Experimental Determinations of the Molar Heat and Entropy of Adsorption and the Activity Coefficient of the Adsorbed Phase for the Methane-Ethane-Silica Gel System

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Calculations of the molar heat and entropy of adsorption for pure methane and pure ethane on silica gel at 25°C. show the heterogeneity of the adsorbent when plotted as functions of the spreading pressure. Plots are given for the activity coefficient of methane and ethane in the adsorbed phase based on experimental data for the entire range of compositions at 25°C. up to a maximum pressure of 1,400 lb./sq.in.abs. Similar results were obtained at 5, 15, and 35°C. The activity coefficients deviate from unity at intermediate compositions.

Adsorption may be classified based on the adsorbent, as nonpolar-homogeneous solid (graphatized carbon), nonpolar-heterogeneous solid (activated carbon), polar-heterogeneous solid (silica gel or alumina), and other (metallic or ionic solids); and based on the adsorbed (binary) phase, as (a) one or both polar, (b) one or both unsaturated and polar, and (c) one or both saturated and nonpolar. For (a) and (b) the activity coefficient in a liquid phase usually deviates from unity; for (c) this large nonideality seldom occurs. In adsorption the solid is an additional determinant of the activity coefficient at low coverage for (a) and (b) when the polar nature or the heterogeneity of the solid may enhance the nonideality or negate the nonideality; at high coverage the adsorbed phase approaches liquid behavior. Large nonideality for (c) can only be the result of the effect of the solid.

The adsorption of methane-ethane on activated carbon (*11*) at 1 atm. was found to be in agreement with the ideal case (*9*). The same gas mixture on silica gel has been studied here because there are only limited data on this system and because the highly polar and heterogeneous silica gel should cause deviations from ideality. The expected deviations were found in the experimental activity coefficients of the adsorbed phase. The heterogeneity of the adsorbent was emphatically confirmed by the change of the heat of adsorption with coverage of the adsorbent. The molar heat and entropy change of adsorption were determined for both pure components.

THEORETICAL

Amounts of Adsorption

From an analysis based on the concept of a three dimensional adsorption zone in which the potential field of the adsorbent and the adsorbate is appreciable, the authors have developed (*7, 8*) a method for the amount of adsorption from chromatographic measurements. Two definitions for the amount of adsorption are (*7*)

$$N^A(i) = v_2\, c_2(i) = [v_R(i) - (v_1 + v_d)]\, c_1(i) \qquad (1)$$

$$N^{GM}(i) = v_2\, [c_2(i) - c_1(i)] = [v_R(i) - (v_1 + v_d + v_2)]\, c_1(i) \qquad (2)$$

The total amount in the adsorption zone is given by Equation (1). Equation (2) gives the net amount in the adsorption zone with the consideration of molecular size. The v are determined experimentally or from computations of experimental measurements. Note that our notation uses i for the component, 1 for the gas phase, and 2 for the adsorbed phase.

Spreading Pressure Definition

At chemical equilibrium the Gibbs free energy of the gas phase is given by

$$dG_1 = \Sigma\, [\mu(i)\; dN_1(i) + N_1(i)\; d\mu(i)] = -S_1\; dT + v_1\; dP + \Sigma\mu(i)\; dN_1(i) \qquad (3)$$

and of the adsorbed phase

$$dG_2 = \Sigma\, [\mu(i)\; dN_2(i) + N_2(i)\; du(i)] = -S_2\; dT + v_2\; dP + \Sigma\mu(i)\; dN_2(i) + A\; d\pi \qquad (4)$$

Here $N_2(i)$ implies $N^A(i)$ given by Equation (1) and v_2 is the volume of the adsorption zone.

The adsorbed phase has one additional variable, the spreading pressure, π, compared to the gas phase due to the presence of the adsorbent. For multilayer adsorption the term ($A\; d\pi$) in Equation (4) becomes small compared to the other terms; at the limit of maximum thickness of the adsorbed phase the term is negligible and Equation (4) becomes the expression for a liquid phase.

