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Activated carbon in the petroleum industry

Part I.¹⁾

by Dr. PAUL ZÜRCHER²⁾ (Lugano)

Abstract

The theory of adsorption has progressed to the point where it can be used as a basis for design.

Activated carbon as a means of recovering gasoline and LPG is a success outside the United States. Whether this process will be economical under American conditions will have to be proved by actual operation.

Fractionation of liquid mixtures by adsorbents is progressing and is about to be tested on a commercial scale. The separation of gases into fractions of high purity is an accomplished fact.

Cyclic and continuous countercurrent methods have been developed in detail. Depending on conditions, the adsorbate is expelled from the carbon either by steam or by a solvent.

Much progress can be expected. Introduction of fluid flow will be a matter of time. Eventually, some older standard methods of fractionation of light hydrocarbons may be driven into the background by the developments in the field of activated carbon and other adsorbents.

Adsorbents have been familiar to the petroleum industry as means of removal of color, resins, diolefins, and as catalysts in desulfurizing, reforming, and cracking.

Made-to-order adsorbents have opened a new field of applications in the separation of gases and of liquids into fractions.

Knowledge of the fundamentals of adsorption is increasing. Recently discovered correlations are applied in the design of plants.

Activated carbon in the petroleum industry

Activated carbon has been known and applied for a long time in a number of industries. Only in the last fifteen years has the petroleum refiner become conscious of the advantages it offers. Adsorption by carbon may replace treatment by sulfur dioxide, phenol, Duo-Sol, furfural, and sulfuric acid. Activated carbon is a tool for the purification of hydrogen, methane, for the separation of olefins from cracked gases, for the recovery of liquefied petroleum gases from natural gas, and for the sharp fractionation of liquid hydrocarbons. Operation of these processes may be carried out at atmospheric temperature and pressure. An adsorbent is often the only means of removing impurities within the boiling range of the product. In other methods, the smaller the amount of impurities, the more difficult becomes their separation. Adsorption may replace several steps of chemical and physical treatment. There are no waste products, and equipment is inexpensive.

In his annual review on the progress of adsorption, Harris (1) states: «Industrial

1) Part II: «Vapor Recovery Plants» will follow in Bull. no. 60, July 1954.

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applications of adsorption are widespread enough that this field has ceased to be a specialty in unit operation and is now taking its rightful place alongside other, older fields.»

Adsorption may be defined as the power of a solid surface to attract and hold substances, usually by physical forces, although chemical reactions may not be excluded in many cases. Depending on the nature of the surface, specific materials are attracted, particularly when the surface is porous. Mineral adsorbents, such as fuller's earth and bauxite, have an inherent power of adsorption which sometimes, but not always, can be improved by treatment. Artificial adsorbents, e.g. activated carbon and silica gel, can be made to perform tasks impossible for natural adsorbents.

Properties of Activated Carbons

Activated carbons are black glossy powders or granules or pellets, 1/16—3/8 inches in diameter. Some products are marketed in the original form of wood chips. The weight per cuft. is 10—34 pounds.

The chemical composition of the carbons varies with the raw material and the method of preparation. Omitting bone char which contains about 90 % ash, the composition of five commercial products is within these limits:

Percent of carbon	90—99
Percent of ash	2—10
Percent soluble in hydrochloric acid	2—7
pH of water extract	6—10.6

There are some carbons made from coal, of excellent quality, of an ash content of 25—30 %, with a pH of 4.5—6.

Extremes in physical properties of American gas adsorbent carbons are:

Apparent density	0.7—0.9 gram/cm ³
Specific gravity	1.75—2.10
Average weight per cuft.	28—34 lb.
Specific heat	0.220—0.240 cal/gram
Adsorptive capacity for CCl ₄ at 82° F.	50—90 weight percent
Heat of wetting with benzene	20—25 cal/gram
Commercial gas velocities	20—120 cuft/min.
Effective bed temperature	40—120 deg. F.

Adsorptive Power

The power of carbons to attract and hold liquids and gases is related to the surface area; the larger this area, the greater is the adsorptive power. The surface area of an adsorbent may be determined by measuring the maximum of dye or gas that can be taken up, forming probably a monomolecular layer. From the space occupied by each molecule, the total area can be calculated. When a substance is adsorbed from a solution, the space taken up by the solvent and the influence of the pH are disregarded.

It is surprising that despite these inaccuracies the surface area of a gram of activated carbon has been calculated to be within the same order of magnitude of 1×10^6 to 6×10^6 square centimeters, or 6000 square meters (2). Cremer (3) concluded that the surface had centers of different adsorptive power. Examination of activated carbons under the electron microscope confirms this statement (4). Emmett (5) reported that the pore area of different carbons was between 17 and 48 A

square. He pointed out that the surface consisted not only of pores and that there might be capillaries of different shape, cracks and crevices with parallel walls. In X-ray studies of 1200 samples of carbons he found indications that much of the carbon was arranged in platelets and concluded that any simple interpretation was impossible. Assuming that the surface of a specially prepared carbon consisted of nothing but pores of a diameter of 20.8 Å, Emmett found that the total length of the pores of one gram of carbon would be 40 000 times the circumference of the earth. By adsorption of toluene from a mixture of iso-octane and toluene, Eagle and Scott (6) determined the diameter of the pores of eight carbons. Their results checked with those of Emmett.

Different carbons have different adsorptive power. In the following tabulation are shown the adsorptive capacities of three commercial carbons for benzol in air.

Adsorptive Capacities of Three Carbons at Different Concentrations of Benzol in Air. Courouleau and Benson (7).

Saturation of benzene in air percent	Carbon		
	A	B	C
90	54.9	48.8	63.0
10	47.6	39.0	44.5
1	39.9	11.2	11.3
0.1	30.7	11.2	11.3

It is clear that the choice of the carbon depends on the concentration of the vapor in air. For the removal of benzol from a very rich mixture, carbon C would be best, but for a very lean mixture, carbon A would be the most efficient.

