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Theory of adsorption from solution and mixed gases

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NOTE TO USERS

THEORY OF ADSORPTION

FROM SOLUTION AND MIXED GASES

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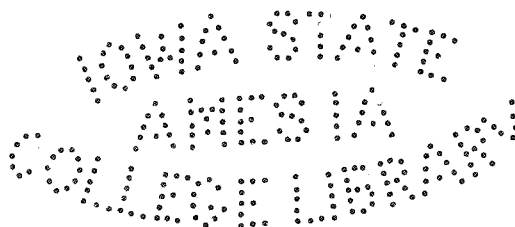
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I. INTRODUCTION

Adsorption from solution is a phenomenon which has been treated extensively from the experimental viewpoint and, although many correlations have been made between bits of data, no satisfactory general theory has been offered. This situation is not amenable to a good understanding of the physical picture occurring when adsorption from solution takes place. To truly understand a physical phenomenon, a firm theoretical basis is the first requisite.

It would be presumptuous to assume that a complete theory of adsorption from solution, even for the case of a binary solution on non-electrolytes, can be developed in one piece of work, but the problem attempted here was to formulate a new approach to the situation in the hope that this approach can be expanded, refined and eventually lead to a complete theory of adsorption from solution.

Adsorption of gas mixtures is closely allied to adsorption from solution and, therefore, the extension of the theory to cover this phenomenon is a secondary goal. The advantages of having one basic theory elucidate these two phenomena is apparent. More correlations could be discovered to increase the value of adsorption for both academic and industrial interest.

Kipling (1) presented an excellent review of the
status of adsorption of solutions of non-electrolytes up
to 1951. He stated rather completely the inherent diffi-
culties in elucidating a clear picture of adsorption from
solution, even in binary solutions which are the only so-
lutions to be discussed. Kipling deplores the reluctance
of chemists to give up the so-called composite isotherm,
which is a surface excess isotherm. More explicitly, the
composite isotherm is the isotherm resulting from plotting
the term

$$\frac{V(C_0 - C)}{M}$$

against C. In the above expression, V is the volume of
solution, C_0 is the initial concentration of component 1,
C is the equilibrium or final concentration of component 1
and M is the weight of adsorbent used.

It is easily seen that the term above can lead to
either positive or negative values. This fact led to the
realization that when dealing with adsorption from solution
the designation of solvent and solute is meaningless.
Many of the early experiments performed in the investi-
gation of adsorption from solution were done over a limited
concentration range. This restriction leads easily to the
concept of solvent and solute and, in fact, in the systems
investigated there was positive adsorption of the component

present in the smaller amount. The next step was to assume
that the solvent was inert or non-adsorbed, leading eventu-
ally to treating the adsorption of the solute as if it
followed one of the more well known gas adsorption isotherms.
Many systems follow the Freundlich equation (2)

$$\frac{x}{m} = kc^{1/n} \,,$$

or

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log c \,,$$

for adsorption of the solute up to a concentration of 0.2
molar. In the Freundlich equation $\frac{x}{m}$ is the adsorption
per unit weight of adsorbent, C is the concentration of
the solute and k and n are constants. The Langmuir equa-
tion (3)

$$\frac{x}{m} = \frac{k'c}{1 + kc} \,,$$

or

$$\frac{m}{x} = \frac{k}{k'} + \frac{1}{k'} \cdot \frac{1}{c} \,,$$

is usually followed to higher concentrations than is the
Freundlich equation.

It is apparent that both of the above equations lead
to an adsorption that always increases with increasing
concentration. In immiscible systems that is the situation

up to the saturation point, but in completely miscible systems ever increasing adsorption is never observed. The necessity of assuming that both components are adsorbed was first stated explicitly by Williams (4). Even though, since that time, most workers have treated adsorption from solution by assuming adsorption of both components, the restriction was usually made that adsorption was monomolecular. Williams was an exception to this generalization, using the equation

$$\frac{x}{x} + \frac{y}{y} = 1 ,$$

in which x and y are calculated adsorption of components 1 and 2, and x and y are the measured pure gas adsorption of components 1 and 2 at saturation pressure. This treatment does not calculate the composite isotherm but uses the composite isotherm as a starting point in the calculation of hypothetical isotherms for components 1 and 2.

The next approach to the problem was an arithmetical treatment by Ostwald and de Izaguirre (5) who indicated the composite isotherms that would result from various combinations of solvent and solute isotherms. The assumption of monomolecular adsorption was also made by Ostwald and de Izaguirre. One of the most important facts shown by Ostwald and de Izaguirre was that even though they, in one case, assumed only solute adsorption, the composite isotherm

had the value zero for mole fraction of solute either zero
or one. From their calculations, this effect is shown to
be due to the volume change that results when adsorption
takes place. The basic equation used by Ostwald and
de Izaguirre was

$$\frac{n_0(x_0-x)}{m} = \frac{n_0\Delta x}{m} = n_1^s(1-x) - n_2^s x , \qquad (1)$$

in which n_0 is the total moles of solution, x_0 and x are
the mole fractions of component 1, before and after ad-
sorption, n_1^s and n_2^s are the number of moles of component 1
and 2 in the adsorbed film and m is the weight of adsorbent.
Bartell and Sloan (6) starting with the equation of Ostwald
and de Izaguirre applied the assumption that both components
followed the Freundlich equation. For the system benzene-
ethanol on charcoal, Bartell and Sloan evaluated the four
constants and obtained a rather close fit to the experi-
mental isotherm. The fit was improved by Kipling and
Tester (7) who used the Langmuir isotherm for the components.
There is a marked discrepancy in the individual component
isotherms in these two treatments and Kipling and Tester
have emphasized that this discrepancy only points out that
the entire process is but slightly understood.

In another paper, Kipling and Tester (8) assumed an
equation similar to that of Williams (4), however, Kipling
and Tester restricted the treatment to monomolecular

adsorption. Their equation was

$$n_1^s A_1 + n_2^s A_2 = A$$

or

$$\frac{n_1^s}{(n_1^s)^0} + \frac{n_2^s}{(n_2^s)^0} = 1 \quad , \tag{2}$$

in which $(n_1^s)^0$ and $(n_2^s)^0$ are the monolayer amounts of components 1 and 2. The values for these monolayers are determined by pure gas isotherms. Equation (1) was combined with Equation (2) to calculate mixed monomolecular vapor adsorption with some measure of success. The restriction to monomolecular adsorption removes much of the value of the treatment.

In the same paper, Kipling and Tester used a kinetic approach to mixed gas adsorption and adsorption from solution. By equating the rates of adsorption and desorption for the two components, they derived the expressions for mixed gas adsorption

$$\sigma_1 = \frac{p_1}{p_1 + Kp_2}$$

and

$$\delta_2 = \frac{p_2}{p_2 + \frac{p_1}{K}} \quad .$$

In the above expressions, δ_1 and δ_2 are the fractions of the surface covered by components 1 and 2, p_1 and p_2 are the partial pressures of components 1 and 2 in the gas phase and K is a constant. By assuming Raoult's law behavior or other treatments, analytic expressions can be derived. A suggested extension to adsorption from solution was made which necessitated obtaining expressions for heats of vaporization and mixing. No applications of this extension were attempted.

Polanyi (9) introduced a theory of adsorption of pure gases which did not give an analytical expression for the isotherms but was a partial explanation of the adsorption process. His theory was adapted to monomolecular and multimolecular adsorption. As this theory, with modifications, appears suited for the treatment of multimolecular adsorption from solution it will be briefly summarized. At any point in the neighborhood of an adsorbent surface there exists an adsorptive potential ε; points having the same value of ε form a surface approximately parallel to the adsorbent surface and together with the adsorbent surface enclose a volume ϕ. The function $\varepsilon(\phi)$ is assumed to be temperature independent.

Given an adsorption isotherm $n(p/p_0)$, the function $\varepsilon(\phi)$ can be calculated by use of the equations

$$\varepsilon = R T \ln \frac{p_0}{p}$$

$$\emptyset = n \, \overline{V}_1$$

in which p is the pressure at which n moles of gas are adsorbed, p_0 is the saturated vapor pressure of the gas and $\overline{V}_1$ is the liquid molar volume at the temperature of the adsorption isotherm. The function $\varepsilon(\emptyset)$ being established from one isotherm, isotherms at any other temperature can be calculated from these two equations. The status of this theory to 1942 has been reviewed by Brunauer (10).

Recently, Hill (11) and McMillan and Teller (12), have theoretically derived the expression

$$\ln \frac{p_0}{p} = \frac{a}{\emptyset^3} \quad ,$$

in which $\emptyset$ is the amount adsorbed per unit and a is a constant. Halsey (13) derived a more general expression

$$\ln \frac{p_0}{p} = \frac{a}{\emptyset^n}$$

in which a and n are constants. These expressions are analytical functions for the Polanyi adsorption potential and this fact makes the Polanyi theory much more attractive than it has been. However, few systems obey these equations and the usefulness of the theoretical approach has

has been severely limited. When a better understanding of the adsorbent-adsorbate interaction is reached, the Polanyi theory will be a valuable basis for the prediction of adsorption isotherms.

Polanyi (14) applied his theory of gas adsorption to adsorption of slightly soluble substances from solution. It is easily shown that this extension is not general. Polanyi's basic equation for adsorption from solution is in modern notation

$$\bar{V}_2 \varepsilon_1 - \bar{V}_1 \varepsilon_2 = -\bar{V}_2 \; RT \ln a_1 \; ,$$

in which a_1 is the activity of component 1 referred to a standard state of pure component 1. By exactly parallel arguments it follows that

$$\bar{V}_1 \varepsilon_2 - \bar{V}_2 \varepsilon_1 = -\bar{V}_1 \; RT \ln a_2 \; ,$$

and therefore

$$\bar{V}_1 \ln a_2 = -\bar{V}_2 \ln a_1 \; .$$

This is impossible, since both a_1 and a_2 have unity as upper bounds, and $\bar{V}_1$ and $\bar{V}_2$ are both positive. This restriction emphasizes the limitations to slightly soluble substances, which reduce the value of the approach of Polanyi.

It is evident that no satisfactory treatment of adsorption from solution has been put forth so far. The

theories discussed above just try to explain the experi-
mental results of adsorption but no effort has been made
to predict adsorption from solution. This absence is one
which should be corrected and as will be seen later, an
effort has been made to alleviate this situation.

III.   EXPERIMENTAL

A.   Materials

As the objective of this problem is to calculate and to check experimentally adsorption from solution and from gas mixtures, the pure gas adsorption isotherms obtained were made with the same materials as were the adsorption from solution isotherms, run by Craig (15) and Hansen (16).

1. Adsorbates

(a) Water. The water used was tap distilled water which was then redistilled from alkaline permanganate solution and stored in standard taper pyrex bottles.

(b) Ethanol. The ethanol used was prepared by Hansen (16). To 300 ml. of commercial absolute alcohol was added 10 g. of magnesium turnings and 0.1 g. of iodine crystals. This mixture was refluxed for several hours. Then about one liter of absolute alcohol was added and refluxed overnight. It was then distilled through a 30 plate Oldershaw column at a reflux ratio of 10:1.

After the first distillation, more alcohol was added to the residue and another batch was distilled off. Both batches were mixed together.

Boiling Point (corrected to 760 mm.)

First batch   78.62-78.69° C.

Second batch   78.65-78.70° C.

(c) Propanol-1. The propanol-1 was purified by
Craig (15). Chemically pure propanol-1, obtained from
Columbia Organic Chemicals Company, Columbia, South
Carolina, was redistilled. A constant boiling middle por-
tion, three-fifths of the total liquid, was retained for
for use. The boiling point, corrected to 760 mm. was
97.6° C.

(d) Butanol-1. The butanol-1 was purified by Craig
(15). Butanol-1, obtained from Columbia Organic Chemicals
Company, was water extracted and the water rich portion
distilled. From partial distillation a butanol-1 rich
phase was obtained and this phase was dried over calcium
sulphate and then distilled from magnesium butoxide pre-
pared in a manner similar to the magnesium ethoxide used
to purify the ethanol. The boiling point, corrected to
760 mm. was 118.28-118.30° C.

(e) Cyclohexane. The cyclohexane was purified by
Hansen (16). The starting material was about 1700 ml. of
cyclohexane obtained from E. I. duPont de Nemours Company.
This was washed with redistilled water and sodium carbon-
ate solution. Sodium hydroxide pellets were added to re-
move excess water. After three hours, the cyclohexane was
decanted and allowed to stand over sodium metal for 12
hours. The cyclohexane was decanted off and distilled

through a 30 plate Oldershaw column with a reflux ratio of 10:1. The boiling point corrected to 760 mm, was 80.72-80.85° C.

2. Adsorbents

(a) Spheron-6. Spheron-6 is a pelletized furnace black made by the Godfrey L. Cabot Company, Boston, Massachusetts. The Spheron-6 was heated to 980° C in vacuum for 24 hours, then stored in covered mason jars. The samples used for the adsorption of water, propanol-1 and butanol-1 were from a batch used by Craig (15) for his solution isotherms. The samples used for the adsorption of ethanol and cyclohexane were from a batch used by Hansen (16).

(b) DAG-1. DAG-1 is a deflocculated artifical graphite produced by the Acheson Colloids Corporation. The DAG-1 was heated to 980° in vacuo for 24 hours and stored in covered mason jars.

B. Adsorption Measurements

The gas adsorption isotherms were determined gravimetrically using a magnetically compensated balance of the type described by Edwards and Baldwin (17). The balance was enclosed in a sealed glass system. Vapor was introduced into this system through a sidearm which led to a bulb containing the liquid whose vapor was being adsorbed.

The pressure at which adsorption occurred was the vapor pressure of the liquid at the temperature of this bulb. Approximately 0.5 g. adsorbent was placed in a platinum bucket which was suspended from one arm of the balance; the other arm of the balance was counterweighted with platinum wire. The adsorbent and the reservoir bulb were thermostatted independently, the adsorbent at 25.00 ± 0.02° C, the bulb reservoir at the temperature necessary for desired pressure to within 0.1° C. Pressures were computed from measured bulb temperatures using vapor pressure data from the International Critical Tables. In the case of butanol-1 this involved extrapolation of measured data, for the lowest temperature at which vapor pressure data was given was 20° C.

The balance was calibrated by means of a set of calibrated weights. The plot of milligrams weight against milliamperes current in the solenoid was perfectly linear throughout the range used in this work. Checks were made to find out if the weight of the adsorbent changed the calibration of the balance. When 1 gram weights were affixed to the arms of the balance, no change in calibration could be detected. The accuracy of the balance used was 0.01 milligram, which corresponds to less than 0.001 millimole of adsorbate. The sensitivity of the balance in the runs was about 1.6 milligrams to 1 milliampere.

The magnet used was an Alnico VII cylinder, 1 milli-meter in diameter and 15 millimeters long. The solenoid consisted of 2000 turns of Formvar coated B. and S. No. 28 copper wire in a length of 75 millimeters. A series of decades adjustable to 10 ohms was in series with the sole-noid. Also in series circuit were a 10 ohm Helipot and a 1 ohm standard resistor. The potential drop across the stan-dard resistor was measured with a Rubicon type B precision potentiometer. The potential in the solenoid circuit was 18 volts, furnished by three 6 volt dry cells in series. A schematic diagram of the apparatus is shown in Figure 1.

C. Temperature Controls

As stated above, the temperature of the adsorbent was held at $25° + 0.02$ C. The bath temperature into which the sidearm containing the adsorbent bucket was controlled by means of a Magna-set thermoregulator, controlling an electronic relay which in turn actuated an infra-red lamp which shone into the water bath from the side. The side of the tube containing the adsorbent bucket was covered with aluminum foil to prevent any extraneous heating of the sample. The bath was stirred by means of a magnetic stirrer.

The temperature of the reservoir bulb was controlled by controlling the temperature of the bath into which the bulb was immersed. The bath temperature was regulated by a thyatron controlled heater operated by the circuit shown

PLATINUM
COUNTERWEIGHT

TO
MEASURING
CIRCUIT

TO VACUUM

RESERVOIR
BULB

SAMPLE
BUCKET

VARIABLE
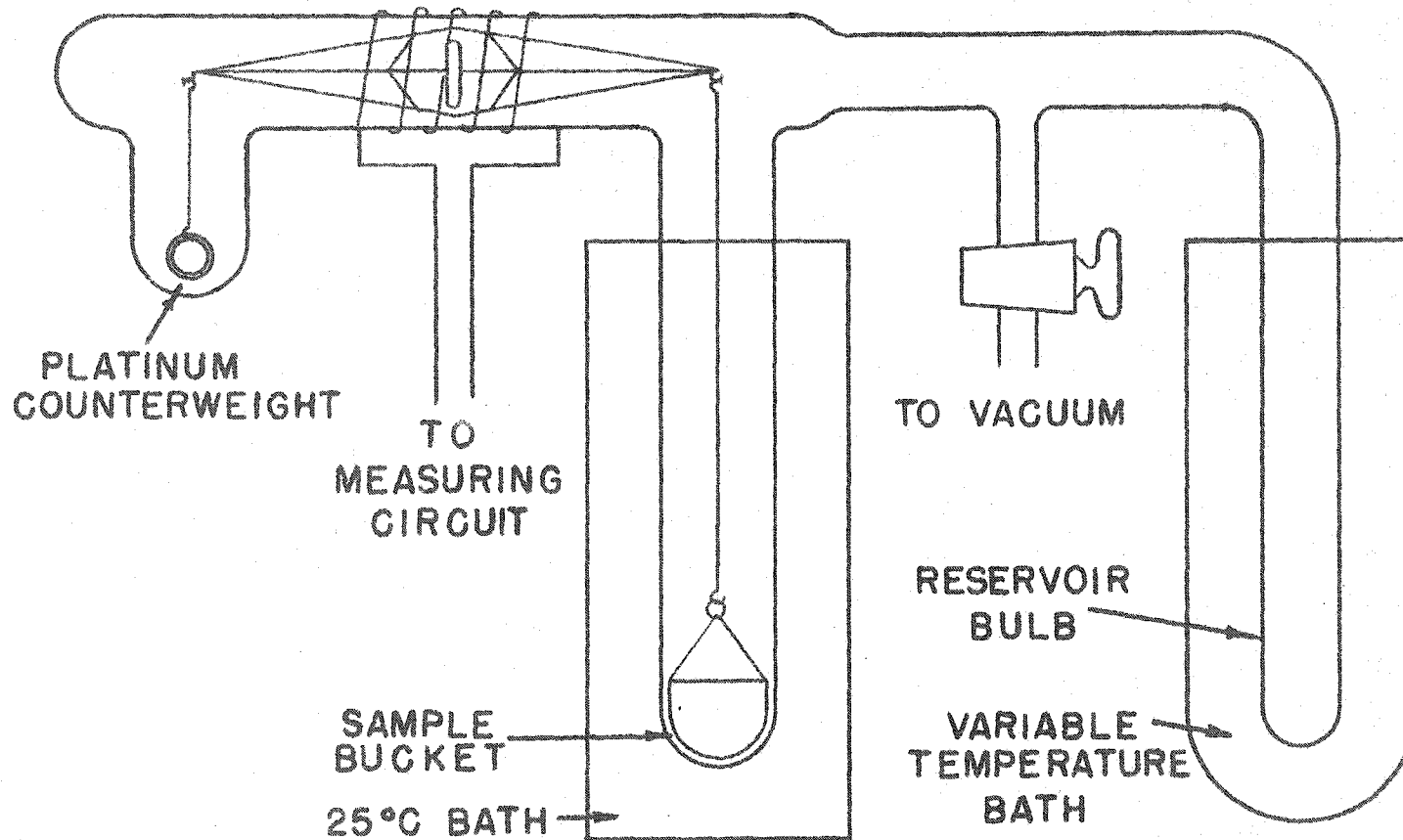TEMPERATURE
BATH

25°C BATH

Figure 1.   Experimental Apparatus.

in Figure 2. This circuit is a modification of one described by Tarnopol (18). In Figure 2, R_T is a resistance thermometer and Dec is a variable balancing decade with a range from 0 to 99.99 ohms in steps of 0.1 ohm. The 20,000 ohm potentiometer across the bridge controls the sensitivity of the circuit and this potentiometer is adjusted until the circuit is almost to the off-on stage. By adjusting to this point, the circuit is a very sensitive proportional controller and stabilizes to constant temperature within a minute. At equilibrium, a constant current flows through the heater, balancing the heat leak to an outer cooling bath.

The resistance thermometer consisted of 8 feet of 1 mil lead wire. The lead wire was wrapped non-inductively around a sheet of mica rectangle, 1 inch by 2 inches. The mica sheet was supported in a brass frame and the lead wire was protected by a piece of screen. Lead was chosen because it has the highest temperature coefficient of resistivity of any wire that was available. The total resistance of the thermometer was about 40 ohms at room temperature. The resistance change for this size thermometer was about 0.16 ohms per degree. This value cannot be given exactly as the thermometers were fragile and a number were made and used.