At constant temperature Equations (3) and (4) reduce to

$$v_1\; dP = \Sigma N_1(i)\;\; d\mu(i) \qquad (3a)$$

$$v_2\; dP + A\; d\pi = \Sigma N_2(i)\;\; d\mu(i) \qquad (4a)$$

Solving for dP from Equations (3*a*) and (4*a*) and equating gives

$$A\; d\pi = \Sigma[N_2(i) - N_1(i)\;\, (v_2/v_1)]\;\, d\mu(i) = v_2\;\, \Sigma[c_2(i) - c_1(i)]\;\, d\mu(i) \qquad (5)$$

An alternative expression for Equation (5) may be derived by using Equation (2) and fugacity instead of chemical potential.

$$A\; d\pi = R\; T\; \Sigma\; N^{GM}(i)\;\, d\, \ln f(i) = R\; T\; \Sigma[N^{GM}(i)/f(i)]\;\, df(i) \qquad (5a)$$

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The integrated form of Equation (5*a*) at constant temperature is

$$(A\pi)/(RT) = \Sigma \int [N^{GM}(i)/f(i)]\ df(i)$$

$$= \Sigma \int_0^{f^o(i)} [N^{GM^o}(i)/f^o(i)]\ df^o(i) \qquad (6)$$

$$+ \Sigma \int_{f^o(i)}^{f(i)} [N^{GM}(i)/f(i)]\ df(i) \qquad (6a)$$

The integration may be carried out along two paths; either along an isotherm for a given gas phase composition using Equation (6), or at constant pressure from a pure component to a given composition using Equation (6*a*).

Molar Heat and Entropy of Adsorption

The enthalpy and entropy change on adsorption have been defined at constant spreading pressure by Hill (3). He showed that the heat of adsorption becomes identical to the enthalpy change only at the restriction of constant spreading pressure.

For pure component adsorption, Equations (3) and (4) reduce to

$$N_1\ d\mu = -S_1\ dT + v_1\ dP \qquad (3b)$$

$$N_2\ d\mu = -S_2\ dT + v_2\ dP + A\ d\pi \qquad (4b)$$

Taking the difference at constant spreading pressure yields the Clausius-Clapeyron equation

$$(\overline{v_1} - \overline{v_2})\ dP = (\overline{S}_1 - \overline{S}_2)\ dT \quad (\text{constant } \pi) \qquad (7)$$

The molar heat of adsorption, $\overline{Q}$, and the molar entropy change of adsorption are given by

$$\overline{Q} = -\Delta\overline{H} = \overline{H}_1 - \overline{H}_2$$

$$= -z\ R\ (1 - \overline{v_2}/\overline{v_1})\ [\partial \ln\ P/\partial\ (1/T)]_\pi \qquad (8)$$

$$\overline{\Delta S} = \overline{S}_2 - \overline{S}_1 = (\overline{H}_2 - \overline{H}_1)/T = \Delta\overline{H}/T \qquad (9)$$

The enthalpy and entropy changes as defined are negative quantities. The volume ratio in Equation (8) may be replaced by the concentration ratio (c_1/c_2) and therefore by [Equation (1)]

$$\overline{v_2}/\overline{v_1} = v_2/(v_R - v_1 - v_d) \qquad (10)$$

Equations (5*a*) and (12) combine to yield

$$A\ d\pi/(RT) = \Sigma N^{GM}(i)\ d\ \ln\ f(i)$$

$$= N^{GM}(t)\ \Sigma x^{GM}(i)\ [d\ \ln\ \gamma^2(i)$$

$$+ d\ \ln\ x^{GM}(i) + d\ \ln\ f^o(i)] \qquad (13)$$

At constant π, the terms $[\Sigma x^{GM}(i)\ d\ \ln\ x^{GM}(i)]$ and $[\Sigma x^{GM}(i)\ d\ \ln\ f^o(i)]$ are mathematically equal to zero. The Gibbs-Duhem relation for the adsorbed phase results

$$[\Sigma x^{GM}(i)\ d\ \ln\ \gamma_2(i)]_{\pi,T} = 0 \qquad (14)$$

Equation (14) states a necessary condition for activity coefficients and may be used to check the internal consistency of the data. There are two possible general cases for deviation of the activity coefficients from unity as governed by Equation (14).

1. monotonic deviation, either positive or negative.
2. maximum-minimum positive—negative sets, one or more, at intermediate compositions. For both cases, of course, the activity coefficient approaches 1.0 as the mole fraction of the component approaches 1.0.