The speed of throughput influences the amount of vapors that can be adsorbed by activated carbons. Ray (8) passed air containing 0.370—0.392 grams of benzol per liter through columns of 30 grams of different carbons at the rate of 500 ml. a minute. From 33.8 to 55.9 grams of benzol were adsorbed per 100 grams of carbon. When the flow of the charge was increased to 1000 ml. a minute, only 30.4—39.4 grams of benzol were taken up.

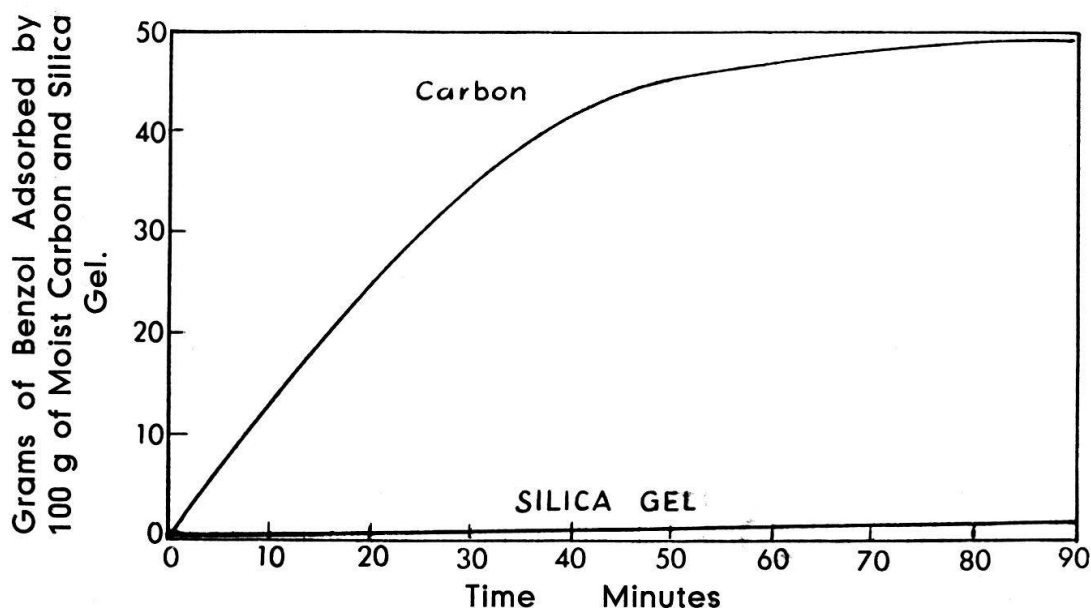


Fig. 1. Adsorption of Benzol Vapor from Dry Air by Activated Carbon and Silica Gel Containing Water (Ray).

Fig. 1 is a graphic picture of the influence of the moisture content of activated carbon and of silica gel on the adsorptive capacity for 0.036 grams of benzol per liter of air at 77° F. The presence of 34.5 % moisture in the carbon did not interfere with the adsorptive power, but as little as 16.38 % moisture in the silica gel had an adverse effect. The break point of the carbon (time elapsed after which vapors are no longer completely adsorbed) occurred after about 22 minutes, while unadsorbed vapors of benzol passed through the silica gel from the start. The property of silica gel to adsorb moisture preferentially has given it a prominent place in drying operations.

Heat of Adsorption

Heat of adsorption (or heat of wetting) is the heat developed when a fluid is contacted with an adsorbent. It is said to be an index of adsorptive power and varies with different gases and liquids. An activated carbon having a high heat of adsorption in contact with many substances will not readily take up their impurities because both the desirable and the undesirable constituents are adsorbed. A list of heats of adsorption for different substances reported by several observers reveals considerable differences depending on the quality of the carbons.

Liquid	Heats of Adsorption, cal. per gram Carbon		
	Carbon ³	Carbon ⁴	Carbon ⁵
Water	12.4		8.4
Ether	28.3		
Benzene	29.4	32.7	21.0
Carbon disulfide	30.0	31.2	29.0
Ethanol	28.4	23.3	
Methanol	30.2		
Ethylene chloride	32.8		
Petroleum ether			23.8

The heat of adsorption of a gas is often much larger than its heat of condensation and increases with decreasing pressure. Gregg (9) compared heats of adsorption of gases with their heats of condensation. In purely physical adsorption the former are one and one half to three times as large as the latter. The heat of adsorption of ethylene is 8,900—7,100 calories per gram mole in a partial pressure range of 0—550 mm. Hg., and the heat of condensation is 2050 calories per gram mole at 32° F. The corresponding values for Carbon dioxide are 7,120—6,120 and 2570. In recent studies, Miller and coworkers (10) showed that the area available on adsorbents to wetting liquids varied depending on the size and shape of the wetting molecules, and that nearly equal heats of adsorption were produced by molecules of similar dimensions. It is claimed that the heat of adsorption decreases with increasing length of the chain of polar molecules (11). Comparing the heat of adsorption and relative adsorbability, Smith and Beebe (12) came to the conclusion that 1) from a mixture of 1-butene and butane, the former is selectively adsorbed on silica gel because the heat of adsorption of 1-butene exceeds that of butane by nearly 3 kilo-

³) Andress and Berl, *Z. Phys. Chem.* 122, 81 (1926).

⁴) Bartell and Fu, *J. Phys. Chem.* 33, 1758 (1929).

⁵) Culbertson and Winter, *J. Am. Chem. Soc.* 59, 308 (1937).

calories per mole; 2) on carbon black the two compounds cannot be separated, their heats of adsorption being similar.

