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.

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[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

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(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).

volume adsorption zone would result in the accumulation of inerts over the adsorbent. For example, if 50 ml. of 99.2% pure acetylene were admitted to an adsorption zone with 6 ml. as the dead space and if 44 ml. were adsorbed on the surface, the dead space gas composition would be 6.7% inerts. Hence, to avoid this, large volumes of acetylene were passed over the surface as in the procedure for equilibrating a mixture. This effectively maintained the inerts concentration at a low value over the adsorbent. Adsorption points for acetylene were thus obtained at a few total pressures up to one atmosphere, the majority of the isotherm being obtained by desorption. (Clearly each slug desorbed results in bodily removal of inerts, hence a desorptive procedure serves to purify the acetylene.)

The analytical procedure employed for the determination of acetylene in ethylene when employed on known mixtures was accurate within ±0.8%. The error is due to slow adsorption of ethylene in the reagent. When pure ethylene is passed through alkaline mercuric cyanide at a total pressure of 1 atmosphere and at room temperature 1 ml. per 100 is lost after ten passes. Since only ten passes through the reagent were employed when mixtures were being analyzed, the error in analysis is not too great.

Results.—The data for adsorption isotherms of acetylene at 25.0° are in Table I and Fig. 1, the isotherm data for ethylene are in Table II and Fig. 1. Table III contains the vapor-adsorbate equilibrium data for the binary mixtures and the total adsorption on either carbon or silica gel. These data are shown graphically in Fig. 2. Table IV contains the results obtained when the mixed adsorbate was evacuated with the desorption pump.

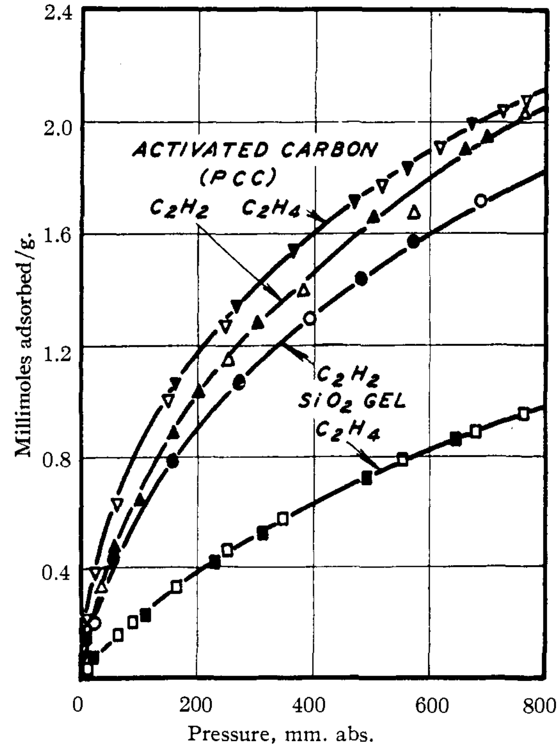

Fig. 1.—Adsorption isotherms of acetylene and ethylene on activated carbon and on silica gel, $T = 25°$: ▼ ▲ ○ □ adsorption; ▽ △ ● ■ desorption.

Table I

Adsorption Isotherms of Acetylene on Activated Carbon (P. C. C. A 366C-EY-51C) and Silica Gel at 25.0 ± 0.1°

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

Carbon P	Carbon n	Silica gel P	Silica gel n
Adsorption		Adsorption	
246.3	1.152	389.3	1.301
376.6	1.408	685.7	1.731
569.3	1.789	Desorption	
758.8	2.050	568.5	1.583
Desorption		477.5	1.452
701.8	1.972	270.0	1.090
658.0	1.920	153.8	0.797
495.5	1.672	57.2	0.435
298.0	1.281	21.0	0.2282
200.1	1.033	9.7	0.1412
153.6	0.889		
92.1	.648		
52.6	.471		
30.1	.3275		
14.6	.1940		

Table II

Adsorption Isotherms of Ethylene on Activated Carbon (P. C. C. A 366C-EY-51C) and Silica Gel at 25.0 ± 0.1°

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

Carbon P	Carbon n	Silica gel P	Silica gel n
Adsorption		Adsorption	
13	0.186	14.2	0.0348
45	0.485	65.4	.1572
104	0.831	87.2	.2030
214	1.22	184.5	.3353
343	1.52	250.5	.4599
498	1.80	347.1	.5797
645	2.00	552.0	.7910
757	2.14	676.6	.8950
Desorption		764.2	.9620
666	2.02	Desorption	
504	1.82	644.3	0.8660
356	1.56	489.7	.7270
203	1.20	310.4	.532
100	0.843	231.5	.428
60	0.639	107.0	.228
		26.5	.0687

Discussion.—The isotherm of ethylene on silica gel at 25.0° follows the Langmuir[6] equation satisfactorily at the higher pressures; the three

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[6] I. Langmuir, This Journal, **38**, 2221–2295 (1916).

TABLE III

VAPOR–ADSORBATE EQUILIBRIUM DATA FOR MIXTURES OF ETHYLENE AND ACETYLENE OVER (1) ACTIVATED CARBON (P. C. C. A 366C-EY-51C) (2) SILICA GEL AT 25.0 ± 0.1°, AND BAROMETRIC PRESSURE (759–763 MM. ABS.)

