HEATS OF IMMERSION

OF

SILICAS IN LIQUIDS

by

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To my wife,

whose patience and cooperation made this work possible.

ABSTRACT

This work embodies the results of an investigation on the heats of immersion of silica adsorbents in pure liquids, and in binary liquid systems where benzene is preferentially adsorbed over the entire concentration range from mixtures with various hydrocarbon solvents. The measurements were carried out in a metal calorimeter at 25° C and 1 atmosphere, to an accuracy of within 1.1%. The apparent adsorption isotherms have also been studied at the same P and T.

On the basis of the assumption of a perfect system behaviour, it has been shown from liquid adsorption data that the separation factor $K^{(N)}$, in terms of mole fractions, depends on the origin of the adsorbent, in mixtures of benzene with cyclohexane. In mixtures of benzene with n-alkanes, $K^{(N)}$ is independent of the chain length of the solvent. The surface areas of the adsorbents calculated from adsorption data, increased in steps of about 80 $m^2/g.$ in the sequence: benzene - cyclohexane, nitrogen (B. E. T.), benzene - n-alkanes.

Heats of immersion in a given pure liquid vary with the source of the sample and with the preparative conditions for a given material, diminishing in the sequence: ethanol, water, toluene, benzene, n-alkanes and cyclohexane. For a given adsorbent the

heats of immersion in n-alkanes are essentially the same.

The isotherm of the relative heat of immersion θ_I was found to vary markedly with the source of the sample and with the nature of the solvent but was unaffected by the preparative conditions of the adsorbent. The relative heat of immersion is defined as follows

$$\theta_I = \frac{H_I - (H_I^\circ)_2}{(H_I^\circ)_1 - (H_I^\circ)_2}$$

where H_I is the heat of immersion of the adsorbent in the mixture; and

$(H_I^\circ)_1$ and $(H_I^\circ)_2$ are the heats of immersion of the adsorbent in the pure liquids 1 and 2, respectively.

The equation developed by Everett for perfect systems was found to be adequate only for the prediction of the system benzene - cyclohexane-silicic acid (Baker Reagent). Semi-empirical equations of the Langmuir type have been proposed and used with success to correlate the binary data for the silica gel (Davidson 28-200 mesh).

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III TABLE OF CONTENTS

IV LIST OF FIGURES

V LIST OF TABLES

VI NOMENCLATURE

A°	Angstrom
A, A', A''	constants
Av.D.	average deviation
a	contact angle, degrees
B, B_1, B', etc.	constants
C	constant in B.E.T. equation
D, D_1, D', D''	constants
E	potential drop, volts
H_I	heat of immersion of a solid adsorbent in a binary liquid mixture., cal./g.
H_I°	heat of immerion of a solid adsorbent in a pure liquid, cal./g.
$H_{dil.}$	heat of dilution on immersion, cal./g.
H_w	heat of wetting, cal./g.
ΔH^M	molar heat of mixing, cal./mole
h_I	heat of immersion of a unit area of solid adsorbent in a liquid medium, cal./m^2
h_I°	heat of immersion of a unit area of solid adsorbent in a pure liquid, cal./m^2
$h_{I(L)}$	absolute heat of immersion, calculated by using the surface area determined from adsorption of binary mixtures, cal./m^2
$h_{I(N_2)}$	absolute heat of immersion, calculated by using the nitrogen surface area (B.E.T.), cal./m^2

h_s	enthalpy of a unit area of degassed adsorbent
$h_{s(L)}$	enthalpy of the unit area solid-liquid interface
I	current, amp.
J	electrical equivalent of heat, 4.184 joules/cal.
K, K', K_1, etc.	constants
$K^{(G)}$	adsorption separation factor based on weights
$K^{(N)}$	adsorption separation factor based on moles
$K^{(V)}$	adsorption separation factor based on volumes
k, k_1, etc.	constants
M	molecular weight, g./mole
$\overline{M}$	mean molecular weight, g./mole
m	milli - , 10^{-3} x .....
N	moles
n	number of observations
n_D	refractive index
P	pressure, atm. or cm. of mercury or mm. of mercury
P_s	saturation pressure, cm. of mercury
Q^M	heat evolved or absorbed on mixing liquids, cal.
$Q_{dil.}$	heat of dilution on immersion, cal.
Q_I	heat evolved on immersion of an adsorbent in a liquid medium, cal.

