

# The Study of Multicomponent Gas-Solid Equilibrium at High Pressures by Gas Chromatography:

## Part II. Generalization of the Theory and Application to the Methane-Propane-Silica Gel System

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The mathematical relation for the retention volume for elution chromatography has been extended to include the case of a multicomponent elution gas mixture in which all the components are adsorbed appreciably on the adsorbent. The total adsorption, component adsorption, and the  $K$  values or the ratio of the gas-phase concentration to the adsorbed-phase concentration for each component are related to the retention volume for the components as measured by a technique which distinguishes the molecules in the elution gas from those in the perturbing sample. Radioactively traced hydrocarbons are used in the application to obtain the retention volumes appropriate for the theory.

The relations derived were applied in studying the adsorption of methane-propane mixtures on silica gel up to a pressure of 1,000 lb./sq. in. abs. The internal consistency of the propane adsorption data with the propane infinite dilution data and the methane data with the pure methane adsorption data obtained by a gravimetric method is demonstrated.

In a preceding paper (2) the applicability of gas-solid chromatography to the measurement of  $K$  values or the ratio of the gas to adsorbed-phase concentration of solutes at essentially infinite dilutions in an appreciably adsorbed pure component was shown. A literature review on publications related to this paper has been presented elsewhere (1, 2).

The purpose of this paper is to extend the theory of gas-solid chromatography to include the case of multicomponent elution gas mixtures, each component of which is appreciably adsorbed. The extension refers to the case in which the perturbation components are distinguishable from the elution gas components. In the foregoing studies, the radioactively traced isotopes of the components in the elution gas are used to provide the distinguishability.

The final working equation presented in the preceding paper (2) for the case of a solute at essentially infinite dilution in the gas-solid system was as follows:

$$K_i = \frac{ZRTw}{\pi(V_{Ri}^0 - V_g)} \quad (1)$$

It is recalled that the major assumptions involved in Equation (1) were as follows: linear adsorption isotherm, large number of theoretical plates, small sample to column volume ratio, constant plate characteristics, constant partition coefficient, and pointwise equilibrium.

In order to extend the applicability of Equation (1) to mixture elution gases, it must be noted that the equation

was derived for a solute at infinite dilution in the carrier gas so that the distinguishability condition required for the general equations does not arise (1). If the solute injected is a radioactively tagged isotope of a nonradioactive component which is present in the elution gas, then the actual sample molecules injected could be detected by an ion chamber electrometer, or similar device for detecting radioactive material. Thus, a small sample with physical properties identical to those of a component of the elution gas would be at essentially infinite dilution in the column, and Equation (1) should again be valid, that is if the conditions described in the infinite dilution treatment of reference 2 are fulfilled. Through the use of minute perturbations, low pressure gradient, constant temperature, and appropriate column length, etc., the assumptions listed should be satisfied as in reference 2. The assumption of pointwise equilibrium has been studied by Stalcup and Deans as reported by Stalcup (5) and validated for nonpolar gas-liquid systems by Stalcup and Kobayashi (7) and by Koonce (3).

At this point, the overall validity of the proposed method rests upon the demonstrated internal consistency of the mixture, the pure component, and the infinite dilution data since static equilibrium data for a comparable system are not available.

A value for the total moles adsorbed is obtainable from the elution data and Equation (3) below. With the assumptions of Equation (1) in mind, the following solution is offered for the case of mixture elution gases using tagged samples.

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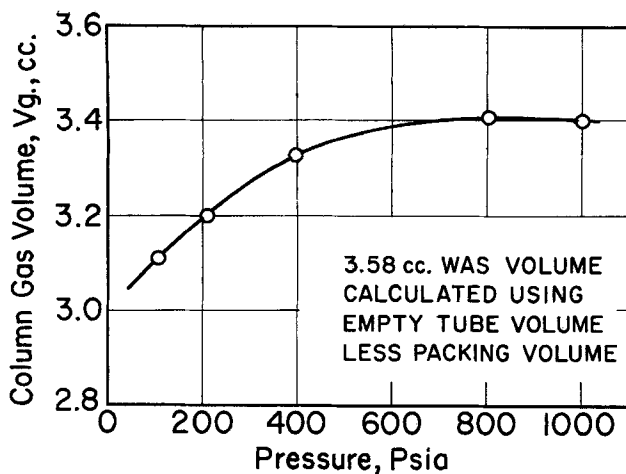


Fig. 1. Column gas volume measured with radioactive methane retention volume vs. column pressure.

