[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Vapor–Adsorbate[1] Equilibrium. I. Propane–Propylene on Activated Carbon and on Silica Gel

BY W. K. LEWIS, E. R. GILLILAND, B. CHERTOW AND W. H. HOFFMAN

The potentiality of separating gases on an industrial scale by adsorptive procedures has led to a study of the equilibria involved when gaseous mixtures of hydrocarbons are in contact with solids of large specific surface area. In these investigations the adsorption isotherms of the individual components, and, in the case of the mixtures, the composition of the vapor and adsorbate in equilibrium with each other, have been determined. The condition of equilibrium has been ascertained, in dealing with mixtures, by approaching the equilibrium from both sides, *i. e.*, a given adsorbate composition would be attained by placing either gas (of a binary system) in contact with the adsorbent and equilibrating by bringing the second gas into contact with the solid. Finally, the reversibility of the phenomena has been investigated by desorption isotherms in the case of the individual components and by desorption and analysis of the adsorbed mixtures.

This report presents the results obtained when gaseous mixtures of propane and propylene were permitted to equilibrate with an activated carbon or a silica gel at 25.0 ± 0.1° and barometric pressure. The propane–propylene system is of interest because the physical properties of these gases are very similar and separation by a standard distillation technique is difficult.

Materials.—Commercial cylinders of C. P. grade gases were employed. When 22% sulfuric acid containing mercuric sulfate was used as an analytical reagent for determining olefins,[2] the propylene was found to be 99.15% olefin and the propane was found to be 0.05% olefin. Refrigeration grade silica gel, 14/20 mesh, with a BET[3] surface area of 751 sq. m. per g. (as determined by the usual low temperature adsorption of nitrogen) was supplied by the Davison Chemical Company of Baltimore. An activated carbon called Black Pearls I with a surface area, similarly determined, of 705 sq. m. per g. was supplied by the Godfrey L. Cabot Co. of Boston. Chemically pure, redistilled mercury was used as the displacing fluid in the apparatus, and the tubing to connect the mercury leveling bulbs to the Pyrex glass apparatus was sulfur-free gum rubber or neoprene.

Apparatus.—The apparatus (Fig. 1) finally evolved consists of a gas measuring buret calibrated in 0.1 ml. equipped with a compensator manometer to correct for temperature and barometer changes during an experiment. The first gas brought into the buret can then be stored in the premix chamber while the second gas is being measured. The gases are mixed by manipulation of the externally mounted bar magnets which causes spinning and raising (or lowering) of the soft iron washer within the glass chamber. The reservoir downstream of the adsorption U-tube permits the gases to be pumped back and forth over the adsorbent from the premix chamber to the reservoir, constancy of pressure being attained by maintaining the mercury level in the reservoir at the level of the mercury in the manometer leg.

By proper manipulation of the stopcock on the premix chamber, this unit may be employed as a desorption pump. If communication with the adsorption zone is brought about, when the level of mercury in this chamber is high, subsequent lowering of the mercury level causes the gas to be pumped into the chamber. After the stopcock is closed, the entrapped gases can be compressed to one atmosphere, pumped into the buret and measured. Repeated desorptions can create a very low pressure in the adsorption zone, since the volume of this zone is generally under 10 ml. while the premix chamber volume is 350 ml.

Glass to glass seals are used throughout except for the connection to the leveling bulbs. Precision bore, high vacuum stopcocks with mercury seals were employed with very small quantities of Apiezon M as lubricant. All capillaries shown in the diagram are 2-mm. bore, elsewhere the bore is 6 or 8 mm. Auxiliary apparatus consisted of a conventional Orsat type gas analysis assembly, a Cenco Hyvac pump for routine evacuations, a thermostat bath with a circulatory pump, a 30° thermometer calibrated in 0.1°, a Tesla coil for checking the evacuated apparatus, specially made clamps for regulating the flow of mercury through the rubber tubing, etc.