R	resistance, ohms.
T	temperature, °C or °K
t	time, min.
V	volume, l. or cc.
$\tilde{V}$	molar volume, cc./mole
$\overline{V}$	mean molar volume, cc./mole
V_p	total volume of adsorbent, cc./g.
W	mass of adsorbent or mass of pure adsorbate, g. or mg.
W^o	mass of adsorbent following evacuation at room temperature or mass of a binary liquid mixture of weight fraction r_1^o, g.
W^i	mass of adsorbent residue following evacuation at higher temperatures, g.
$X_i^{(G)}$	apparent adsorption of species i from a binary mixture on to the adsorbent, g/g.
$X_i^{(N)}$	apparent adsorption of species i from a binary mixture on to the adsorbent, mole/g. or m. mole/g.
$X_i^{(V)}$	apparent adsorption of species i from a binary mixture on to the adsorbent, cc./g.
x	mole fraction

Greek Letters:

α	temperature coefficient of thermistor resistance, ohms/100 ohms/° C
β	constant in thermister equation, °K
Γ_i	absolute magnitude of adsorption of species i, μ mole/m^2

σ	constant in Freundlich's equation
ϵ	internal energy, cal./m^2
θ	fraction of adsorbent covered with adsorbed first layer of molecules
θ_I	relative heat of immersion
θ_I'	corrected relative heat of immersion: $\frac{\theta_I \tilde{V}_2}{\theta_I \tilde{V}_2 + (1 - \theta_I) \tilde{V}_1}$
μ	micro -, 10^{-6} x .....
ρ	density, g./cc
Φ_i	molar area of species i on the surface of the adsorbent, m^2/mole or m^2/m. mole
ϕ_i	volume fraction of species i
$\mathcal{S}_s$	surface area of adsorbent, m^2/g.
$\mathcal{S}_{s(L)}$	surface area of adsorbent determined from adsorption of binary liquid mixtures, m^2/g.
$\mathcal{S}_{s(N_2)}$	surface area of adsorbent determined from adsorption of nitrogen (B. E. T.) m^2/g.

Subscripts:

o	saturation conditions
1, 2	species of a binary mixture
c	calibration, corrected
i	species
l	liquid
m	at monolayer coverage, maximum
s	adsorbate-free solid

Superscripts:

a	adsorbed
e	equilibrium
o	initial condition, pure liquid

VII TERMINOLOGY

1. The term "solute" is used with reference to heats of immersion of binary mixtures, to designate component 1, namely, benzene.
2. The term "heat of mixing" ΔH^{M} is used with reference to an excess enthalpy of mixing at constant T and P.
3. The term "ideal mixture" is used with reference to the case where $\Delta H^{M} = 0$.
4. The term "perfect mixture" is used with reference to the special case of an ideal binary mixture where the molar areas of the adsorbed species are the same.
5. The term "Adsorption isotherm" is used with reference to the net amount of a pure substance adsorbed at constant T over the range $0 < P/P_{o} < 1$, the bulk phase being a gas or a vapor. It is also used with reference to the net adsorption of a mixture from a fluid bulk phase, at constant T and over the entire concentration range.
6. The term "individual adsorption isotherm" is used with reference to the net adsorption of species 1 and 2 from a binary mixture, at constant T.
7. The term "composite adsorption isotherm" is used to express, directly, the experimental results in the adsorption from binary liquid mixtures on solid adsorbents over the range $0 < x_{1}^{e} < 1$, at T and P.

8. The term "absolute heat of immersion" h_I is used with reference to the heat, in calories, released on immersion of a unit surface area of adsorbent in a liquid medium at T and P.

   $h_{I(N_2)}$ when based on the unit area of adsorbent determined from nitrogen adsorption (B.E.T.); and

   $h_{I(L)}$ when based on the unit area of adsorbent determined by adsorption from binary liquid mixtures.

9. The term "heat of immersion" H_I is used with reference to the heat, in calories, released on immersion of a unit mass of solid adsorbent in a liquid medium, at T and P.

10. The term "isotherm of heats of immersion" is used with reference to the heats of immersion determined over the complete concentration range at 25° C. and 1 atm. referred to an isothermal equilibrium of the components of a binary mixture between two phases, one or more of which is present at a surface or interface.