Since there is no fixed liquid on the packing, the sum of mole fractions of adsorbed elution gas components must equal 1:

$$\sum_{i=1}^N x_i = 1.0$$

Using Equation (1) and the definition of  $K_i$ , one may express  $x_i$  as

$$x_i = \frac{y_i \pi (V_{Ri}^{**} - V_g)}{Z R T w}$$

where  $V_{Ri}^{**}$  is the corrected retention volume for the tagged sample, but  $w x_i = w_i$ , and  $\sum_{i=1}^N w_i = w$ , so that

$$w_i = \frac{y_i \pi (V_{Ri}^{**} - V_g)}{Z R T} \quad (2)$$

and the total moles adsorbed

$$w = \frac{\pi}{Z R T} \sum_{i=1}^N y_i (V_{Ri}^{**} - V_g) \quad (3)$$

Thus, by measuring the retention volumes of radioactive samples of all the components of the elution gas, the total moles as well as the moles of each component adsorbed can be calculated.

Now, since  $w$  is known, all the  $K_i$  can be calculated from Equation (1). By rearranging Equations (3) and (1) into the following form, one need not calculate  $w$  explicitly to obtain the  $K$  values:

$$K_i = \frac{w Z R T}{\pi (V_{Ri}^{**} - V_g)} = \frac{1}{(V_{Ri}^{**} - V_g)} \sum_{j=1}^N y_j (V_{Rj}^{**} - V_g) \quad (4)$$

or

$$K_i = y_i + \sum_{j=1, j \neq i}^N y_j \frac{(V_{Rj}^{**} - V_g)}{(V_{Ri}^{**} - V_g)} \quad (5)$$

Equations (3) and (5) are proposed for calculating the adsorption isotherms and equilibrium distribution coefficients of multicomponent gas mixtures, subject to the same assumptions as Equation (1). There is the additional assumption that the C-14-tagged samples have the same physical properties, namely distribution coefficients, and hence retention volumes, as the untagged mixture components. This assumption has been verified over the temperature range of this study by running both radio-

active and thermal conductivity peaks at infinite dilution and obtaining equal retention volumes. When quantum effects become appreciable at very low temperatures, discrepancies between the tagged and untagged molecules should appear.

## EXPERIMENTAL APPARATUS

The experimental equipment used in this study has been described elsewhere (3). It was the same as that described in the preceding paper (2) with one added feature. An ion chamber detector with a vibrating reed electrometer amplifier was used to detect the perturbation of the radioactive samples. Since the ion chamber required a purge gas, the carrier gas flow rate was measured with an orifice meter calibrated against the soap bubble flowmeter. Elution gas composition as well as atmospheric pressure and temperature were taken into consideration for the calibration. The mercury levels of the flowmeter were read with a high precision cathetometer.

The two gas mixtures used were made up by pumping liquid propane into cylinders pressurized with methane, then heating the cylinder at one end for several days to assure complete mixing. The two mixtures used were analyzed by gas chromatography to be 2.31 and 4.72 mole % propane in methane. The mixture analyses were repeated several times, with the relative deviation from the mean composition being less than 0.5%.

## FREE GAS VOLUME DETERMINATION

The gas volume  $V_g$  used in calculating the mixture data was determined as follows. With pure methane as elution gas, radioactive methane was injected as sample. Since in this case both gas and adsorbate are pure methane, the  $K$  value or distribution coefficient for the sample is 1, as C-14 methane has the same physical properties as normal methane. Thus, if  $V_{Ri}^{**}$  is measured and  $K$  is taken as 1, Equation (1) can be used to calculate  $V_g$ , since the amount adsorbed had been determined previously (2). The gas volumes measured in this way are plotted in Figure 1. This method of obtaining  $V_g$  is recommended over either calculating it directly or using the helium retention data, if the necessary equipment is available and if the pure component isotherm is known beforehand for the elution gas. The pressure variation shown in Figure 1 may be related to that observed by Tiller (8) in filtration studies. Further work will be needed to develop our understanding of the phenomenon.