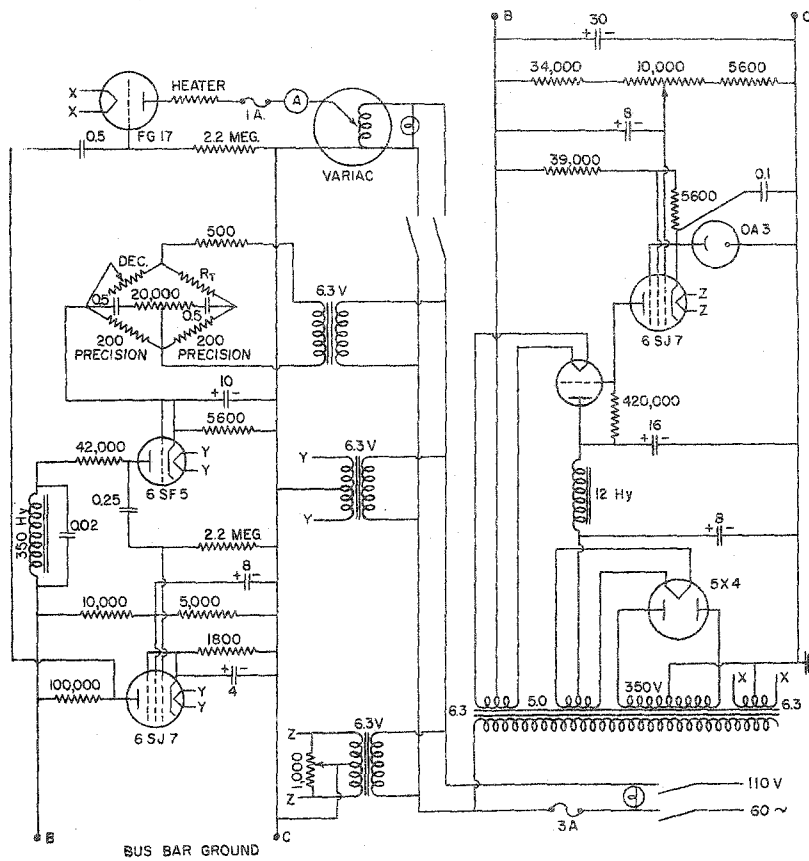The heater in the reservoir bulb bath was a coil of 20

Figure 2. Temperature Control Circuit.

ohms of nichrome wire placed in the bottom of the bath.
Stirring was accomplished with a two blade paddle stirrer
which was run fast enough to cause evident turbulence on
the top of the bath liquid. Trichloroethylene made an
excellent bath liquid and was also used as the liquid in
the dry-ice-cooled outer bath. The inner bath container
was a Dewar flask to minimize the heat leak. The entire
reservoir bulb cooling bath is shown in Figure 3.

D. Results

The adsorption results obtained with the apparatus de-
scribed above are given in Tables 1-7. The smoothed iso-
therms used in the calculations are shown in Figures 4-10.
Prior to the gas adsorption measurements the adsorbents
were outgassed at 25° C for 12 hours. The surface area of
the adsorbents as determined by the Brunauer-Emmett-Teller
method using nitrogen adsorption was 114 square meters per
gram for the Spheron-6 and 102.4 square meters per gram for
the DAG-1.

Hysteresis on desorption appeared negligible in the
case of ethanol, propanol-1, butanol-1 and cyclohexane on
Spheron-6. In the case of propanol-1 on DAG-1 the hystere-
sis was extremely small. The adsorption-desorption isotherm
of water on Spheron-6 showed an appreciable hysteresis over
the entire reduced pressure range. The amount of hysteresis
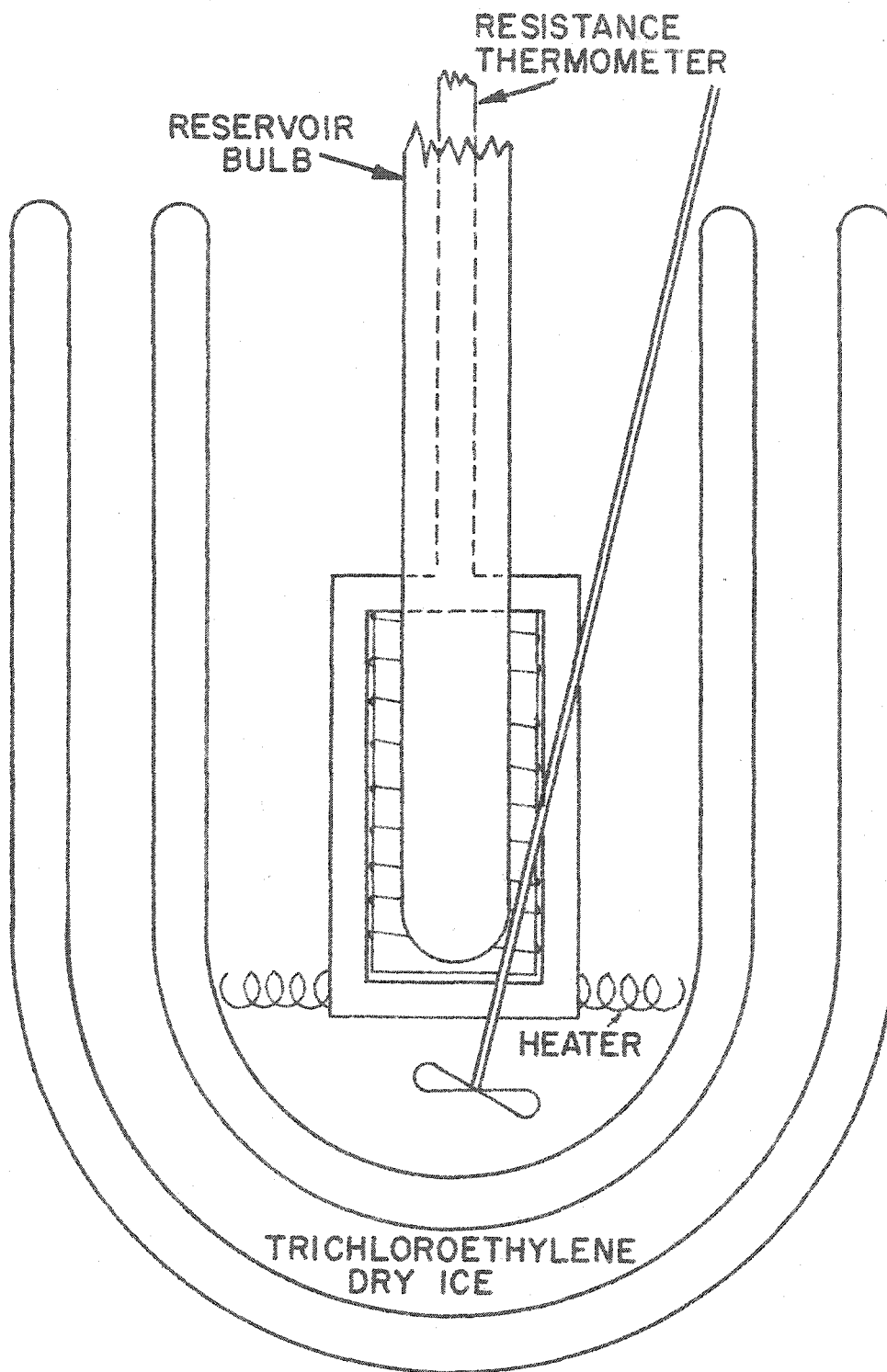
Figure 3. Reservoir Bulb Bath.

Table 1

Adsorption of Water Vapor by Spheron-6

Adsorption		Desorption	
Reduced Pressure	Millimoles/g.	Reduced Pressure	Millimoles/g.
0.045	0.013	0.857	1.554
.075	.048	.833	1.530
.099	.062	.760	1.512
.149	.123	.725	1.444
.201	.217	.625	1.424
.283	.344	.585	1.316
.331	.454	.522	1.201
.350	.499	.469	1.031
.416	.684	.374	0.812
.455	.772	.254	0.505
.497	.900	.174	0.348
.514	.902	.126	0.225
.589	1.102	.060	0.139
.656	1.218		
.700	1.273		
.800	1.377		
.875	1.464		
.942	1.618		
.970	1.815		

Table 2

Adsorption of Propanol-1 Vapor by Spheron-6

Adsorption		Desorption	
Reduced Pressure	Millimoles/g.	Reduced Pressure	Millimoles/g.
0.054	0.102	0.965	1.774
.096	.148	.923	1.528
.158	.293	.867	1.234
.203	.374	.804	1.047
.326	.475	.775	1.027
.386	.653	.691	0.944
.441	.665	.558	0.791
.507	.741	.498	0.742
.620	.867	.425	0.667
.728	1.024	.365	0.579
.793	1.055	.265	0.463
.831	1.135	.171	0.335
.897	1.426	.076	0.151
.941	2.051		
.982	2.144		

Table 3

Adsorption of Butanol-1 Vapor by Spheron-6

Adsorption		Desorption	
Reduced Pressure	Millimoles/g.	Reduced Pressure	Millimoles/g.
0.015	0.097	0.910	1.417
.030	.147	.804	1.106
.053	.197	.681	0.888
.100	.280	.604	0.761
.156	.337	.320	0.506
.206	.398	.110	0.300
.292	.482	.054	0.204
.393	.582		
.495	.668		
.600	.766		
.708	.875		
.778	.988		
.853	1.130		
.918	1.275		
.964	1.445		

Table 4

Adsorption of Water Vapor by DAG-1

Adsorption		Desorption	
Reduced Pressure	Millimoles/g.	Reduced Pressure	Millimoles/g.
0.051	0.018	0.600	1.652
.104	.028	0.258	1.641
.211	.036		
.320	.042		
.416	.051		
.509	.062		
.657	.085		
.775	.113		
.893	.186		
.976	.245		
.988	1.680		

Table 5

Adsorption of Propanol-1 Vapor by DAG-1

Adsorption		Desorption	
Reduced Pressure	Millimoles/g.	Reduced Pressure	Millimoles/g.
0.042	0.235	0.966	1.796
.080	.332	.927	1.669
.124	.437	.889	1.372
.205	.490	.825	1.183
.261	.518	.719	0.979
.378	.620	.660	.907
.477	.705	.572	.828
.591	.809	.508	.778
.693	.946	.448	.727
.793	1.106	.382	.678
.852	1.303	.314	.604
.891	1.400	.218	.505
.941	1.674	.133	.402
.989	1.856	.058	.251

Table 6

Adsorption of Ethanol Vapor by Spheron-6

Adsorption		Desorption	
Reduced Pressure	Millimoles/g.	Reduced Pressure	Millimoles/g.
0.049	0.115	.793	1.402
.057	.159	.758	1.391
.095	.227	.647	1.288
.101	.245	.613	1.211
.205	.500	.550	1.150
.207	.543	.436	1.034
.291	.701	.338	0.878
.389	.904	.242	0.686
.418	.936	.144	0.413
.478	1.018		
.490	1.062		
.605	1.190		
.705	1.320		
.828	1.465		
.842	1.514		
.897	1.663		
.902	1.696		
.936	1.920		

Table 7

Adsorption of Cyclohexane Vapor on Spheron-6

Adsorption		Desorption	
Reduced Pressure	Millimoles/g.	Reduced Pressure	Millimoles/g.
0.051	0.268	0.764	0.968
.100	.339	.640	.703
.148	.370	.503	.586
.200	.389	.402	.491
.303	.446	.296	.448
.406	.510	.203	.397
.506	.574	.099	.317
.601	.666	.051	.273
.660	.742	.029	.216
.709	.806		
.750	.899		
.810	1.077		
.878	1.437		
.926	2.096		
.958	3.738		

was nearly 0.2 millimoles per gram over the range

0.2 $\frac{P}{P_0}$ 0.7, the difference decreasing to 0.1 milli-

moles per gram at $\frac{P}{P_0}$ = 0.1 and 0.9. The adsorption iso-

therm shown was used in the calculations; it lay between

the isotherms reported by Anderson and Emmett (19) for

Spheron-6 and Spheron-6 outgassed at 950° C to 1000° C.

The hysteresis for the adsorption of water on DAG-1

was extreme, in fact, it was impossible to desorbe much of

the adsorbed water. One explanation for this phenomena is

that the adsorption which takes place at a $\frac{P}{P_0}$ of 0.976 is

not an actual adsorption of the water but rather the water

goes between the layers of the graphite and forms an inter-

stitial compound. The Spheron-6 is not a graphite structure

and, therefore, there is no possibility of the formation of

an interstitial compound. X-ray diffraction powder pictures

of the DAG-1 before and after adsorption showed no change

in the C axis. In agreement with this, the results of

Hennig (20) on the take up of bromine by graphite also

showed no indication of a change in the C axis. Formation

of interstitial compounds is, therefore, not a reasonable

explanation of the hysteresis; Hennig's hole or micropore

theory appears to be the best explanation available, and

it is not particularly satisfying.

IV. THEORY

A. Adsorption from Solution

As has been mentioned before, the principal efforts of this work will be to further the understanding of adsorption from solution and also to make it possible to predict adsorption from solution having only pure gas adsorption data. The logical extension of calculating mixed gas isotherms was also made. The theory developed is explained in detail.

Consider a solid adsorbent in equilibrium with a binary liquid solution of components 1 and 2. Let $\Delta\phi$ be an infinitesimal volume increment enclosed between two equipotential surfaces ϕ and $\phi + \Delta\phi$. Assuming $\Delta\phi$ to be invariant, the conditions for equilibrium between material in $\Delta\phi$ and in the bulk solution follows from the invariance in the total free energy under constrained infinitesimal mass transfer. These conditions give

$$\delta F = 0 = (\mu_{1\phi} - \mu_{1b})\,\delta\, n_{1\phi} + (\mu_{2\phi} - \mu_{2b})\,\delta\, n_{2\phi}\,,$$

subject to the constraint

$$\delta\Delta\phi = 0 = \tilde{\tilde{V}}_{1\phi}\,\delta\, n_{1\phi} + \tilde{\tilde{V}}_{2\phi}\,\delta\, n_{2\phi}\,.$$

From the usual Lagrangian multiplier approach it follows that

$$-\lambda = \frac{\mu_{1\phi} - \mu_{1b}}{\tilde{V}_{1\phi}} = \frac{\mu_{2\phi} - \mu_{2b}}{\tilde{V}_{2\phi}} \qquad (3)$$

in which μ_1 and $\tilde{V}_{1\phi}$ are the chemical potential and partial molar volume of component 1 at the position ϕ and μ_{1b} is the chemical potential of component 1 in the bulk solution.

The activity of component 1 is defined by

$$\mu_1 = \mu_1^\circ + RT \ln a_1 \quad ,$$

Therefore

$$\mu_{1\phi} - \mu_{1b} = \mu_{1\phi}^\circ - \mu_{1b}^\circ + RT \ln \frac{a_{1\phi}}{a_{1b}} \quad , \qquad (4)$$

in which the activity $a_{1\phi}$ is referred to pure liquid component 1 at ϕ and a_{1b} to pure liquid 1 in the bulk solution. From Equations (3) and (4) it follows that

$$\mu_{1\phi}^\circ - \mu_{1b}^\circ + RT \ln \frac{a_{1\phi}}{a_{1b}} = \frac{\tilde{V}_1}{\tilde{V}_2} \left(\mu_{2\phi}^\circ - \mu_{2b}^\circ + RT \ln \frac{a_{2\phi}}{a_{2b}} \right) \quad ,$$

or

$$\frac{a_{1\phi}}{a_{2\phi}^a} = \frac{a_{1b}}{a_{2b}^a} e^{-\frac{(\mu_{1\phi}^\circ - \mu_{1b}^\circ) - a(\mu_{2\phi}^\circ - \mu_{2b}^\circ)}{RT}} \quad , \qquad (5)$$

where

$$a = \frac{V_{1\phi}}{V_{2\phi}} \quad .$$

The following assumptions are now made:

(1) $\mu_{i\phi}^{o} - \mu_{ib}^{o} = -\varepsilon_1(\phi)$, the Polanyi adsorption potential of pure component 1 at ϕ as obtained from the gas adsorption isotherm of component 1.

(2) $\tilde{V}_{1\phi}$ is the same function of $x_{1\phi}$, the mole fraction of 1 at ϕ as V_{1b} is of x_{1b}, the mole fraction in bulk.

(3) $\dfrac{a_{1\phi}}{a_{2\phi}}$ is the same function of $x_{1\phi}$ as $\dfrac{a_{1b}}{a_{2b}}$ is of x_{1b}, the latter function being determinable experimentally by activity measurements.

In the treatment of the experimental data, the molar volumes of the pure liquids have been used rather than the partial molar volumes. For the systems used, this is an excellent approximation. Although this simplification makes the calculations considerably more straightforward, it is not a necessary one.

With these assumptions Equation (5) becomes

$$\frac{a_{1\phi}}{a_{2\phi}} = \frac{a_{1b}}{a_{2b}} \, e^{\dfrac{\varepsilon_1(\phi) - a\varepsilon_2(\phi)}{RT}} \tag{6}$$

which is of the form

$$G(x_{1\phi}) = G(x_{1b}) \; f(\phi) \; .$$

For a specified x_{1b} and ϕ, $G(x_{1\phi})$ is determined by Equation (6) and, therefore, by assumption Equation (3), x_1 is obtained by inversion. For any value of x_{1b} the

predicted adsorption is therefore

$$\frac{V \Delta c}{m} = \int_0^\infty \left(\frac{x_{1\phi}}{\overline{V}_\phi} - \frac{x_{1b}}{\overline{V}_b} \right) d\phi \quad ,$$

in which $\overline{V}_\phi$ and $\overline{V}_b$ are the molar volumes at ϕ and in the bulk respectively. The value of $\frac{V \Delta c}{m}$ is found by graphical integration.

It should be noticed that, if $\mathcal{E}_1(\phi)$ happens to be of the form $\frac{k_1}{\phi^3}$ as would be expected from the treatment of Hill (11) and McMillan and Teller (12) then $f(\phi)$ becomes $\exp \frac{K}{\phi^3}$ where $K = \frac{1}{RT}(K_1 - a K_2)$. Because of the nature of $G(x_{1\phi})$, $x_{1\phi}$ will always be greater or always less than x_{1b} so that inversion of adsorption appears to be impossible in this case. If the form of $\mathcal{E}_1(\phi)$ follows the treatment of Halsey (13) and the values of n are not the same for two components, inversion of the adsorption isotherm is possible. The possibility of using analytical forms for $\mathcal{E}_1(\phi)$ appears attractive, but no satisfactory function has yet been developed.

An analogous treatment using an area constraint instead of a volume constraint could be made. This area constraint treatment must of course be subject to the validity of the assumptions mentioned above. Its utility is in the treatment of gases which give unimolecular adsorption isotherms and, therefore, is closely allied to the

earlier treatments of adsorption from solution.

B. Adsorption of Mixed Gases

The theory as adapted to mixed gas adsorption must be
modified to include the fundamental differences between ad-
sorption from solution and adsorption of mixed gases. In
adsorption from solution the density of the material sur-
rounding the adsorbent is practically constant out to and
including the bulk solution. As shown by Lowry and
Olmstead (21), when a gas is adsorbed at a temperature
well below its critical temperature there is a rather
sharp change in the density of the adsorbed gas, from the
liquid density next to the surface of the adsorbent, to the
gas density. The point at which this change takes place
is designated as ϕ_{max} and as adsorption is a surface ex-
cess, ϕ_{max} is the limit of integration in the determi-
nation of the amount of gas adsorbed. Thus the equation
for the adsorption of component i is

$$N_a = \int_0^{\phi_{max}} \frac{x_i \phi}{\overline{V}_\phi} \, d\phi - \frac{x_{ig}}{\overline{V}_g} \phi_{max} \quad .$$

The term $\dfrac{x_{ig}}{\overline{V}_g}$ is negligible as the value of the molar

volume of the gas is large.

ϕ_{max} is the volume corresponding to the greatest

distance from the adsorbent surface at which the adsorptive
forces are capable of liquefying the gas being adsorbed.
For a single component gas this can be established in
principle as the solution of the equation

$$\mu_{1\phi}^{\circ} - \mu_1 = 0 \quad ,$$

and for a system of binary mixed gases on adsorption is

$$x_1(\mu_{1\phi} - \mu_1) + x_2(\mu_{2\phi} - \mu_2) = 0 \quad .$$

From the definition of the chemical potential given earlier
it follows that

$$x_1(-\varepsilon_1 + RT \ln\frac{a_{1\phi}}{a_{1b}}) + x_2(-\varepsilon_2 + RT \ln \frac{a_{2\phi}}{a_{2b}}) = 0 \quad .$$

C. Discussion of Assumptions

The limitations of the three basic assumptions in-
cluded in this development are the causes of the limitations
inherent in the theory. A discussion of the validity of
the assumptions should point out these limitations, how-
ever, the very nature of most assumptions must lead to the
conclusion that the agreement of theory with experiment is
the best check of the accuracy of the assumptions. In the
assumptions used in the theory developed here, the first
one is a part of the basic foundation of the theory, the
last two are necessary because of the impracticallity of

measuring the partial molar volumes in the adsorbed phase
and the activity coefficients in the adsorbed phase.

As the assumption that the difference in the reference
states is equal to the Polanyi adsorption potential is
fundamental to the theory, the nature of $\varepsilon(\phi)$ is an im-
portant consideration. The clearest indication of the
nature of $\varepsilon(\phi)$ is contained in Hill's paper (11).
Basically, $\varepsilon(\phi)$ is attributed to the total van der Waal's
attraction between a molecule in the adsorption region and
all of the molecules in a semi-infinite slab of adsorbent.
Between each molecule in the slab and the molecule in the
adsorption region there exists an interaction energy of
the form $\dfrac{K}{r^6}$, r being the distance between interacting
molecules. Integrating this over the slab to a total
interaction energy of the form $\dfrac{\beta}{x^3}$, where x is the distance
of the adsorbed molecule from the slab, this distance being
proportional to ϕ. Hill, in his treatment, included a
term to correct for the interaction of the molecules in
the adsorbed phase, but this term changed only the value
of the β in the total interaction energy.