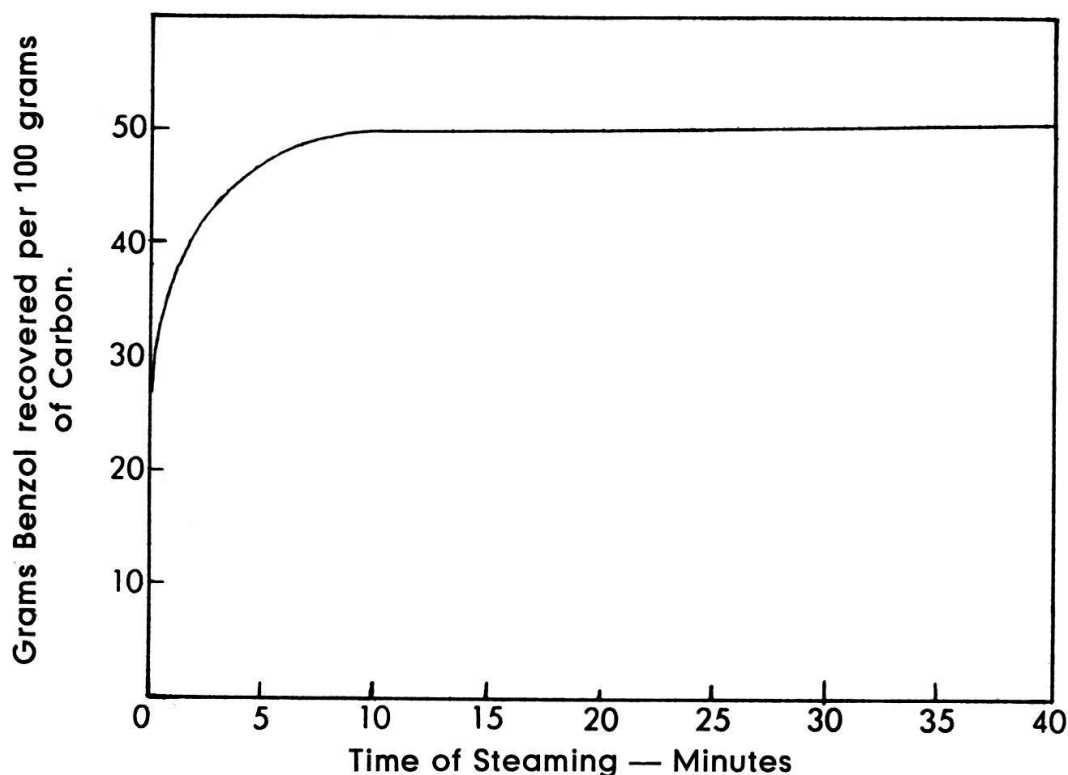


Fig. 2. Desorption of Benzol by Wet Steam. Benzol Held by Carbon at Saturation, 57% by Weight (Ray).

As a carbon is gradually charged with a liquid or a gas, its heat of adsorption changes continuously until complete saturation is reached. Usually, the heat of adsorption decreases with rising temperature, but many cases are known where it increases. These exceptions may be explained by assuming catalytic polymerization caused by the adsorbent.

The proportional adsorption of a mixture of substances from a solvent varies with the temperature.

Accurate knowledge of the heat of adsorption of a chosen carbon is important to the designing engineer. He has to provide means of holding the temperature in the contacting vessel within rather narrow limits.

Hydrogen Ion Concentration

Hydrogen ion concentration of an adsorbent may be important in the purification of liquids. A low pH favors the adsorption of acids and dyes. The refiner need not worry about the pH of this carbon. Adsorption of non-electrolytic substances depends on the carbon alone. However, a case may occur, where hydrogen chloride is to be removed from a mixture of gases. Special adsorbents capable of picking up hydrogen chloride have been prepared by Hassler (13).

Rate of Adsorption

The rate of adsorption of a vapor by a solid is proportional to the difference between the partial pressure of the vapor in the gas in contact with the solid and the

partial pressure of the condensed vapor on the surface of the solid. Adsorption on a fresh carbon is very rapid. As vapors condense on the surface of the solid, adsorption decreases until the vapor pressure of the adsorbed material is equal to the partial vapor pressure in the charge. At this point adsorption ceases. In gas masks (14), seven thousand parts per million of the war gas chloropicrin in air are adsorbed to the extent of 99.99 % in three hundredths of a second. Nitrogen at pressures of 0.36–6.75 mm. Hg is condensed on carbon to the extent of 95 % in two minutes, and equilibrium is reached in 30 minutes.

Chemical adsorption may be instantaneous or measurably slower. Its rate increases with the temperature (15).

Desorption

The operation of removing the adsorbate from the solid surface is termed DESORPTION. Heat alone will drive gases and vapors from the adsorbents below cracking temperatures. Steam, however, is much more efficient. Ray (8) passed wet steam through a bed of activated carbon saturated with 57 % by weight of benzol. In less than ten minutes most of the benzol was desorbed. Thirty minutes of additional steaming had very little effect. A total of about 51 grams or 90 % of the benzol were desorbed (Fig. 2).