Procedure.—Experience in this Laboratory has taught that when a fresh sample of adsorbent is to be employed in adsorption studies, if a high degree reproducibility and reversibility of the phenomena are to be realized, the adsorbent surface must be "flushed" at least twice with one of the components of the gas mixture under investigation. Earlier workers in the field[4] have also made this finding; it is reported because it must not be overlooked. Flushing the surface involves a preliminary evacuation of the adsorbent at an elevated temperature (refluxing glycol at 192° for activated carbon, and glycol–water at 160° for silica gel have been found satisfactory) followed by cooling, saturating the surface with one of the gases to be used and re-evacuation at the proper temperature. This technique is strikingly analogous to rinsing an analytical buret with the standard reagent to be measured by that buret. After at least two such flushings of the fresh adsorbent sample, routine desorption in preparation for an experiment merely consists in evacuating at the proper temperature for a period of one hour.

The gas volume (called hereafter the dead space) surrounding the adsorbent is determined by admitting a known volume of helium to the evacuated adsorption zone (maintained at 25.0 ± 0.1°) and recording the pressure.

After the system is flushed and the dead space is determined, the system is again evacuated. Adsorption isotherms of the individual gases are determined by admitting successive small known quantities of gas to the adsorption zone and recording the pressure after a ten to fifteen minute wait for equilibrium. After the pressure in the

---

[1] The word adsorbate is used in this article to indicate material held by the solid.

[2] Francis and Lukasiewics, *Ind. Eng. Chem.*, *Anal. Ed.*, **17**, 703 (1945).

[3] Brunauer, Emmett and Teller, THIS JOURNAL, **60**, 309–319 (1938).

[4] H. S. Harned, *ibid.*, **42**, 372 (1920).