The basic van der Waal's interaction, if occurring
through a dielectric, can be shown by a trivial modification
of the treatment given by Pauling and Wilson (22) to de-
pend inversely on the square of the dielectric constant,

which would lead to the same dependence on the part of $\varepsilon(\phi)$. This would have no effect on the form of $\varepsilon(\phi)$ in single component adsorption, but could in principle cause $\varepsilon_i(\phi)$ to vary, at fixed ϕ, with composition of material enclosed between ϕ and the adsorbent surface in multicomponent adsorption. One consideration which lessens the effect of the dielectric constant upon $\varepsilon(\phi)$ is present when orientation of the adsorbed molecules takes place. When the position of the dipoles is fixed, the dielectric constant is proportional to the square of the refractive index and, therefore, does not change much with composition.

The partial molar volumes of substances in the neighborhood of an adsorbent surface might differ from their values in bulk solution of the same composition because of orientation and compression due to the adsorption potential. For liquids well below critical temperatures and under the effect of moderate adsorption potentials, deviations from bulk solution should be minor. In the case of the activity coefficients of the components, strong orientation may alter the interaction between the components. This orientation would depend strongly upon the dipole moments of the components and especially upon the polar character of the adsorbent. With non-polar adsorbents and moderate adsorption potentials, it is felt that the variation of the activity coefficients should be negligible.

V. TREATMENT OF DATA AND CONCLUSIONS

A. Method of Calculation

The experimental data used in the calculations were
points picked off the smooth curves drawn through the ad-
sorption isotherms shown in Figures 4 - 10. The ad-
sorption isotherms were chosen instead of the desorption
isotherms because the method used by Craig (15) and Hansen
(16) in obtaining the adsorption from solution data indi-
cated this treatment. The adsorbent sample was put into
a known solution and after equilibrium was reached, the
resulting solution was analyzed. The points that resulted
in an increase of the mole fraction of water could be con-
sidered to have resulted from the desorption of water.
However, in no case where there was desorption of water
was the mole fraction of the water greater than 0.7.
From this consideration it appears reasonable to believe
that the likelihood of the adsorbent initially becoming
saturated with water and then desorbing to equilibrium is
small. The fact that equilibrium in solution adsorption
was reached in two minutes, which was the shortest possi-
ble time in which a measurement could be made, is another
point against the desorption process.

Other data needed to complete the calculations are the
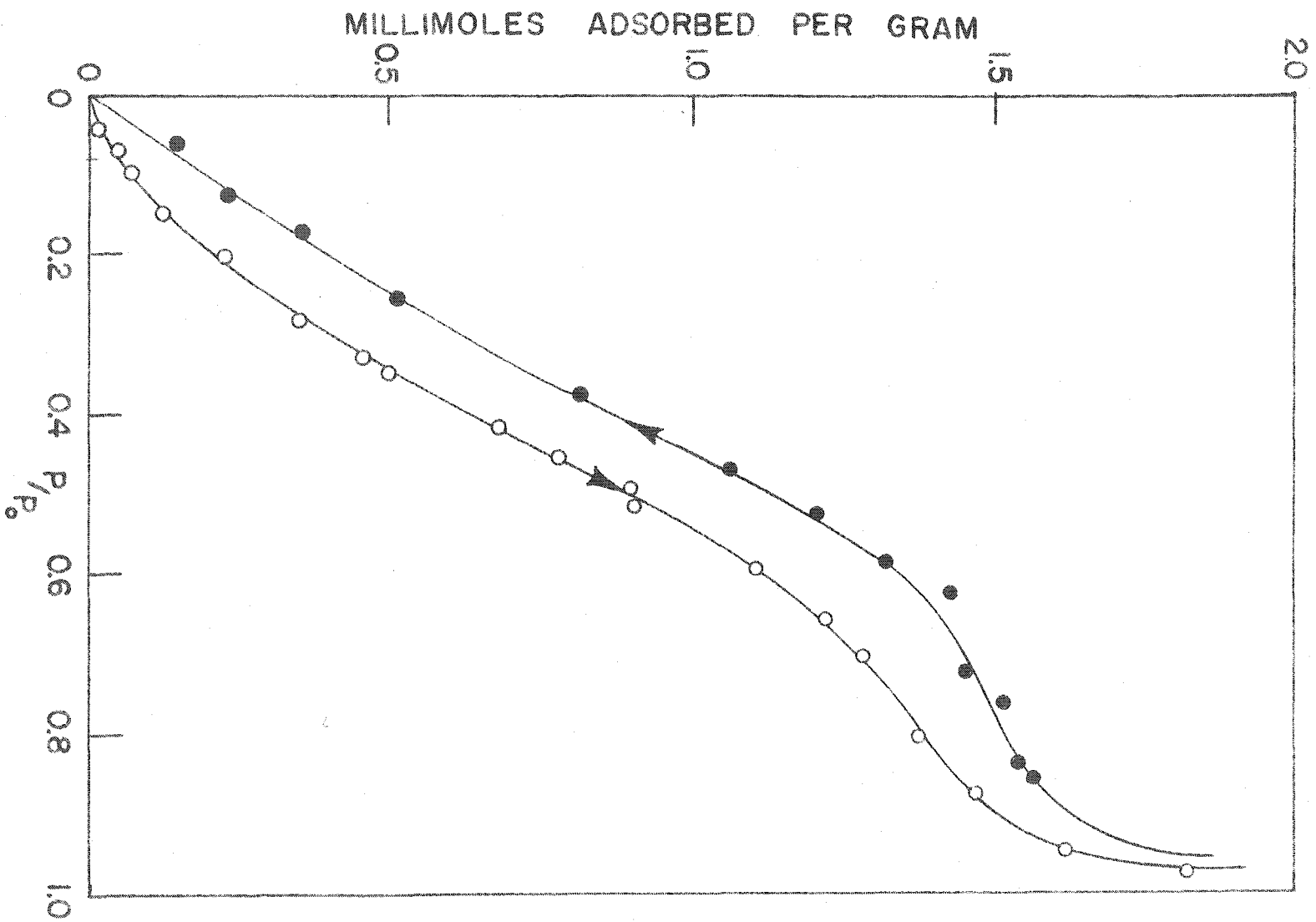activity coefficients and the molar volumes of the binary

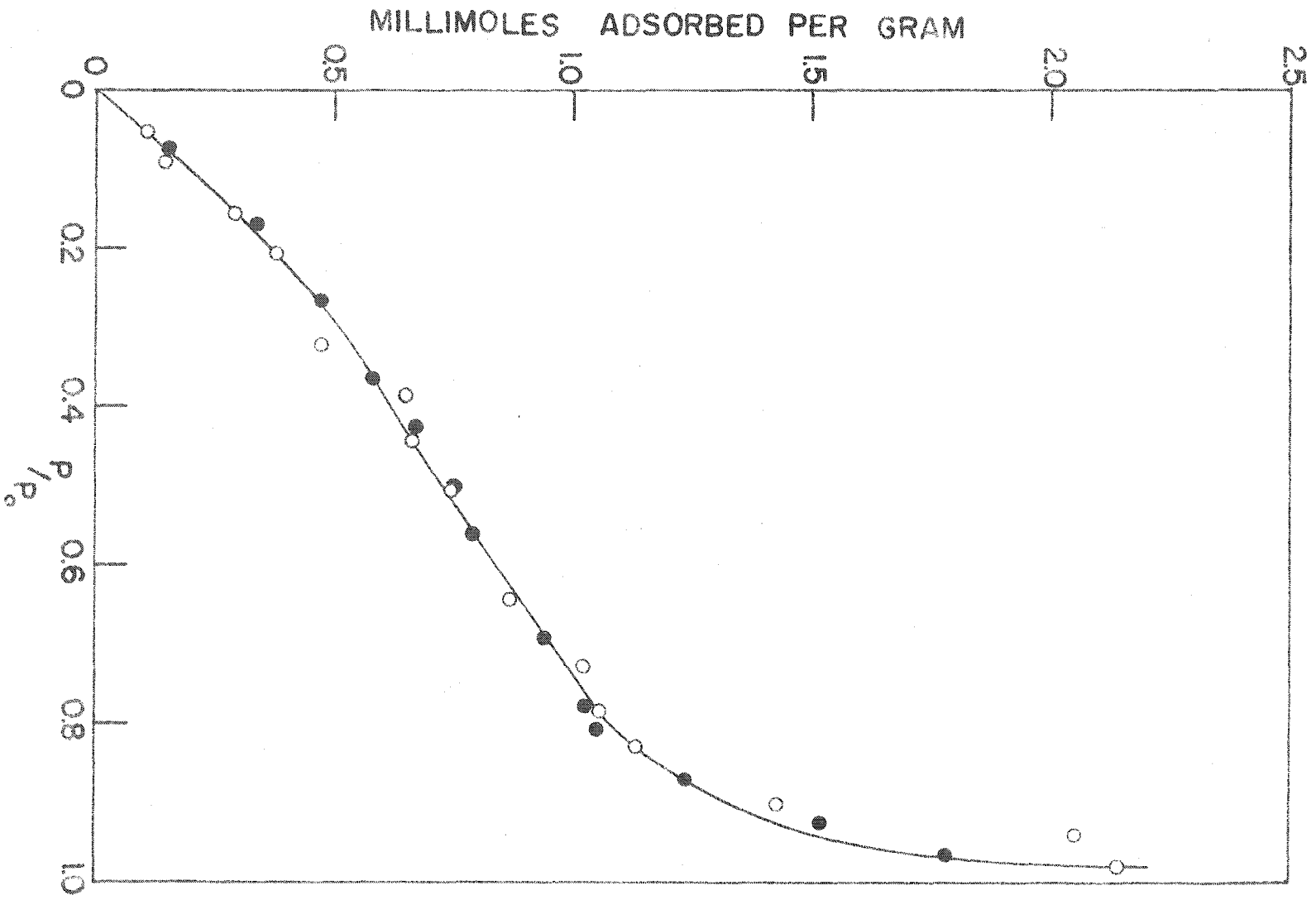Figure 4. Adsorption of Water on Spheron-6 at 25°C.

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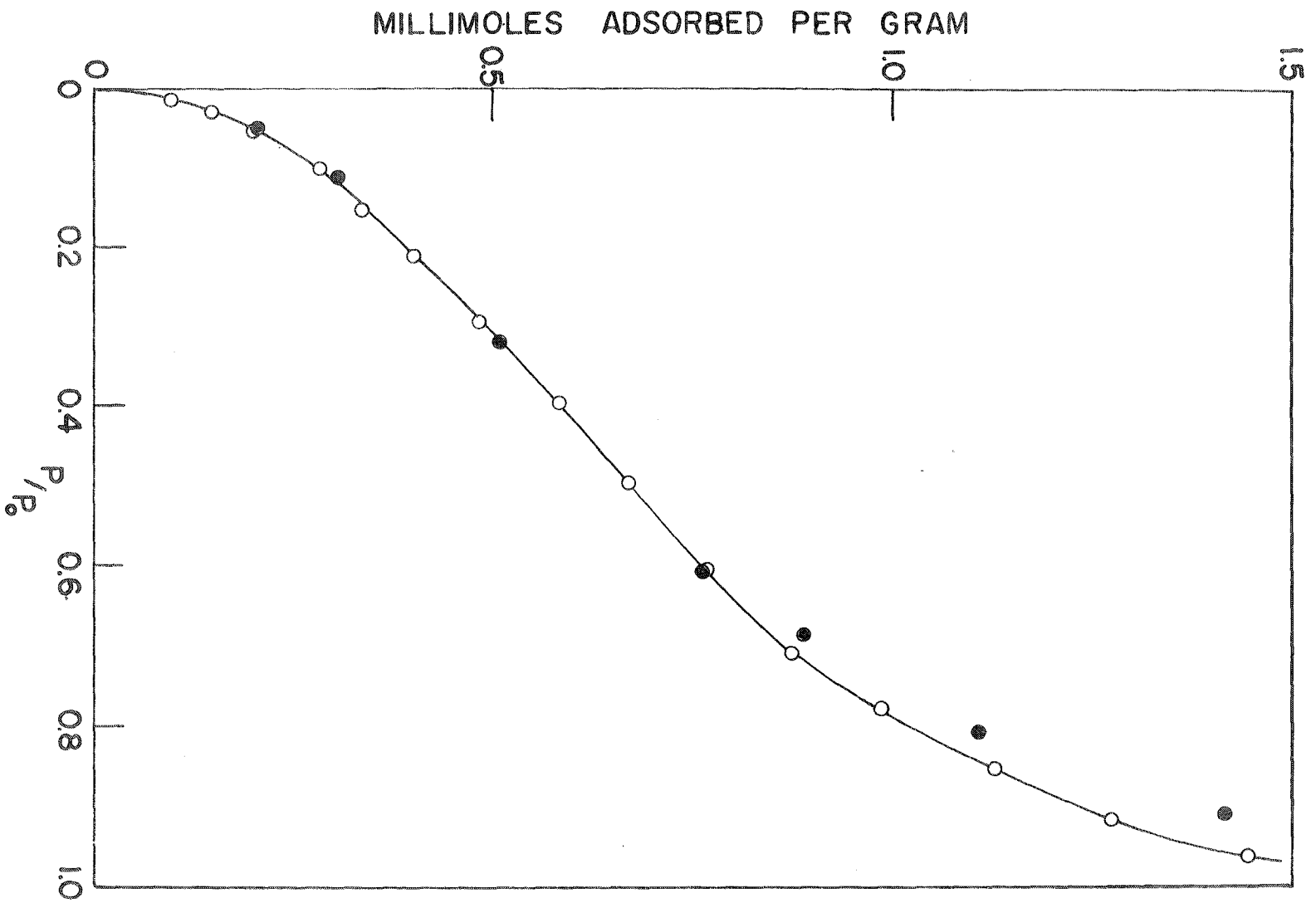Figure 5. Adsorption of Propanol-1 on Spheron-6 at 25°C.

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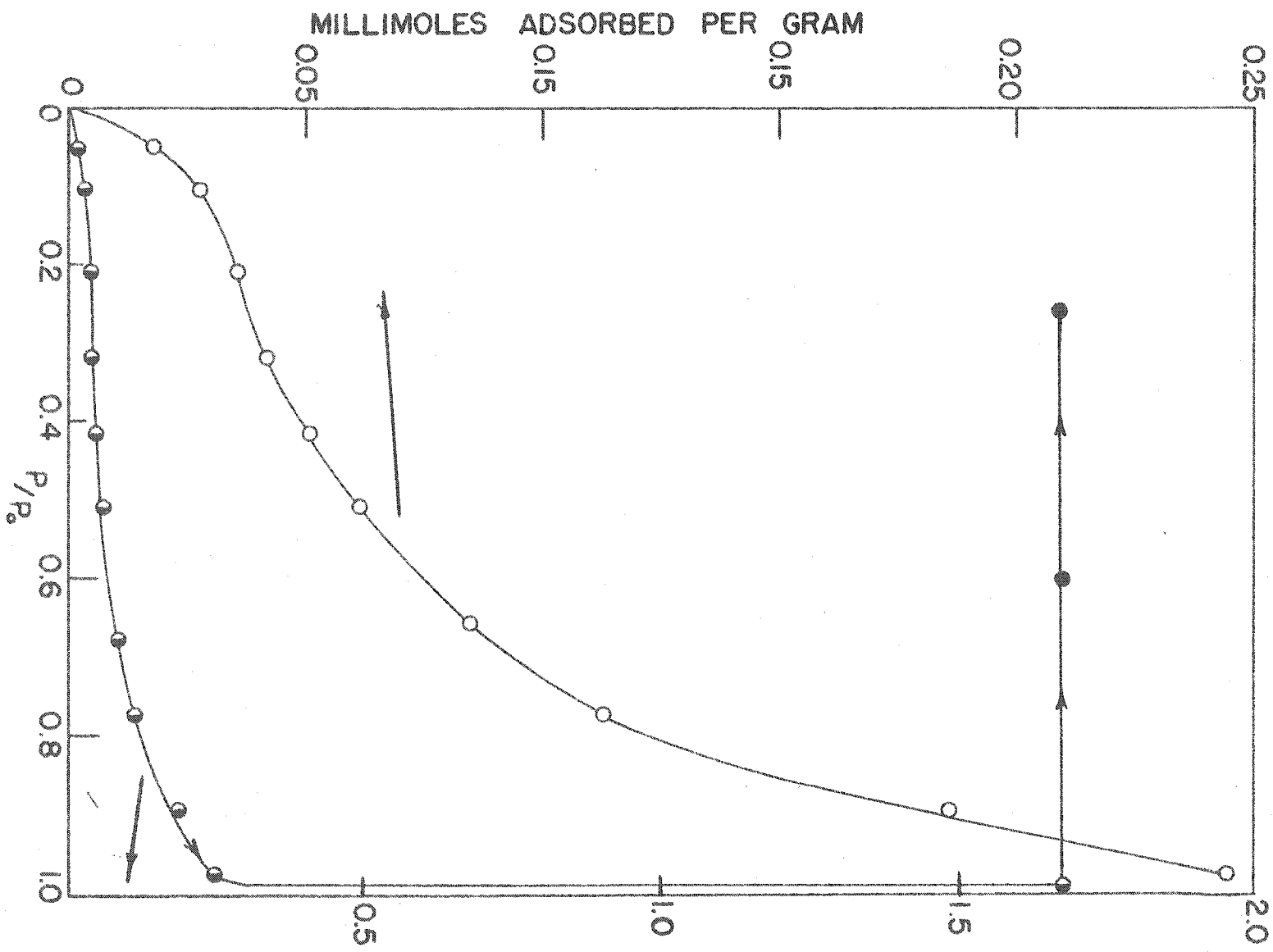Figure 6. Adsorption of Butanol-1 on Spheron-6 at 25°C.

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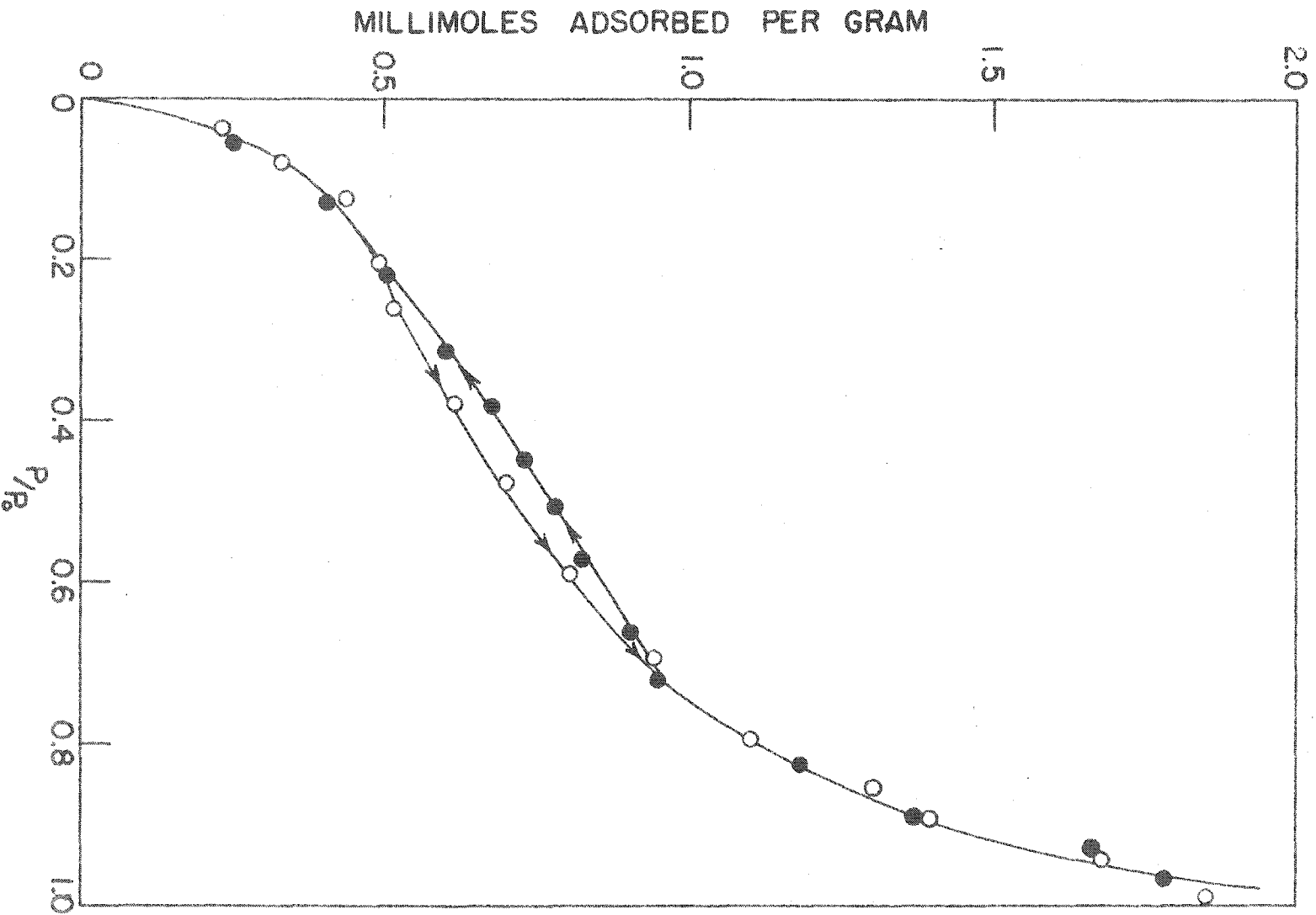Figure 7. Adsorption of Water on DAG-1 at 25°C.