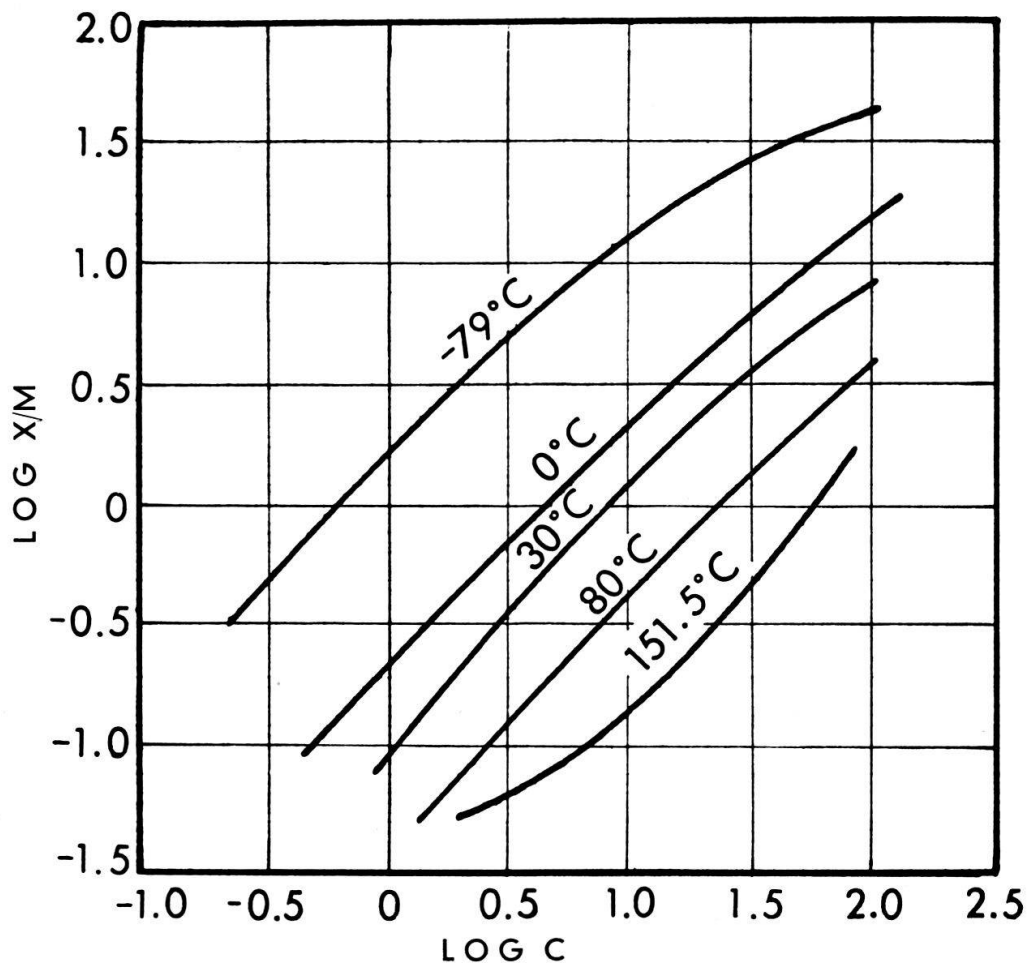


Fig. 3. Freundlich's Isotherms for Nitrogen on Charcoal at Different Temperatures (Titoff).

Much higher temperatures are necessary to drive out all of the adsorbed material. In his adsorption studies with equal volumes of iso-octane and n-heptane, Hibschan (16) desorbed the mixture from a four-foot column of activated carbon by application of heat alone and with 14 grams of steam at 580° F. The first fractions collected were analyzed for iso-octane content.

Effect of Desorption Temperatures and of Steam on Selectivity

Yield ml/100 g Carbon	Desorption Conditions				Fresh Carbon
	910° F	Heat 700° F	600° F	Steam 580° F	
	Filtrate Composition, Vol. % Iso-octane				
5	79	69	63	74	81
25	65		56	67	68
50	59		54	61	60

A small amount of steam at 580° F. was much more effective than heating without steam to 600° F.

Desorption with steam at 580° F. was 32 times more efficient than with steam at 212° F.

Adsorption Isotherms

The forces that cause adsorption are complex and not completely explored. Freundlich (17) derived an empirical equation from a number of suggestions made early in the twentieth century. It is related to the equilibrium between the concentration of the solute remaining in the solution and the amount adsorbed on the solid surface. In the equation

$$x/m = KC^{1/n}$$

x is the amount of material absorbed

m is the weight of the adsorbent

C is the concentration of the material remaining in solution

K and n are constants.

The logarithmic form

$$\text{Log } (x/m) = \text{Log } K + 1/n \text{ Log } C$$

is the equation of a straight line with the slope 1/n and the intercept K if C is unity. If the logarithmic curve obtained by measurements of adsorption is not a straight line, the equation cannot be applied for calculation. The line will bend at both ends, K and 1/n being no longer constants. Titoff (18) plotted the log of x/m against log C for nitrogen adsorbed on activated carbon at different temperatures. Only the data for zero degree C gave a straight line (Fig. 3).

In order to determine the capacity of a certain quantity of an adsorbent, a series of batch treatments is conducted with varying amounts of adsorbent and equal quantities of solution or gas at constant temperature. The solution or gas of each batch is analyzed at fixed intervals until equilibrium has been reached. For each batch, the values of x/m are plotted on the ordinate, and the values of C on the abscissa. Usually, for a solvent containing one adsorbable solute, a smooth curve is obtained. This curve is called ADSORPTION ISOTHERM. The term 1/n indicates the change in the concentration of the adsorbate with respect to the concentration

