

吸着平衡에 관한 研究

김 동 수*

A Study of Equilibrium Relations in Gas Adsorption System

*Dong-Soo Kim

The 31st Chem. Engrn. Lab. ROKA

Abstract

A simple technique is described for calculating adsorption equilibria for components in a gaseous mixture, using only data for the corresponding pure-component adsorption equilibria on the same adsorbent. By using experimental data for the binary mixture, the activity coefficient is calculated, also.

The proposed technique is based on the ideal solution theory, where Raoult's Law applies. Predicted adsorption equilibria for Ethane-Ethylene mixtures at 20°C and 60°C gave excellent agreement, but an Ethylene-Carbon dioxide mixture showed some non-idealities, which were expected because of the chemical dissimilarities.

The simplicity of the calculation, which requires no data for the mixture, makes it useful for engineering application to non-polar and chemically similar gas mixtures.

I. Introduction

The gas-adsorbate equilibria for pure components and mixtures of gases on solid surfaces were studied for different temperatures, pressures, and surface coverages. Also a technique was studied for calculating the adsorption equilibria for the components in a gaseous mixture using adsorption equilibrium data for each of the pure components at the same equilibrium conditions, and on the same adsorbent, based on the concept of an ideal adsorbed solution.

II. Theoretical Backgrounds and Method of Calculations

Many forces of attraction exist between a gas and solid, depending on the physical structure of the solid, and the chemical nature of both the gas and the solid. Since the adsorption problem is very complicated and broad, this study is limited to only a physical adsorption, assuming there is no significant chemical reaction on the adsorbed phase.

Despite the large number of investigations of the adsorption of gas on the solids, relatively few definite conclusions can be made about the properties of the adsorbed layer. One of the basic reasons for

*The 31st Chem. Engrn. Lab. ROKA

this is because of the simultaneous dependency of adsorption on pressure and temperature. When gases are being adsorbed, intervals of change in the relative pressures are investigated which are not comparable in length. Therefore only the bulk properties of all three phases are considered, and there is no need to limit the adsorption to a monolayer adsorption.

It is necessary to have a more specific system to which mathematical relations apply. As mentioned above, because the interfacial region is ill defined, it is necessary to replace this situation with a hypothetical one, which for purposes of thermodynamic analysis is intended to be equivalent. According to J. Willard Gibbs¹⁾, the actual region may be thought as an imaginary situation where the gas phase persists unchanged up to the solid surfaces, and then the abnormalities occur on the solid surface, but they are presumed not to change during the adsorption process.

Although the two-dimensional phase is presumed to be in thermal and mechanical equilibrium with both the solid and the gas phase, it is in phase equilibrium only with the gas phase. It is assumed that phase equilibrium is always established between the adsorbate, considered as a two-dimensional phase, and the bulk phase.

Finally, theory was carried out under the assumption that a gas-adsorbate equilibrium may be considered to be an analogous process to a gas-liquid equilibrium process, and the Gibb's phase rules are applied and interpreted as described in Ross and Oliver²⁾.

With the assumptions made above, one may be able to derive the equations to be used without much difficulties, and the derivations will be omitted.

One can predict how the equilibrium will be affected by pressure, temperature and surface coverage by using the equation of equilibrium relations:

$$\frac{y_i}{x_i} = \frac{\gamma_i^a}{\gamma_i^g} K_i \quad (1)$$

where y_i and x_i refer to the concentrations of the

component i in the gas phase and adsorbed phase, γ_i^g and γ_i^a refer to the activity coefficient of component i in the gas phase and adsorbed phase respectively, and K_i is the equilibrium constant for component i . Since the activity coefficients in the gas phase at lower pressures are approximately equal to unity, the above equation is reduced to

$$\frac{y_i}{x_i} = \frac{\gamma_i^a}{\gamma_i^g} K_i = \gamma_i^a K_i \quad (2)$$

Equilibrium constant, K_i , will be calculated by Gibbs-Helmholtz Equation:

$$\ln K = \frac{-\Delta H_{ad}}{R} \left(\frac{1}{T} - \frac{1}{T_e} \right) \quad (3)$$

where ΔH_{ad} is the heat of adsorption at a temperature T , and T_e is the temperature at equilibrium.