For infinite dilution Equation (12) can be rewritten as

$$\gamma_2{}^\infty(i) = (P\ \gamma_1{}^\infty(i)/\{[x^{GM}(i)/y(i)]\ f^o(i)\})_{\pi,T} \qquad (12a)$$

RESULTS

The experimental data used for the calculations are given elsewhere (8).[*] Methane-ethane mixtures whose compositions are given in Table 1 were adsorbed on silica gel with a specific surface area of 803.5 sq. m./g. The adsorbed phase was assumed to be 8.0Å. thick. In the moderate pressure region the data were accurate within 1%; at pressures below 40 lb./sq.in.abs. and above 1,000 lb./sq.in.abs. the accuracy was no worse than 3%. In the calculation of the spreading pressure the amount of adsorption N^{GM} has little dependence on the assumption of the thickness of the adsorption zone, for the concentration of the adsorbent as a function of the distance from the solid surface becomes constant at about twice the collision diameter for this system (7).

TABLE 1. COMPOSITIONS OF GAS MIXTURES ANALYZED BY MASS SPECTROMETER (mole %)

Mixture:	1	2	3	4	5	6	7	8
CH_4	99.98	98.56	94.27	89.42	79.49	60.07	33.60	0.00
C_2H_6	0.02	1.44	5.58	10.58	20.51	39.79	66.40	99.94
air and others	—	—	0.15	—	—	0.14	—	0.06

The partial differential in Equation (8) is not defined at zero spreading pressure; therefore, the limit is taken as

$$[\partial \ln\ P/\partial(1/T)]_{\pi=0}$$

$$\equiv \lim_{\pi \to 0} [\partial \ln\ (P/\pi)/\partial(1/T)]$$

$$= \{\partial \ln\ [(A\ P)/(R\ T\ N^{GM})]/\partial(1/T)\}_{P=0}$$

$$= T - [\partial \ln\ (N^{GM}/P)/\partial(1/T)]_{P=0} \qquad (11)$$

Activity Coefficient of Adsorbed Phase

The activity coefficient of the adsorbed phase at constant temperature and spreading pressure may be defined as

$$\gamma_2(i) = \{f(i)/[x^{GM}(i)\ f^o(i)]\}_{\pi,T} \qquad (12)$$

Spreading Pressure

The spreading pressure was calculated by Equation (6) along an isotherm for each gas composition. Representative results at 25.00°C. are shown in Figure 1. The accuracy is the same as that given above. The spreading pressure rises sharply with pressure at lower gas phase pressure, but the rate decreases as the total pressure increases. The contribution of the surface energy term ($A\pi$) in the total Gibbs free energy [Equation (4)] becomes less and less at higher pressure. For a liquid phase supported on a solid, the ($A\pi$) term is negligibly small compared with the other terms and the usual expression for the Gibbs free energy results.

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[*] Detailed experimental results are available from University Microfilm, Ann Arbor, Michigan. Post Doctoral Monograph, S. Masukawa, Rice University (1967).

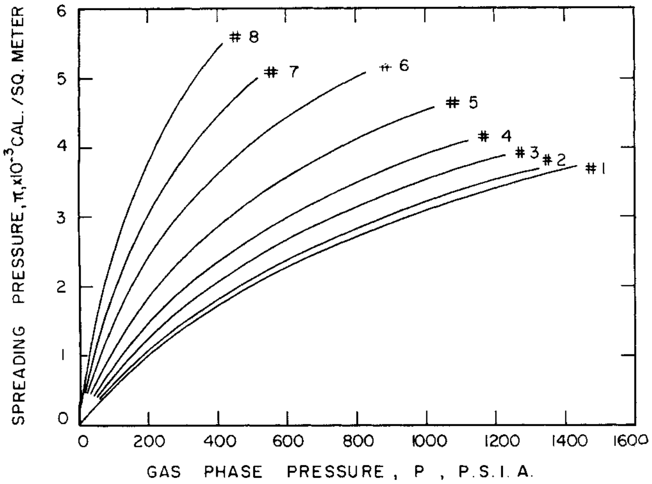

Fig. 1. Spreading pressure of adsorbed phase as function of gas phase pressure and gas mixture, methane-ethane-silica gel system at 25°C.