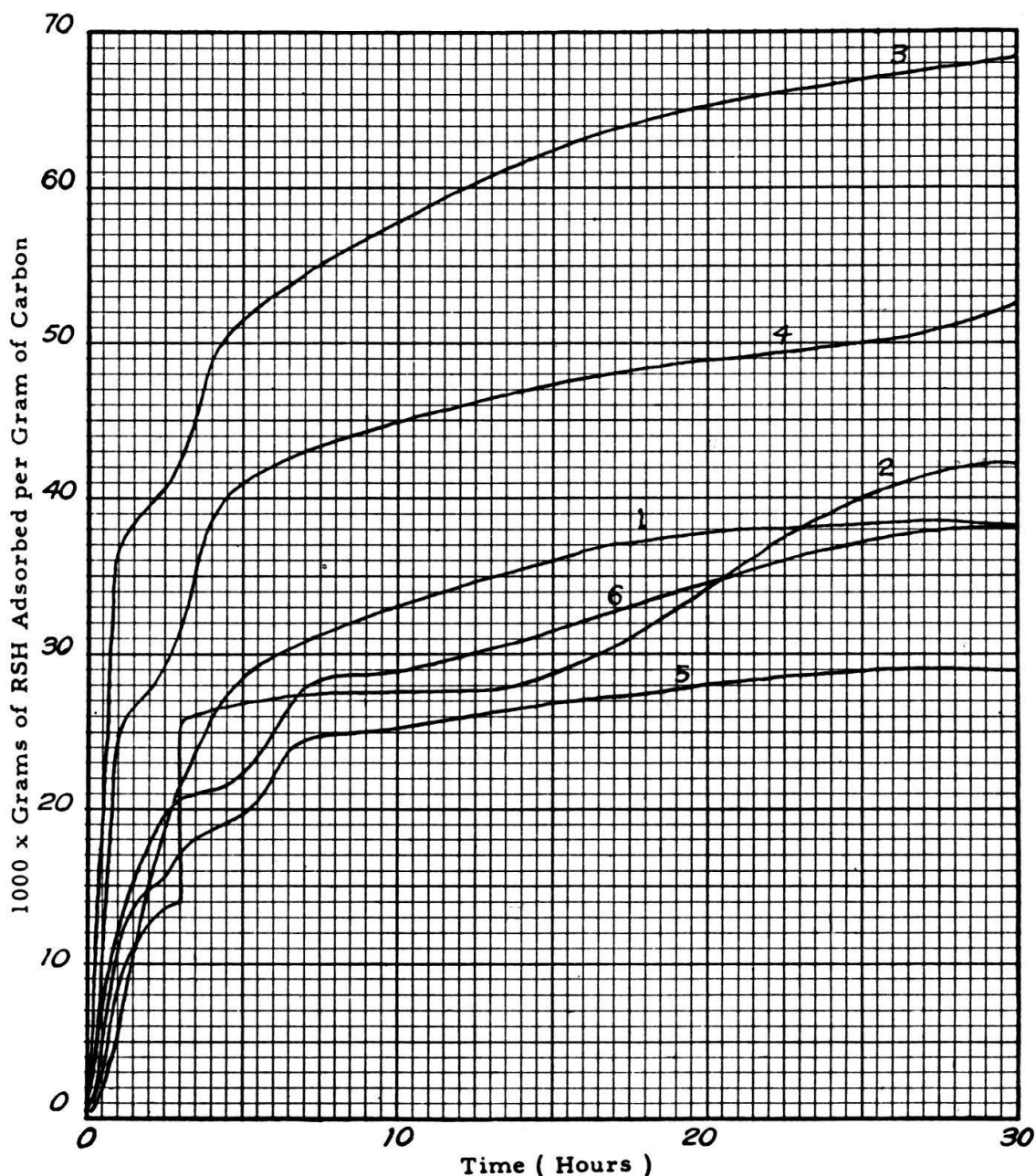


Fig. 4. Rate of extraction of Mercaptans from Straight-Run Gasoline at 83° F. (Curve 1, n-Propyl; 2, iso-Propyl; 3, n-Butyl; 4, iso-Butyl; 5, tertiary Butyl; 6, n-Amyl (Courtesy Petroleum Refiner).

of the solute remaining in solution. If $1/n$ is unity, the curve will be a horizontal line signifying that there is no preferential adsorption.

Freundlich's equation is applicable only to very dilute solutions and vapors. These are generally encountered in industrial problems, and for this reason the equation is much used for technical purposes.

Several fundamental concepts are the bases of older theories that are often applied in modern research. The Gibbs equation (19) proposes surface tension. Zsigmondy (20) preferred capillary attraction. Ponlanyi (21) calculated the free energy change when molecules pass from the gaseous to the adsorbed state. Isotherms at any tem-

perature were predicted from experimental isotherms at one temperature. Lewis and coworkers used this method (22).

According to Langmuir (23) adsorption takes place in monomolecular layers and is due to unsaturated valence forces on the surface of the crystal lattices. Manus (24) preferred electrostatic attraction. McBain and others believe in multilayer adsorption (25), (26). This idea has been confirmed in more recent studies (27), (28).

The equations of Bohart and Adams (29), and of Mecklenburg (30) are still serving as research tools. Dole and Klotz used the latter. Othmer and coworkers (32, 33, 34) correlated adsorption with pressure, temperature, and concentration of gases and vapors and prepared a nomograph for the determination of adsorption isotherms over a wide range of temperatures.

Mention is made of the equation of Koble and Corrigan (35), in which all isotherms are straight and parallel lines. At very high and very low values of the equilibrium pressure of the adsorbed gas, calculated and experimental results differ considerably. Nevertheless, this method of evaluation seems to be more accurate than that of Freundlich.

One of the many theories may fit one case perfectly, while it cannot be applied in another. Brunauer and coworkers (36) found in the literature five types of adsorption isotherms for gases and liquids on several adsorbents and at different temperatures. This is the reason why research men try out several theories, their goal being to combine fundamentals into one generally applicable formula. Keeping in mind the great variety of activated carbons available, one is not surprised by the statement of Robinson (37) that the problem is like an unfinished jigsaw puzzle in which there can be recognized a number of details but not the general picture.

Isotherms are of irregular shape when adsorption and chemical reactions take place on the surface of activated carbon. Voreck and coworkers (38) percolated naphtha through a column of activated carbon saturated with caustic soda solution. All mercaptans dissolved in the naphtha were removed by the adsorbent. Isotherms were unusual, indicating a combination of chemical reaction, adsorption, diffusion, and possibly ion exchange (Fig. 4).

Adsorption of Mixtures of Gases and Liquids

When a mixture of gases or liquids passes through a layer of adsorbent carbon, all compounds will at first be equally taken up until the adsorbent is almost saturated. From this point on, fractionation begins within the adsorbent layer, and the more volatile material is driven out. At equilibrium, the less volatile constituents form the bulk of the adsorbate. Only a few examples of this subject can be given, the literature being very voluminous.

Hirschler and Amon (39) studied the adsorption of many binary liquid mixtures on silica gel and on activated carbon. Adsorption isotherms of saturated hydrocarbons of paraffin-paraffin, paraffin-naphthene, and naphthene-naphthene systems were prepared. With carbon as adsorbent, most isotherms were U-shaped, for instance that of a mixture of n-heptane and methylcyclohexane. The isotherm of the same mixture with silica gel as adsorbent was S-shaped. From a binary-type mixture, a portion of each component may be recovered in substantially pure form on carbon. Adsorption of liquids on carbon generally increases with increasing molecular weight

in a homologous series. In contrast, adsorption on silica gel decreases with increasing molecular weight in a homologous series. The authors summarize: «Materials of

