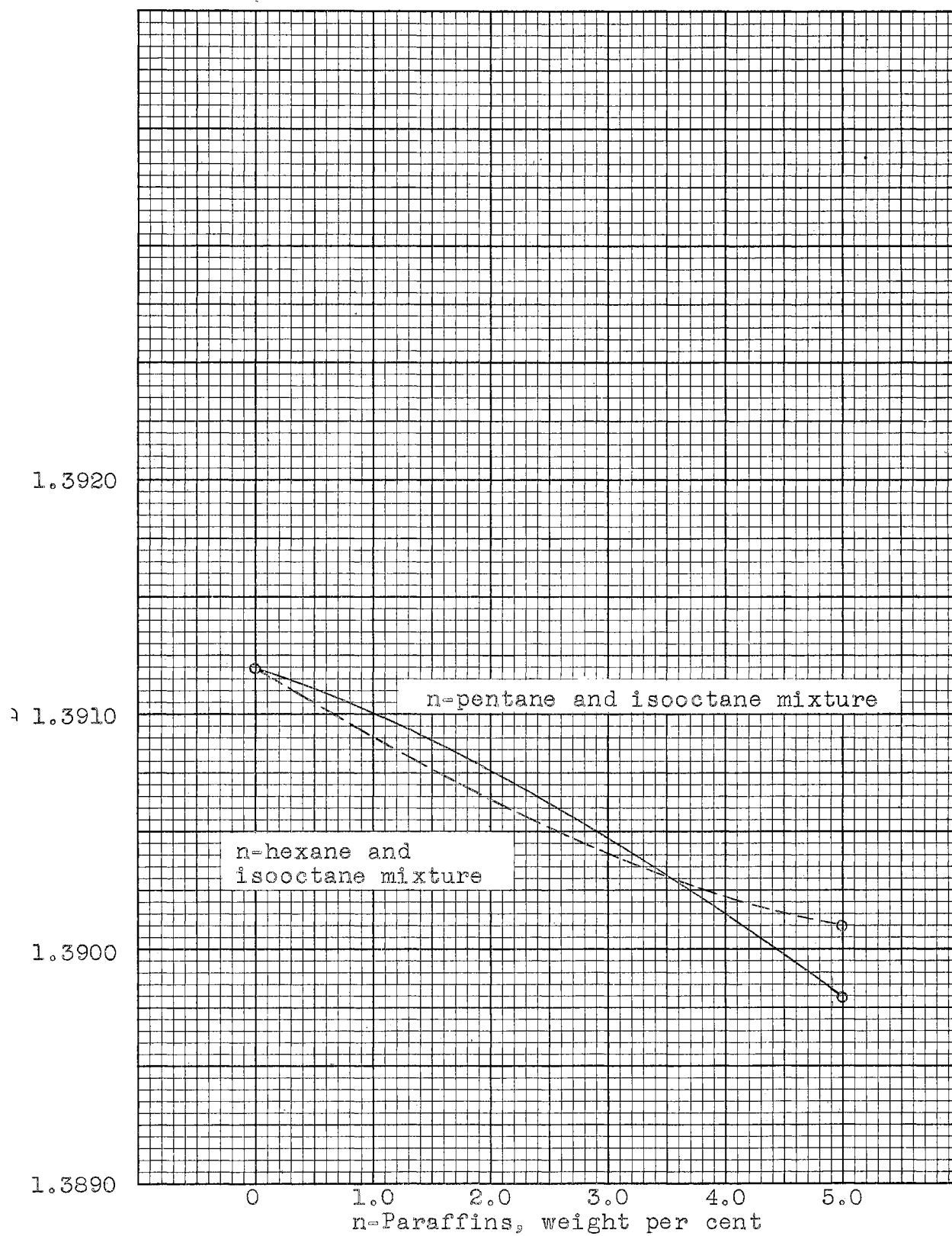
Figure 13 Refractive Index of n-Paraffins and Isooctane
Mixture

APPENDIX B

EXPERIMENTAL DATA

TABLE XI

EXPERIMENTAL DATA ON EQUILIBRIUM CAPACITY OF
N-PARAFFINS ON MOLECULAR SIEVE TYPE 5A

Adsorbate	Wt. of sample (gm.)	Wt. adsorbed (gm.)
n-pentane	21.8120	2.0020
	19.7500	1.7020
n-hexane	20.6565	2.0615
	22.1140	2.1215
	20.2300	1.9650
n-heptane	20.1010	2.4105
	21.0500	2.5130
n-octane	19.8185	2.6165
water	20.4660	4.0010

Average room temperature - 68°F

TABLE XII

EXPERIMENTAL DATA ON THE SEPARATION OF N-PARAFFINS FROM 5.0 WEIGHT PER CENT N-PARAFFIN IN CYCLOHEXANE MIXTURE

Charge rate - 10 ml./min.