Heat and Entropy of Adsorption

The molar heat and entropy changes of adsorption for methane and ethane were calculated by Equations (8), (9), and (10) at several spreading pressures. The logarithm of the total pressure versus the reciprocal of the absolute temperature for various spreading pressures is given in Figures 2 and 3 for methane and ethane adsorption, respectively. Figure 4 gives the ratio of the molar volumes, $\bar{v}_2/\bar{v}_1$, for the 25.00°C. calculated by Equation (10). Although most determinations of the initial heat of adsorption assume the ratio to be zero at zero pressure, the results shown in Figure 4 indicate the assumption to be erroneous for lighter gases (here methane and ethane).

With an assumption of zero $\bar{v}_2/\bar{v}_1$, the heat of adsorption at zero pressure was calculated to be 3.70 and 6.09 kcal./mole for methane and ethane in this work. These values are comparable to those reported by Kiselev, et al. (*6*). Their results were 3.85 and 5.95 kcal./mole for methane and ethane adsorption on a silica gel of specific surface area 715 sq.m./g. at 20 to 90°C.

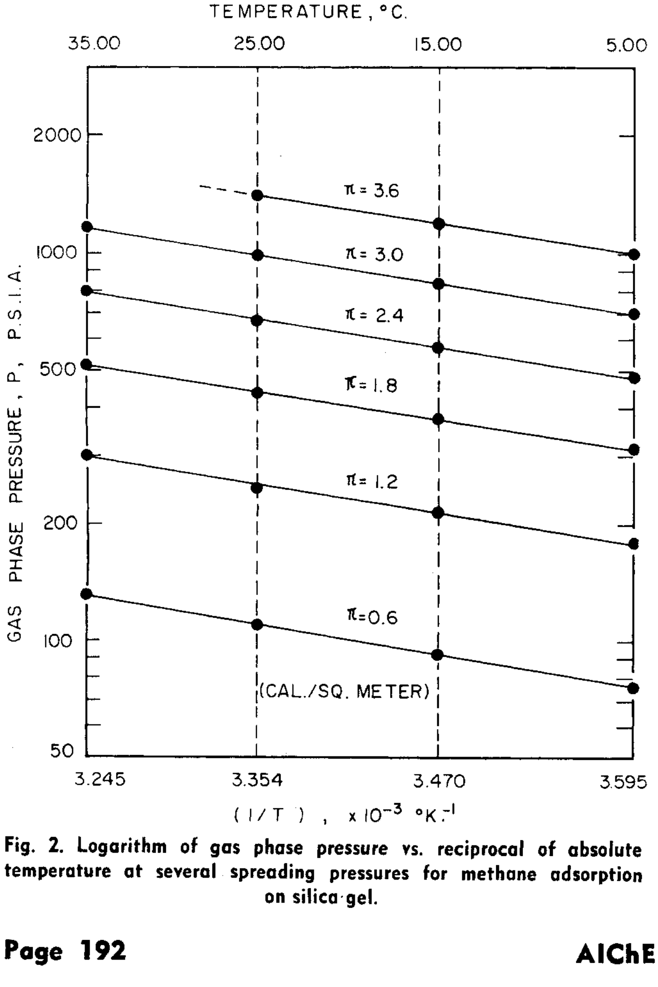

Fig. 2. Logarithm of gas phase pressure vs. reciprocal of absolute temperature at several spreading pressures for methane adsorption on silica gel.

