Adsorption Phase Equilibrium Correlations

Light-hydrocarbon Vapors on Activated Charcoal

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Data correlations are presented for equilibrium adsorption of pure hydrocarbon vapors and their mixtures. The systems represented are C_1 to C_4 hydrocarbons (olefins and paraffins) on gas-adsorbent grades of activated charcoal. The mixture data are limited to binary and ternary gas systems. The adsorption conditions represented among the correlated data cover ranges of 77° to 175°F. temperature and 0 to 100 lb./sq. in. gauge. With the use of empirical adsorption constants, a common correlation of specific adsorption capacity for the various hydrocarbons is presented; it applies for either pure components or their mixtures. A correlation is given also for adsorption relative volatilities. Approximate adsorption heats, a limited amount of high-temperature steam adsorption data, and sample calculations on application of the correlations are included. The prediction methods are recommended for adsorption conditions up to 250°F. and 250 lb/sq. in. gauge for the particular systems studied.

A companion paper (*11*) describes a new development for continuous adsorptive separation of gas mixtures called the Fluid Char Adsorption (FCA) Process. The development required considerable laboratory study to evaluate alternate adsorbents and to obtain vapor-adsorption data for FCA process designs and interpretation of pilot plant results. This paper includes such data* on light-hydrocarbon–activated-charcoal systems, methods developed for correlating the phase equilibrium relations, and application of the correlations to adsorption-tower design.

Adsorption can be a valuable supplement to conventional techniques for some of the more difficult gas separations encountered in industry. The general category of adsorption applications includes separation of difficult-to-condense gas mixtures and removal of materials such as water and solvent vapors (present in low concentrations) from various process-gas streams. It is a necessary requirement, of course, that the adsorbent used exhibit good selectivity among the key mixture components or fractions to be separated. The fractionation of materials such as methane and ethylene with activated charcoal fits into this category, and intensive study has been given to use of the FCA process for separation of refinery light hydrocarbons. The data and correlations presented here are specific to this application.

Some of the methods and concepts used in the design of a continuous adsorption system differ from those applied for the older fixed-bed unit. In the FCA design, for example, finely divided activated char is handled as a fluidized solid in a multistage bubble-plate column. The gas to be separated is contacted with char in a continuous countercurrent tower operation closely analogous to that of a rectified (reboiled) oil absorber. Thus design of FCA columns requires stepwise plate calculations involving material and heat balances, phase equilibrium relations, and plate efficiencies—quite similar to calculations for design of fractionators handling vapor-liquid systems. This similarity and the indicated design methods served as guides to the mixture adsorption variables correlated: specific adsorption capacities, adsorption relative volatilities, and adsorption heats. The method of applying the vapor-mixture adsorption correlations is illustrated by sample calculations which parallel those for vapor-liquid equilibria.

GAS-ADSORPTION PHASE EQUILIBRIUM DATA AND CORRELATIONS

The first step in the light-hydrocarbon–adsorption study was the evaluation of adsorbents. Preliminary isotherm and attrition data indicated activated coconut chars to be the best available adsorbents for separating light hydrocarbons according to molecular weight. A special petroleum-derived char was subsequently developed which possessed adsorption-desorption-attrition properties substantially identical to those of the familiar Columbia *G* activated coconut charcoal. The data presented in this paper all pertain to light-hydrocarbons and steam on either Columbia *G* or the special char used for pilot plant studies (*11*).

A substantial quantity of mixture ad-

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*Adsorption isotherms and vapor-adsorbate data obtained by Esso Research and Engineering Company are given in tabular form in Appendix Tables A and B. Derivation of the basic correlating equation for the mixture data is available in Appendix A. These appendices are obtainable from the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., as document 4785 for $1.75 for microfilm or $2.50 for photoprints.