Flowrator reading - 1.28

Refractive Index Data

Cut No.	Fraction(ml.)	Run 1	Run 2	Run 3	Run 4
1	0 - 50	1.4238	1.4238	1.4238	1.4238
2	50 - 100	1.4238	1.4238	1.4238	1.4238
3	100 - 150	1.4238	1.4238	1.4238	1.4238
4	150 - 200	1.4238	1.4238	1.4238	1.4238
5	200 - 250	1.4237	1.4238	1.4237	1.4237
6	250 - 300	1.4237	1.4238	1.4237	1.4237
7	300 - 350	1.4237	1.4237	1.4237	1.4237
8	350 - 400	1.4237	1.4237	1.4236	1.4237
9	400 - 450	1.4237	1.4237	1.4236	1.4236
10	450 - 500	1.4236	1.4237	1.4235	1.4236
11	500 - 550	1.4236	1.4237	1.4235	1.4235
12	550 - 600	1.4235	1.4237	1.4235	1.4235
13	600 - 650	1.4235	1.4236	1.4234	1.4235
14	650 - 700	1.4232	1.4236	1.4233	1.4234
15	700 - 750	1.4229	1.4235	1.4232	1.4233
16	750 - 800	1.4227	1.4232	1.4231	1.4232
17	800 - 850	1.4224	1.4229	1.4229	1.4231
18	850 - 900	1.4222	1.4225	1.4228	1.4230
19	900 - 950	1.4219	1.4222	1.4226	1.4229
20	950 - 1000	1.4217	1.4220	1.4224	1.4229
21	1000 - 1050	1.4215	1.4219	1.4223	1.4228
22	1050 - 1100	1.4211	1.4217	1.4221	1.4227
23	1100 - 1150	1.4208	1.4214	1.4219	1.4226
24	1150 - 1200	1.4204	1.4212	1.4218	1.4224
25	1200 - 1250	1.4202	1.4210	1.4216	1.4223
26	1250 - 1300	1.4202	1.4209	1.4214	1.4222
27	1300 - 1350	1.4202	1.4209	1.4213	1.4221
28	1350 - 1400	1.4201	1.4209	1.4213	1.4220
29	1400 - 1450	1.4201	1.4208	1.4212	1.4219
30	1450 - 1500	1.4201	1.4208	1.4212	1.4218

		Run 1	Run 2	Run 3	Run 4
Initial bed temp. °F		65	70	57	70
Maximum bed temp. °F		81	90	73	85

TABLE XIII

EXPERIMENTAL DATA ON THE SEPARATION OF N-HEPTANE FROM
5.0 WEIGHT PER CENT N-HEPTANE IN METHYLCYCLOHEXANE,
ETHYLBENZENE AND ISOPROPYLBENZENE MIXTURE

Charge rate - 10 ml./min.

Flowrator reading		- -	1.15	1.20	1.20

Refractive Index Data

Cut No.	Fraction(ml.)		Run 5	Run 6	Run 7
1	0 -	50	1.4228	1.4959	1.4905
2	50 -	100	1.4228	1.4959	1.4902
3	100 -	150	1.4228	1.4959	1.4898
4	150 -	200	1.4228	1.4959	1.4891
5	200 -	250	1.4228	1.4958	1.4882
6	250 -	300	1.4228	1.4958	1.4870
7	300 -	350	1.4228	1.4958	1.4866
8	350 -	400	1.4228	1.4955	1.4855
9	400 -	450	1.4228	1.4951	1.4850
10	450 -	500	1.4227	1.4948	1.4847
11	500 -	550	1.4227	1.4941	1.4846
12	550 -	600	1.4227	1.4934	1.4845
13	600 -	650	1.4226	1.4930	1.4844
14	650 -	700	1.4226	1.4926	1.4842
15	700 -	750	1.4226	1.4922	1.4841
16	750 -	800	1.4225	1.4918	1.4840
17	800 -	850	1.4225	1.4913	1.4840
18	850 -	900	1.4224	1.4910	1.4839
19	900 -	950	1.4223	1.4907	1.4839
20	950 -	1000	1.4221	1.4904	1.4839
21	1000 -	1050	1.4220	1.4901	1.4839
22	1050 -	1100	1.4219	1.4898	1.4839
23	1100 -	1150	1.4217	1.4896	1.4839
24	1150 -	1200	1.4215	1.4894	1.4839
25	1200 -	1250	1.4213	1.4893	1.4839
26	1250 -	1300	1.4211	1.4893	1.4839
27	1300 -	1350	1.4211	1.4892	1.4839
28	1350 -	1400	1.4211	1.4892	1.4839
29	1400 -	1450	1.4210	1.4891	1.4839
30	1450 -	1500	1.4210	1.4891	1.4839

Initial bed temp. °F	65	68	70
Maximum bed temp. °F	85	85	80

TABLE XIV

EXPERIMENTAL DATA ON THE SEPARATION OF N-PARAFFINS FROM
5.0 WEIGHT PER CENT N-PARAFFIN IN ISOOCTANE MIXTURE

Charge rate - 10 ml./min.