The heat of adsorption is defined as the enthalpy in the gas phase minus the enthalpy in the adsorbed phase and will be calculated by the Clausius-Clayperon Equation:

$$\frac{dP}{dT} = \frac{\Delta H_{ad} P}{RT^2} \quad (4)$$

Rearranging Equation (4),

$$\Delta H_{ad} = \left(\frac{dP}{dT} \right) \frac{RT^2}{P} = - \frac{d(\ln P)R}{d\frac{1}{T}} \quad (5)$$

The calculated equilibrium constant will be compared with x 's and y 's obtained experimentally in Equation (1).

$$\gamma_i^a = \frac{y_i}{x_i K_i} \quad (1)$$

From the above equation, γ_i^a will be calculated. Once γ_i^a and K_i are obtained, approximate equilibrium compositions may be predicated at any point of desired pressures and temperatures in a limited range where the assumptions hold.

III. Compilation of Data and Processing of Data

Several binary adsorption systems are investigated using the corresponding data for a pure component adsorption system by Szepesy and Illes^{3),4),5)}. A set of data expressed in terms of pressure vs. temperature at several different surface coverages is desired for the calculation of the heat of adsorption by Equation (5). They were obtained by reading off the pressure on the isotherms at the intervals of 5 cu. cm of gas/g of solid surface coverage. It can be seen from Equation (5) that slopes of the curve of the data expressed in terms of $\ln P$ vs. $\frac{1}{T}$ is the value of heat of adsorption multiplied by gas constant R . Therefore pressure and temperature from the given data must be related first. To fit the experimental data, the following equation was used.

$$\ln P = A + \frac{B}{T-C} \quad (6)$$

where A, B and C are empirical constants. Equation (6) is used frequently for the studies of pressure-temperature relations in the calculations of the heat of condensation in a liquid vapor system to give very satisfactory results. To calculate A, B and C in Equation (6), the computer subprogram *FMCG*, which is used to find a minimum of a function of several variables by the method of conjugate gradient, was used for each surface coverage⁶⁾.

When A, B and C were obtained, Equation (6) was substituted into Equation (5) to give

$$\frac{\Delta H_{ad}}{R} = \frac{-d(\ln P)}{d\frac{1}{T}} = \frac{BT^2}{(T-C)^2} \quad (7)$$

The calculated values of H_{ad} are shown in Figure 1.

Then activity coefficient is calculated by Equation (2), using binary data obtained experimentally by Szepesy and Illes.

$$\gamma_i^a = \frac{y_i}{x_i K_i} \quad (2)$$

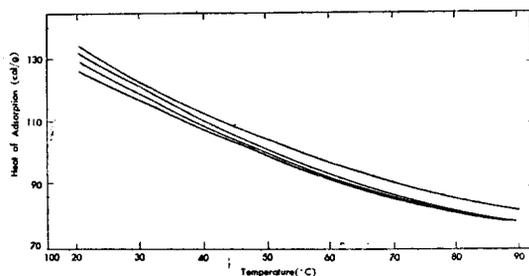


Fig. 1. Heat of adsorption-temperature relationships for different coverages.

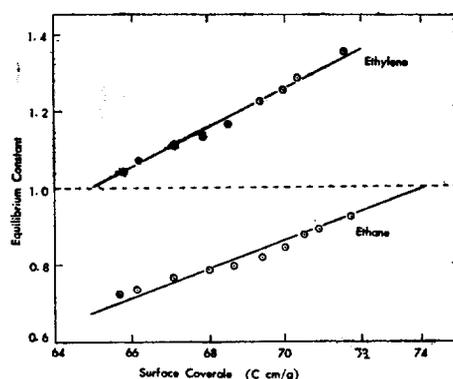


Fig. 2. Ethane-Ethylene Mixture (at 20°C).

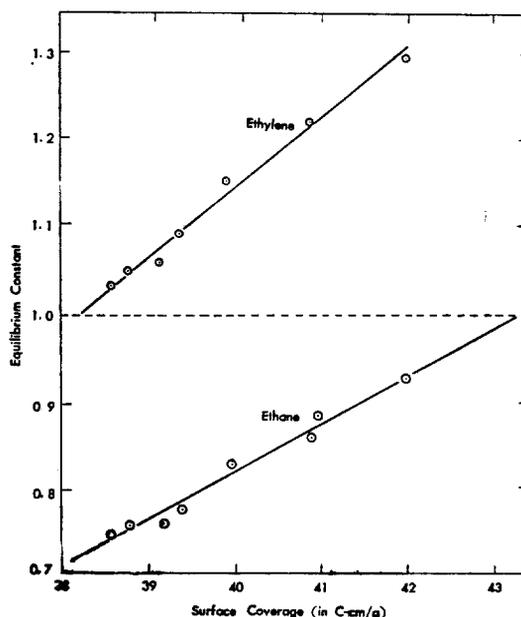


Fig. 3. Ethane-Ethylene Mixture (at 60°C).