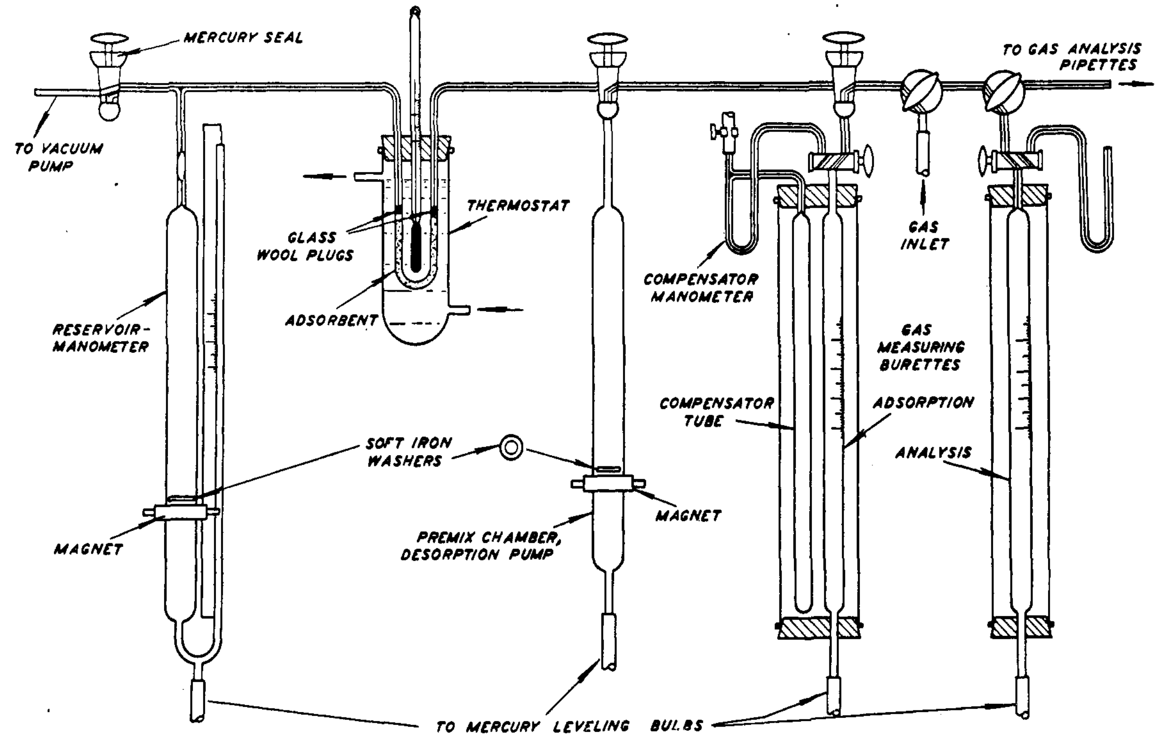

Fig. 1.—Apparatus for determining vapor–adsorbate equilibrium.

adsorption zone has been built up to the maximum desired pressure, successive small quantities are desorbed with the desorption pump and are measured in the gas buret, pressures in the adsorption zone again being recorded. The reversibility of the phenomenon is thus checked. At 25.0 ± 0.1°, the desorption isotherm can be readily studied down to a pressure of 2 mm. of mercury abs. To attain further desorption it is expeditious to raise the temperature in the adsorption zone.

When mixture runs are to be carried out with either a new adsorbent or new gas system, it is advisable to devote the first two experiments to finding out whether the same equilibrium values for the adsorbate and gas phase compositions are attainable independent of which gas has been on the surface first. Hence, the first experiment involves adding a known volume of the first gaseous component to the evacuated adsorption U-tube and permitting about forty minutes residence therein before adding a known volume of the second gas to the system. (Note, no premixing is employed in these initial experiments.) Passes back and forth through the U-tube for forty to sixty minutes (two or three minutes per pass) are generally sufficient. The unadsorbed gas is then measured in the buret and is analyzed. After re-evacuation of the adsorption zone at the proper temperature level, the same procedure is repeated, this time, however, the order in which the gases are fed to the system is reversed.

If the two equilibrium values thus obtained lie close to one another this procedure of adding first one gas then the other may be followed throughout, or the premix chamber may be used as described above before any gas is admitted to the evacuated adsorption zone.

Reversibility of the adsorption of mixtures is readily determined by using the premix chamber as a desorption pump as described above. In general, it is best to pump off as much gas as possible before raising the temperature in the bath surrounding the adsorption zone. The desorbed gases can be measured in the buret and analyzed.

Results.—The data for the adsorption isotherms of propane and of propylene on silica gel and on activated carbon at 25.0 ± 0.1° are in Tables I and II, respectively, and are presented graphically in Fig. 2. The results for mixtures of these gases on the adsorbents mentioned are to be found in Table III and in Fig. 3, equilibrium distribution and total adsorption being shown.

TABLE I

ADSORPTION ISOTHERMS OF PROPANE ON ACTIVATED CARBON (GLC) AND SILICA GEL AT 25.0 ± 0.1°

n = millimoles adsorbed per g. adsorbent; P = pressure, mm. abs.

Carbon[a]		Silica gel[b]		Silica gel Desorption	
P, mm.	n[c]	P, mm.	n[c]	P, mm.	n[c]
15.7[d]	0.791	11.1	0.0564	703.0	1.501
44.0	1.141	25.0	.1252	611.1	1.350
54.2	1.223	43.5	.1980	505.9	1.199
84.0	1.416	71.4	.2986	419.0	1.061
107.0[d]	1.532	100.0	.3850	118.3	0.456
139.0	1.646	158.9	.5441	57.2	.2690
177.0	1.769	227.5	.7020	35.1	.1912
215.5	1.872	304.2	.843	12.0	.0931
278.0	2.006	387.0	1.010	4.5	.0436
331.5	2.105	468.0	1.138		
429.5[d]	2.254	569.0	1.288		
536.0	2.373	677.8	1.434		
585.7	2.454	775.0	1.562		
640.7[d]	2.479				
680.2	2.510				

[a] Vol. of dead space = 7.70 ml. [b] Vol. of dead space = 6.76 ml. [c] Based on adsorbent weight as received. Three to five per cent. of the as received adsorbent is easily removable volatile matter. The "as received" basis is used throughout this series. [d] Obtained on duplicate run of adsorption isotherms.