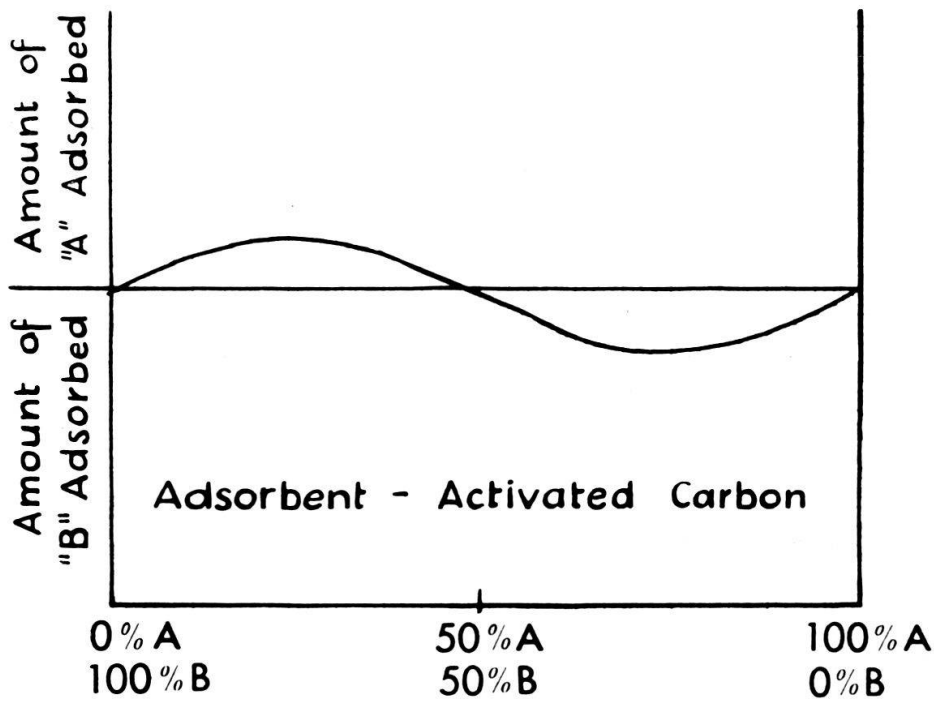


Fig. 5. Adsorption isotherm where components of about the same adsorbability are present in about equal proportions (Petroleum Processing, Dec. 1950).

high purity may be obtained from many commercially available or synthetic hydrocarbons. Unsaturated and high-molecular weight hydrocarbons, may so be separated

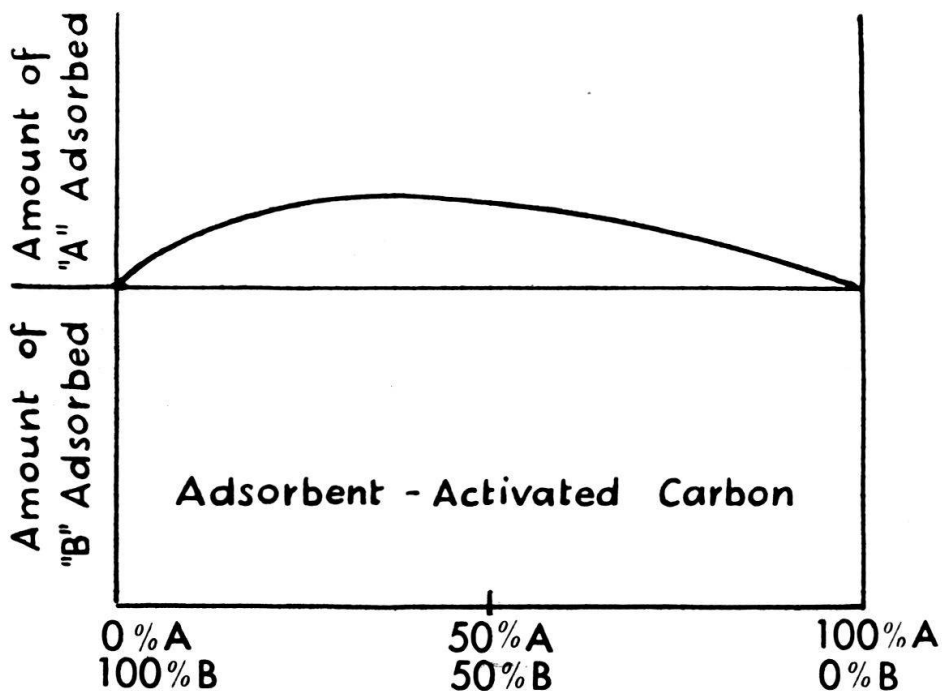


Fig. 6. Adsorption isotherm where one component is selectively adsorbable through substantially entire concentration range (Petroleum Processing, Dec. 1950).

by adsorption. Its wide application, speed, and the use of very simple and inexpensive apparatus make adsorption one of the most powerful and convenient tools available for the separation of saturated hydrocarbons.»

In U.S. Paten 2,518,236, Hirschler (40) describes the separation of a mixture of 97.8 % ethylbenzene and 2.2 % o-xylene by percolation through activated carbon at 50—60° F. The first 46 % of the filtrate contained 99.3 % ethylbenzene, and an additional 22 % had 98.7 % ethylbenzene.

The adsorption isotherms change with the composition of the charge. The curve is of the S-type when about equal amounts of components are present. It is of U-shape where one component is selectively adsorbed through substantially the entire concentration range. Some aromatics have intermediate isotherms between the two main types (Fig 5, 6, 7).

Hibschan (16) percolated mixtures of heptane and iso-octane through his four-foot column of activated carbon and analyzed the cumulative yields per 100 grams of carbon. His results were:

Cumulative Yield ml/100 g C	% Iso-Octane in Feed		
	25 Filtrate	50 Composition, Vol%	80 Iso-Octane
5	38	81	94
25	35	70	90
50	31	63	87

Preferential adsorption of heptane took place in all concentrations. However, after about the same amounts of filtrate had been collected from all mixtures, there was no difference in the composition of the charge and the product. Countercurrent flow would be required to collect higher concentrations of iso-octane.