When the activity coefficients are obtained, they may be combined with equilibrium composition at any surface coverage within the range of data investigated. The calculated results are shown on the following figures and tables.

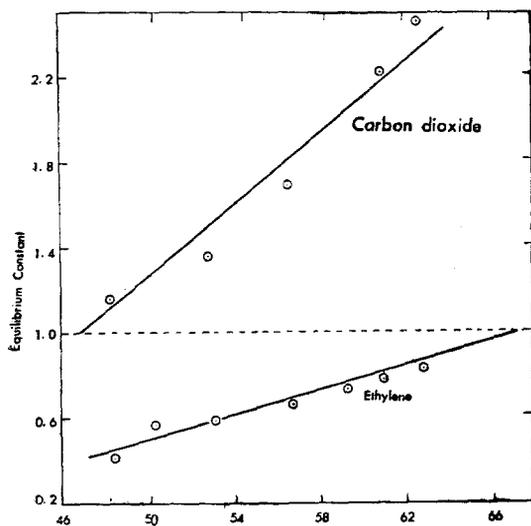


Fig. 4. Carbon Dioxide-Ethylene(at 20°C).

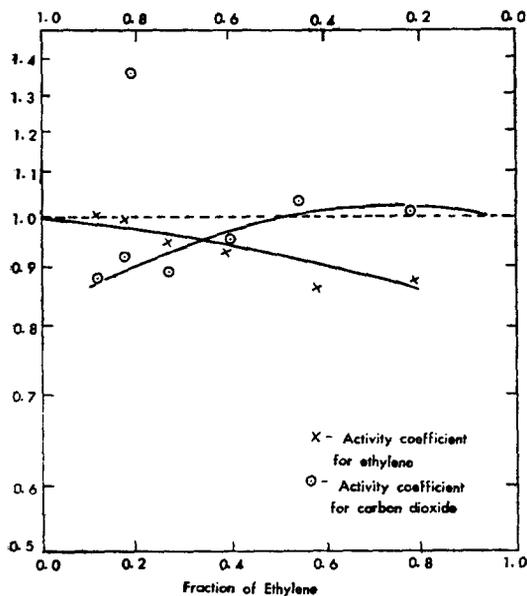


Fig. 5. Ethylene-Carbon dioxide Mixture(at 20°C).

Table. 1. Ethane-Ethylene Mixture at 293.16°K

Ethane					
$\frac{y_i}{x_i}$	T_e	K	a	x	V
0.7098	301.16	0.7127	0.9960	0.163	65.64
0.7323	301.06	0.7296	1.0046	0.269	66.02
0.7559	300.16	0.7559	1.0000	0.381	67.01
0.7951	299.76	0.7679	1.0354	0.488	67.79
0.8270	299.06	0.7895	1.0475	0.578	68.49
0.8378	298.16	0.8183	1.0239	0.672	69.25
0.8777	297.56	0.8382	1.0472	0.736	69.81
0.8590	296.86	0.8621	1.0383	0.791	70.30
0.9149	296.46	0.8761	1.0443	0.834	70.68
0.9328	295.26	0.9175	1.0166	0.863	71.56

Ethylene					
$\frac{y_i}{x_i}$	T_e	K	a	x	V
1.0561	292.56	1.0292	1.0256	0.838	65.65
1.0970	292.16	1.0529	1.0419	0.732	66.02
1.1502	291.16	1.1011	1.0446	0.619	67.01
1.1953	290.36	1.1364	1.0518	0.512	67.79
1.1237	289.76	1.1677	1.0594	0.422	63.49
1.3323	288.86	1.2165	1.0952	0.328	69.25
1.340	288.36	1.2446	1.0765	0.264	69.81
1.4000	287.36	1.3031	1.0818	0.166	70.68