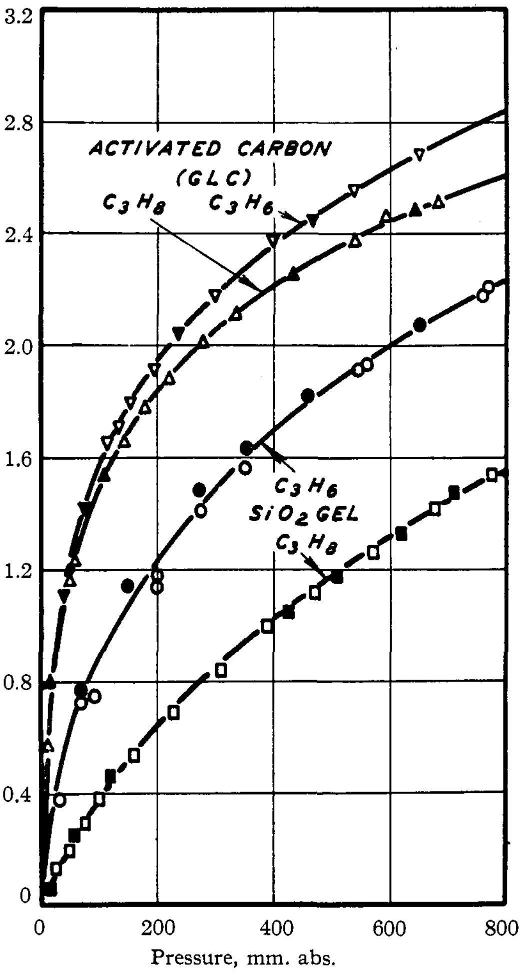

Fig. 2.—Adsorption isotherms of propane and propylene on activated carbon and on silica gel at 25.0 ± 0.1°: ▽ △ ○ □, adsorption; ▼ ▲, duplicate isotherm; ● ■, desorption.

Randomly chosen results on the data obtained when desorptions were carried out with the desorption pump are found in Table IV.

TABLE II

ADSORPTION ISOTHERMS OF PROPYLENE ON ACTIVATED CARBON (GLC) AND SILICA GEL AT 25.0 ± 0.1°

n = millimoles adsorbed per g. adsorbent. P = pressure, mm. abs.

Carbon[a]		Silica gel[b, c]			
P, mm.	n	P, mm.	n	P, mm.	n
Adsorption		Adsorption		Desorption	
16.5	0.567	34.2	0.3738	650	2.073
36.0[d]	1.107	71.4	0.7227	459	1.814
47.7	1.171	91.6	0.7472	457.9	1.808
71.0[d]	1.419	194.3	1.129	355.6	1.633
118.5	1.648	198.3	1.168	281.8	1.473
131.0	1.703	271.5	1.401	155.4	1.125
154.0	1.786	253.2	1.562	74.2	0.7596
192.0	1.913	550.7	1.918	4.4	0.1090
231.0[d]	2.041	555.2	1.928		
294.0	2.168	760.6	2.184		
398.5	2.366	768.2	2.197		
464.5[d]	2.456				
537.5	2.552				
649.5	2.677				

[a] See Table I. [b] See Table I. [c] Obtained with propylene containing 3.08% inert since the original propylene (0.85% inert) was consumed. [d] Duplicate isotherm.

All the results are based on using $PV = \mu RT$ as the equation of state of each gas. Values of μ were calculated from the ethylene charts of York.[5]

Precision of Results.—The precision of the volumetric measurements should be high since the volumes measured usually exceeded 20 ml. and the burets employed are calibrated with 0.1 ml. marks. Hence, the precision desired governs the weight of the adsorbent sample, provided also the dead space is kept small compared to the total adsorption.