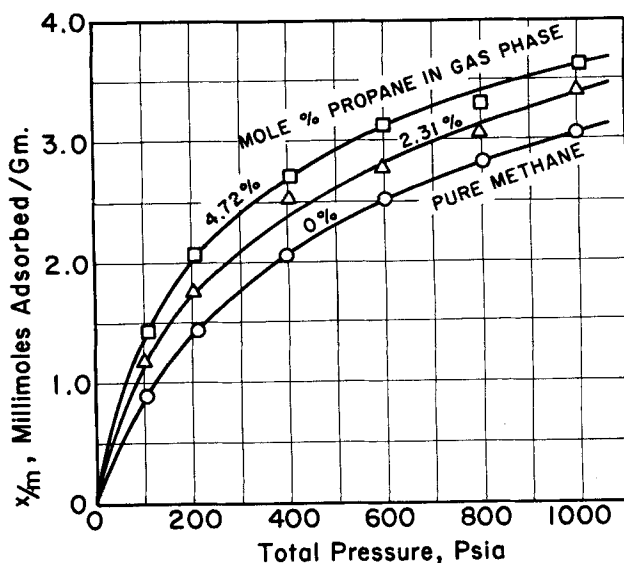


Fig. 2. Total adsorption from methane-propane mixtures vs. pressure on silica gel at 20°C.

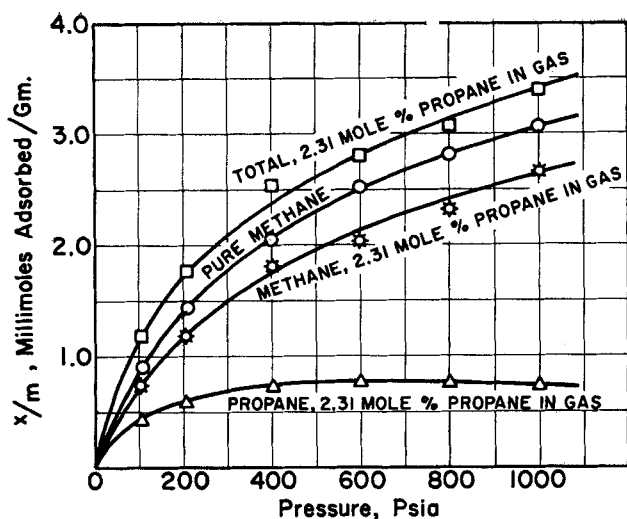


Fig. 3. Comparison of various adsorption isotherms on silica gel at 20°C.

### MIXTURE RESULTS

It is felt that the mixture data run in this study are offered to demonstrate the validity of the mixture theory presented in the theoretical section. All the runs were made at 20°C. with the two mixtures described previously.

Adsorption isotherms calculated from Equation (2) are plotted in Figures 2, 3, and 4. The data for propane in the mixtures show very little scatter in both cases, while the methane data show somewhat greater scatter. The scatter of the methane data is explained by the closeness of the methane retention volumes and the free gas volume, resulting in sensitive variations of the methane adsorbed and its  $K$  values. This same slight scatter appears in Figure 2, where the mixture isotherms are compared with the pure methane. The relative deviation of the methane data from the smoothed values is 5%. The comparison shows that the presence of propane increases the total amount adsorbed, but the incremental increase decreases with increasing propane concentration in the gas. Figures 3 and 4 show that the methane and propane molecules are competing for the available sites, since the amounts of methane adsorbed from the mixtures are less than those adsorbed with pure methane. It should be noted also that the total adsorptive capacity is increased over pure methane for the mixtures containing propane,

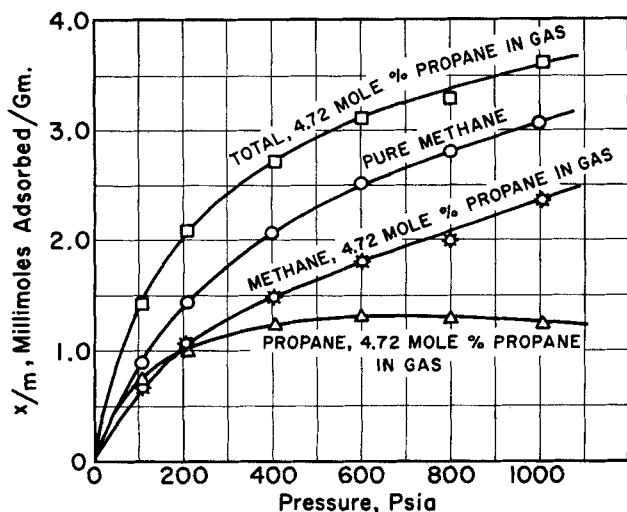


Fig. 4. Comparison of various adsorption isotherms on silica gel at 20°C.