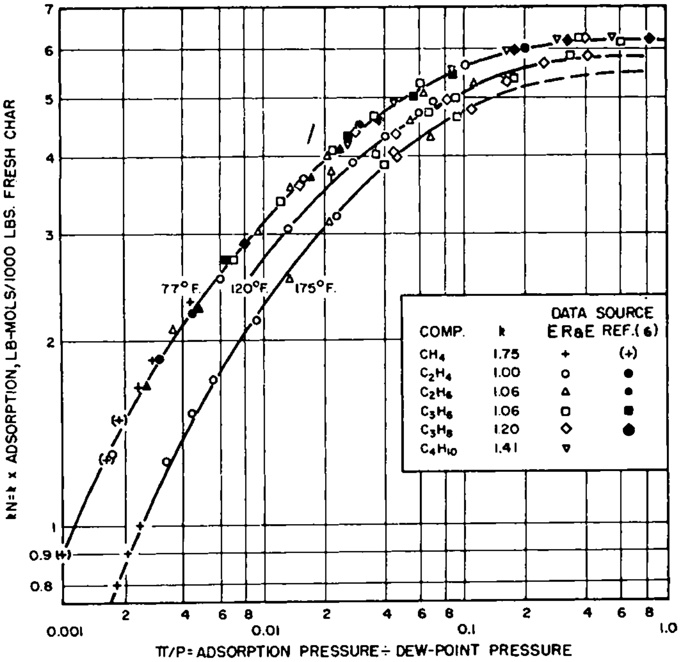

Fig. 1. Adsorption isotherm correlation: pure hydrocarbons on activated charcoal.

sorption data was obtained for design studies and for evaluation of pilot plant results on adsorptive separation of refinery residue gas. This gas contains H_2, N_2, CO, CO_2, H_2S, CH_4, C_2's, C_3's, and small amounts of C_4^+. Gas compositions vary appreciably in a multistage adsorber for separating a gas of this complexity. Thus a correlation of mixture adsorption was undertaken at an early stage of preliminary design studies. It was felt that the best approach to predicting mixture behavior would be through a correlation of pure-component adsorption data, and the correlations presented below for light-hydrocarbon adsorption on activated chars were developed with this line of approach.

Pure-component Absorption

A number of investigators have presented theories and correlations pertaining to pure-component adsorption. Among the most important contributions are works published by Langmuir (*5*), Brunnauer, Emmett, and Teller (*1*), Polanyi (*9*), and London (*7*). A convenient starting point for the authors' correlations was provided by the "adsorption-potential" concept derived by Polanyi and London. The combined derivations of these two workers gave a method for predicting adsorption of various pure components at different temperatures and pressures from a single pure-component isotherm, all pertaining to the same homopolar adsorbent such as charcoal. The adsorption-potential prediction method was modified by Dubinin et al. (*3*) to provide the more conveniently applicable form:

$$\left(\frac{T}{V}\log\frac{P}{\pi}\right)_v = \text{constant} \qquad (1)$$

On applying their data, Dubinin et al. found this relation to hold for various pure adsorbates on a single char at varying adsorption conditions.

Equation (1) is obviously not applicable when supercritical temperatures are involved. Most of the components in refinery residue gas, for example, would be above their critical temperatures at practical adsorption conditions. It was theorized, however, that the molecular packing of an adsorbed gas (above and below its critical temperature) should

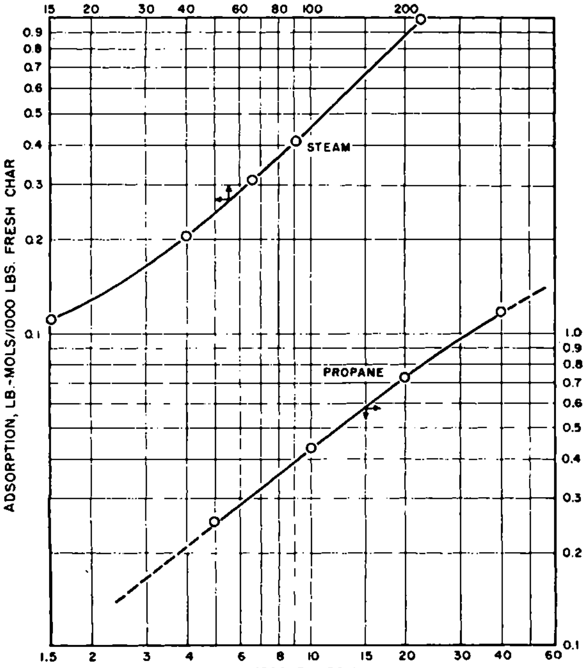

Fig. 2. Steam and propane adsorption on activated char at 500°F.