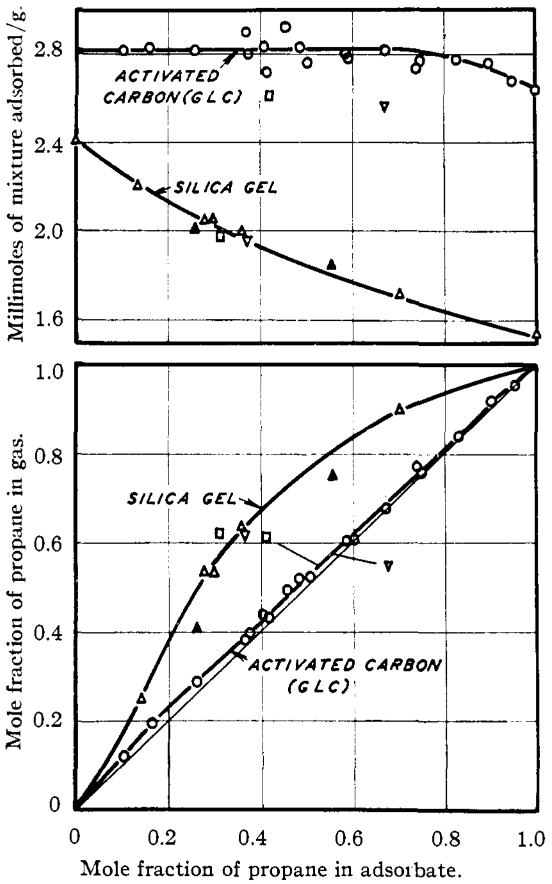

Fig. 3.—Isothermal, isobaric adsorption of propane-propylene mixtures on silica gel and on activated carbon; atmospheric pressure and 25°; total adsorption and vapor-adsorbate equilibrium: △ ○ premixed gases, 20 passes; ▽ propane on surface first; □ propylene on surface first; ▲ non-equilibrium, 2 passes on silica gel.

---

(5) R. York and E. F. White, *Trans. Am. Inst. Chem. Eng.*, **40**, 227 (1944).

TABLE III

VAPOR–ADSORBATE EQUILIBRIUM DATA FOR MIXTURES OF PROPANE AND PROPYLENE OVER (1) ACTIVATED CARBON (GLC), (2) SILICA GEL, AT 25.0 ± 0.1° AND ATMOSPHERIC PRESSURE (752–773 MM. ABS.)

X = mole fraction of propane in adsorbate; Y = mole fraction of propane in gas phase; N = millimoles of mixture adsorbed per gram of adsorbent.

Activated carbon				Silica gel			
Y	X	N	π	Y	X	N	π
0.1104[a,b]	0.0993	2.819	755.6	0.2445[a]	0.1078	2.197	769.2
.1881[a,b]	.1613	2.831	759.0	.299	.2576	2.013	760.9
.2816[a,b]	.2596	2.823	760.0	.4040[b]	.2956	2.052	767.8
.3799[a,b]	.3675	2.907	757.0	.530	.2816	2.041	761.0
.3959[a]	.3728	2.794	762.0	.5333[a]	.3655	1.963	753.6
.4328[a,b]	.4147	2.772	755.7	.5356[a]	.3120	1.967	766.3
.4351[a,b]	.4077	2.838	766.0	.6140[c]	.3591	1.974	754.0
.4910[a,b]	.4575	2.927	769.0	.6220[d]	.5550	1.851	753.6
.5188[a]	.4819	2.831	771.0	.6252[a]	.7007	1.701	754.0
.522[a]	.5036	2.763	755.0	.7480[f]	.723	1.686	760.0
.5460[c]	.6675	2.56	756.3	.671	.096	2.180	
.5983[b,e]	.5865	2.793	759.0	.8964[a]	.253	1.993	760.0
.6010[a,b]	.5925	2.777	756.5	.921	.401	1.426	760.0
.6107[d]	.4112	2.605	756.9				
.6736[a,b]	.6688	2.820	767.0				
.7577[a]	.7477	2.770	771.0				
.7695[a,b]	.7391	2.725	753.1				
.8410[b,e]	.8315	2.768	763.0				
.9158[a,b]	.8992	2.745	761.3				
.9528[a,b]	.9517	2.670	772.4				