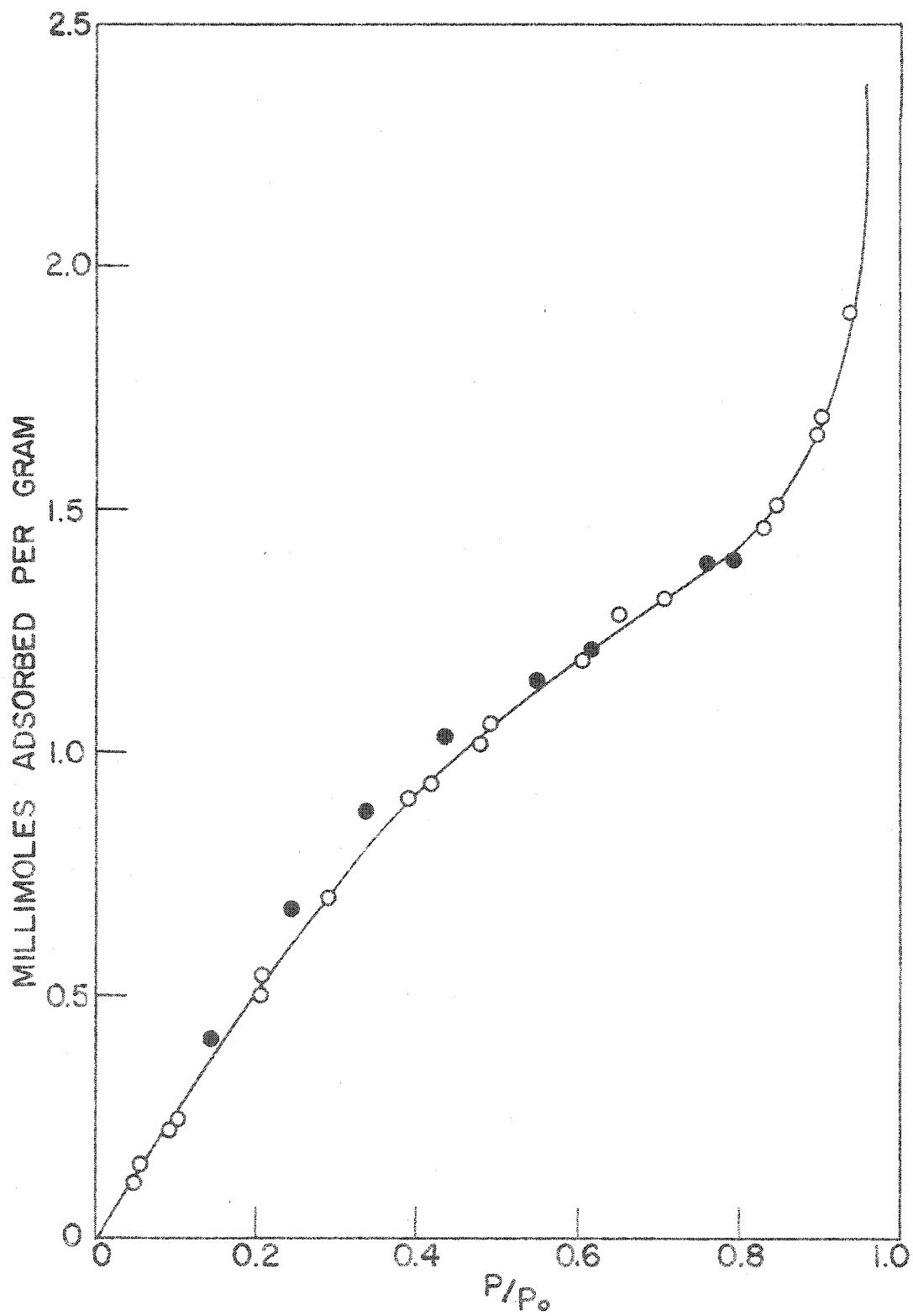Figure 8. Adsorption of Propanol-1 on DAG-1 at 25°C.
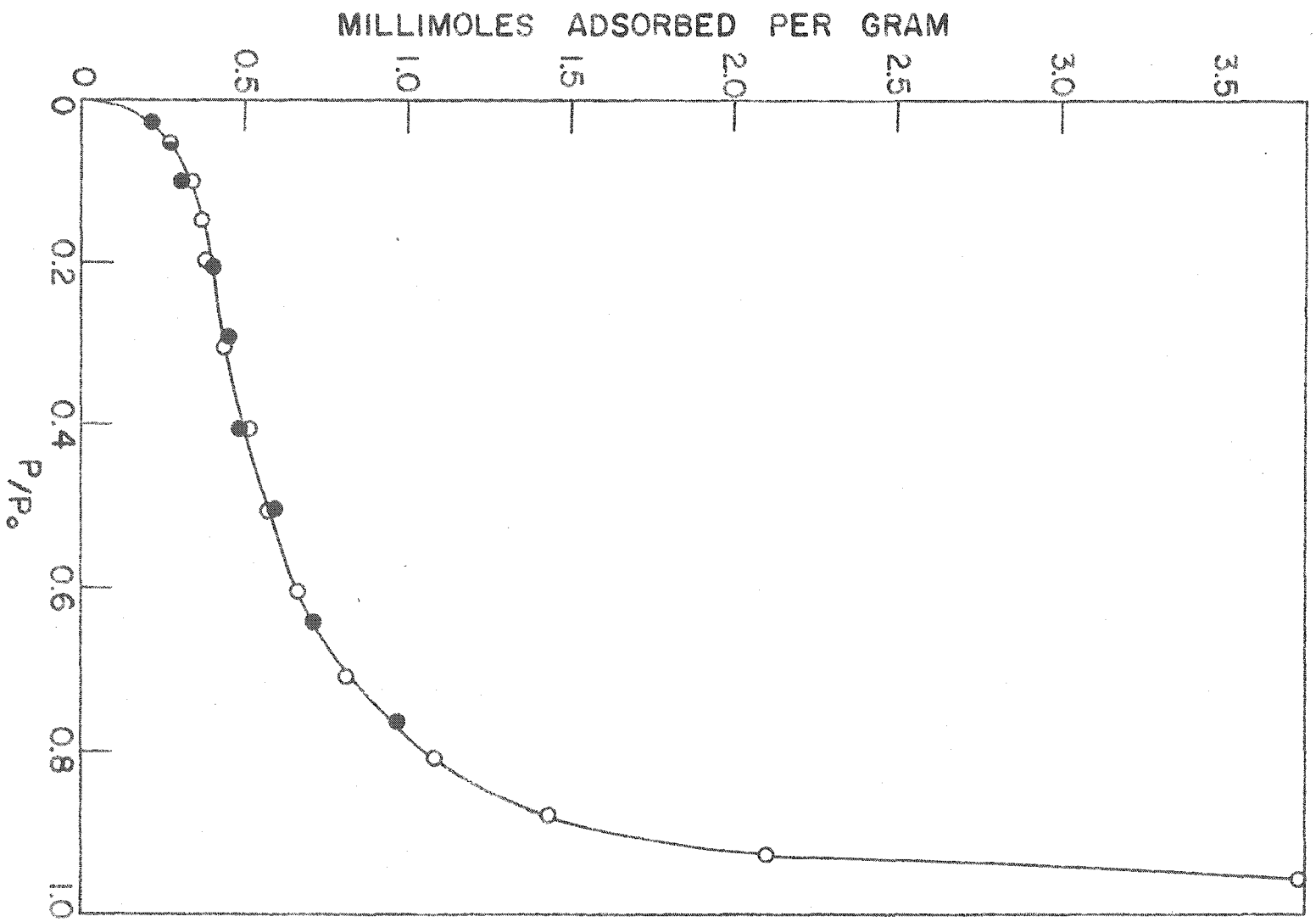
42

Figure 9. Adsorption of Ethanol on Spheron-6 at 25°C.

Figure 10. Adsorption of Cyclohexane on Spheron—6 at 25°C.

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solutions used. The systems chosen were those for which the necessary information was available. The molar volumes for the water-propanol-1 system and the water-butanol-1 system were calculated from the density data for these systems given in the International Critical Tables. The density data for the ethanol-cyclohexane system was calculated from data obtained by Hansen (16), who made up 50 ml. samples, and weighed the amount of the components. The data while not extremely precise gave every indication that the molar volume was a linear function of the mole fraction. For the system nitrogen-oxygen at 78.2° K., which was the system studied by Arnold (23), a linear function of mole fraction was assumed, which is reasonable in view of the nearly ideal behavior of this system. Arnold made a rather complete and exacting study of the adsorption of the gas mixture of oxygen and nitrogen at 78.2° K., and his isotherms were used to compare with calculated gas mixture adsorption.

The activity coefficients used were obtained from various sources. Activity data for the water-propanol-1 system were obtained by Miller (24). The water-butanol-1 system was studied by Randall and Weber (25) and by Butler, Thomson and Maclennan (26). The work of Butler, Thomson and Maclennan was done at 25° C. which was the temperature needed for the present work and was therefore

used. The data of Randall and Weber were taken at 30° C, but checked closely the data used. The activity for the ethanol-cyclohexane system was taken from the owrk of Washburn and Handorf (27). All the systems mentioned above deviate greatly from ideality; in fact the water-butanol-1 system has a large region of immiscibility. In comparison with these, according to Dodge and Davis (28) the oxygen-nitrogen system at 78° K is almost ideal.

The actual calculations were made in the following manner. From the experimental adsorption isotherm, points were taken and a plot of $_1(\emptyset)$ versus $\emptyset$ was made. In all the calculations $\emptyset$ was in units of cubic millimeters at the liquid density of the substance whose vapor was adsorbed. Such plots were made for both components of the system being studied. For the two component points of equal $\emptyset$ were taken and the quantity $\log \exp \frac{\epsilon_1 - \epsilon_2}{kT}$ tabulated as a function of $\emptyset$. Using the activity data a plot was made of $\log \frac{a_1}{a_2}$ versus x_1, x_1 being the mole fraction of component 1. The molar volume data was used to make a graph of $\frac{x_1}{V}$ versus x_1. From these last two graphs, a plot of $\frac{x_1}{V}$ versus $\log \frac{a_1}{a_2}$ was constructed. To calculate an adsorption point corresponding to a certain bulk solution, the value of $\log \frac{a_1}{a_2}$ for the bulk solution was added to each value in the list of the

function log $\exp\left(\frac{\varepsilon_1 - \alpha\varepsilon_2}{RT}\right)$. This new table of values is
a list of the values of the function log $\frac{a_1\phi}{a_2^\alpha\phi}$ as a
function of ϕ in the adsorbed phase. From the graph men-
tioned above, a list of the values of the function $\frac{x_1}{\bar{V}}$ as
a function of ϕ for the adsorbed phase was made. The
value of $\frac{x_1}{\bar{V}}$ for the bulk solution was subtracted from the
$\frac{x_1}{\bar{V}}$ terms for the adsorbed phase and a graph was made of
$\left(\frac{x_1}{\bar{V}}\right)_\phi - \left(\frac{x_1}{\bar{V}}\right)_b$ versus ϕ. This plot was graphically in-
tegrated to obtain the $\frac{V\Delta c}{m}$ corresponding to the bulk
equilibrium concentration.

When adsorption of gas mixtures is to be calculated
the values of $\frac{x_1}{\bar{V}}$ and $\frac{x_2}{\bar{V}}$ are plotted against ϕ. In order
to obtain the value for ϕ_{max} the function

$$x_1\left(-\varepsilon_1 + RT\ln\frac{a_1\phi}{a_{1g}}\right) + x_2\left(-\varepsilon_2 + RT\ln\frac{a_2\phi}{a_{2g}}\right)$$

is plotted against ϕ and the value of ϕ when the above
function crosses the zero axis is the value of ϕ_{max}.
This value of ϕ is the upper limit of the integration
when the graph of $\frac{x}{\bar{V}}$ is integrated and the value obtained
by integration is the amount of adsorption at the reduced
pressure of the gas phase. The value of log $\frac{a_1}{a_2^\alpha}$ used ini-
tially is calculated from the partial pressures of the
components in the gas mixture; however, $\bar{V}_1$ and $\bar{V}_2$ are the
liquid molar volumes of the components.

B. Calculated Adsorption from Solution

1. Original theory

Using the theory and method of calculation previously outlined, the adsorption isotherms for the following systems were calculated; water-propanol-1 on Spheron-6, water-butanol-1 on Spheron-6, water-propanol-1 on DAG-1, and ethanol-cyclohexane on Spheron-6. These isotherms are shown in Figures 11-14. The circles on the aqueous systems are the experimental data of Craig (15) and the circles on the ethanol-cyclohexane system are the experimental data of Hansen (16). The original theory was used to calculate the solid lines for the water-propanol-1 and the water-butanol-1 adsorption on Spheron-6.

The calculated isotherms are seen to be in qualitative agreement with experimental results except in the case of the water-butanol-1 system. As the curves of $\left(\frac{x_1}{\overline{V}}\right)_{\varnothing} - \frac{x_1}{\overline{V}}\bigg|_b$ versus $\varnothing$ are essentially different in the four systems, a representative curve is shown for each system. These are given in Figures 15-18. It is these curves which give a physical picture of the adsorption process and some rather surprising effects are apparent. In the adsorption isotherms of water-propanol-1 and water-butanol-1 on Spheron-6 the physical picture led to a modification of the theory.
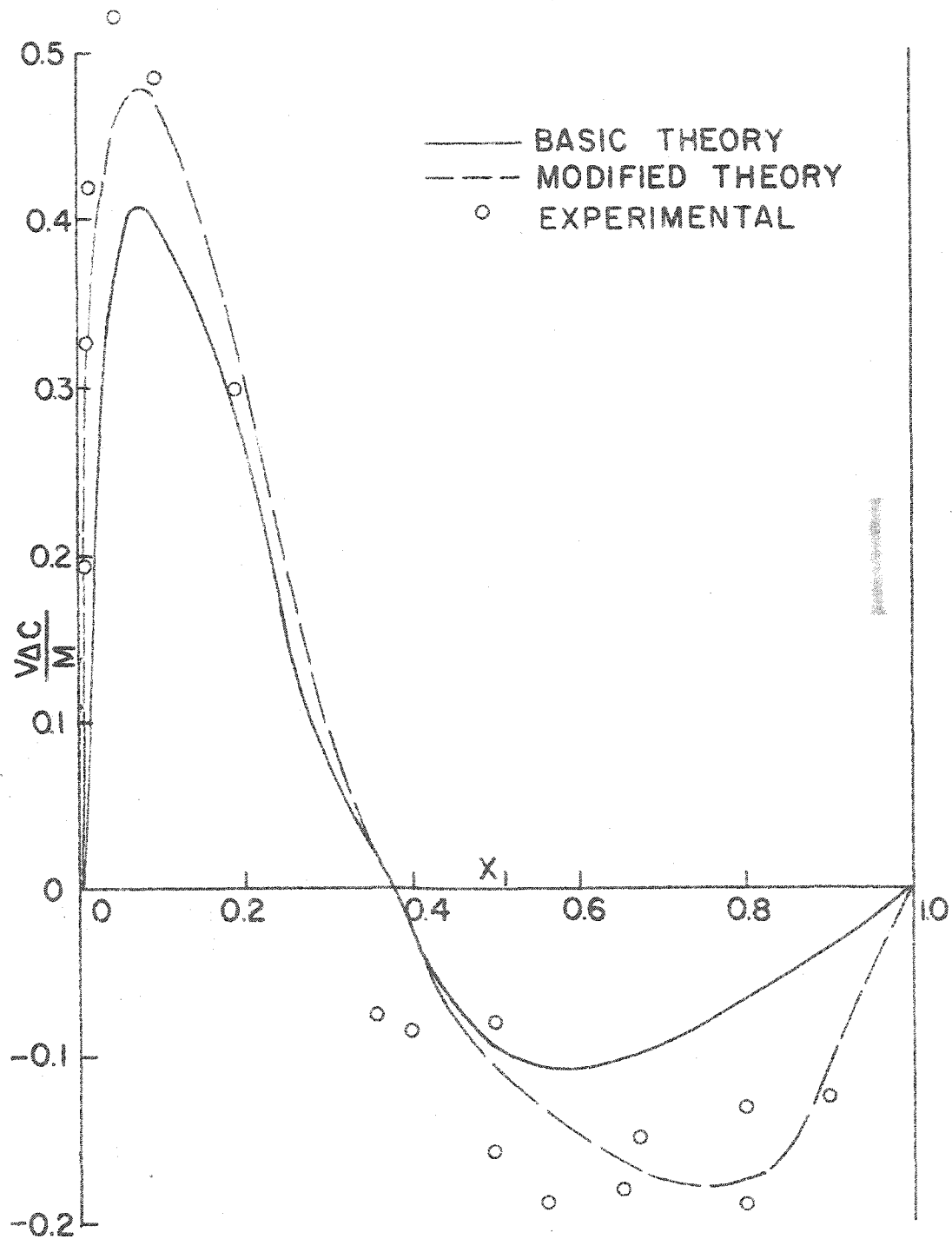
Figure 11. Adsorption of Propanol-1 from Aqueous
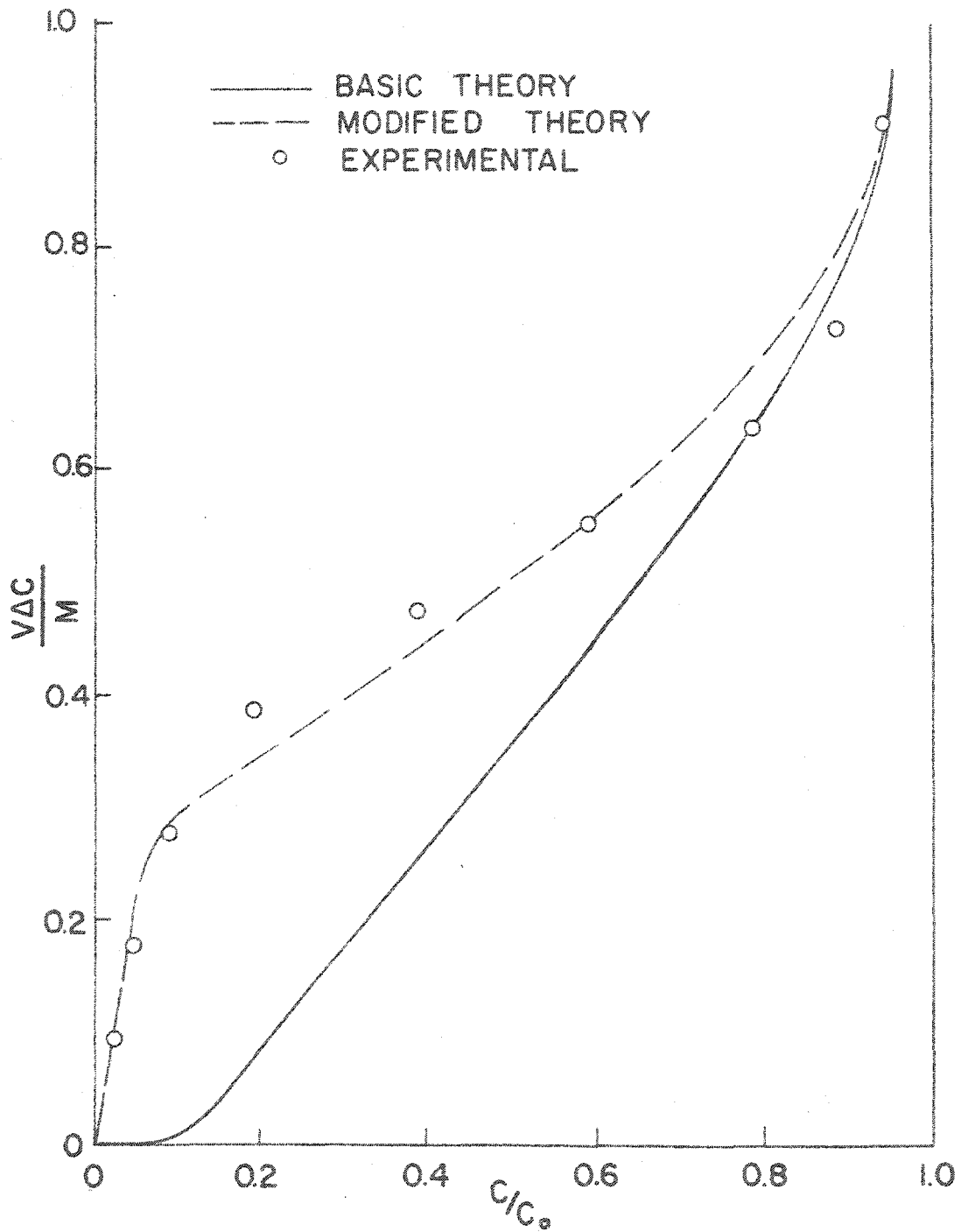Solution by Spheron-6 at 25°C.