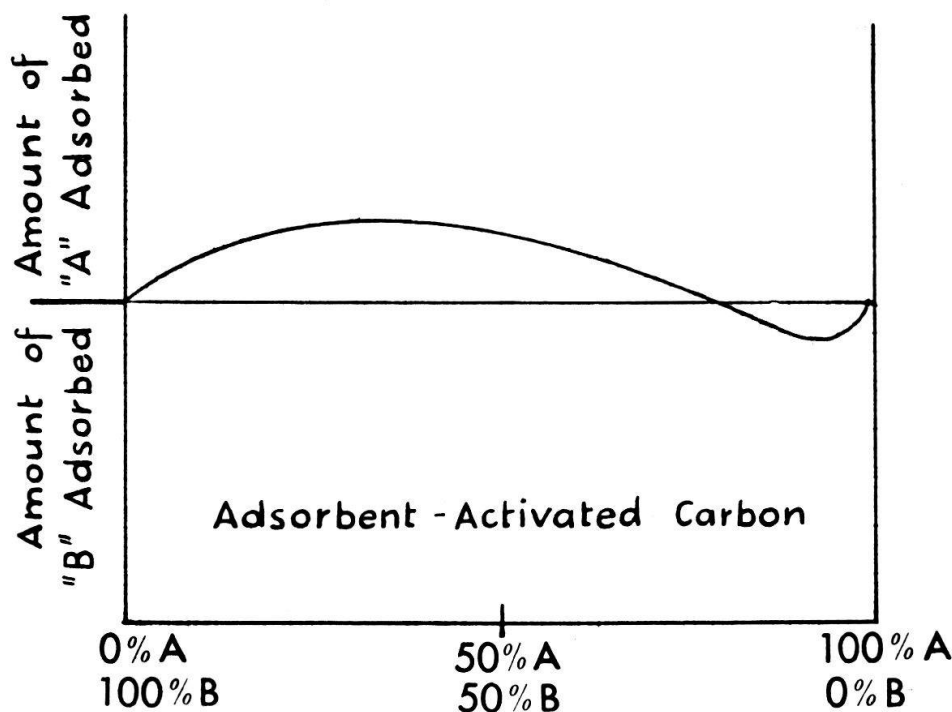


Fig. 7. Adsorption isotherm showing intermediate type of behavior exhibited by some pairs of aromatics (Petroleum Processing, Dec. 1950).

In vapor-phase treatment, the first eight percent collected were substantially pure iso-octane, but more carbon was required to obtain higher concentrations of iso-octane, than in the liquid-phase separation. For high iso-octane yields, the liquid method is preferred because it is more selective.

In a 1 : 1 blend of iso-octane with mixtures of pentane and hexane, separation was inferior.

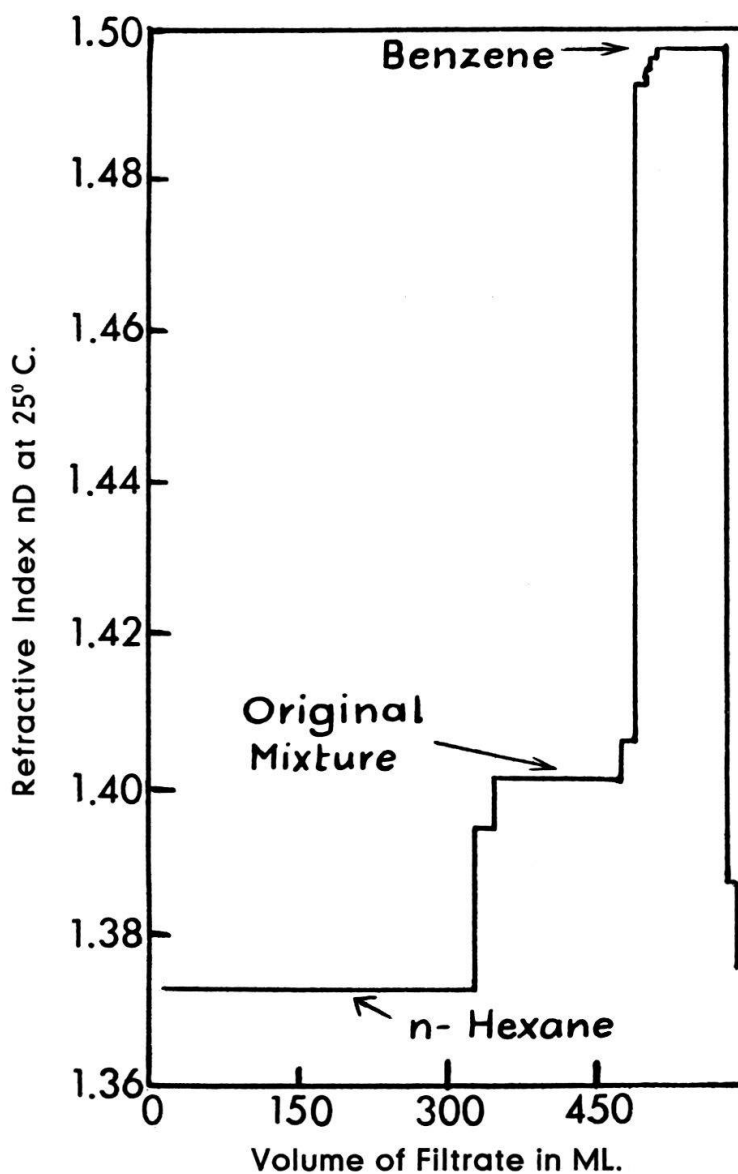


Fig. 8. Experiment 3.
0.25 vol. Benzene, 0.75 vol n-Hexane
(Mair, Westhaver and Rossini).

Hibschman concludes that for the purpose of purification of unsaturated hydrocarbons, carbon will often produce much better saturation than silica gel if the most weakly adsorbed component is to be purified.

