NOMENCLATURE

B, C, D = constants in Redlich-Kister equation
ΔG_x^E = excess free energy of mixing, cal/mole of the mixture
P_T = total pressure, mm Hg
x_i = mole fraction of component i in liquid
y_i = mole fraction of component i in vapor

GREEK LETTERS

γ_i = activity coefficient of component i

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Adsorption Isotherms at High Pressures

Comment on Data of Stacy et al.

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The adsorption isotherms of methane on carbon and on silica gel at 38–121°C up to 650 atm pressure, reported by Stacy et al., have an abnormal shape and give too high adsorption values. High-pressure adsorption isotherms theoretically should, and experimentally always do, exhibit a maximum at 100–200 atm pressure. The solitary exception in the case of Stacy et al. is apparently due to an error in their dead-space determination; the gas simply compressed into the unaccounted part of the dead space has completely masked the true adsorption.

In two recent papers in this Journal, Stacy et al. (*6, 7*) have reported the adsorption isotherms of methane on carbon and on silica at 38–121°C and pressures up to 650 atm. These isotherms continuously increase with pressure. All hitherto published high-pressure adsorption isotherms (for reviews see *2, 3*), however, show a distinct maximum in the isotherm at 100–300 atm pressure, provided the measurements have been carried out to at least 200 atm pressure. Examples are (*2*): the adsorption of CH_4 and H_2 on charcoal; CO_2, N_2O, and SiF_4 on charcoal; CH_4 on coal; Ar and N_2 on active carbon; N_2 and CO on alumina; and CH_4 on silica gel. It is possible even to predict (*4*) the pressure $P_{\max}$ at which adsorption isotherms should exhibit a maximum: $P_{\max} = (T/T_c)^2 P_c$, where T is the temperature of adsorption and T_c and P_c are the critical temperature and critical pressure of the adsorbate gas. This relationship holds good for ordinary adsorbents with not too fine pores. For microporous adsorbents with pores of molecular dimensions (e.g., activated charcoal or molecular sieves), the maximum in adsorption isotherm is reached even earlier: $P_{\max}$ = 60–80% of $(T/T_c)^2 P_c$. In the light of such results the data of Stacy et al. are examined and indications are given of the source of error which may have masked the true adsorption.

Stacy et al. (*6*) report [see correction (*6a*)] that the accuracy in the determination of the dead-space volume in their apparatus is only 1%. This is 0.66 cc for the dead-space volume of 66.4 cc. The quantity of gas which can be simply compressed into this 0.66 cc at high gas densities, attained at pressures of 300–600 atm, can be too large compared to the physical adsorption of methane at the same pressure on only 14.6 grams of carbon or 12.9 grams of silica used as the adsorbent at 38–121°C. This may perhaps have masked the true adsorption.

At pressures of 200–650 atm, the dimensional changes (compressibility as also the swelling on adsorption) of carbon and the penetration of methane into the interlamellar space in the graphitic planes in carbon will be appreciable (*5*), and what one measures can no longer be called adsorption in the ordinary sense of the term. Since Stacy et al. find continuously increasing isotherms for silica gel (*7*) as well, the inaccuracy in the dead-space determination seems to be the major source of error in their high-pressure adsorption isotherms.

It is also instructive here to compare the adsorption of methane on silica gel reported by Stacy et al. with the data for the same adsorbent-adsorbate system obtained by Gilmer and Kobayashi (*1*) in 1964 at temperatures of −40°, −20°, 0°, 20°, and 40°C and pressures up to 137 atm. Such comparisons of physical adsorption are permissible even if the chemical nature of the two silica surfaces may not be very similar. The BET surface areas for the two silicas are 145 and 532 m^2/g, respectively. The nitrogen monolayer values (v_m) corresponding to these two surface areas are 1.48 and 5.4 mmol/g. These values may be taken as a rough indication for the maximum at-

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Table I. Adsorption of Methane on Silica

Gilmer and Kobayashi (*1*)			Stacy et al. (*7*)		
T = 40°C, S = 532 m^2/g v_m = 5.4 mmol/g			T = 37.8°C, S = 145 m^2/g v_m = 1.48 mmol/g		
Pressure, atm	Adsorption, mmmol/g	θ	Pressure, atm	Adsorption, mmol/g	θ
50	2.3	0.43	50	1.1	0.74
100	2.9	0.54	100	2	1.3
140	3.2	0.59	140	3	2.0
Even at −40°C			200	4	2.7
50	4.5	0.83	400	6.5	4.4
100	4.3	0.80	600	8	5.4
140	3.8	0.70			

tainable surface coverage on these adsorbents by any adsorbate gas above its critical temperature (for methane $T_c = -82.9°C$), and hence can be used for calculating the degree of coverage θ. In Table I the results of Stacy et al. for 37.8°C are compared with those of Gilmer and Kobayashi for 40°C. The adsorption data of Stacy et al. indicate multimolecular adsorption ($\theta > 1$), which is highly improbable so far above the critical temperature of the adsorbate.

It must be emphasized here that the adsorption isotherms of Gilmer and Kobayashi (*1*) at −40°, −20°, and 0°C show clear maxima at pressures of 63, 82, and 96 atm, respectively, while their 20° and 40°C isotherms already level off at 120–40 atm. This behavior of high-pressure adsorption isotherms is normal and expected and has indeed been observed by all previous workers in this field (for a list of work since 1930, see Table 1 in ref. *2*). In contrast to these, the adsorption isotherms of Stacy et al. continuously increase with pressure even at 600–50 atm. This strengthens the suspicion that the gas simply compressed into some unaccounted part of the dead space in their apparatus has masked the true adsorption.

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ORGANIC SECTION

Catalytic Hydrogenation of Polynuclear Hydrocarbons

Products of Partial Hydrogenation of Dibenz(*a,j*)anthracene, Benzo(*ghi*)perylene, Dibenz(*a,c*)anthracene, 3-Methylcholanthrene, 7,12-Dimethylbenz(*a*)anthracene, and Anthanthrene

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The catalytic hydrogenation reactions of the title compounds were studied. A total of 18 products were isolated and characterized. Some of these compounds were products of reduction at noncontiguous carbon atoms, the reactive centers in one case being separated by seven bonds. The mass spectral fragmentation of derivatives of 3-methylcholanthrene and 7,12-dimethylbenz(*a*)anthracene is characterized by a strong tendency to lose methyl groups.

As a result of our interest in the relationship of chemical structure to carcinogenic activity among polynuclear hydrocarbons (*6, 8*), we have recently completed a study (*7, 9*) of the carcinogenicity of a number of partially hydrogenated derivatives of dibenz(*a,j*)anthracene (I), benzo(*ghi*)perylene (II), dibenz(*a,c*)anthracene (III), 3-methylcholanthrene (IV), 7,12-dimethylbenz(*a*)anthracene (V), and anthanthrene (VI). We report the preparation and characterization of those hydrogenation products.

Some of the reactions followed unexpected steric courses. The production of the 1,2,3,7,8,9-hexahydro derivative (VIb) in the hydrogenation of anthanthrene implied that net 1,8- (or greater) addition of hydrogen had occurred. Similarly, IIb and IVc are the products of reduction at noncontiguous carbon atoms.

The mass spectra of the hydrogenated hydrocarbons showed that the added hydrogens were most easily lost so that the peak corresponding to the completely aromatic structure was

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