Figure 12. Adsorption of Butanol-1 from Aqueous
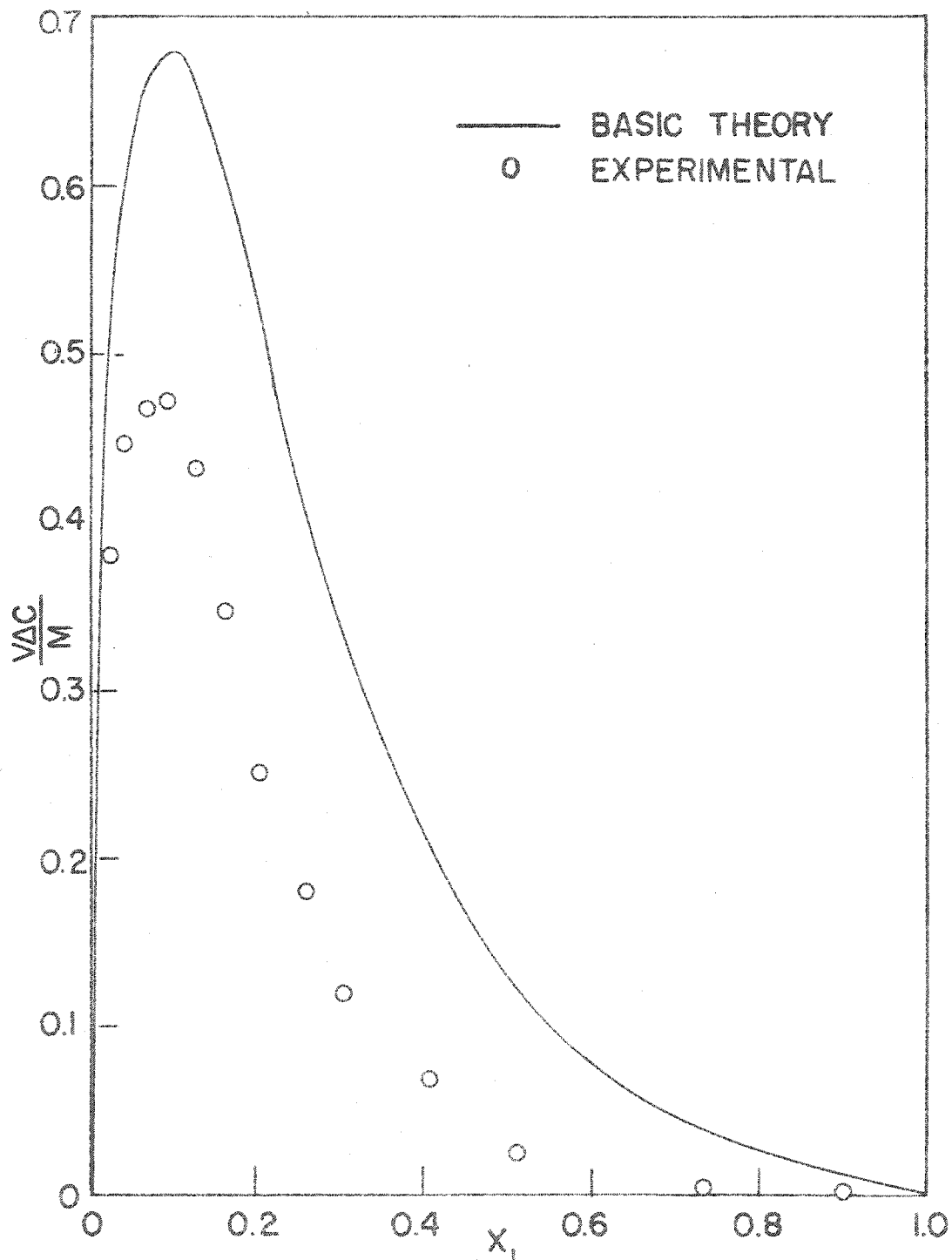Solution by Spheron-6 at 25°C.

Figure 13. Adsorption of Propanol-1 from Aqueous
Solution by DAG-1 at 25°C.
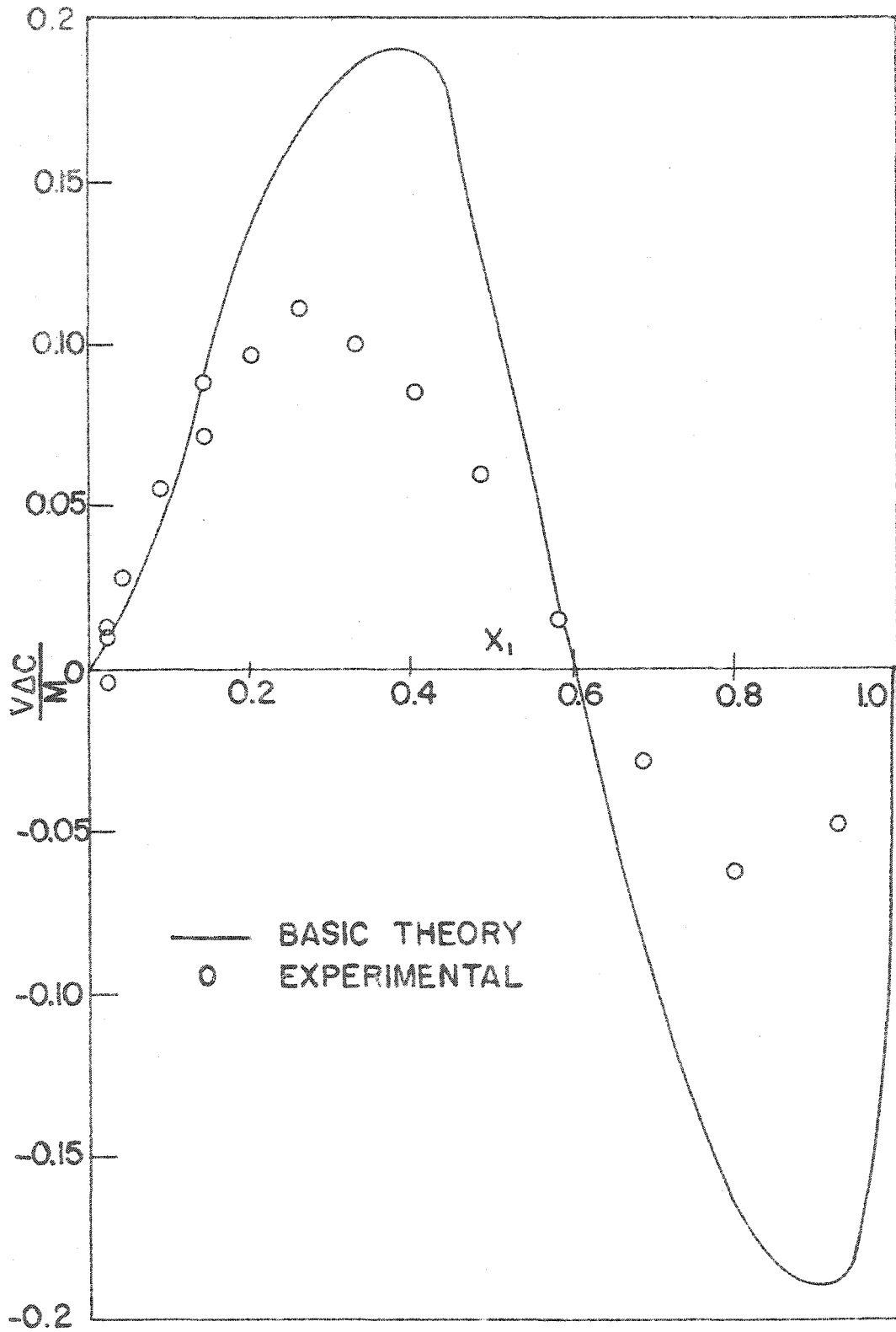
Figure 14. Adsorption of Cyclohexane from Ethanol Solution by Spheron-6 at 25°C.
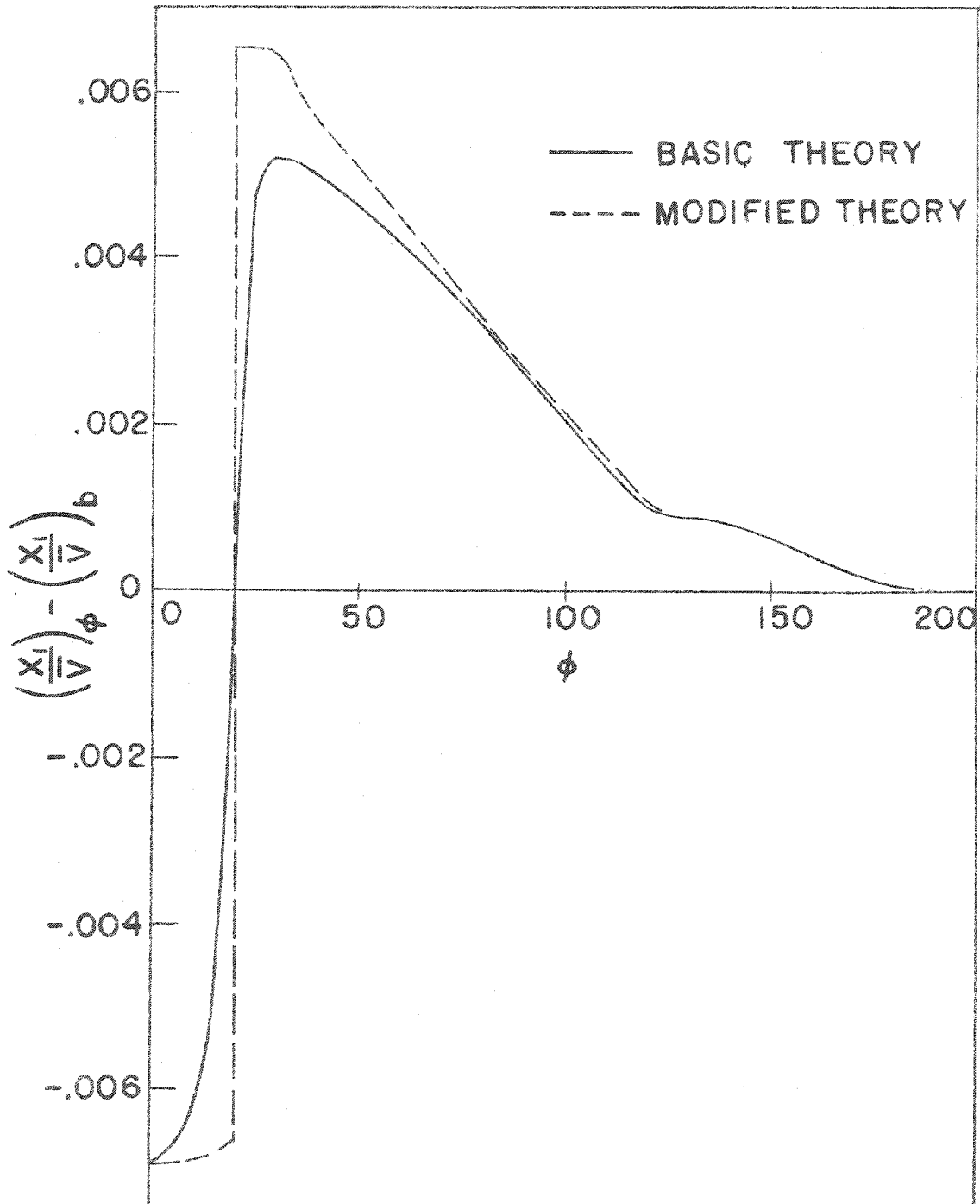
Figure 15. $\frac{x_1}{V}\phi - \frac{x_1}{V}b$ versus ϕ Curve for the System Propanol-1-Water-Spheron-6. Propanol-1 is Component 1 with Mole Fraction 0.200.

Figure 16. $\dfrac{x_1}{\overline{V}}\Bigg|_{\emptyset} - \dfrac{x_1}{\overline{V}}\Bigg|_{b}$ versus $\emptyset$ Curve for the System Butanol-1-Water-Spheron-6. Butanol-1 is Component 1 with Mole Fraction 0.200.

Figure 17. $\frac{x_1}{\overline{V}}\,\phi - \frac{x_1}{\overline{V}}\,b$ versus ϕ Curve for the System Propanol-1-Water-DAG-1. Propanol-1 is Component with Mole Fraction 0.100.
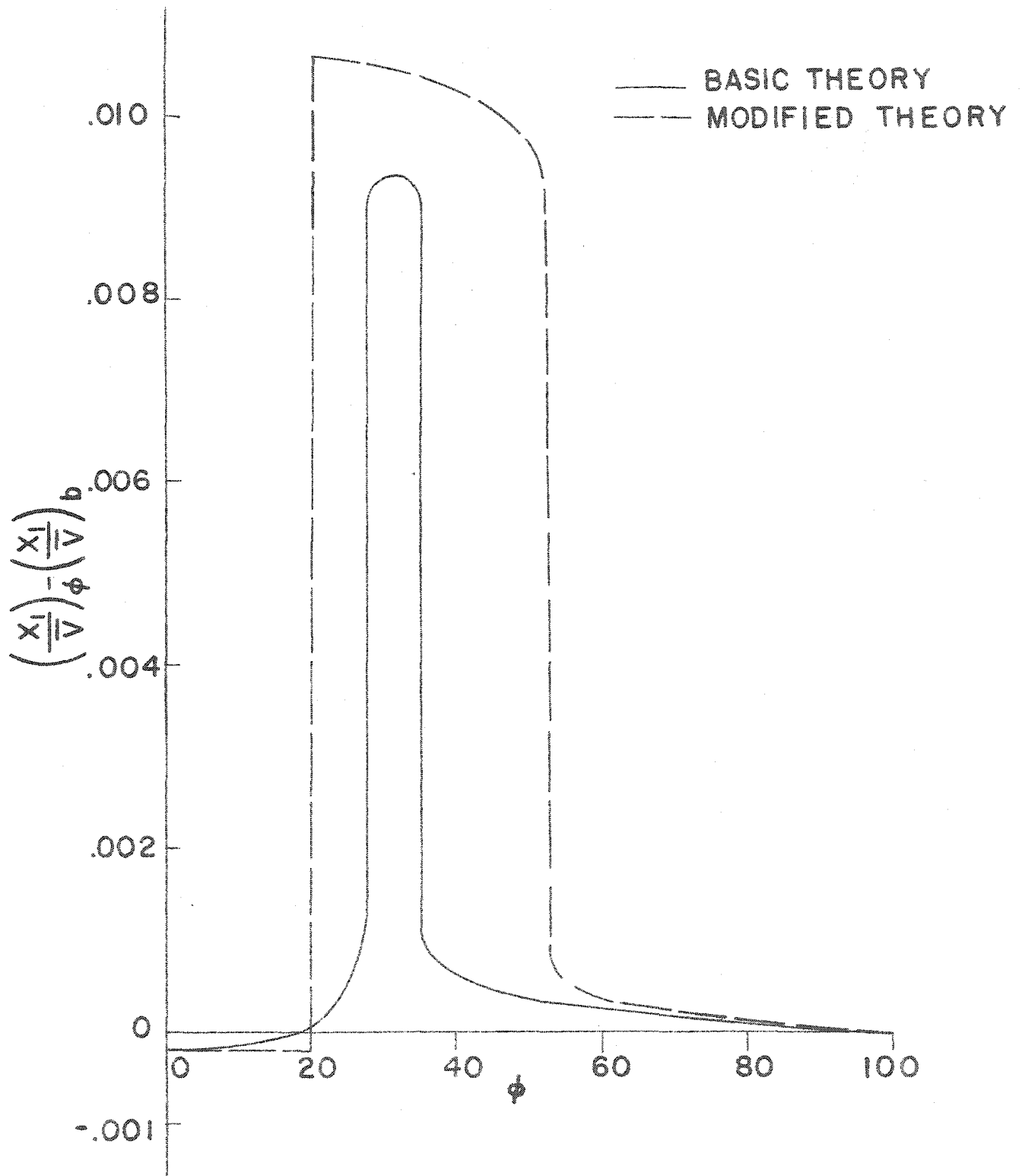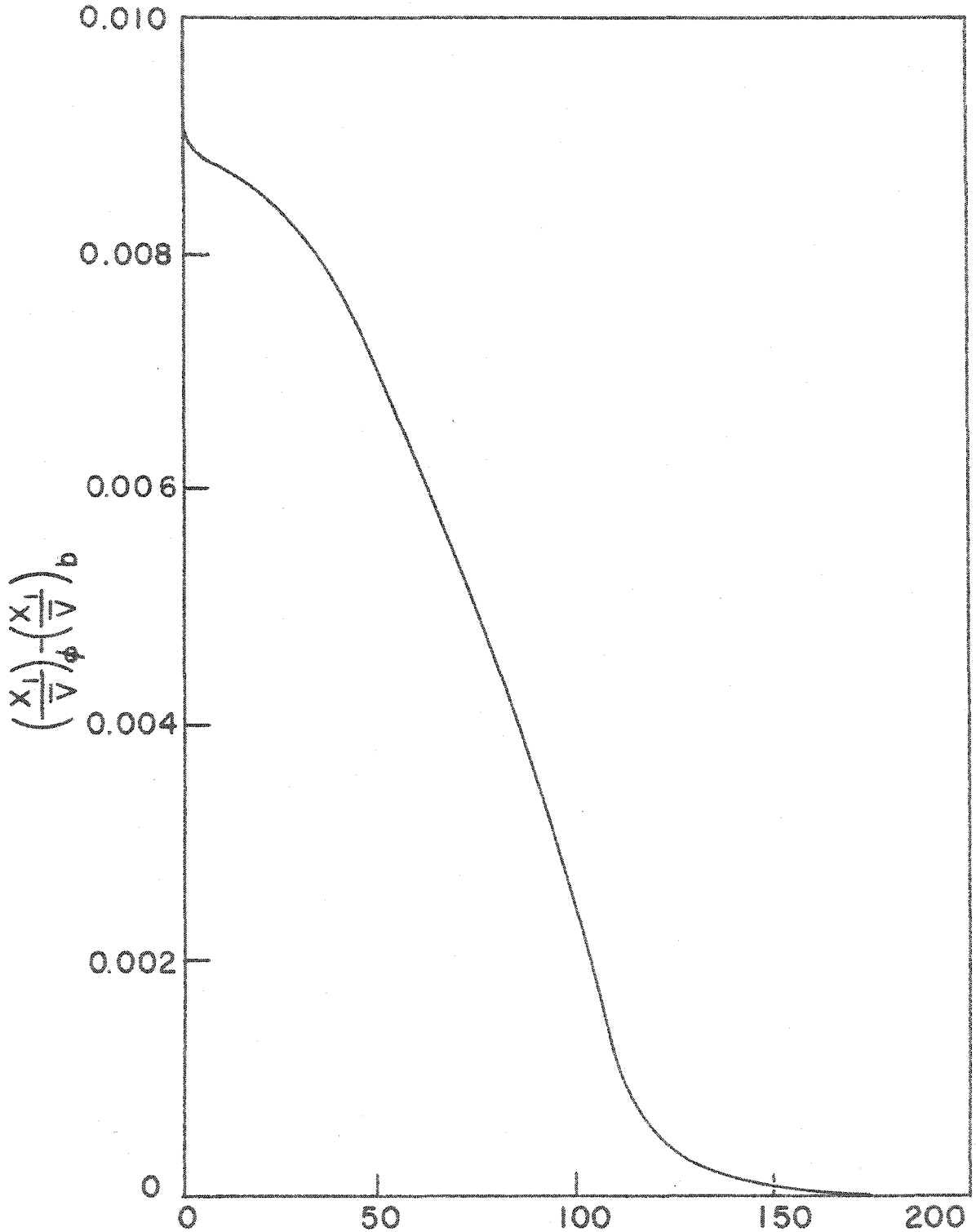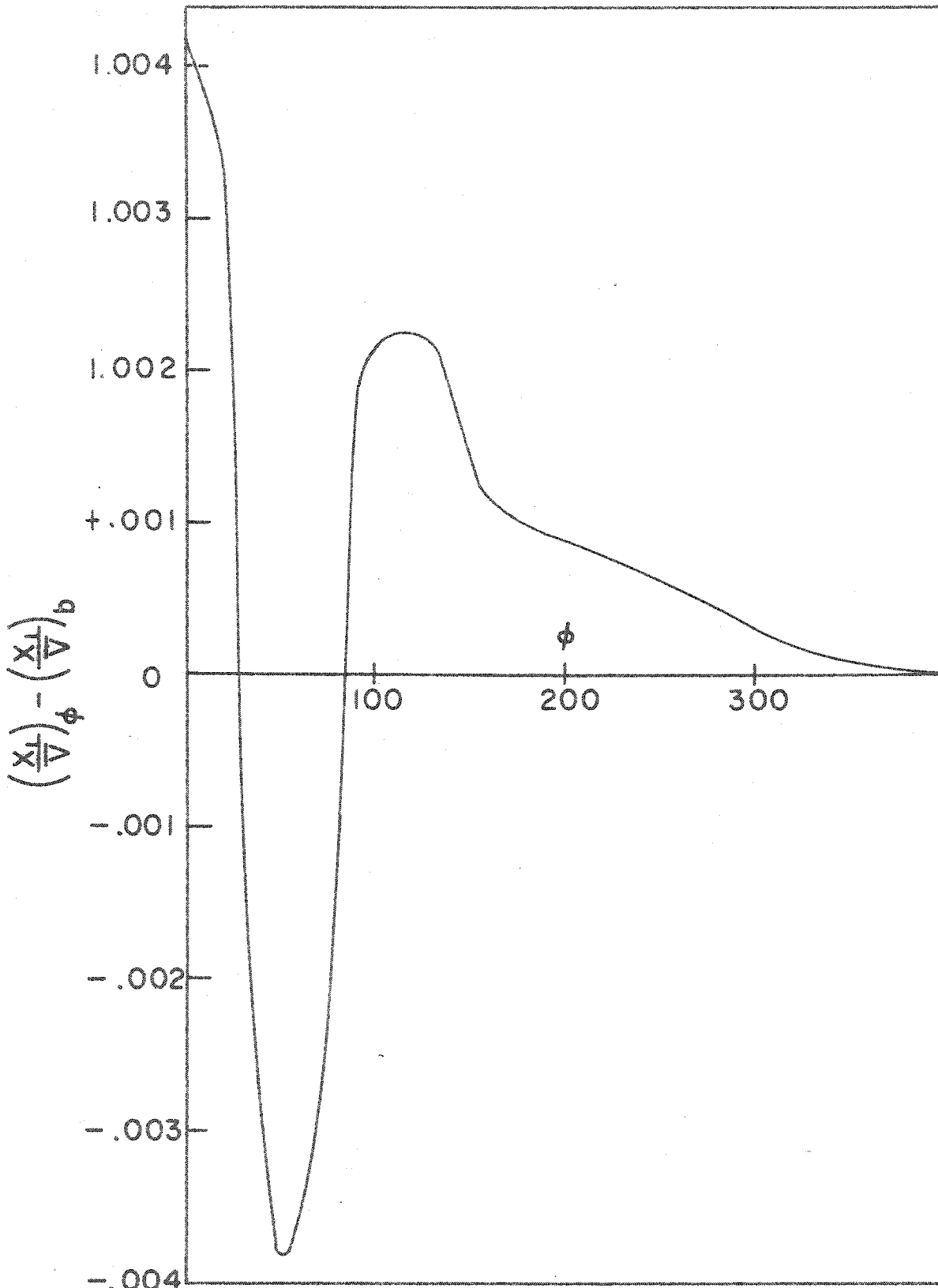
Figure 18. $\frac{x_1}{\overline{V}}\phi - \frac{x_1}{\overline{V}}\,b$ versus ϕ Curve for the System Cyclohexane-Ethanol-Spheron-6. Cyclohexane is component 1 with Mole Fraction 0.400.