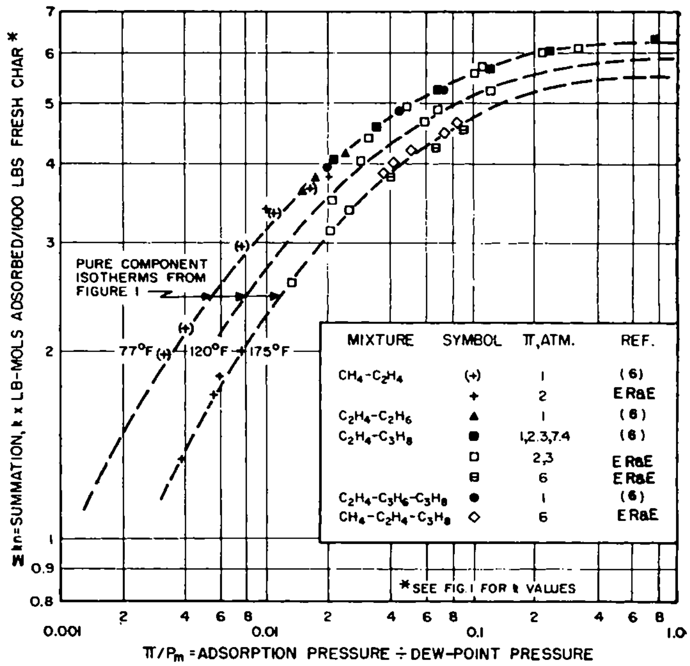

Fig. 3. Adsorption isotherm correlation: hydrocarbon mixtures on activated charcoal.

approach that of normal liquid, owing to the strong adsorption forces. Also, it was observed that the molal saturated-liquid volumes of light hydrocarbons are not too far apart and that the ratios of these volumes change very little with temperature. It was further presumed that extrapolated pressures at supercritical temperatures, obtained from a Clapeyron *P-T* plot, would satisfy the adsorption-potential relation derived by Polanyi. These considerations and subsequent testing of the data led to the following modification of Equation (1) as a basis for correlating pure light-hydrocarbon adsorption on the same char at temperatures above and below critical values:

$$(kN)_t = \phi(\pi/P) = N_\gamma' \qquad (2)$$

The correlation constant *k* (different for each component) and the constant-temperature restriction were provided to correct for imperfections in the theories and assumptions discussed above.

Pure-component adsorption data on C_1-C_4 hydrocarbons are correlated with Equation (2) in Figure 1. *kN* (constant times moles adsorbed on a constant weight of adsorbent) is plotted vs. "relative pressure" (π/P) at constant temperature. The data cover ranges of 77° to 175°F. temperature and 0 to 100 lb./sq. in. abs. pressure. The laboratory equipment and techniques used to obtain the data were substantially the same as described by Lewis et al. (*6*). These coworkers obtained similar data on Columbia *G* char at 77°F., which are included in Figure 1 for comparison.

Extrapolated vapor pressures, as previously described, are used in Figure 1 for supercritical temperatures. The dimensionless correlation constant *k* is defined as adsorption of the arbitrary reference component, ethylene, relative to that for the component in question at the same temperature and relative pressure; *k* for ethylene is always unity, by definition. The *k* values listed in Figure 1 were determined empirically from the 77°F. data. The various components all approach the average 77°F. correlation curve very closely with individual *k* values constant over the whole range of relative pressure. The same *k* values were used also for the 120° and 175°F. correlation isotherms. A minimum of data were obtained at the latter temperatures, and overlapping of the various components with respect to relative pressure is somewhat limited. As shown below, however, these correlations were found to be quite satisfactory when applied to prediction of mixture behavior.

Isotherm data on C_3 and steam are presented in Figure 2 for adsorption at 500°F., a representative temperature for desorption with steam. C_3's are substantially the only hydrocarbons present in significant amounts in the desorption zone of an adsorber for refinery C_1-C_2-C_3 separations. At the highly superheated conditions used for desorption in the pilot unit (*11*) (relative pressure in the range of 0.1), steam and light hydrocarbons were observed to adsorb substantially independently of each other at their respective partial pressures. The adsorption behavior of steam-hydrocarbon vapor near the dew point, however, is quite complex. Conditions of low superheat for such mixtures could be encountered in an adsorber refluxed with wet desorbate or in a low-temperature desorber steaming zone.

At total pressures in the range of 0 to 100 lb./sq. in. abs., it was found that adsorption of hydrogen, nitrogen, and carbon monoxide from refinery gas is negligible relative to hydrocarbon adsorption.

Gas-mixture Adsorption

A substantial amount of two- and three-component-mixture adsorption data on C_1, C_2, and C_3 hydrocarbons were obtained at 77°F. and 0 to 100 lb./sq. in. abs. Similar spot measurements were made at 120° and 175°F. These and similar data of Lewis et al. (*6*) are correlated in Figure 3 with a relation analogous to Equation (2) (Figure 1) for single components:

$$\left(\sum kn\right)_t = \phi(\pi/P_m) = N_r' \qquad (3a)$$

or

$$\sum n/N_r = 1 \qquad (3b)$$

The curves of Figure 1, representing the pure-component correlation iso-

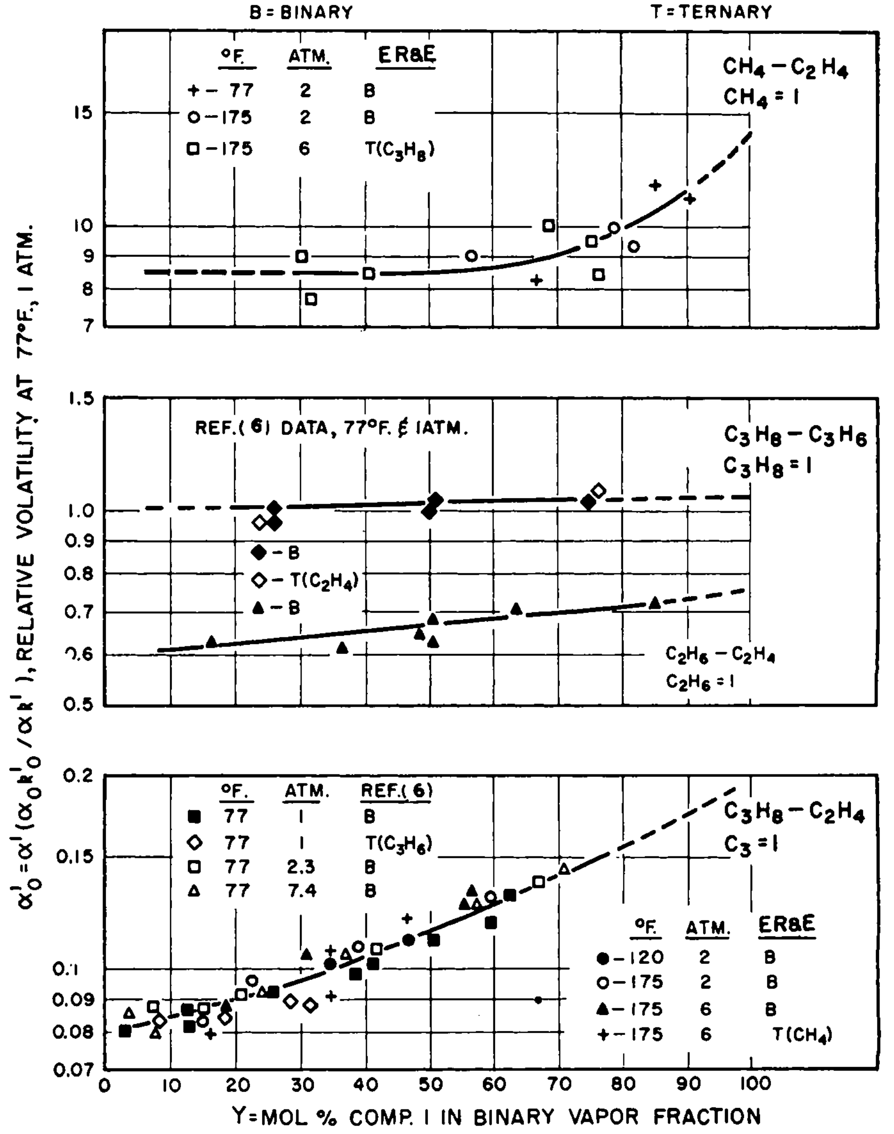

Fig. 4. Adsorption relative-volatility correlations: hydrocarbon mixtures on activated charcoal.

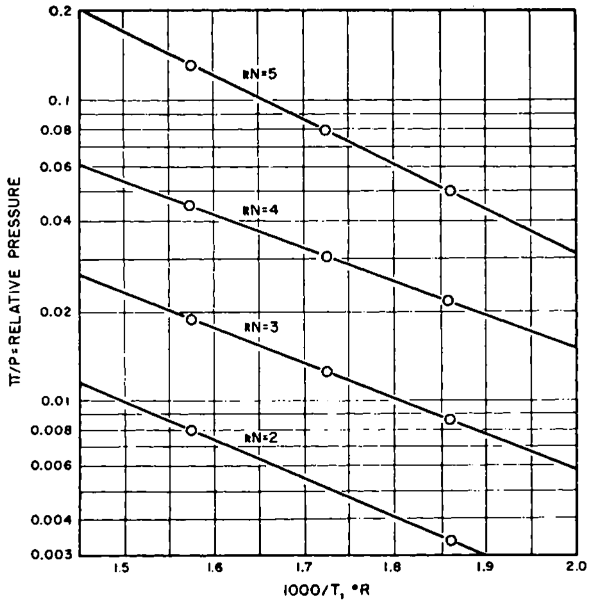

Fig. 5. **Light-hydrocarbon adsorption on activated char: extension of correlation isotherms**