X = mole fraction of ethylene on surface; Y = mole fraction of ethylene in gas phase; N = millimoles of mixture adsorbed per gram of adsorbent; π = pressure mm. abs.

Activated carbon				Silica gel			
Y	X	N	π	Y	X	N	π
0.0903	0.0852	2.057	761.9	0.2422	0.0686	1.622	761.9
.1366	.1242	2.033	759.3	.562	.292	1.397	761.0
.112	.140	2.026	760.6	.714	.458	1.298	763.4
.186	.232	2.031	761.7	.814	.592[a]	1.193	761.8
.289	.344	2.068	758.8	.838	.630[b]	1.170	763.6
.345	.428	2.030	761.1	.932	.864	1.078	763.5
.453	.567	2.070	768				
.551	.653[b]	2.085	759.2				
.553	.661[a]	1.992	757.3				
.842	.903	2.078	760.8				

[a] Ethylene on surface first. [b] Acetylene on surface first.

TABLE IV

Adsorbate recovery: C_2H_2–C_2H_4

Activated Carbon

		Total
Ml. of C_2H_2 fed to apparatus, S. T. P.	90.60	
Ml. of C_2H_4 fed to apparatus, S. T. P.	12.89	103.49
Ml. of unadsorbed mixture retd. to buret S. T. P.[a]	52.40	
Ml. of evac. gas (adsorbate + dead volume)[b]	51.50	103.90
Silica Gel		
Ml. of C_2H_2 fed, S. T. P.	62.48	
Ml. of C_2H_4 fed, S. T. P.	60.62	123.10
Ml. unads. mix retd. to buret, S. T. P.[c]	85.50	
Ml. evac. (adsorbate + dead vol.)[d]	37.40	122.90

[a] % C_2H_2 = 88.8. [b] % C_2H_2 = 86.3. [c] % C_2H_2 = 43.8. [d] % C_2H_2 = 65.7.

remaining isotherms, however, obey neither this equation nor the Freundlich relationship. It will be observed from the isotherms of the individual gases that while the carbon sample has the greater affinity for ethylene over the entire pressure range investigated, the silica adsorbent has a greater preference for acetylene. However, the activated carbon adsorbs more of these hydrocarbons than does the silica gel.

These preferences are maintained when the adsorbent is confronted with mixtures of these two gases, the silica gel showing, however, rather more discrimination. Thus, the relative volatilities, (see ref. 1) which vary with composition, are greater over silica gel than over activated carbon.

As in the case with propane–propylene[1] the carbon adsorbent has the greater capacity for the hydrocarbons. In each case the total quantity adsorbed per gram of carbon is substantially independent of composition, whereas with silica gel there is almost a linear variation in adsorbent capacity. It will be noted that with these adsorbents it has been possible to approach the equilibrium from both directions, *i. e.*, the same concentrations are attained independent of which gas resided on the adsorbent first. Finally, a study of Table IV indicates that the adsorptions reported herein are entirely reversible.

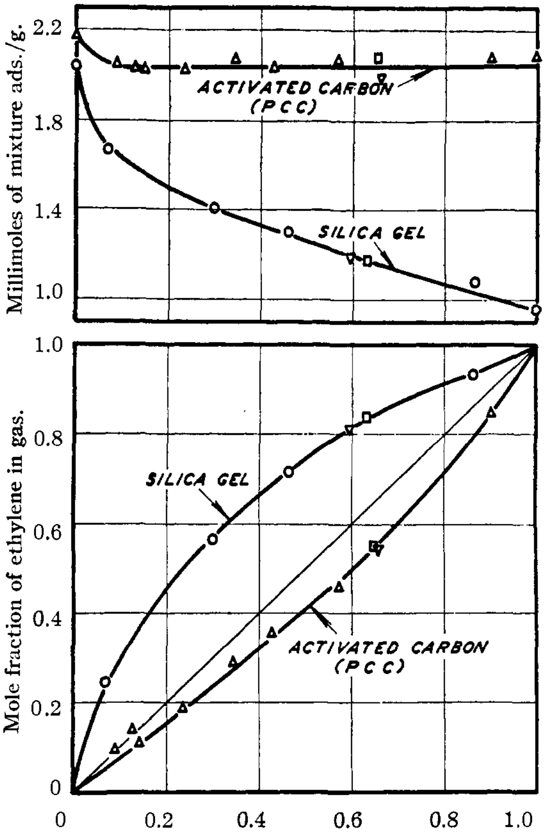

Fig. 2.—Isothermal, isobaric adsorption of acetylene–ethylene mixtures, atmospheric pressure, T = 25°, total adsorption and vapor–adsorbate equilibria on activated carbon and on silica gel: ○,△ premixed gases; □ acetylene on surface first; ▽ ethylene on surface first.

Summary

1. Adsorption–desorption isotherms have been measured for acetylene and for ethylene on silica gel and on activated carbon at 25°.

2. Vapor–adsorbate equilibrium curves at barometric pressure and 25° have been determined for mixtures of these two gases on each adsorbent.

3. Acetylene is more volatile than ethylene over the activated carbon employed and is the less volatile component over the silica gel employed.

4. The adsorption phenomena reported herein are reversible.

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