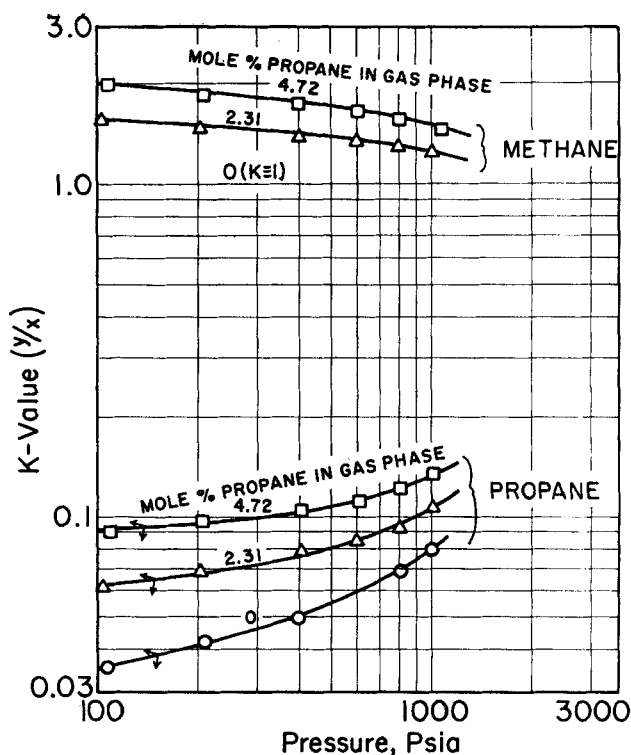


Fig. 5.  $K$  value vs. pressure for methane and propane in the system methane-propane-silica gel at 20°C.

again in qualitative agreement with Lewis et al. (4) for their atmospheric pressure data on the same system.

$K$  values for methane and propane calculated from Equation (4) are plotted in Figure 5. The original data from which the  $K$  values were obtained are reported elsewhere (1). These  $K$  values show very little scatter, and even the methane values fall very close to the smooth curve. It can be seen from the plot that the  $K$  values for both components are tending toward one, consistent with the previously made postulate of the existence of a critical pressure for adsorption (2).

The  $K$  values for methane and propane are plotted vs. composition in Figures 6 and 7, respectively. Severe

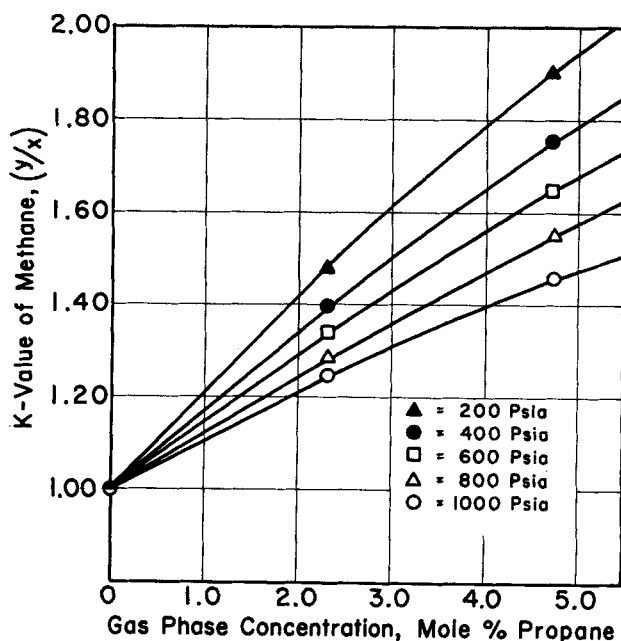


Fig. 6.  $K$  value of methane vs. concentration along isobars for system methane-propane-silica gel at 20°C.