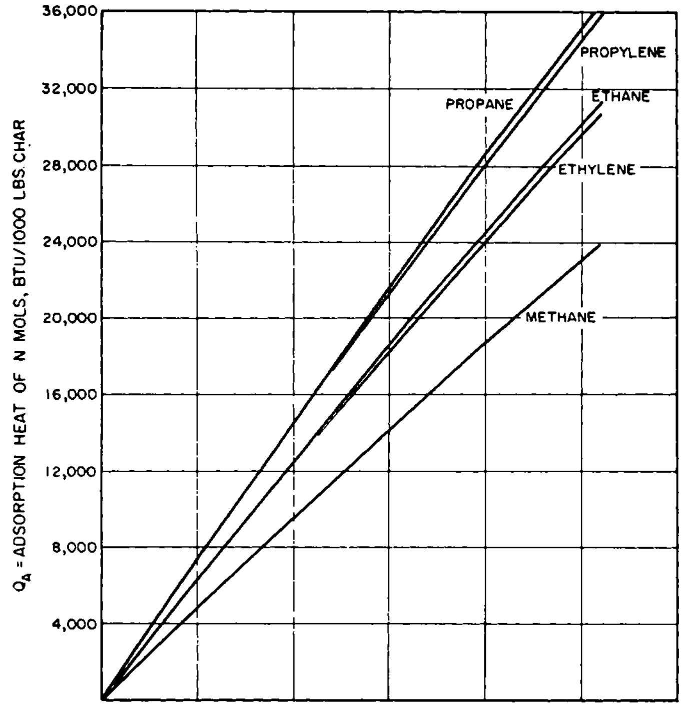

Fig. 6. **Approximate isothermal adsorption heats: light hydrocarbons on activated charcoal.**

therms, are superimposed on the mixture data in Figure 3. Thus the gas-mixture adsorption is indicated to be correlated satisfactorily by the pure-component isotherms of Figure 1. The same k constants derived from single-component data may be used for mixtures, $\Sigma\, kn$ being substituted for kN in Figure 1, and π/P_m for π/P.

The Figure 3 correlation obviously is not sufficient for a complete resolution of mixture adsorption. The adsorption relative-volatility concept (α') was introduced as the necessary supplement. The mixture adsorption relation observed by Lewis et al. (*6*) was very helpful in deriving a correlation basis for relative volatility:

$$\sum n/N_\pi = 1 \qquad (4)$$

[It is interesting to note the similarity of this relation and Equation (3b).] In order to develop a more fundamental correlation of relative volatility, mathematical expressions were sought for the adsorption isotherm correlation function ϕ for substitution in Equation (3a). A Freundlich type of relation (*4*) was substituted, Equations (3a) and (4) were combined, and the following α' correlation equation was developed:*

$$\alpha_0' = \alpha'\left(\frac{\alpha_0 k_0'}{\alpha k'}\right) = f\left(\frac{y}{y'}\right) \qquad (5)$$

This expression relates adsorption relative volatility to pure-component adsorption, vapor composition, and liquid relative volatility. Actually the Raoult-law value of the latter was indicated by the derivation, but the fugacity value was found to give a better correlation. Lewis and coworkers (*6*) correlated α' as a function of n/n' and pure-component adsorption.

Adsorption relative-volatility data on light-hydrocarbon mixtures are correlated in Figure 4, based on Equation (5). (The same data are represented in Figure 3.) α' values vary as much as threefold over the whole range of binary composition. The combined effects of temperature and pressure over the range covered produce the same order of variation. However, the data deviate by a maximum of about 15% from the averaged correlation curves. This deviation is not very significant in terms of estimated adsorber-char rates and separation stages.

The derivation of Equation (5) was based on binary-mixture adsorption. It was observed, however, that α' for two components is primarily a function of composition ratio (y'/y or n/n'), temperature and total pressure, and substantially independent of mixture complexity. This observation is in agreement with that of Lewis et al. (*6*). Thus Figure 4 may be applied for a given binary fraction of a complex mixture; e.g., k' and α' for each constituent relative to the same reference component are evaluated at the same π, t, and y/y' as for the complete mixture. The equilibrium adsorption of each constituent (n) from a multicomponent gas mixture can then be estimated with Figure 3†, Equation (5), and the following relation:

$$n' = \sum kn/\sum (ky/\alpha' y') \qquad (6)$$

Extension of Correlation Isotherms; Adsorption Heats

Clapeyron plots provide a means of interpolating or extrapolating the correlation isotherms. With reference to

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*On substitution of a Langmuir type of relation for the ϕ function, a very simple relative volatility expression is obtained: $\alpha' = k\alpha$. This relation applies quite well for close-boiling pairs, as borne out by the data in Figure 4. (Relative pressure for close-boiling pairs at constant π and t varies very little over the whole range of composition.)