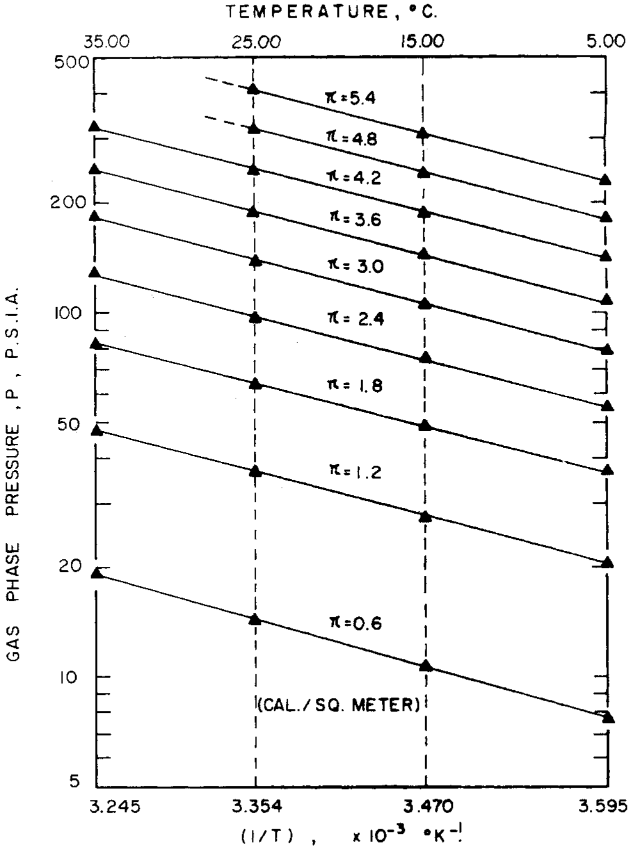

Fig. 3. Logarithm of gas phase pressure vs. reciprocal of absolute temperature at several spreading pressures for ethane adsorption on silica gel.

The enthalpy and entropy changes on adsorption calculated from Equation (8) at 25.00°C. for methane and ethane are shown in Figure 5. The uncertainty was ± 0.1 kcal./mole. With the actual $\bar{v}_2/\bar{v}_1$ the heat of adsorption at zero pressure was 3.06 and 5.99 kcal./mole for methane and ethane. The sharp decrease in magnitude of the enthalpy change at lower spreading pressures illustrates the existence of highly active parts on the solid surface even though the area fraction is rather small. Further evidence of the heterogeneity of the adsorbent silica gel is given by the existence of a maximum in the adsorbed volume per molecule reported elsewhere (*7*).

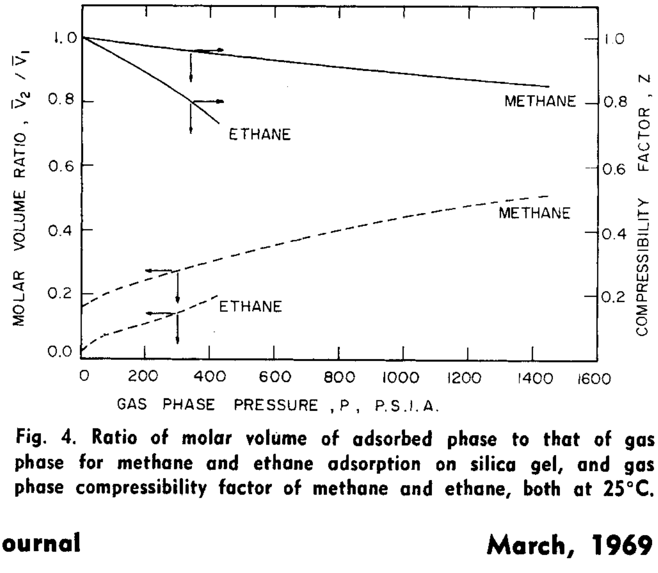

Fig. 4. Ratio of molar volume of adsorbed phase to that of gas phase for methane and ethane adsorption on silica gel, and gas phase compressibility factor of methane and ethane, both at 25°C.

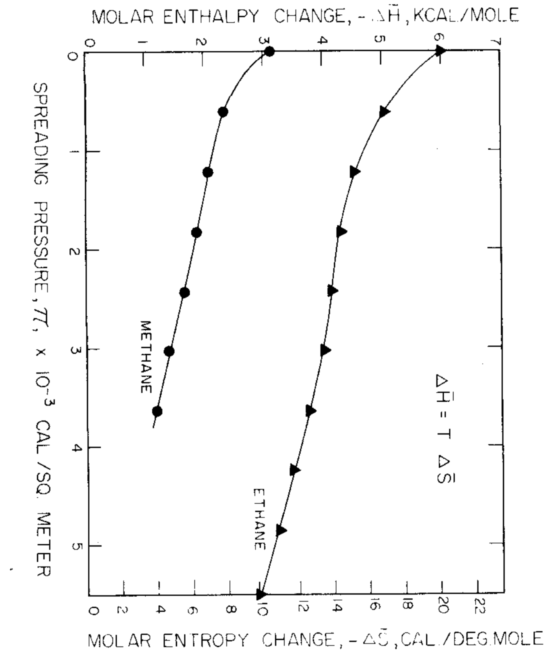

Fig. 5. Molar enthalpy and entropy changes on adsorption vs. spreading pressure, methane and ethane on silica gel at 25°C.