[a] Premixed gas, 20 passes. [b] Fresh sample of adsorbent used. [c] Propane on surface 1st for forty min., propylene added, 20 passes. [d] Propylene on surface 1st for forty min., propane added, 20 passes. [e] Premixed gas, 10 passes. [f] Premixed gas, 2 passes, non-equilibrium.

TABLE IV

DESORPTION RECOVERY OF PROPANE–PROPYLENE MIXTURES

Activated Carbon (GLC)	
Ml. of C_3H_8 fed to apparatus, S. T. P.	24.74
Ml. of C_3H_6 fed to apparatus, S. T. P.	115.85
Total ml. fed to apparatus	140.59
Ml. of mix. retd. to buret, S. T. P.	68.80
Ml. of evac. gas (adsorbate + dead space gas)	72.00
Total ml. recovered from apparatus	140.80
Silica Gel	
Ml. of C_3H_8 fed to apparatus, S. T. P	18.62
Ml. of C_3H_6 fed to apparatus, S. T. P.	89.22
Total ml. fed to apparatus	107.84
Ml. of mix retd. to buret, S. T. P.	44.01
Ml. of evac. gas	63.37
Total ml. recovered from apparatus	107.38

Discussion.—The individual isotherms of propane and propylene, respectively, on the activated carbon appear to follow the empirical Freundlich equation somewhat better than the theoretical Langmuir[6] equation. While the pressure range involved herein is mainly outside that suggested by Brunauer, *et al.*,[3] the few points in this range do follow their relationship. Because none of these isotherm equations fit the data satisfactorily over the pressure range studied herein, none of the constants of the equations is reported, though over portions of the isotherms there is reasonable agreement with either the Freundlich or Langmuir equation.

The Langmuir adsorption equation for a binary mixture at equilibrium is given as

$$n_p = \frac{a_p b_p p_p}{1 + b_o p_o + b_p p_p} \text{ for the paraffin and}$$

$$n_o = \frac{a_o b_o p_o}{1 + b_p p_p + b_o p_o} \text{ for the olefin}$$

where n = millimoles of gas adsorbed per gram of adsorbent at a partial pressure in the mixture of p; a and b are constants and the subscripts o and p refer to the olefin and paraffin, respectively.

Division of one equation by the other yields

$$\frac{n_o}{p_o} \times \frac{p_p}{n_p} = \frac{Y_p}{X_p} \times \frac{X_o}{Y_o} = \frac{a_o b_o}{a_p b_p} = \text{constant}$$

where Y = mole fraction in gas phase, and X = mole fraction in adsorbate.

The left member of the above equation is analogous to the relative volatility for vapor–liquid systems,[7] hence the same terminology will be employed. The Langmuir equation states that at constant temperature the relative volatility of a binary mixture over an adsorbent is constant and independent of the adsorbate composition and the total pressure. For the system propane–propylene over the activated carbon used the relative volatility has been found to be substantially constant at barometric pressure at a value rather close to one. It is clear from Fig. 3 that such a low relative volatility means that the adsorbent does not differentiate greatly between these hydrocarbons.

(6) I. Langmuir, THIS JOURNAL, **38**, 2221–2295 (1916).

(7) Walker, Lewis, McAdams and Gilliland, "Principles of Chemical Engineering," McGraw-Hill Book Co., New York, N. Y., 1937.

In the case of silica gel as an adsorbent, it will be noted that the adsorption per gram on silica gel is less than that on activated carbon for each of the gases studied. The mixture behavior is also different. First, while there was little selection of one component over the other by the carbon, the silica gel differentiated rather strongly between the two gases with the result that propylene is, quite clearly, less volatile than propane. Second, the relative volatility is not independent of composition (as simple calculations will show), but varies markedly. Third, the affinity of silica gel for the hydrocarbon mixture not only is lower than the affinity of the activated carbon, but also it varies with compostion in an almost linear fashion.