†Figure 7, discussed below, is equivalent to Figures 1 and 3.

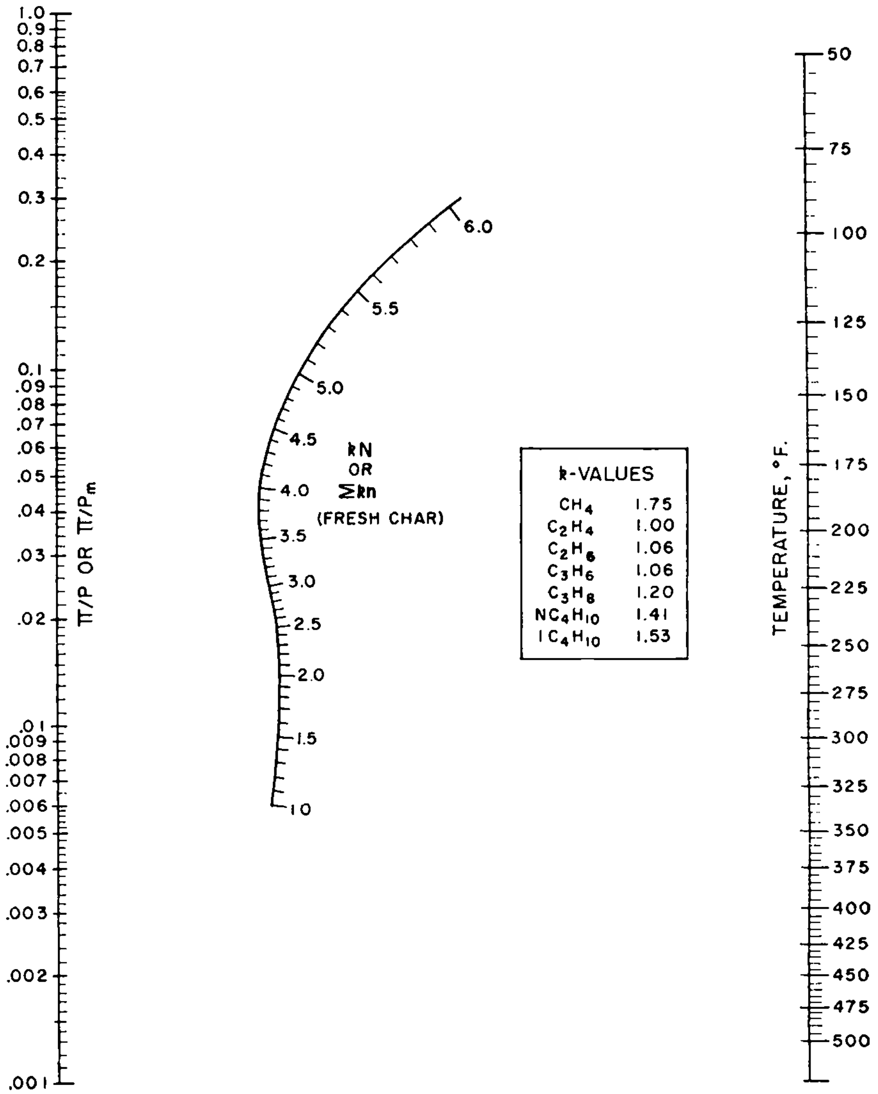
Figure 5, log relative pressure is noted to vary linearly with reciprocal absolute temperature at constant mass adsorption. As approximations of isothermal adsorption heats H_A for light hydrocarbons, slopes of the curves in Figure 5 were taken equal to $(H_L - H_A)/2{,}300R$ for all the hydrocarbons at the same value of kN. H_L is necessarily a calculated quantity estimated with the Clapeyron relation and may not be real or representative of the true liquefaction heat.

The estimated differential adsorption heat H_A decreases with increasing N. Integral adsorption heats were estimated as

$$Q_A = \int_0^N H_A \, dN \qquad (7)$$

Estimated integral adsorption heats for light hydrocarbons on Columbia G char are plotted in Figure 6 as a function of N. These values at $N = 1$ are roughly twice the corresponding heats of liquefaction. Heats of adsorption for steam, which were estimated similarly in the range of 0.3 to 1 relative pressure, are close to liquefaction heats, indicative of capillary condensation. For estimation of adsorption heats of mixtures, it has been assumed that adsorption heat for each component is the same as for the pure component at $N = n$ and that adsorption heats are additive.