The first case to be discussed is the adsorption of water and propanol-1 on DAG-1. The $\left(\frac{x_1}{v}\right)_\emptyset - \left(\frac{x_1}{v}\right)_b$ curve shows that there is a concentration of propanol-1 at all values of $\emptyset$ out to the point where bulk concentration is reached. This follows logically from the shape of the adsorption isotherms of water and propanol-1 on DAG-1. The adsorption of the water is so very slight that the $\mathcal{E}(\emptyset)$ for water has no effect when compared with that for propanol-1. When the theoretical isotherm is compared with the actual, the observation is made that the adsorption calculated is too large. Trouble experienced in obtaining the adsorption isotherm of water, coupled with the irreversibility of the isotherm makes this system one in which agreement could be expected to be poor. The shape of the calculated isotherm agrees with the shape of the experimental isotherm giving support to the theory.

The adsorption isotherm of water propanol-1 by Spheron-6 is one in which an inversion occurs. The calculated isotherm is in qualitative and rough quantitative agreement with the theoretical. When Figure 15 is examined, certain pecularities in the behavior of this system become apparent. Figure 15 indicates that up to a $\emptyset$ of 20 mm.^{3}, the adsorbed phase is almost pure water and beyond this point the alcohol concentrates. Assuming that the adsorbed phase is pure water and using the liquid

density of water, the mean area per water molecule can be calculated and was found to be 17.1 Å^2. According to Brunauer (10, p 274) the area of a water molecule is 11.5 Å^2; the observed water adsorption therefore is more than 50% of the value corresponding to a complete water monolayer.

Water and butanol-1 are not completely miscible and the isotherm shown in Figure 12 is the isotherm from the water rich phase. The mole fraction of butanol-1 corresponding to saturation concentration is 0.0188. As is seen from Figure 16, the shape of the $\left(\frac{x_1}{\bar{v}}\right)_\emptyset - \left(\frac{x_1}{\bar{v}}\right)_b$ versus $\emptyset$ curve for the water-butanol-1 system is similar to the $\left(\frac{x_1}{\bar{v}}\right)_\emptyset - \left(\frac{x_1}{\bar{v}}\right)_b$ curve for the water-propanol-1 system. The composition of the adsorbed phase is again almost pure water up to a $\emptyset$ of 20 mm.^{3} The situation in the water-butanol-1 case is different for $\emptyset > 20$ mm.^{3} as there are discontinuities in the $\left(\frac{x_1}{\bar{v}}\right)_\emptyset - \left(\frac{x_1}{\bar{v}}\right)_b$ curve resulting from the formation of the butanol-1 rich phase. The adsorption isotherm calculated from the original theory is given by the solid line in Figure 12. The agreement with experiment is excellent at high reduced concentration, but at low reduced concentration the calculated adsorption is much too low. In fact, the calculated adsorption isotherm has a positive curvature at all activities, while

the experimental adsorption isotherm is sigmoid in shape. The modified theory as described later improves the agreement.

The adsorption isotherm of the ethanol-cyclohexane system on Spheron-6 is given in Figure 14. One unusual aspect of this isotherm is the positive curvature of the isotherm at low mole fraction of cyclohexane. The data of Hansen (16) also indicate this behavior although in a less pronounced manner. This behavior is unusual as practically all adsorption from solutions are concave toward the zero axis at the ends. The $\left(\frac{x_1}{\bar{v}}\right)_{\phi} - \left(\frac{x_1}{\bar{v}}\right)_b$

versus ϕ plot for this system (Figure 18) is most unusual; for $0 < \phi < 28$ mm.^{3} there is a concentration of cyclohexane, for $28 < \phi < 85$ mm.^{3} there is a concentration of ethanol and for $\phi > 85$ mm.^{3} there is again a concentration of ethanol. In spite of this complicated situation, the calculated adsorption isotherm agrees qualitatively with the experimental; the position of the inversion point checks closely; at both ends, however, the absolute value of the calculated isotherm is too great.

2. Modified theory

The curves of $\left(\frac{x_1}{\bar{v}}\right)_{\phi} - \left(\frac{x_1}{\bar{v}}\right)_b$ versus ϕ suggest a possible modification of the original theory. Due to the

existence of surface oxides on Spheron-6 it would be
reasonable to assume that the water is concentrated in
the immediate neighborhood of the surface in the form of
an oriented dipole film. This picture is supported by
the curves referred to. Under these circumstances the
following assumptions could be made:

1. For $\emptyset < 20$ (region of the dipole layer) the
Polanyi potential incorrectly represents the ad-
sorption of alcohol in the presence of an oriented
dipole layer (in the same region), and since it is
less than $\alpha \mathcal{E}_2(\emptyset)$ in this region ($\mathcal{E}_2$ is the
Polanyi potential of water, $\alpha = V_1/V_2$) it appears
not entirely unreasonable to neglect it entirely
for $\emptyset < 20$.

2. For $\emptyset > 20$ molecules are subjected, in addition
to their Polanyi potentials, to a potential due to
the oriented dipole layer. Since the dipole densi-
ty is known as well as polarizabilities and dipole
moments of molecules involved it should be possible
to estimate the order of magnitude of this effect.

Consider the adjacent diagram.

Let σ be the number of dipoles per cm^2
in the oriented layer, μ_1 and α_1 the
dipole moment and polarizability of each,
μ_2 and α_2 the corresponding quantities for the molecule
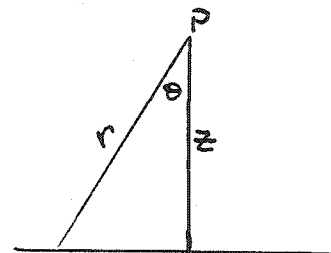
at P interacting with the dipole layer. With a dipole at distance r the interaction energy is

$$u = - \frac{\alpha_1 \mu_2^2 + \alpha_2 \mu_1^2}{r^6} \, .$$

The total interaction energy is then

$$U = -\int_0^{\frac{\pi}{2}} \frac{(\alpha_1 \mu_2^2 + \alpha_2 \mu_1^2)}{z^6/\cos^6 \theta} \cdot 2\pi \sigma' z \tan\theta \, d(z\tan\theta)$$

$$= - \frac{\pi(\alpha_1 \mu_2^2 + \alpha_2 \mu_1^2)}{2 z^4} \sigma \quad \text{(per molecule)}$$

Setting $z = \frac{\emptyset - 10}{1000 \, A}$, $\emptyset$ in mm.[3]

$\alpha = 3P/4\pi N_0$, where P is the molar polarization

$\bar{\mu} = \mu \times 10^{+18}$ = dipole moment in Debyes

$A = 114 \times 10^4 \, \text{cm}^2/\text{gm}$

$\sigma = 10^{16}/17.1 = 5.85 \times 10^{14}$ dipoles/cm^{2}

$1 \, \text{erg/molecule} = N_0/4.183 \times 10^7$ calories/mole

there results

$$U = - \frac{8.86 \times 10^6 (P_1 \bar{\mu}_2^2 + P_2 \bar{\mu}_1^2)}{(\emptyset - 10)^4} \quad \text{cal/mole} \, .$$

Necessary further data are:

For water, $P = 3.716$, $\bar{u} = 1.84$

For propanol-1, $P = 17.577$, $\bar{u} = 1.7$

For butanol-1, $P = 22.20$ $\bar{u} = 1.7$.

Substituting, the additional interaction energy terms are:

for propanol -1 $\varepsilon_{int} = \dfrac{6.22 \times 10^{8}}{(\emptyset - 10)^{4}}$ cal/mole

for butanol-1 $\varepsilon_{int} = \dfrac{2.60 \times 10^{8}}{(\emptyset - 10)^{4}}$ cal/mole.

In calculating ε_{int}, only the interaction of the dipole layer with the alcohol has been considered; the interaction of this layer with water is assumed to have been accounted for in the measured $\varepsilon_2(\emptyset)$.

Isotherms calculated using the modifications in effective adsorption potentials outlined are shown as dashed lines in Figures 11 and 12; corresponding $\left(\dfrac{x_1}{\bar{v}}\right)_{\emptyset} - \left(\dfrac{x_1}{\bar{v}}\right)_b$

curves are shown as dashed lines in Figures 15 and 16. There is some improvement in the agreement between theory and experiment in the system water-propanol-1-Spheron-6, but in the system water-butanol-1-Spheron-6 the improvement in agreement is very pronounced. Solution adsorption results suggest the formation of a butanol-1 rich phase on top of the water layer even at low butanol concentrations; with the dipole-induced dipole interaction energy added

the effective adsorption potential is sufficient to account for this phase theoretically.

The water-propanol-1 adsorption on DAG-1 gave no indication of any layering effect, and therefore no correction or modification was applied. The ethanol-cyclohexane adsorption on Spheron-6 is felt to be too complex to submit to the treatment just described. Just what modifications of the theory should be made to improve the agreement of experiment and theory are not known. It seems impracticable to assume a system of complex dipole-induced dipole interactions as such a treatment removes much of the vigor of the approach used.

C. Calculated Adsorption of Gas Mixtures

The excellent work done by Arnold (23) on the adsorption of mixtures of nitrogen and oxygen on anatase, a form of titanium dioxide, together with his pure gas isotherms furnished sufficient data to test the theory of mixed gas adsorption. Figure 19 shows the experimental and calculated isotherms. Agreement in this case is quantitative as to total adsorption but the individual isotherms only show qualitative agreement, the calculated adsorption of nitrogen being too low and the calculated adsorption of oxygen too high.
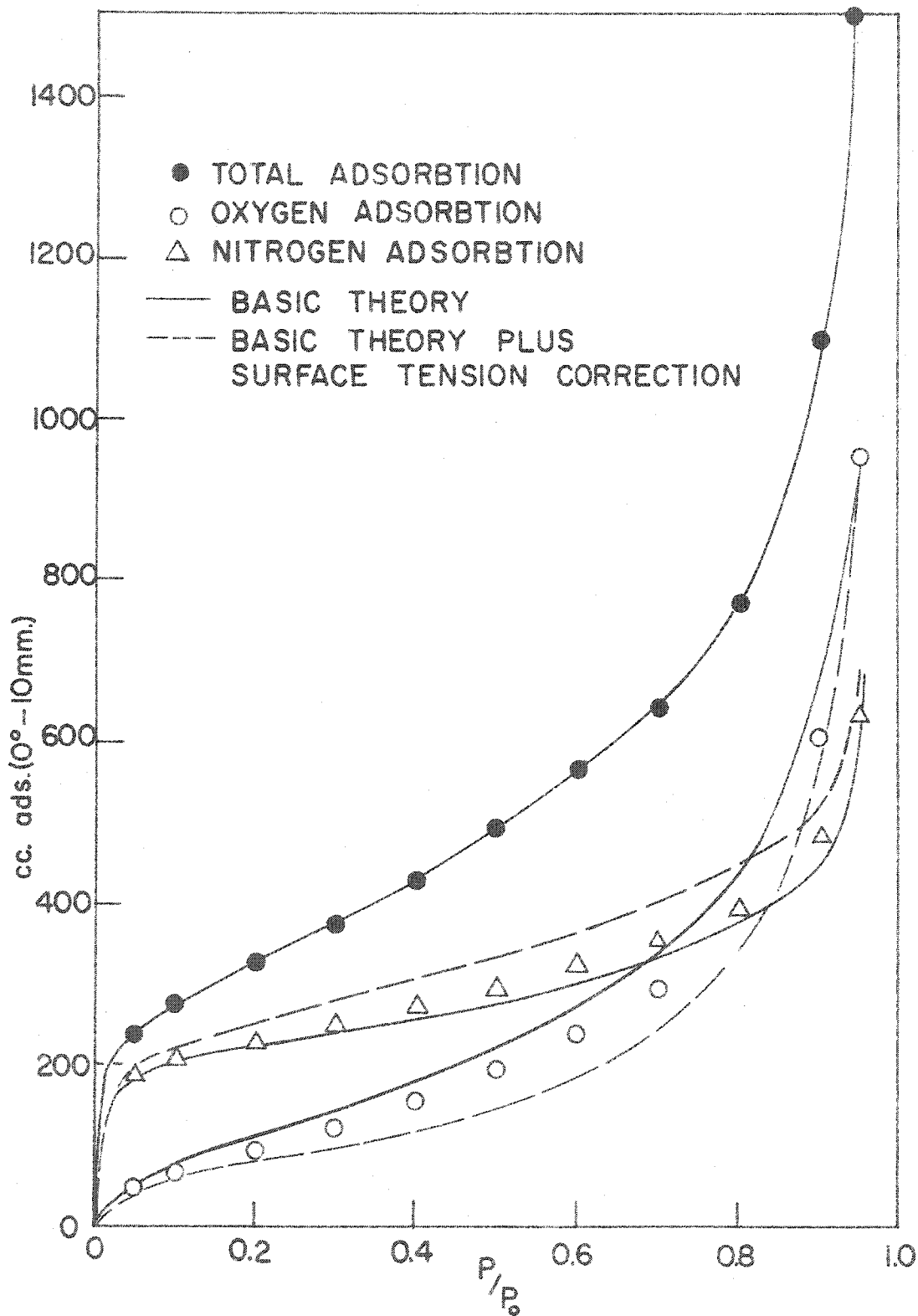
Figure 19. Adsorption Isotherm for the Gas Mixture
Oxygen-Nitrogen on Anatase at 78.2° K.

One complication in mixed gas adsorption which does not appear in adsorption from solution is the formation of a liquid-vapor interface. This, of course, is using the assumption that the adsorbed phase is a liquid. At the liquid-vapor interface, due to energy requirements, the component having lower surface tension will concentrate; in the oxygen-nitrogen system this component is nitrogen. This effect is in the right direction to bring the calculated individual isotherms into agreement with the experimental isotherm.

Figure 20, the $\frac{x}{v}$ curves for oxygen and nitrogen, shows that nitrogen is preferentially adsorbed on the surface, but the composition of the adsorbed phase becomes almost constant at the point where $\emptyset$ equals 12 mm.^{3} Using the area of the anatase, determined by the Brunauer-Emmett-Teller theory to be 13.8 square meters per gram, a $\emptyset$ of 4.55 mm.^{3} was calculated to be a monolayer. This is the thickness of the outer layer of the adsorbed phase in which, due to surface tension, the nitrogen is concentrated. The treatment devised to account for this effect is not very satisfying but there appears to be no more appropriate treatment available. Assuming the proper description of the surface layer to be obtained by required zero variation in free energy on infinitesimal mass transfer subject to a constraint of fixed total area
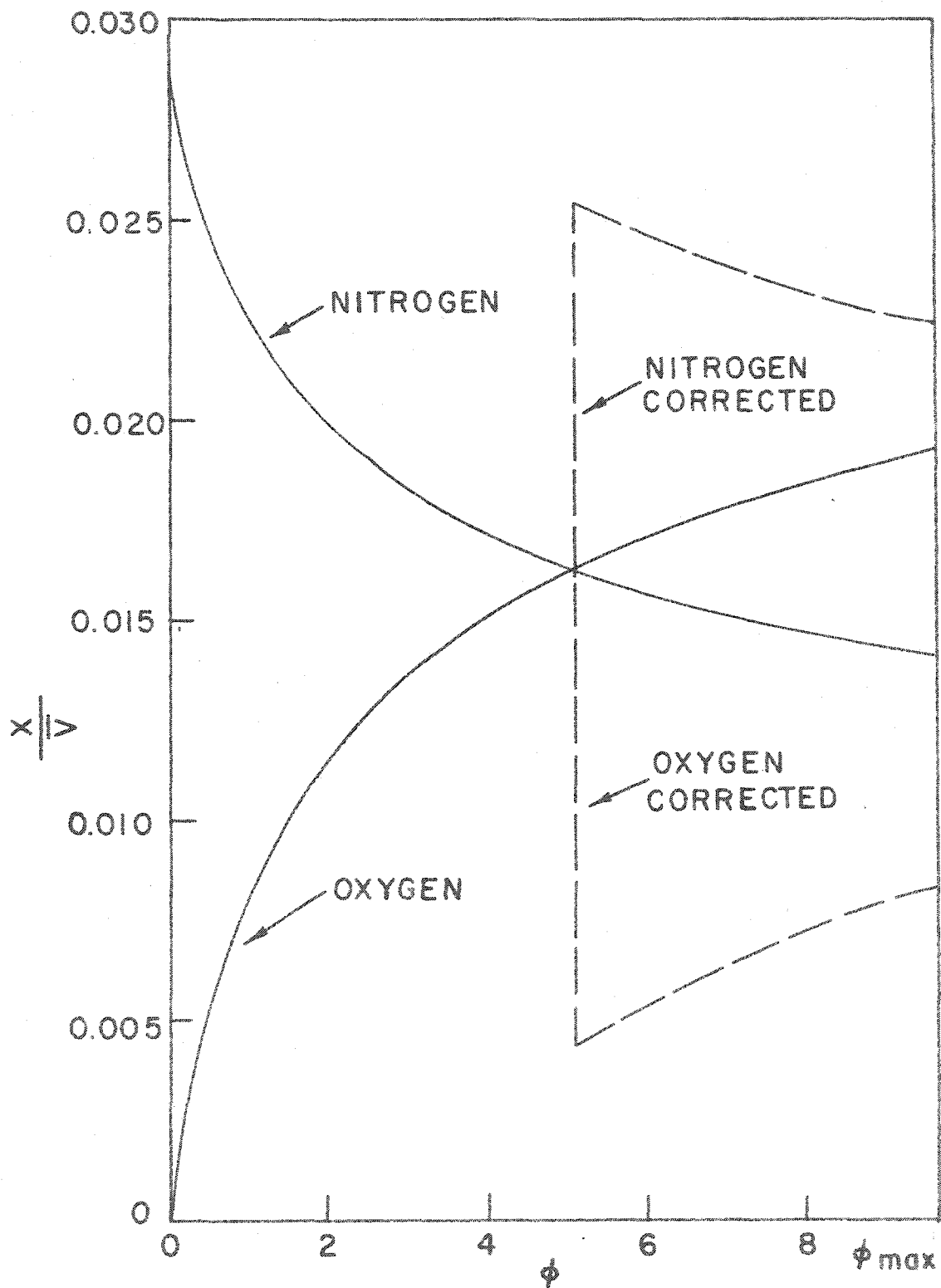
Figure 20. $\frac{x_1}{V}$ Curves for the System Oxygen-Nitrogen-Anatase.

it follows by arguments completely parallel to those used in development of the basic theory that

$$\frac{-\mathcal{E}_1' + RT \ln \frac{a_{1\emptyset}}{a_{1g}}}{A_1} = \frac{-\mathcal{E}_2' + RT \ln \frac{a_{2\emptyset}}{a_{2g}}}{A_2}$$

in which A_1 and A_2 are the molar areas of the two components. Now if the free surface energy of the liquid-vapor interface is presumed to vary linearly with surface area fraction from that of component 1 to that of component 2 there will be, on replacing component 1 by an equivalent area of component 2 at this interface, a free energy change of $A(\gamma_2 - \gamma_1)$ in addition to that due to their different adsorption potentials; accordingly it has been assumed that

$$-\mathcal{E}_1' = -\mathcal{E}_1(\emptyset) + \gamma_1 A_1$$
$$-\mathcal{E}_2' = -\mathcal{E}_2(\emptyset) + \gamma_2 A_2$$

γ_1 and γ_2 being the surface tensions of components 1 and 2, $\mathcal{E}_1(\emptyset)$ and $\mathcal{E}_2(\emptyset)$ being their Polanyi adsorption potentials. Accordingly

$$\frac{-\mathcal{E}_1 + RT \ln \frac{a_{1\emptyset}}{a_{1g}}}{A_1} + \gamma_1 = \frac{-\mathcal{E}_2 + RT \ln \frac{a_{2\emptyset}}{a_{1g}}}{A_2} + \gamma_2 \ .$$

In the nitrogen-oxygen system A_1 and A_2 are substantially equal; setting $A_1 = A_2 = A$ there results

$$\frac{a_{1\phi}}{a_{2\phi}} = \frac{a_{1g}}{a_{2g}} \quad \frac{{}_1 - {}_2 + A({}_2 - {}_1)}{RT} \quad .$$

This equation was then used to calculate nitrogen and oxygen concentrations in the region,

$$\phi_{max} - 4.55 \quad \phi \quad \phi_{max}$$

(supposedly the molecular layer bounded by the vapor phase) while the concentrations of nitrogen and oxygen for lower values of ϕ were taken unmodified from the prior calculation. The modified results are shown as dashed lines in Figures 19 and 20; the calculated total adsorption is still in excellent agreement with that observed but the individual isotherms have been over corrected.

Failure of this treatment to account correctly for the liquid vapor interface adsorption correction is not entirely surprising, for the treatment is not self-consistent. Thus, the correction is handled on an area constraint basis, but the potentials are calculated on a volume constraint basis and used in the correction. A more satisfactory procedure would be to infer adsorption at the liquid-vapor interface from surface tensions of oxygen-nitrogen solutions, but unfortunately no such data are available at present.