It is to be noted that the adsorbent capacity has been based on the weight of adsorbent "as received." Since on an as received basis some three to five per cent. of the adsorbent weight is lost as a result of outgassing, the capacities reported are on the low side. This factor does not influence the mixture equilibrium results.

The data of Table IV indicate the high degree of recoverability of the adsorbate. Within the limits of precision, recovery may be termed substantially complete.

Summary

In addition to the determination of the adsorption isotherms of propane and propylene on (a) activated carbon and (b) silica gel at 25.0 ± 0.1°, the equilibrium behavior of binary mixtures of these two rather similar gases (physically) was also determined over each of the adsorbents at the same temperature. All adsorptions were entirely reversible.

There is very little difference in the relative volatility of these gases over activated carbon; there is substantial difference over silica gel. However, the adsorption capacity per unit weight of carbon is greater for these hydrocarbons than that of silica gel. In both these vapor–adsorbate equilibria propane is the more volatile component, whereas in the vapor–liquid equilibrium for this hydrocarbon system propane is the less volatile component.

CAMBRIDGE 39, MASS. RECEIVED MARCH 10, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Vapor–Adsorbate Equilibrium. II. Acetylene–Ethylene on Activated Carbon and on Silica Gel

BY W. K. LEWIS, E. R. GILLILAND, BERNARD CHERTOW AND W. MILLIKEN

Vapor–adsorbate equilibrium has been investigated for binary gaseous mixtures of acetylene and ethylene at 25.0° and barometric pressure. As in the previous work on propane–propylene mixtures[1] adsorption–desorption isotherms for each gas were determined on (a) activated carbon and (b) silica gel. Equilibrium data were collected with mixtures as in the earlier report, the equilibrium concentrations having been approached from both directions. In addition, desorption studies of mixtures permitted observations to be made on the reversibility of the adsorption.

Materials.—Commercial C. P. grade ethylene of 99.5 mole % minimum purity was employed. This gas was totally absorbed in 22% sulfuric acid saturated with mercuric sulfate[2] when its olefin content was determined. In addition, when subjected to a catalytic hydrogenation analysis[3] the ethylene, after corrections were made for gas law deviations, was found to be 100% unsaturated.

The acetylene was drawn from commercial cylinders wherein it is kept in acetone solution. According to the manufacturers, the acetylene contained in addition to acetone vapor the following as impurities

	%		%
O_2	0.03	NH_3	0.005
N_2	.15	H_2S	.005
PH_3	.026	CO, CO_2, H_2, CH_4	.05

After a clean-up system (consisting of freshly de-aerated water for scrubbing out the acetone and sulfuric acid for drying) was installed, the acetylene purity was 99.2 mole % when determined in alkaline mercuric cyanide.[4] The activated carbon, 28 × 60 mesh, was supplied by the Pittsburgh Coke and Chemical Company (Designation EY-51-C) and had a BET[5] surface area of 805 sq. m. per g. The silica gel has already been reported on.[1]

The apparatus and procedure were substantially those employed before[1] with but a modification in the determination of the acetylene isotherm. Because of about 0.8% unadsorbable impurity, it is obvious that any adsorption isotherm determined by successive additions of small known volumes of acetylene to a constant

---

(1) W. K. Lewis, *et al.*, THIS JOURNAL, **72**, 1153 (1950).

(2) Francis and Lukasiewics, *Ind. Eng. Chem.*, *Anal. Ed.*, **17**, 703 (1945).

(3) R. F. Robey and C. E. Morrell, *ibid.*, **14**, 880–883 (1942).

(4) Wood, *Fuel*, **9**, 289 (1930).

(5) Brunauer, Emmett and Teller, THIS JOURNAL, **60**, 309–319 (1938).