Figures 1 and 5 are combined in the form of an alignment chart, Figure 7, to permit more convenient estimates of kN or Σkn at various temperatures and relative pressures.



k-VALUES	
CH_4	1.75
C_2H_4	1.00
C_2H_6	1.06
C_3H_6	1.06
C_3H_8	1.20
NC_4H_{10}	1.41
IC_4H_{10}	1.53

Fig. 7. Light-hydrocarbon adsorption on activated charcoal (Figures 1 and 5 combined).

Limitations to the Adsorption Correlations

Quite extensive data on pure components and mixtures were obtained for the 77°F. correlation isotherms. At the higher temperatures (referring to Figure 1) the various pure components overlap to a somewhat limited extent with respect to relative pressure. The isotherm correlations were found to be adequate for mixture predictions, however, as borne out by spot data covering the range of adsorption and rectification conditions for the pilot plant (Figure 3).*

Cadogan (*2*) applied his thesis data to evaluate the authors' correlations. He found the constant k values listed in Figure 1 to be satisfactory for correlating light hydrocarbons on Columbia G char at constant temperature and over a wide range of relative pressure. His data on an activated carbon derived from coal, however, indicated a variation in k with temperature. On applying the Figure 1 correlation to the extensive adsorption data of Ray and Box (*10*), the authors observed a drift in hydrocarbon k values with both temperature and relative pressure. In view of these considerations, the reader is warned against applying Figures 4, 6 and 7 for conditions far outside the data range, other than for rough approximations, limited to 250°F. and 250 lb./sq. in. In a wide range of adsorption conditions the Figure 7 correlation no doubt should allow for variations in k values with temperature and relative pressure. These variations could be handled conveniently with alignment charts. Furthermore, as suggested by the derivations made in developing Equation (5), a varying k may be more satisfactory than k' for correlating adsorption relative volatility.

It is interesting to note that adsorption relative pressure is equal to Σx, estimated by Raoult's Law. This term may be considered as the total mole fraction of gases dissolved in a nonvolatile liquid at the same equilibrium gas composition, temperature, and total pressure as for the adsorption system considered. These considerations and the original "adsorption potential" or work concept of Polanyi (*9*) suggest the use of Σx estimated by the fugacity method, rather than relative pressure, for isotherm correlations. The fugacity method was tested and found to give correlation as good as but no better than relative pressure for both pure components and mixtures. As mentioned previously, however, fugacity α was substituted for the Raoult's Law value in Equation (5) in order to improve the Figure 4 correlation. The fugacity α value would have appeared in the derivation if fugacity Σx had been used for the isotherm correlations. Equilibrium liquid mole fractions might provide a satisfactory basis for a more general correlation of gas adsorption, by use of actual vapor-liquid data or Σx estimates based on fugacities and allowance for nonideal liquids.

Sample Calculations

Data and calculated results on equilibrium adsorption from a hypothetical gas mixture are summarized in Table 1. The first column in the table gives the equilibrium gas composition. The adsorption conditions are 6.5 atm. abs. pressure and 160°F. The following sample calculations

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*The correlation methods should apply for other adsorbents, possibly even polar solids, as the correlation term k could allow for variation in adsorbate polarity. A new set of k values would have to be determined for each adsorbent.

demonstrate the suggested method of applying the correlations: $\Sigma y/P = 0.0071$ (Table 1); $\pi/P_m = 6.5(0.0071) = 0.0461$; $\Sigma kn = 4.13$ (Figure 7). Sample calculations of values in Table 1, with CH_4 used as an example: $P = 485$ atm. (Ref. *8*); $\pi/P = 0.0134$; $N_\pi = 1.56$ (Figure 7). Similarly, $N_\pi' = 4.15$ (pure ethylene adsorption at 6.5 atm. and 160°F.); $k' = 4.15/1.56 = 2.66$. Similarly, $k_0' = 3.25$; $\alpha/\alpha_0 = 0.72$ (Ref. *8*); $\alpha'/\alpha_0' = 0.59$ [Equation (5)]*; $y/(y + y') = 0.8$; $\alpha_0' = 10$ (Figure 4); $\alpha' = 0.59\ (10) = 5.9$; $n/n' = 0.4/(0.1 \times 5.9) = 0.68$ [α' definition]; $k = 1.75$ (Figure 7); $kn/n' = 1.18$; $\Sigma kn/n' = 11.25$ (Table 1); $n' = \Sigma kn/\Sigma(kn/n') = 0.37$ [Equation (6)]; $n = 0.37\ (0.68) = 0.25$ lb.-mole CH_4 adsorbed/1,000 lb. fresh char.