D. Discussion of Errors

The treatment of probable errors in the above calculations is a rather difficult subject to handle. There is no obvious way to estimate the change in the calculated adsorption isotherms with a change in the original gas adsorption isotherms. Because of this problem, the water-propanol-1 isotherm on Spheron-6 was recalculated assuming the pure component isotherms were in error. The broken lines in Figure 21 show the range of calculated isotherms resulting from assumed differences in the original gas adsorption isotherms. The isotherm marked A was calculated assuming the adsorption of the water was 0.06 millimoles higher than was actually found. This difference was linearly reduced to zero in the range of $0.25 \quad P/P_0 \quad 0$. The propanol-1 adsorption used to calculate curve A was assumed to be lower than that found by using a constant amount of 0.080 for $P/P_0 \quad 0.7$ and a linear decrease to zero for $0.70 \quad P/P_0 \quad 0.$

The opposite assumptions were made for calculating curve B. It is apparent that the results depend closely
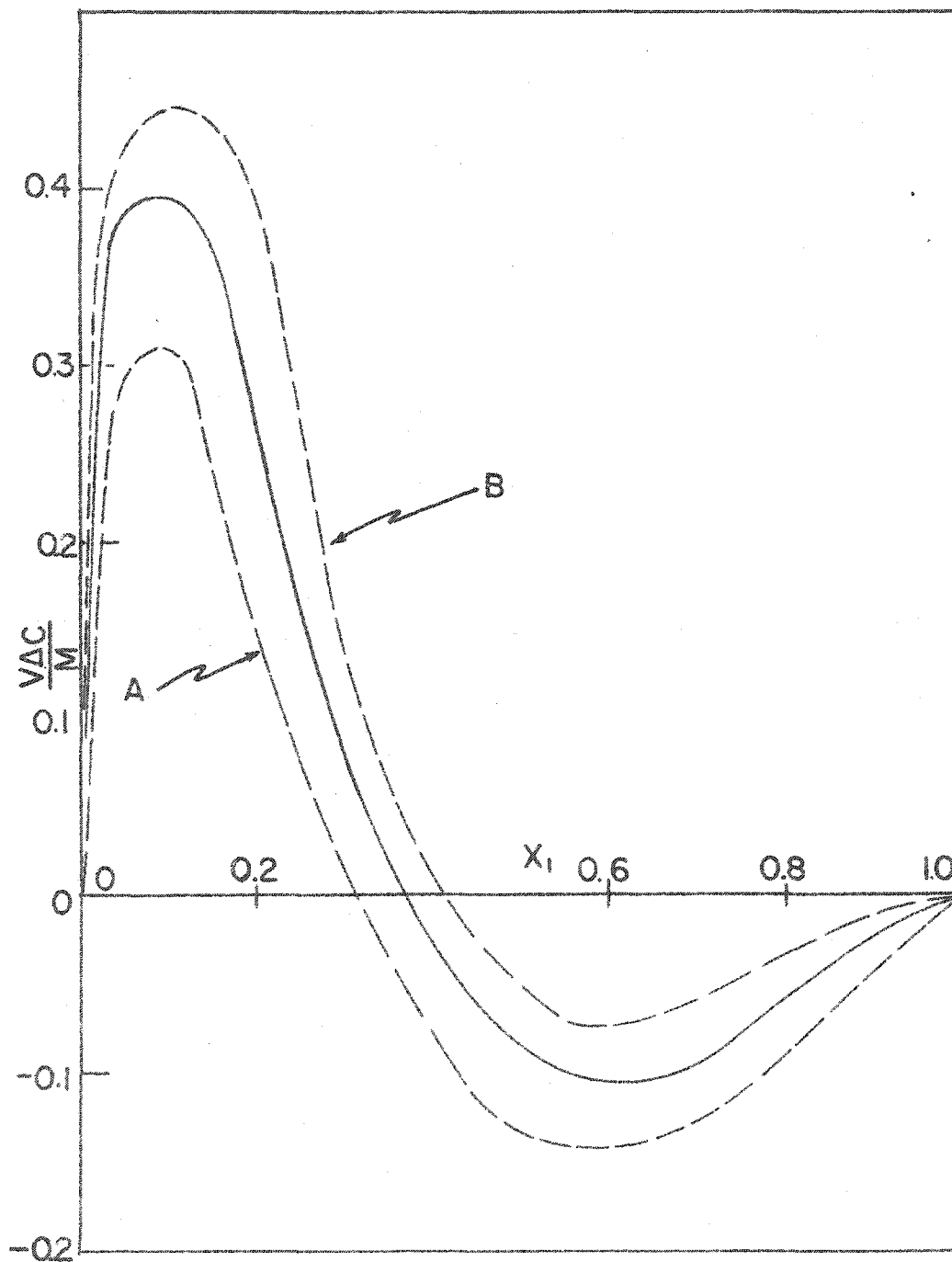
Figure 21. Spread of Adsorption of Propanol-1 from
Aqueous Solution by Spheron-6 Assuming Errors
in Gas Adsorption Isotherms.

upon the original isotherms. There is no change in the essential shape of the isotherm but there is a definite displacement of the isotherm. The spread of the isotherms varies from a maximum of 0.14 millimoles per gram at the point of the maximum in the adsorption isotherm to a difference of 0.08 millimoles per gram at the point of the minimum in the adsorption isotherm. Any other combination of errors within those stated above in the original gas adsorption isotherms will cause the calculated isotherm to lie between the broken lines in Figure 21.

One interesting aspect of the treatment above is the variation in the size of the water layer. Using the high water adsorption isotherm and the low propanol-1 isotherm, the water layer went out to a $\emptyset$ of 22.9 mm.^{3}, with the low water and the high propanol-1, the value of $\emptyset$ for the water layer was 18.2 mm.^{3}

Figure 22 shows results of similar calculations for the system butanol-1-water-Spheron-6. The same errors were assumed for the water isotherm, and the butanol-1 error was assumed to vary linearly from 0 at P/P_0 = 0 to ± 0.10 at P/P_0 = 0.95. Curve A results from the lowered butanol-1 isotherm and increased water isotherm, curve B from the increased butanol-1 isotherm and lowered water isotherm. Indicated water layer volumes are 22.1 mm.^{3} and 18.1 mm.^{3} respectively.
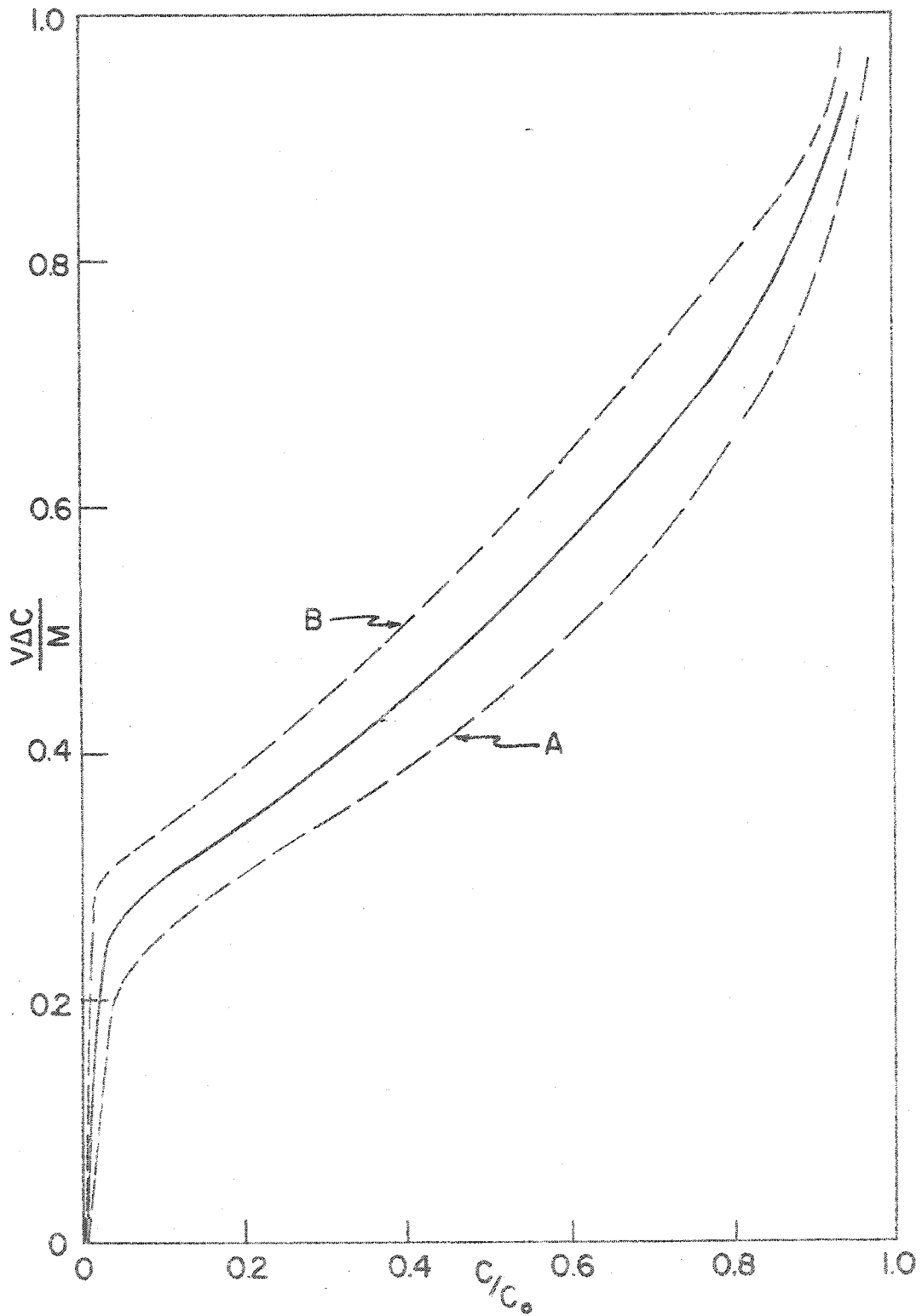
Figure 22. Spread of Results of Butanol-1-Water-Spheron-6
After Assuming Scatter in Original Isotherms.

E. Conclusions

In the discussion of the conclusions which can be drawn from the theory and results presented, the assumption will be made that the theory is correct. It is correct insofar as the assumptions are correct and, therefore, the discussion is essentially founded on the boiler that the three basic assumptions are theoretically sound. As the types of isotherms calculated are basically different and the results in all cases showed good qualitative agreement with experiment the theory with its modifications appears to be a satisfactory approach to the problem of adsorption from solution and of mixed gas adsorption.

The first, and probably most obvious, manner in which this theory differs from others is in its description of the concentration gradient as a function of the distance from the surface, and contrasts sharply with the component isotherm treatment of Kipling (1). It must be remembered that Kipling and others treated systems as if the adsorption was monomolecular. No systems were treated here in which the pure components gave monomolecular adsorption isotherms from the gas state and so no description of the physical picture of this type of adsorption can be given. with systems in which the components show multimolecular

adsorption in the gas phase, there is no reason or validity for the belief that a monomolecular treatment will give a true definition in describing adsorption from solution. Kipling's desire that the composite isotherm be dropped in favor of the pure component isotherm has little foundation in light of the theory here advanced; and the composite isotherm is felt to be the logical, even though not the most descriptive, way of giving the results of adsorption from solution.

The most significant result of the theory is the complete picture of the concentration of the components in the adsorbed phase. Coupled with this is the fact that this concentration is found by starting with the pure component isotherms instead of starting with the solution isotherm and working backwards. Curves of the type shown in Figures 15 - 18, which will be called concentration curves, can be used to explain the types of composite isotherms resulting from adsorption from solution. The concentration curves are closely related to the plot of the term $\log \exp \dfrac{\varepsilon_1 - \alpha \varepsilon_2}{RT}$ for the system. It can be seen that the shape of this latter plot is determined by the value of the term $\varepsilon_1 - \alpha \varepsilon_2$, which will be called the effective adsorption potential.

In any binary system in which $\varepsilon_1 - \alpha \varepsilon_2$ is always positive or always negative, inversion of the isotherm is

impossible. If the effective adsorption potential is
always positive, as is the case of water-propanol-1 on
DAG-1 with the alcohol called component 1, the composite
isotherm will show a positive adsorption of component 1.
If the effective adsorption potential is negative, the
isotherm will show negative adsorption of component 1.

In every other type of effective adsorption potential,
in miscible systems, inversion must take place. This is
the result of the shape of the $\log \frac{a_1}{a_2^\alpha}$ curve. The slope
of this curve is high for both low and high mole fraction
of component 1 and in the intermediate range has a rather
low slope. This means that in the intermediate range the
mole fraction changes greatly with a slight change in $\log$
$\frac{a_1}{a_2^\alpha}$ while the opposite effect takes place in the high and
low mole fraction range. It must be remembered that the
essential shape of the concentration curve does not change
and that the concentration curve crosses the bulk con-
centration line at the same points for all equilibrium
concentrations. Thus the entire concentration picture in
the adsorbed phase can be estimated rather closely by a
knowledge of the effective adsorption potential. To de-
termine the exact shape of the entire isotherm, however,
one must integrate the concentration curves at a number
of mole fractions of bulk solution.

The effective adsorption potentials for both the water-propanol-1 on Spheron-6 and the water-butanol-1 on Spheron-6 with alcohol as component 1, are negative up to a ∅ of 20 mm.[3] This agreement, both as to sign and point of sign change, is a good indication that the theory has some definite merit, and suggests that the cause of this water layer is probably the interaction of the water with the surface oxides on the Spheron-6. The sample of Spheron-6 that was used in the adsorption of ethanol and cyclohexane was a recently evacuated sample rather than that used for the other isotherms. Even though no water adsorption isotherm was run on this newer sample, it is fairly certain that less hysteresis would result on desorption from this sample than from the older sample.

There is no obvious reason for the behavior of the ethanol-cyclohexane system on Spheron-6. The formation of a region of preferential concentration of cyclohexane next to the surface is extremely peculiar. The steepness of the cyclohexane isotherm at both low and high reduced pressure is related to this behavior but no explanation for either phenomenon based on van der Waal's interactions appears possible.

The concentration curves for the adsorption of the mixture of gaseous oxygen and nitrogen show nothing unusual. The results of the calculations are fairly close

to experiment, and when the correct method of applying
the surface tension modification is found, agreement
should be excellent. Mention should be made of another
case where the surface tension correction might apply,
which is the case of adsorption from solution in which
the components show monomolecular adsorption in the gas
phase. The interface between the adsorbed monolayer and
the bulk solution should be one that would require a sur-
face tension treatment.

One outstanding result of the results described
above is that in agreement with Kipling (1) it is clear
that one should not speak of adsorption from solution,
but of adsorption of solution.

VI. SUMMARY

1. A new theoretical approach to adsorption from solution and gas mixtures is presented.

2. Basic assumptions of the theory are first, that the difference in standard state chemical potential between a component in bulk and the same component in a given position in the neighborhood of the adsorbent surface is equal to the Polanyi adsorption potential as determined by pure component vapor adsorption, and second, that the activity of a component (referred to pure liquid component at the position of interest) is the same function of concentration whether in bulk or near the surface. Implications and probable limitations of these assumptions are discussed.

3. Isotherms for the adsorption of water, ethanol, propanol-1, butanol-1, and cyclohexane on the carbon black Spheron-6 and for the adsorption of water and propanol-1 on the artifical graphite DAG-1 from the vapor phase at 25° C were determined gravimetrically. Desorption isotherms were also determined on all of the above systems except propanol-1-DAG-1. Water showed a moderate hysteresis on Spheron-6; hysteresis of other substances on this adsorbent was negligible. Propanol-1 showed a slight hysteresis on DAG-1; water adsorbed on DAG-1 could not be

desorbed at 25° C.

4.   The theory developed was used with the experimental gas adsorption isotherms to calculate the isotherms for adsorption from solution in the systems water-propanol-1-Spheron-6, water-butanol-1-Spheron-6, ethanol-cyclohexane-Spheron-6, and water-propanol-1-DAG-1, and the results compared with experimental results of R. P. Craig and R. D. Hansen. Good qualitative agreement between calculated and observed isotherms was obtained for all systems except the system water-butanol-1-Spheron-6.

5.   The theory permits description of the adsorption process in terms of concentrations of constituents as functions of distance from the adsorbent surface. In both of the Spheron-6-water-alcohol systems this description indicated a nearly complete monomolecular layer of water in the immediate neighborhood of the adsorbent surface. This water layer is attributed to surface oxygen complexes of the Spheron-6.

6.   The theory was modified to account for van der Waal's interaction between alcohol molecules and an oriented water dipole layer in the water-alcohol-Spheron-6 systems. This modification markedly improved agreement between calculated and observed solution adsorption isotherms for both systems and especially for the system water-butanol-1 -Spheron-6.

7. The adsorption of nitrogen and oxygen from nitrogen-oxygen mixed vapors on anatase at 78.2° K was calculated using pure gas isotherms of Arnold and compared with experimental mixed gas isotherms of the same worker. The theory predicted total adsorption almost exactly, but underestimated the adsorption of nitrogen and overestimated that of oxygen.

8. The necessity of modifying the theory to account for adsorption at the liquid-vapor interface formed when condensible vapors are adsorbed on solids is pointed out, and it is shown that this effect is in the direction needed to improve results in the nitrogen-oxygen-anatase system.

9. A rather crude modification of the theory is developed to account for adsorption at the liquid-vapor interface in mixed gas adsorption and its limitations discussed. The modification overcorrects the theory in the nitrogen-oxygen-anatase system.

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VIII. ACKNOWLEDGMENT

IX. APPENDIX

The method of calculation of adsorption from so-
lution is a rather involved procedure and will be de-
scribed in detail. The complete calculation of the point
corresponding to a bulk solution of water-propanol-1 on
Spheron-6 with a mole fraction of propanol-1 of 0.2 will
be given. In all the calculations the propanol-1 is
called component 1 and the water is component 2.

Figures 4 and 5 show the pure vapor adsorption iso-
therms used in the calculations. The plot is of milli-
moles adsorbed per gram of adsorbent as a function of the
reduced pressure. A smooth curve is drawn through the
points and from this curve Table 8 is constructed.

is defined as $RT \ln P_0/P$ and $\emptyset$ is defined as $N_a \bar{V}$ where
N_a is millimoles adsorbed and $\bar{V}$ is the millimolar volume
of the component in $mm.^3$/millimole. This gives $\emptyset$ the
units of $mm.^3$