Activity Coefficient

The activity coefficient of the adsorbed phase was calculated by Equations (12) and (12*a*) at spreading pressures of 0.60, 1.80, and 3.60 × 10^{-3} cal./sq.m. The necessary gas phase fugacity data were obtained by the partial volume method (5) using the smoothed gas phase compressibility factors (7). Figure 6 shows the activity coefficients versus the adsorbed phase composition for the three spreading pressures at 25.00°C. Similar results were found at 5.00, 15.00, and 35.00°C. To our knowledge these are the first reported determinations of the activity coefficient of the adsorbed phase over the entire composition range. Sturdevant (*10*) obtained qualitatively similar positive and negative deviations for the 50-50 methane-propane-activated charcoal system at 30°C.

The maximum uncertainty in the activity coefficient occurs from errors in the composition at both ends of the composition range and is ± 3%. In the 10 to 90% composition range the uncertainty due to composition is less than 1%. An error in x^{GM} causes the activity coefficients for the two components to change in opposite directions. Error in $f(i)$ results from error in the calculated spreading pressure π, which is 1 to 2% at most at moderate pressures and no more than 3% at low and high pressures. The shifts in the activity coefficients from error in $f(i)$ are in the same direction. Error in f^0 is less for ethane than for methane and is of the same order of magnitude or less than the error for $f(i)$. A change in f^0 shifts the entire curve for that component. If all of the errors act in the same direction the total maximum error in the activity coefficient will be 5% only at the extremities of the composition range.

The Gibbs-Duhem relation is obeyed qualitatively in Figure 6 with type *ii* deviations; however, the test was not rigorously applied. The maximum and minimum of the activity coefficient are sharper at smaller spreading pressures and at lower temperatures. At high spreading pressures and temperatures the curves approach those of the usual type *i* deviations seen in liquid mixtures.

The physical image of spreading pressure is not as evident as that of the gas phase pressure or molecular density. Spreading pressure is related to fugacities and amounts of adsorption in a complicated manner. The heterogeneity of a solid surface directly affects the amount of adsorption and, therefore, the spreading pressure of the adsorbed phase. The restriction of constant spreading pressure on the activity coefficient given in Equations (12) and (12*a*) might transfer the heterogeneity effect to the activity coefficient. Another possible explanation for the nonideal behavior of this system may be the polar nature of silica gel, which would cause induced dipole moment (*1*, *2*) in the adsorbed ethane molecules thus resulting in nonideal interaction between the methane and ethane as compared to the interaction in a homogeneous or liquid phase. The nonideality of mixing is known to arise from the mutual interaction of unlike molecules or from the cross term in the mathematical expression (*4*). For even an almost ideal combination such as methane-ethane, deviations from ideality may occur when the adsorbent-adsorbate interaction affects the adsorbate-adsorbate interaction.

In fact, the interaction between adsorbed molecules and adsorbent is much larger than that among gas molecules in the free gas phase or liquid phase. For example, at 25°C. for ethane the enthalpy change on condensation is 1 kcal./mole while the enthalpy change on adsorption is about 3 to 6 kcal./mole. The effect of the polar, heterogeneous solid is sufficient to break the ideal mixing rule of the adsorbates for mixtures of lighter paraffins such as methane and ethane. At higher spreading pressures corresponding to higher coverage it is explained that the ideality of mixing of the adsorbates is restored for this system to some extent due to the partial shielding of the polar heterogeneous solid surface by the adsorbate molecules themselves.