Flowrator reading - 1.0

Refractive Index Data

Cut No.	Fraction(ml.)	Run 8	Run 9
1	0 - 50	1.3912	1.3912
2	50 - 100	1.3912	1.3912
3	100 - 150	1.3912	1.3912
4	150 - 200	1.3912	1.3912
5	200 - 250	1.3911	1.3911
6	250 - 300	1.3911	1.3911
7	300 - 350	1.3911	1.3911
8	350 - 400	1.2911	1.3911
9	400 - 450	1.3911	1.3911
10	450 - 500	1.3911	1.3910
11	500 - 550	1.3910	1.3910
12	550 - 600	1.3910	1.3910
13	600 - 650	1.3910	1.3910
14	650 - 700	1.3910	1.3910
15	700 - 750	1.3910	1.3909
16	750 - 800	1.3910	1.3909
17	800 - 850	1.3910	1.3909
18	850 - 900	1.3910	1.3908
19	900 - 950	1.3909	1.3908
20	950 - 1000	1.3908	1.3907
21	1000 - 1050	1.3906	1.3906
22	1050 - 1100	1.3904	1.3905
23	1100 - 1150	1.3902	1.3904
24	1150 - 1200	1.3901	1.3903
25	1200 - 1250	1.3900	1.3902
26	1250 - 1300	1.3899	1.3901
27	1300 - 1350	1.3899	1.3901
28	1350 - 1400	1.3898	1.3901
29	1400 - 1450	1.3898	1.3901
30	1450 - 1500	1.3898	1.3901

Initial bed temp. °F		74	72
Maximum bed temp. °F		89	92

TABLE XV

EXPERIMENTAL DATA ON THE SEPARATION OF 5.0 WEIGHT PER CENT
MIXED N-PENTANE, N-HEXANE AND N-HEPTANE IN
CYCLOHEXANE MIXTURE

Charge rate - 10 ml./min.

Flowrator reading - 1.20

Refractive Index Data

Cut No.	Fraction(ml.)	Run 10
1	0 - 50	1.4238
2	50 - 100	1.4238
3	100 - 150	1.4238
4	150 - 200	1.4238
5	200 - 250	1.4237
6	250 - 300	1.4237
7	300 - 350	1.4237
8	350 - 400	1.4237
9	400 - 450	1.4237
10	450 - 500	1.4236
11	500 - 550	1.4235
12	550 - 600	1.4234
13	600 - 650	1.4233
14	650 - 700	1.4231
15	700 - 750	1.4229
16	750 - 800	1.4227
17	800 - 850	1.4225
18	850 - 900	1.4222
19	900 - 950	1.4220
20	950 - 1000	1.4218
21	1000 - 1050	1.4215
22	1050 - 1100	1.4213
23	1100 - 1150	1.4211
24	1150 - 1200	1.4209
25	1200 - 1250	1.4208
26	1250 - 1300	1.4207
27	1300 - 1350	1.4207
28	1350 - 1400	1.4206
29	1400 - 1450	1.4206
30	1450 - 1500	1.4206

Initial bed temp. °F   84
Maximum bed temp. °F   96

TABLE XVI

EXPERIMENTAL DATA ON THE PURIFICATION OF COMMERCIAL GRADE METHYLPENTANE

Charge rate - 24 ml./min.

Flowrator reading - 1.50

Refractive Index Data

Cut No.	Fraction(ml.)	Run 11
1	0 - 100	1.3760
2	100 - 200	1.3760
3	200 - 300	1.3760
4	300 - 400	1.3759
5	400 - 500	1.3751
6	500 - 900	1.3749
7	900 - 1300	1.3748
8	1300 - 1700	1.3748

Initial bed temp.	60
Maximum bed temp.	78

TABLE XVII

EXPERIMENTAL DATA ON THE PURIFICATION OF
TECHNICAL GRADE CYCLOHEXANE

Charge rate - 14.0 ml./min.