Table. 2. Ethane-Ethylene Mixture at 333.16 °K

Ethane					
$\frac{y_i}{x_i}$	T_e	K	a	x	V
0.9026	336.16	0.9242	0.9766	0.750	42.49
0.8445	339.16	0.8584	0.9838	0.579	41.37
0.8037	341.16	0.8170	0.9839	0.459	40.41
0.7799	343.16	0.7686	0.9464	0.359	39.85
0.7770	344.46	0.7536	1.0310	0.278	39.62
0.7661	344.96	0.7452	1.0280	0.218	39.29
0.778	345.16	0.7392	1.0500	0.171	39.09

Ethylene					
$\frac{y_i}{x_i}$	T_e	K	a	x	V
1.252	324.16	1.295	0.9667	0.250	42.49
1.2138	326.16	1.221	0.9941	0.421	41.37
1.1664	328.16	1.152	1.0125	0.541	40.41
1.1232	330.66	1.088	1.0324	0.642	39.85
1.0859	331.16	1.058	1.0263	0.7222	39.62
1.0652	331.66	1.044	1.0203	0.7820	39.29
1.0458	332.16	1.0280	1.0173	0.829	39.09

Table. 3. Carbon Dioxide-Ethylene Mixture at 293.16°K

<u>Carbon Dioxide</u>					
$\frac{y_i}{x_i}$	T_e	K	a	x	V
1.1804	290.65	1.1500	1.0264	0.776	48.20
1.3150	287.15	1.3600	1.0514	0.546	52.79
1.6069	283.15	1.6825	0.9550	0.379	56.47
1.8736	279.15	2.0950	0.8943	0.261	59.09
2.0400	278.15	2.2150	0.9207	0.175	60.92
2.1765	276.15	2.4750	0.8793	0.119	62.70

<u>Ethylene</u>					
$\frac{y_i}{x_i}$	T_e	K	a	x	V
0.3750	314.66	0.4255	0.8813	0.224	48.20
0.4823	307.66	0.5656	0.8527	0.454	52.79
0.6296	302.56	0.6784	0.9281	0.621	56.47
0.6955	300.56	0.7347	0.9466	0.739	59.09
0.7793	299.16	0.7794	0.9998	0.825	60.92
0.8410	297.66	0.8264	1.0177	0.881	62.70

Results and Conclusions

Although many similar studies have been conducted none could be used in comparing the results. Unlike condensation problems, there can be an infinite number of systems with the same binary mixture, depending on the kind of adsorbent, size of the adsorbent and degree of activity. Since Szepeszy and Illes did not give any information on how the adsorbent was prepared, there is no way of comparing the calculated results with any other works.

However, the general characteristics of adsorption could be seen and the results are as predicted.

The equilibrium constant-total surface coverage relations were first studied. As expected, the lighter components had the higher values of equilibrium constants at any surface coverage and as the surface coverage increased, the equilibrium constants increas-

ed. See Figure 2~4. As indicated in Equation (3), and from the general definitions in thermodynamics, equilibrium constants are unity at equilibrium points, which may be used as a check point in the calculations.

As expected, the activity coefficients for the Ethane-Ethylene system at 20°C and 60°C were very close to unity throughout the fractional surface coverage. The Carbon dioxide-Ethylene system gave lower activity coefficients which decreased as the fractional coverages increased. See Figure 5. These are reasonable because the calculations were made at lower pressures and at low pressure, one would expect the activity coefficients to be one. For Carbon dioxide-Ethylene mixture, although carbon dioxide is as nonpolar as ethylene is, the differences in the formation and molecular structure could cause non-idealities. These non-idealities are consistent with the activity coefficients calculated from the liquid vapor system.

Literature Cited

1. Gibbs, J. W.; Scientific Papers, Vol. 1, p. 219, Longmans Green and Company, New York (1906).
2. Ross, S., and J. P. Oliver; On Physical Adsorption, Interscience, New York (1964).
3. Szepeszy, L., and V. Illés; "Adsorption of Gases and Gas Mixtures, I", Acta. Chim. Hung., **35**, 53 (1963).
4. Szepeszy, L., and V. Illés; "Adsorption of Gases and Gas Mixtures, II", Acta. Chim. Hung., **35**, 37 (1963).
5. Szepeszy, L., and V. Illés; "Adsorption of Gases and Gas Mixtures, III" Acta. Chim. Hung., **35**, 245 (1963).
6. Fletcher, R., and C. M. Reeves, "Computer Journal", **7**, Iss. 2, 149 (1964).