CONCLUSIONS

The heat and entropy changes of adsorption were determined for methane and ethane on silica gel as functions of the spreading pressure at 25.00°C. The results indicated the heterogeneity of silica gel. The activity coefficient of the adsorbed phase was determined experimentally over the entire composition range for the methane-ethane-silica gel system. The activity coefficient deviates from unity over much of the composition range. The

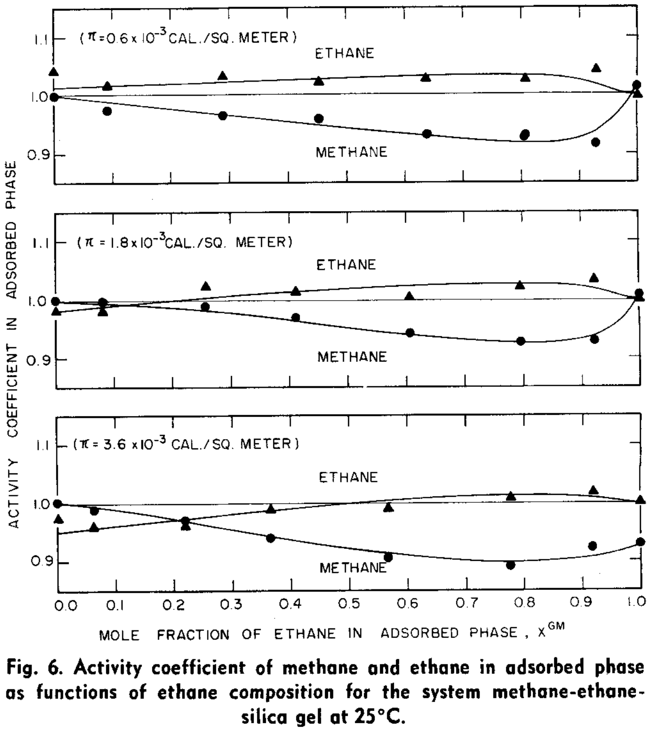

Fig. 6. Activity coefficient of methane and ethane in adsorbed phase as functions of ethane composition for the system methane-ethane-silica gel at 25°C.

main reason for the deviation in this system is ascribed to the polar nature and the heterogeneity of the adsorbent which results in nonideal interactions among the adsorbate molecules through adsorbent-adsorbate interaction.

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NOTATION

A = total surface area of adsorbent, sq. m.
$c(i)$ = molecular concentration of species i, mole/cc.
$f(i)$ = fugacity of species i, lb./sq.in.
G = Gibbs free energy, k cal./mole.
H = enthalpy, k cal./mole
(i) = molecular species
$N(i)$ = number of molecules i
$N^{GM}(t)$ = summation of $N^{GM}(i)$ for all (i)
P = pressure, lb./sq.in.
Q = heat of adsorption, k cal./mole
R = gas constant
S = entropy, cal./molecule/°C.
T = absolute temperature, °K.
v = volume expressed at column conditions, cc.
$x(i)$ = mole fraction of species i in the adsorbed phase
$y(i)$ = mole fraction of species i in the gas phase
z = compressibility factor
Δ = change on adsorption
$\gamma(i)$ = activity coefficient of species i, k cal./mole
$\mu(i)$ = chemical potential of species i, cal./sq.m.
π = spreading pressure of the adsorbed phase

Superscripts

o = pure component
A = absolute adsorption
G = Gibbs adsorption
GM = Gibbs adsorption taking into account molecular size
— = molar
∞ = infinite dilution

Subscripts

1 = gas phase
2 = adsorbed phase
R = experimental retention quantity
d = uncompensated dead space in tubings

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Maximum Temperature Rise in Gas-Solid Reactions

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A shell progressive kinetic model is used to determine the temperature rise in a spherical pellet for a gas-solid diffusion controlled reaction. The effects of heat and mass transfer resistances in the gas film as well as inside the pellet are investigated. The predicted temperature rise may be severe enough to cause sintering to catalyst pellets in which reactions such as combustion of coke occur.

During exothermic gas-solid reactions, such as regeneration of catalyst pellets from carbonaceous deposits, the interior temperature of the solid may differ considerably from that of the gas. These temperature effects may cause severe damage to the catalyst and reduce its activity (*2*). The present work is concerned with the maximum temperature rise in such a system.

For the case of a pseudohomogeneous reaction Damköhler (*5*) obtained an upper bound on the maximum steady state temperature difference between the interior and exterior temperatures of a catalyst. Prater (*8*) suggested the use of this bound for catalyst regeneration. Recently, Wei (*13*) used an elegant method to demonstrate that during the transient period the temperature in certain hot spots can greatly exceed the maximum steady state temperature. His analysis predicts that the smaller the hot spots the higher the upper bound, and he gave an

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