Similarly, n is calculated for each of the other mixture constituents to obtain the equilibrium adsorption of each component on the fresh char represented by Figure 7 (right-hand column of Table 1). Note that the adsorption of inert gas (H_2, N_2, CO) is negligible and was assumed to be zero in the sample calculations. Adsorption relative volatilities for deactivated chars were found to vary insignificantly over an activity range of 75 to 100%. Thus n values for fresh char multiplied by char activity give satisfactory estimates of mixture adsorption on deactivated chars. Pure-component adsorption at atmospheric conditions, relative to that on fresh char, provides a satisfactory index of adsorbent activity. The method of estimating adsorption heats is described in the discussion of Figure 6.

TABLE 1. SAMPLE DATA AND CALCULATION RESULTS ON MIXTURE ADSORPTION

Comp.	y	P	100 y/P	N_π	α/α_0	α_0'	α'	n/n'	k	kn/n'	n
H_2, N_2, CO	0.25	—	0	—	—	—	—	—	—	—	0
CH_4	0.40	485	0.083	1.56	0.72	10.0	5.90	0.68	1.75	1.18	0.25
C_2H_4	0.10	137	0.073	4.15	1.00	1.00	1.00	1.00	1.00	1.00	0.37
C_2H_6	0.15	89	0.169	4.30	1.10	0.68	0.80	1.88	1.06	1.99	0.70
C_3H_8	0.10	26	0.385	4.77	1.63	0.11	0.17	5.90	1.20	7.08	2.18
Totals	1.00		0.710							11.25	3.50

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NOTATION

f = function of y/y' or Y, Equation (5)

H_A = differential isothermal adsorption heat at N, obtained from slope of log π vs. $1/T$ at constant N, B.t.u./lb.-mole

H_L = isothermal heat of liquefaction obtained from slope of log P vs. $1/T$, B.t.u./lb.-mole

k = adsorption isotherm correlation constant, defined as N_r'/N_r

k' = N_π'/N_π. The term N_π represents component 1 in Figure 4.

N = equilibrium adsorption from pure vapor at π and t, lb.-moles/1,000 lb. adsorbent

N_r = N at same relative pressure (and temperature) as for an equilibrium vapor mixture or a reference component

N_r' = N_r for arbitrary reference component (ethylene) = Σkn or kN at r and t

N_π = N at the same pressure (and temperature) as for a mixture

N_π' = N_π for reference adsorption relative-volatility component

n = equilibrium adsorption of one component from a vapor mixture, lb.-moles/1,000 lb. adsorbent (n represents component 1 in Figure 4).

n' = n for reference adsorption relative-volatility component

P = equilibrium vapor pressure of pure liquid at t, atm.; values at supercritical temperatures obtained by extrapolation, log P vs. $1/T$; values used for correlations obtained from Maxwell (*8*)

P_m = dew-point pressure of equilibrium-adsorption vapor mixture at t, based on Raoult's Law; $P_m = 1/\Sigma(y/P)$, atm.

Q_A = integral isothermal adsorption heat of N [Equation (7)], B.t.u./1,000 lb. adsorbent

r = relative pressure, π/P or π/P_m

R = perfect-gas law constant = 1.99 B.t.u./(lb.-mole)(°R.)

t, T = temperature of equilibrium adsorption system, °F. and °R., respectively

v = equilibrium adsorption of pure vapor, expressed as saturated liquid volume at t, cc./g. adsorbent

V = molal saturated liquid volume of pure component at t, cc./g.-mole

x = equilibrium liquid mole fraction at y, π, and t = component 1 in Figure 4

x' = x for reference relative volatility component

y = mole fraction of one component in adsorption vapor mixture = component 1 in Figure 4

y' = y for reference relative-volatility component

Y = mole fraction in a binary fraction of a vapor mixture = $y/(y + y')$

α = liquid relative volatility = $yx'/y'x$ at π, t; fugacity values obtained from Maxwell (*8*) used in Figure 4

α' = adsorption relative volatility at Y, π, and t, defined as $yn'/y'n$

π = total absolute pressure of equilibrium adsorption system, atm.

Σ = summation of all mixture quantities

ϕ = adsorption-isotherm correlation function of relative pressure at constant t; same for Equations (2) and (3*a*)

Subscripts

m = a mixture quantity

0 = arbitrary standard conditions of π = 1 atm. and t = 77°F.

r = a pure-component adsorption value at the same relative pressure and temperature as for a mixture or another pure component

v = constant v

t = constant t

π = a pure-component adsorption value at the same total pressure and temperature as for a mixture

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*Before adsorber-design calculations, it is convenient to prepare constant-pressure working plots of α'/α_0' vs. temperature by application of Equation (5). This procedure minimizes calculations on N_π, k', α/α_0, etc.