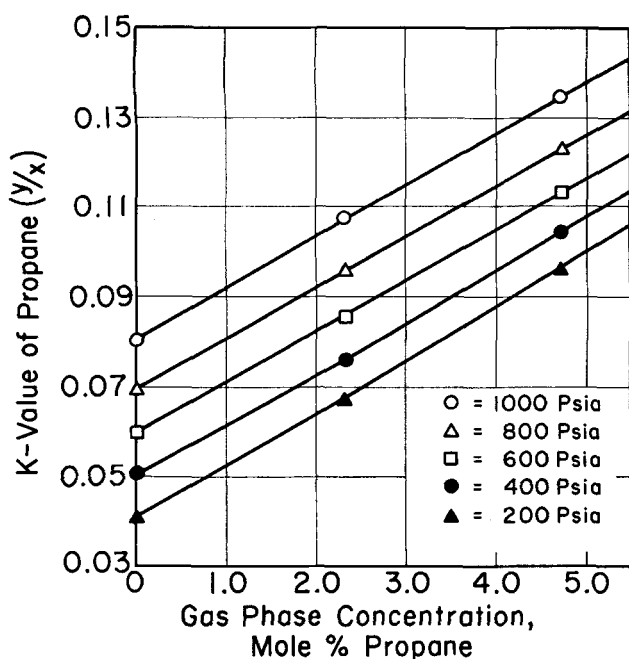


Fig. 7.  $K$  value of propane vs. concentration along isobars for system methane-propane-silica gel at 20°C.

composition dependence is shown by these curves, particularly for the propane. The slight scatter shown by the cross plots is verification of precision of the method.

In Figure 6 the  $K$  value of methane extrapolates smoothly into the  $K = 1.00$  point located at 0 mole % propane in the gas phase. This is to be expected, since the  $K$  value of methane should be 1.00 in the pure methane-silica gel system.

On the other hand the  $K$  values of propane at finite concentrations of propane in the elution gas should be consistent with the infinite dilution  $K$  values for propane in the methane-silica gel system as reported in references 1 and 2. Figure 7 clearly demonstrates that this is so. The methane concentration  $K$  values show a slight curvature over the range covered in this study.

Reference to the retention volumes presented elsewhere (1) show that thermal conductivity and the radioactive retention volumes for propane are not the same in the mixture but they are the same when only nonradioactive propane appears in the perturbation. This observation is consistent with the observations made by Stalkup and Kobayashi (7) and Koonce (3) for the gas-liquid system. The interpretation of this phenomenon for the gas-solid system is presently being developed.

## CONCLUSION

The internal consistency and consistency of the mixture data with the infinite dilution data lend support to the applicability of the technique to the determination of high-pressure adsorption  $K$  values for mixtures. The consistency of the mixture isotherms with the pure methane data and with the infinite dilution propane data appear to substantiate the theory proposed for the application of the chromatographic technique to the determination of adsorption isotherms, particularly to multicomponent mixtures. The  $K$  values determined chromatographically both for infinite dilution and finite concentration are characteristic of the adsorption equilibrium systems studied. The consistency of the  $K$  value data in both cases offers further support to the assumption of equilibrium and negligibility of the effect of peak asymmetries (1).

Application of the chromatographic technique with radioactive samples to the study of mixtures through the

theory developed here is particularly encouraging. The  $K$  values and adsorption isotherms agree quite well with the pure gas and extend smoothly to the infinite dilution case for the solutes. Thus, the necessity of calibrating the system volume and sampling of the gas phase can be eliminated from the study of mixture adsorption. However, it must be noted that the technique as developed here is applicable only to gaseous systems and would have to be studied further before being applied to liquids or two-phase gas-liquid systems.

The chromatographic study of multicomponent adsorption systems has been shown to be consistent with data obtained by a gravimetric method (2) and infinite dilution adsorption  $K$  values. The procedure discussed should provide a rapid, accurate method for further investigations into adsorption equilibrium.

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## NOTATION

- $K$  =  $K$  value,  $y/x$ , ratio of mole fraction in gas to that in absorbate  
 $P$  = absolute pressure  
 $R$  = gas constant/mole  
 $T$  = absolute temperature, °K.  
 $V$  = gas velocity, cm./min. volume/mole  
 $V_g$  = total accessible gas volume of flow system, cc.  
 $V_R$  = retention volume by thermal conductivity detection corrected to column conditions, cc.  
 $V_R^{**}$  = retention volume by radioactive detection corrected to column conditions, cc.  
 $\frac{X}{M}$  = specific adsorption, millimoles adsorbed/g. silica gel  
 $Z$  = compressibility factor,  $PV/RT$ , for gas  
 $i$  = subscript denoting component  $i$   
 $t_r$  = retention time by thermal conductivity detection, time from sample injection to peak emergence, min.  
 $t_r^*$  = retention time by radioactive detection, min.  
 $w$  = total moles adsorbed on column, moles  
 $w_i$  = moles of component  $i$  adsorbed on column, moles  
 $x_i$  = mole fraction of component  $i$  in adsorbate  
 $y_i$  = mole fraction of component  $i$  in gas phase  
 $\pi$  = total column pressure, lb./sq. in. abs. or atm.

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