Using the $(\emptyset)$ data from Table 8, Figure 23 is con-
structed. From Figure 23 the values of $_1$ and $_2$ for
various values of $\emptyset$ are picked off and Table 9 is completed
using the values of $\bar{V}_1$ and $\bar{V}_2$ which were used to calculate
$\emptyset$. Figure 24 is not used in the calculations but is in-
cluded to show a representative curve of the function

$$\log \, ext \frac{_1 - \bar{V}_1/\bar{V}_2 \, _2}{RT} \, .$$

Figure 23.   ($\emptyset$) Curves for Propanol-1 and Water on Spheron-6
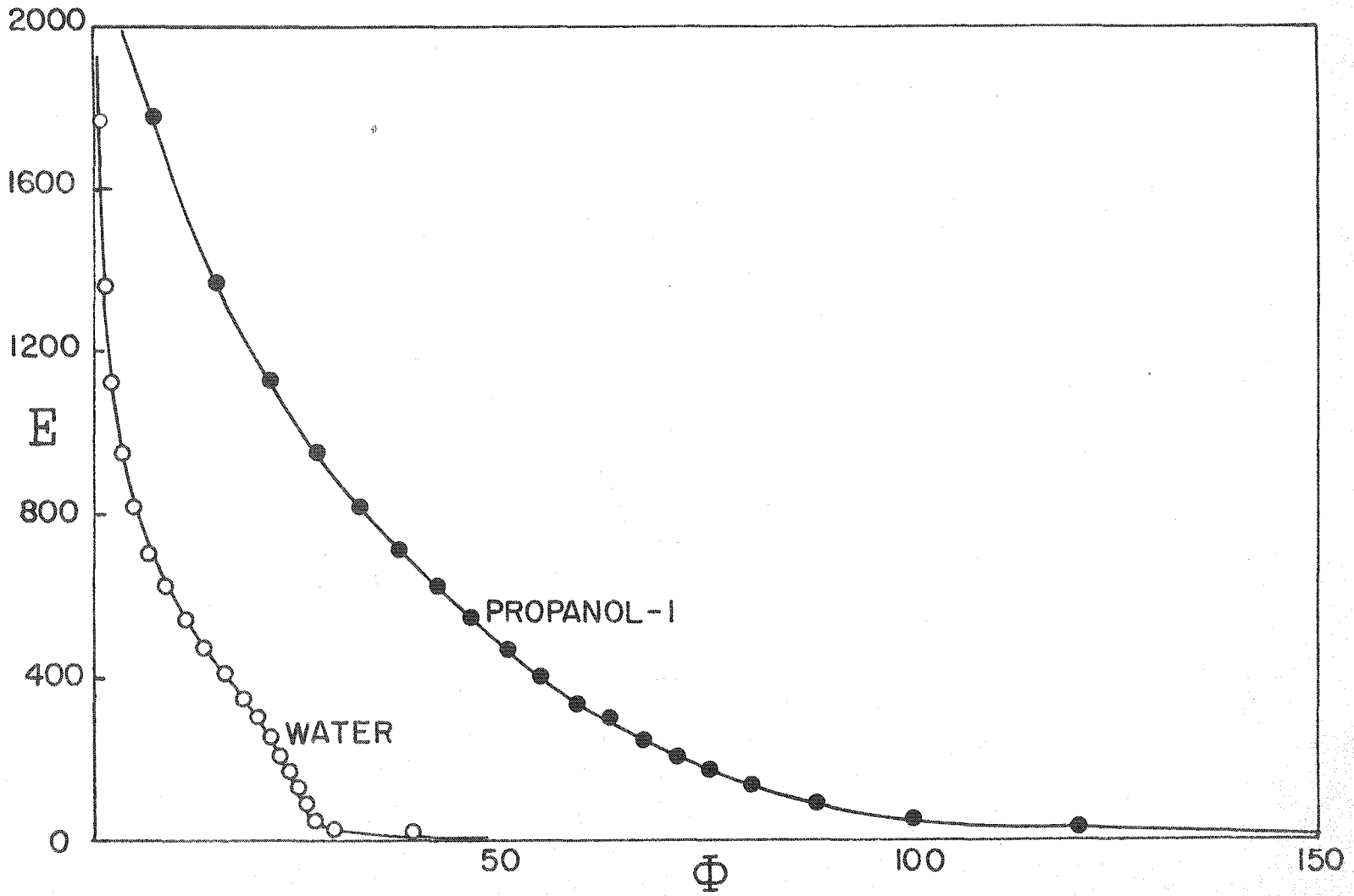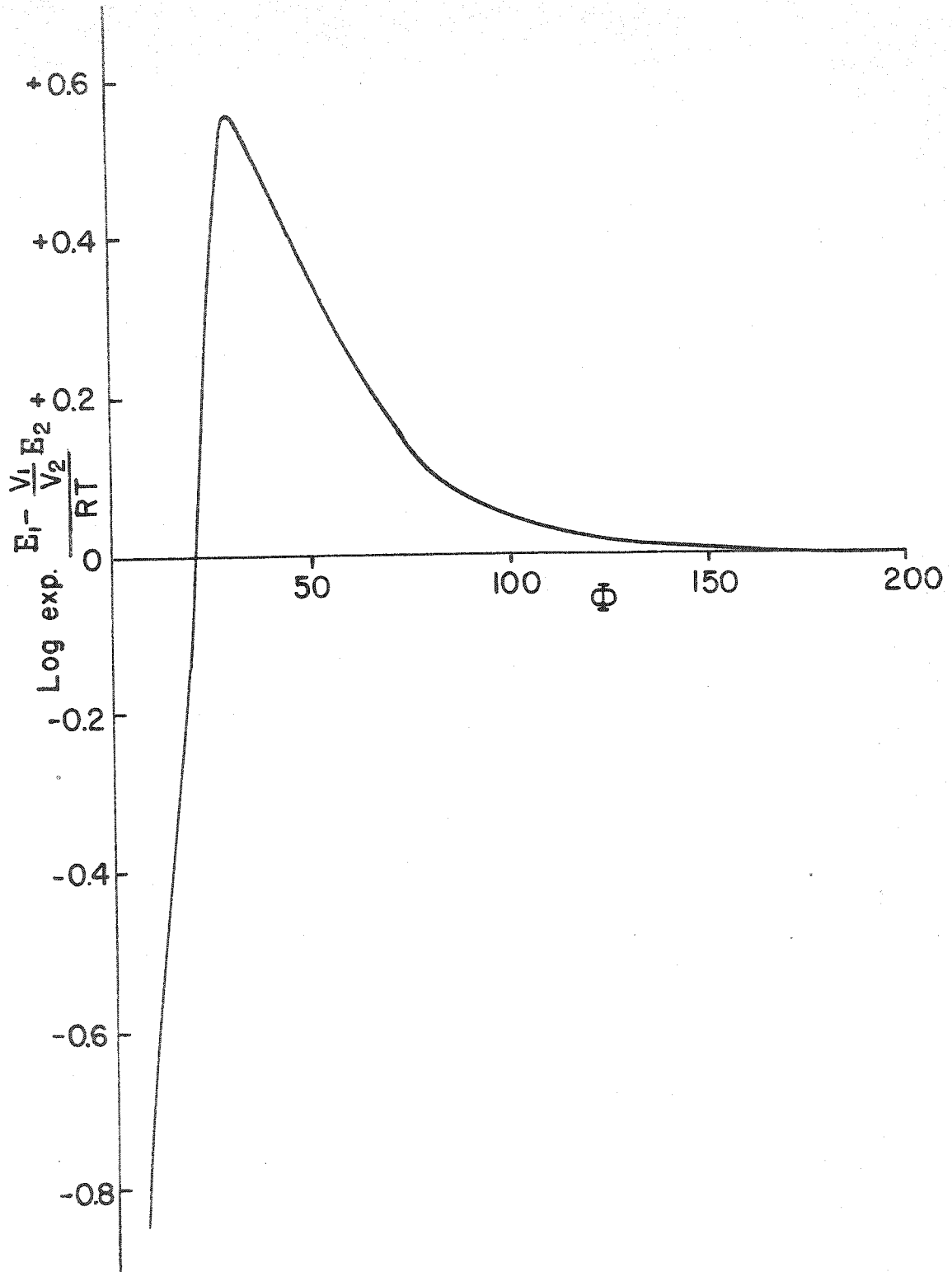
Figure 24. Plot of Effective Adsorption Potential Term.

Table 8

Calculation of (Ø)

Spheron-6

$\frac{P}{P_0}$	Propanol-1				Water	
	$\frac{N_0}{g} \frac{mmol}{gram}$	$\phi_1(mm^3)$	$RT \ln \frac{P_0}{P}$ (cal.)		$\frac{N_0}{g} \frac{mmol}{gram}$	$\phi_2(mm^3)$
.05	0.102	7.66	1775		0.40	0.022
.1	.199	14.95	1364		1.16	.064
.15	.286	21.48	1124		2.17	.120
.2	.364	27.34	954		3.47	.192
.25	.438	32.90	821		5.06	.280
.3	.502	37.71	713		6.90	.382
.35	.562	42.21	622		9.04	.500
.4	.619	46.49	543		11.37	.629
.45	.677	50.85	473		13.75	.761
.5	.734	55.13	411		16.08	.890
.55	.789	59.26	354		18.29	1.012
.6	.843	63.32	303		20.20	1.118
.65	.898	67.45	255		21.70	1.201
.7	.951	71.43	211		22.95	1.270
.75	1.005	75.49	170		24.03	1.330
.8	1.070	80.37	132		25.05	1.386
.85	1.181	88.70	96		26.02	1.440
.9	1.343	100.87	62		27.10	1.500
.95	1.605	120.55	30		29.72	1.645
.98	2.085	156.60	12		39.00	2.158

$$\bar{V}_1 = 75.11 \frac{mm^3}{millimole} \qquad \bar{V}_2 = 18.07 \frac{mm^3}{millimole}$$

Table 9

Calculation of Adsorption Potential Term

Ø	1	2	$\frac{V_1}{V_2}\ 2$	$1\ \frac{V_1}{V_2}\ 2$	$\log e\ \dfrac{1\ \frac{V_1}{V_2}\ 2}{RT}$
4	2163	908	3775	−1612	−1.1815
7	1822	709	2947	−1125	−0.8246
10	1621	590	2453	− 832	−0.6098
15	1367	441	1833	−466	−0.3416
20	1172	310	1289	− 117	−0.0858
25	1015	129	536	+ 479	+0.3511
30	885	30	125	+ 760	+0.5571
35	768	18	75	693	0.5079
40	662	11	48	614	0.4500
50	488	3	12	476	0.3489
60	342	0	0	342	0.2507
70	221			221	0.1620
80	137			137	0.1004
90	89			89	0.0652
100	62			62	0.0454
110	45			45	0.0330
120	31			31	0.0227
130	20			20	0.0147
140	14			14	0.0103
150	11			11	0.0081
160	9			9	0.0066
170	8			8	0.0059

Activity data from the literature are used to calculate $\log a_1/a_2 \, V_1/V_2$ as a function of x_1, the mole fraction of component 1. Table 10 shows this set of calculations. The calculations thus far completed are enough to complete the manipulation of the basic equation

$$\frac{a_1}{a_2 \dfrac{\overline{V}_1}{\overline{V}_2}}\Bigg|_{\emptyset} = \frac{a_1}{a_2 \dfrac{V_1}{V_2}}\Bigg|_{b} \; e^{\dfrac{1 - \dfrac{\overline{V}_1}{\overline{V}_2}}{RT} 2} \quad .$$

To the value of $\log (a_1/a_2 \, V_1/V_2)_b$ for the bulk solution are added the values of $\log \dfrac{1 - V_1/V_2}{RT} \; 2$ for various $\emptyset$. This gives a list of the values of $\log (a_1/a_2 \, V_1/V_2)_\emptyset$ as a function of $\emptyset$. For each $\emptyset$, the corresponding mole fraction can be determined.

The function which is integrated is

$$\int_o \left(\frac{x_1}{V}\bigg|_\emptyset - \frac{x_1}{V}\bigg|_b \right) d\emptyset \quad .$$

In order to evaluate this integral, the molar volume as a function of mole fraction is needed. This function can be calculated from density data in the literature. If no density data are available a good approximation is to assume the molar volume a linear function of the mole fraction. To simplify the evaluation of the integral, Table 11 is made and a plot of x_1/V versus $\log a_1/a_2 \, V_1/V_2$, as shown in Figure 26 is constructed.

Table 10

Calculation of Activity Function

x_1	a_1	a_2	$\log a_1$	$\log a_2$	$\frac{V_1}{V_2} \log a_2$	$\log \frac{a_1}{a_2} V_1/V_2$
0	0	1.000	–	0	0	–
.02	0.235	0.991	–0.6289	–0.0039	–0.0162	–0.6127
.04	0.374	0.983	–0.4271	–0.0075	–0.0312	–0.3959
.06	0.486	0.974	–0.3134	–0.0114	–0.0474	–0.2660
.08	0.528	0.965	–0.2774	–0.0155	–0.0644	–0.2130
.1	0.559	0.956	–0.2526	–0.0195	–0.0811	–0.1715
.2	0.610	0.935	–0.2147	–0.0292	–0.1214	–0.0933
.3	0.634	0.924	–0.1979	–0.0343	–0.1426	–0.0553
.4	0.657	0.905	–0.1824	–0.0434	–0.1804	–0.0020
.5	0.694	0.865	–0.1586	–0.0630	–0.2619	+0.1033
.6	0.740	0.803	–0.1308	–0.0953	–0.3962	+0.2654
.7	0.796	0.713	–0.0991	–0.1469	–0.6107	0.5116
.8	0.860	0.555	–0.0655	–0.2557	–1.0629	0.9974
.9	0.927	0.333	–0.0329	–0.4776	–1.9853	1.9524
.92	0.941	0.276	–0.0264	–0.5591	–2.3242	2.2978
.94	0.953	0.218	–0.0209	–0.6615	–2.7499	2.7290
.96	0.967	0.254	–0.0146	–0.8125	–3.3776	3.3630
1.00	1.000	0	0	–	–	+

Table 11

Calculation of $x_1/\bar{V}$ Function

x_1	$\bar{V}$	$x_1/\bar{V}$	$\log \frac{a_1}{a_2}\bar{V}_1/\bar{V}_2$
0	18.07	0	--
.02	19.08	0.00105	-0.6127
.04	20.09	0.00199	-0.3959
.06	21.12	0.00284	-0.2660
.08	22.18	0.00361	-0.2130
.1	23.24	0.00430	-0.1715
.2	28.94	0.00691	-0.0933
.3	34.50	0.00870	-0.0553
.4	40.16	0.00996	-0.0020
.5	45.96	0.01088	+0.1033
.6	51.62	0.01161	+0.2654
.7	57.35	0.01219	0.5116
.8	63.22	0.01269	0.9974
.9	69.03	0.01304	1.9524
.92	70.33	0.01308	2.2978
.94	71.58	0.01313	2.7290
.96	72.70	0.01320	3.3630
1.00	75.11	.01331	+

The actual evaluation of a calculated adsorption point is given in Table 12. The value of log $a_1/a_2 \, V_1/V_2$ and of x_1/V corresponding to the bulk concentration are taken from Table 11. To the value of log $(a_1/a_2 \, V_1/V_2)_b$ are added the values of log cnt $\dfrac{1-V_1/V_2}{RT} \cdot 2$ as a function of β from Table 9. This gives a list of the value of log $(a_1/a_2 \, V_1/V_2)\beta$. The values of x_1/V corresponding to these last values are taken from Figure 25. The value of $(x_1/V)_b$ is subtracted from this list, which is of $(x_1/V)\beta$ and the difference is plotted against β as shown in Figure 26. This last curve is graphically integrated to give the area of the ad-sorption in millimoles per gram of adsorbent. The units of the integral are such that no conversion factor is needed.
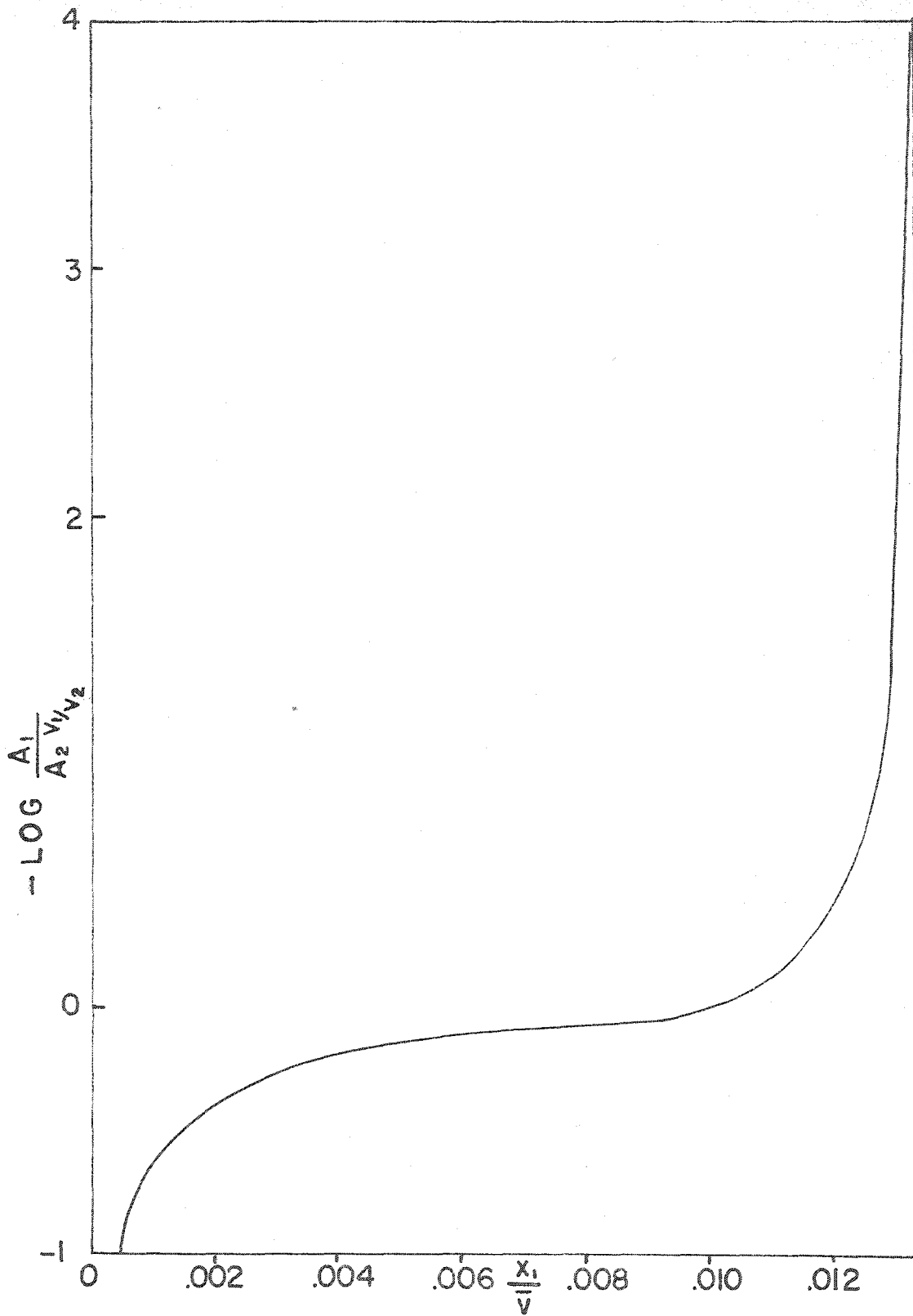
Figure 25. Plot of $\frac{x_1}{V}$ versus $\log(a_1/a_2{}^{V_1/V_2})$.

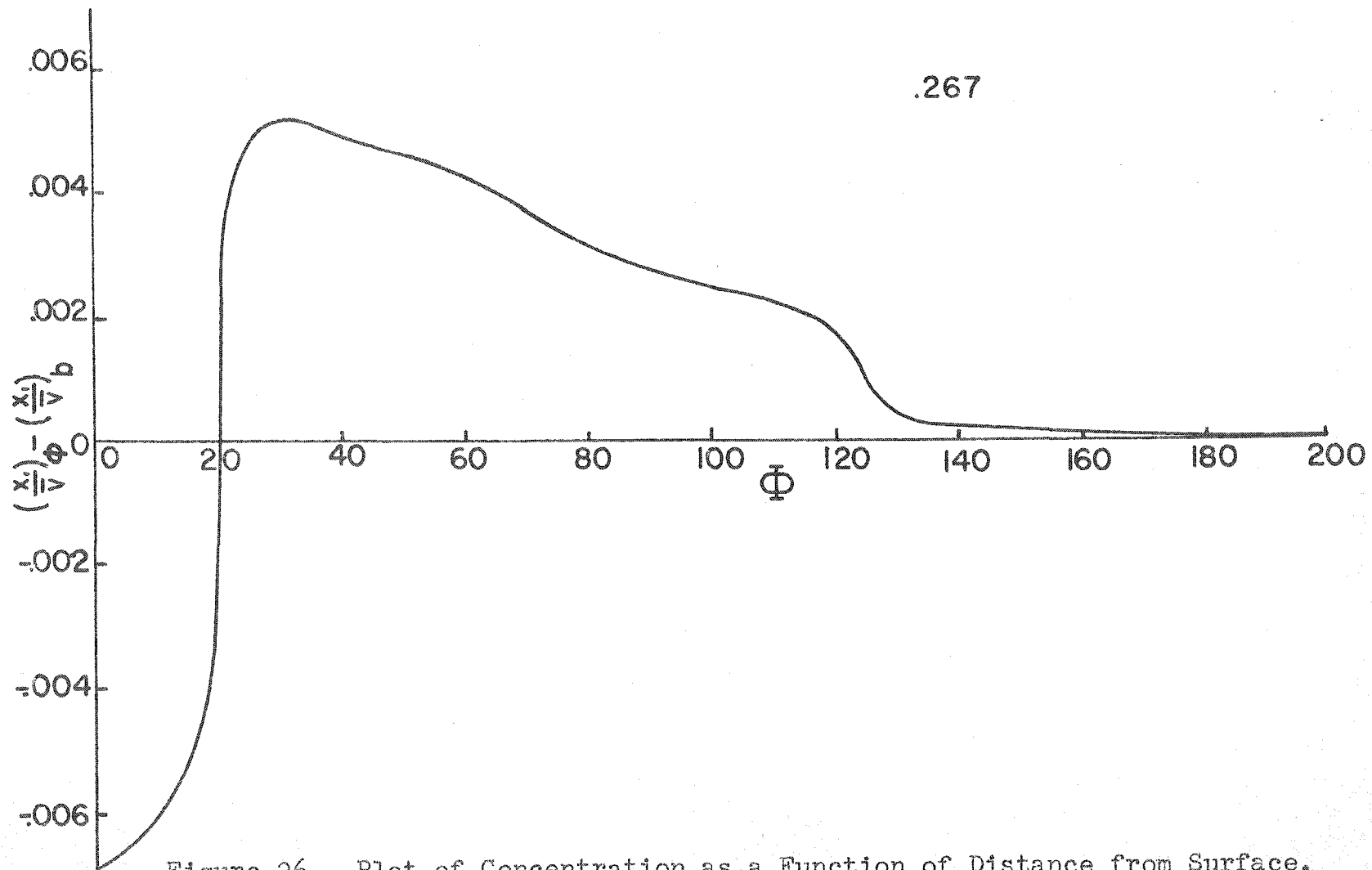Figure 26. Plot of Concentration as a Function of Distance from Surface.

Table 12

Calculation of Concentration with Distance from Surface

ϕ	$\log(a_1/a_2\, V_1/V_2)\phi$	$(x_1/\overline{V})\phi$	$(x_1/\overline{V})\phi - (x_1/\overline{V})b$
4	−1.2748	0.00030	−0.00661
7	−0.9179	0.00049	−0.00642
10	−0.7031	.00083	−0.00608
15	−0.4349	.00172	− .00519
20	−0.1791	.00411	− .00280
25	+0.2578	.01155	+ .00464
30	+0.4638	.01209	+ .00518
35	+0.4146	.01200	.00509
40	+0.3567	.01183	.00492
50	+0.2556	.01154	.00463
60	+0.1574	.01112	.00421
70	+0.0687	.01059	.00368
80	+0.0071	.01006	.00315
90	−0.0281	.00965	.00274
100	−0.0479	.00939	.00248
110	−0.0603	.00860	.00169
120	−0.0706	.00814	.00123
130	−0.0786	.00731	.00040
140	−0.0830	.00710	.00019
150	−0.0852	.00704	.00013
160	−0.0867	.00700	.00009
170	−0.0874	.00698	.00007

$\overline{\log(a_1/a_2\, V_1/V_2)b} = 0.0933$ $x_1^b = 0.2$ $(x_1/V)b = 0.00691$