Flowrator reading - 1.32

Refractive Index Data

Cut No.	Fraction(ml.)	Run 12
1	0 - 50	1.4242
2	50 - 100	1.4240
3	100 - 150	1.4238
4	150 - 200	1.4238
5	200 - 250	1.4238
6	250 - 300	1.4238
7	300 - 350	1.4238
8	350 - 400	1.4238
9	400 - 450	1.4238
10	450 - 500	1.4238
11	500 - 550	1.4238
12	550 - 600	1.4238
13	600 - 650	1.4238
14	650 - 700	1.4238
15	700 - 750	1.4238
16	750 - 800	1.4238
17	800 - 850	1.4238
18	850 - 900	1.4238
19	900 - 950	1.4238
20	950 - 1000	1.4238

Initial bed temp. °F	56
Maximum bed temp. °F	59

TABLE XVIII

MATERIALS RECOVERED ON REGENERATION OF
THE MOLECULAR SIEVES ON RUN 1-10

Run No. and Adsorbate	n-Paraffin Recovery		Dynamic Loading	n_D at 20°C	
	Vol.-ml.	Wt.-gm.	Wt. per cent	#1	#2
1 (n-C_5)	33.3	19.9	5.2	-	1.3592
2 (n-C_6)	43.0	26.2	6.8	1.3751	1.3760
3 (n-C_7)	53.2	36.6	9.5	1.3876	1.3876
4 (n-C_8)	59.3	41.0	10.7	1.3974	1.3974
5 (n-C_7)	48.9	32.8	8.6	1.3878	1.3877
6 (n-C_7)	43.9	29.6	7.7	1.3903	1.3899
7 (n-C_7)	17.7	12.0	3.1	1.3880	1.3889
8 (n-C_5)	24.2	15.0	3.9	-	1.3575
9 (n-C_6)	39.1	25.5	6.6	1.3761	1.3750
10 (n-C_5) (n-C_6) (n-C_7)	32.8	21.6	5.6	1.3831	1.3760

TABLE XIX

VOLUME OF N-PARAFFIN RECOVERED ON REGENERATION FOR RUN 1-4

Sieve temp. °F	Run 1		Run 2		Run 3		Run 4	
	#1	#2	#1	#2	#1	#2	#1	#2
250	-	-	-	2.2	2.2	-	5.5	-
300	-	-	0.5	6.2	6.5	-	10.1	-
350	-	3.9	2.0	9.3	11.5	-	11.0	-
400	-	11.0	4.2	11.7	16.0	1.0	12.0	-
450	-	15.2	6.0	15.0	18.9	1.4	13.1	-
500	-	18.6	7.2	17.8	21.1	1.8	16.0	0.1
550	-	24.8	9.2	20.4	23.9	1.9	20.0	0.2
600	-	29.6	11.0	20.8	27.5	2.0	25.1	0.4
650	-	32.7	13.5	22.2	34.0	2.1	33.0	0.6
660*	- +	33.3	14.0 +	29.0	42.8 +	10.4	48.2 +	3.6 7.5**
	33.3 ml.		43.0 ml.		53.2 ml.		59.3 ml.	

*   Run 1 and Run 2 - after 1 hour

    Run 3 - after 1 1/2 hours

    Run 4 - after 2 hours

**   Volume recovered in range 150°-200°F

TABLE XX

VOLUME OF N-HEPTANE RECOVERED ON REGENERATION FOR RUN 5-7

Sieve temp. °F	Run 5		Run 6		Run 7	
	#1	#2	#1	#2	#1	#2
250	-	-	-	-	-	-
300	5.0	-	1.6	-	-	-
350	9.8	0.7	4.0	-	-	-
400	13.5	1.4	6.0	-	-	-
450	15.5	2.8	8.1	-	-	-
500	17.5	4.3	10.5	-	-	-
550	20.0	5.0	14.0	0.7	-	-
600	23.0	6.5	18.0	1.0	-	-
650	26.5	8.2	23.9	1.7	3.5	0.7
660*	34.9 + 14.0		36.5 + 7.4		12.2 + 5.5	
	48.9 ml.		43.9 ml.		17.7 ml.	

* After 1 1/2 hours

TABLE XXI

VOLUME OF N-PARAFFIN RECOVERED ON REGENERATION FOR RUN 8-10

Sieve temp. °F	Run 8		Run 9		Run 10	
	#1	#2	#1	#2	#1	#2
250	–	–	–	–	–	–
300	–	–	–	1.6	–	1.0
350	–	2.8	3.1	4.2	–	3.4
400	–	7.2	5.8	7.0	0.5	6.0
450	–	10.4	7.0	9.2	1.0	8.0
500	–	14.2	8.1	11.3	1.4	9.2
550	–	18.0	10.0	14.2	3.5	10.8
600	–	22.0	11.5	16.5	6.0	12.3
650	–	24.2	13.5	19.6	10.0	13.8
660*	– +	24.2	14.1 +	25.0	14.5 +	18.3
	24.2 ml.		39.1 ml.		32.8 ml.	

* After 1 hour

VITA

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