Correlation of adsorption with fractionation was investigated with blends of a number of aromatics with paraffin hydrocarbons by Mair and others (41). The following procedure was used. A mixture was percolated through a bed of adsorbent until the percolate began to flow from the bottom of the column. At this moment, charging was stopped, and alcohol was slowly added at the top. The first fractions collected contained a high percentage of non-adsorbable material. Then a sudden change occurred, and the effluent had the composition of the charge. The last portion of the percolate consisted of almost pure adsorbate. Figs 8, 9 show in graphic form the change in the refractive index of mixtures of benzene and n-hexane (pure benzene 1.50142; pure hexane 1.37536). From these and similar tests, the authors derived the separation factor:

$$a = \frac{(N_A/N_B)^a}{(N_A/N_B)^l}$$

N_A and N_B are the mole fractions of the two liquids in the mixture, and a and l are the adsorbed and the liquid phases.

The separation factor was calculated to be 5.6, 3.4 and 2.4 respectively for systems of benzene-n-hexane containing 0.212, 0.506 and 0.820 volume fractions of benzene.

Lewis and coworkers (42) determined the equilibrium diagrams of 35 binary and some ternary mixtures of gaseous hydrocarbons at pressures from 0.33 to about 20 atmospheres absolute at temperatures from 32 to 104° F. with silica gel and with a number of activated carbons. In a summary of the possible correlations they state in part: «The quantity of a mixture adsorbed per gram of adsorbent as a function of the adsorbate composition can be predicted satisfactorily from the knowledge of the quality of each pure gas adsorbed at the temperature and total pressure of the mixture. Molecular weight, molecular structure of the mixture, liquid boiling point influence preferentially adsorption. At constant molecular weights and boiling points, molecular structure of the components of the mixture is of greater significance when the adsorbent is silica gel. When all factors: molecular weight, boiling point, molecular structure play a part, activated carbon adsorbs higher molecular weight gases; silica gel preferentially adsorbs on the basis of both liquid boiling point and gas molecular structure and polarity.»

Satisfactory correlation of the quantity of mixture adsorbed is derived from the correlation equation:

$$\sum_j^n N_1/N_1' = 1$$

where N is the quantity adsorbed from the gas mixture per gram of adsorbent, N' is the quantity adsorbed as in pure gas isotherms, in mg. moles per gram of adsorbent. With the N_1 and N_1' correlation known, satisfactory x, y , diagrams can often be obtained for binary mixtures of gases.

Lewis and coworkers (22) determined the adsorption equilibria of low-molecular weight hydrocarbons for silica gel and activated carbons at 77° F. and one atmosphere pressure. Some isotherms were taken at temperatures as high as 472° F. and 20 atmospheres. Conclusions derived from the results are:

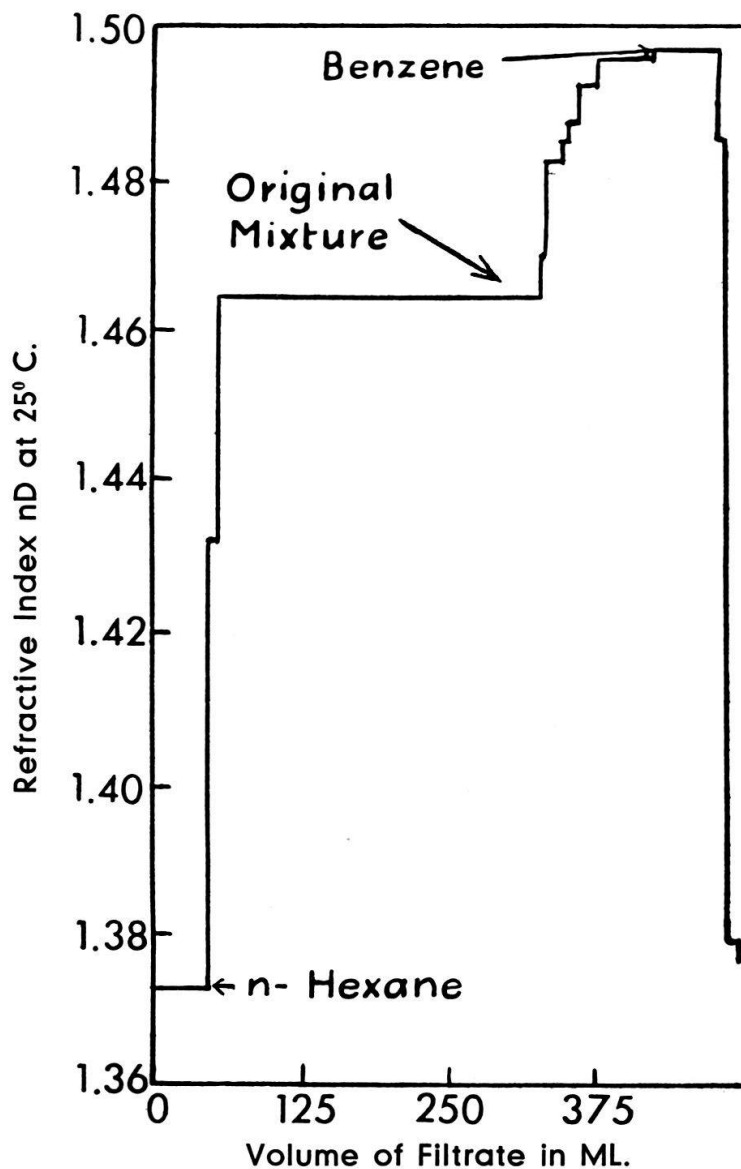


Fig. 9. Experiment 7.
0.75 vol. Benzene, 0.25 vol. n-Hexane (Mair,
Westhaver and Rossini).

The amount of gas adsorbed on carbon increases with increased molecular weight or critical temperature.

Increased pressure does not increase adsorption when saturation values are reached.

Temperature increase reduces adsorption considerably.

With a modified Polanyi equation it is possible to estimate adsorption at higher and lower temperatures and pressures from a minimum of experimental data.

Capacities of adsorbents for hydrocarbon gases differ widely. One carbon may adsorb as much as 60 % more gas than another and two to nine times as much as silica gel at atmospheric pressure.

Eagle and Scott (6) recommend a blend of toluene and iso-octane for the evaluation of adsorbents at very low feed rates and believe that from a knowledge of equilibria the operation of an adsorption column may be predicted.

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