11. The term "relative heat of immersion" θ_I is used to compare experimental results of heats of immersion of an adsorbent in various binary systems, or heats of immersion of different adsorbents in a given binary system. It is defined as follows

$$\theta_I = \frac{H_I - (H_I^\circ)_2}{(H_I^\circ)_1 - (H_I^\circ)_2}$$

where $(H_I^\circ)_1$ and $(H_I^\circ)_2$ are the heats of immersion in the pure components 1 and 2, respectively.

VIII INTRODUCTION

The design of adsorption equipment requires knowledge of the adsorption equilibrium data of the systems undergoing such operation. These data, to be complete, should incorporate the relation between the composition of the adsorbed phase in equilibrium with the bulk mixture and the heat effect accompanying the operation.

In the development of the theory of immersion of solid adsorbents in binary liquid mixtures, a prominent part has been given to the adsorption of molecules on monomolecular films. Historically, the monomolecular theory of adsorption was first applied to the adsorption of gases and vapors on solid adsorbents. In so doing, a body of terminology, equations, assumptions, and several approaches was developed and is in use today. Many of these ideas and forms are applied to the immersion of solids in binary liquid mixtures by mere substitution or by redefinition of symbols. Or, at other times, a new set of assumptions is made to apply to the liquid case, and a new development presented. Further the model of monomolecular adsorption has been extended (1) to the determination of the specific surface area of adsorbents and, moreover, it has been shown how it is possible to calculate the heats of immersion of adsorbents in binary liquid mixtures from considerations of adsorption for perfect systems.

Most studies of heats of immersion have been limited to a single liquid adsorbate. Relatively few investigations have been

concerned with the heats evolved upon adsorption of binary liquid mixtures onto a solid adsorbent. This is not surprising, in view of the difficulties encountered in this type of work and which may be classified into two main groups, experimental and interpretative.

In heat of immersion calorimetry, a degassed adsorbent is contained in a glass bulb. The bulb may on occasion (2) be partially filled with helium in order to minimise the effect of temperature lags. The bulb is broken under the liquid and the heat evolved is determined. The rise in temperature ranges from a few hundredths to a few tenths of a degree and is usually measured by a multiple junction thermocouple or by a thermistor.

The heat produced in the breaking of a glass bulb has been shown by some authors (2) to constitute an appreciable percentage of the total heat evolved, while others (3) have reported a negligible heat change.

For pure liquids, the adsorbate is dried with an adsorbent prior to loading in the calorimeter (2), and a small amount of adsorbent is positioned in the calorimeter to ensure against a possible contamination of the adsorbate in the calorimeter vessel (4).

For mixtures, the adsorbate is agitated in a closed flask with the adsorbent, then analysed, and finally loaded into the caleri-

meter vessel (5). This technique, however useful it may be, will not necessarily prevent contamination of the adsorbate mixture prior to the determination.

Objective of This Work

The first phase of this work was concerned with the construction and testing of a suitable calorimeter for the determination of heats of immersion of adsorbents in binary liquid mixtures.

Secondly, in view of the importance of liquid separation processes based on adsorption and because the literature is almost devoid of heats of immersion data of binary liquid mixtures, it was decided to initiate an investigation of the heats of immersion of silica adsorbents in binary liquid systems, using benzene as a solute. The adsorbates were chosen as being representative of two types of liquid systems, namely: (a) a binary liquid system where the molar areas of the components may be considered to be equal; and (b) mixtures of a solute with solvents of a homologous series. The adsorbents differed from each other in pore radius, in surface area, and in adsorption activity.

IX LITERATURE SURVEY

The following literature survey has been focused mainly on: (i) The basic thermodynamic equations that govern the adsorption of molecules from a liquid medium onto a solid adsorbent; (ii) The adsorption of water, of a selected group of pure hydrocarbons, and of hydrocarbon mixtures, on silica adsorbents, with reference to the following:

A. Equilibrium adsorption from binary liquid mixtures.

B. Heats of immersion

1. Pure liquids

2. Binary mixtures.

C. Main types of calorimeters used in the determination of heats of immersion.

General reviews on heats of immersion of adsorbents in pure liquids have been given by Clark and Thomas (6), Razouk (7) and Chessick (8).

A. EQUILIBRIUM ADSORPTION FROM BINARY LIQUID MIXTURES

When a solid adsorbent is immersed in a binary liquid mixture, in general, the two components may be adsorbed to different extents, so that the concentration of component 1 relative to component 2 in the bulk of the mixture may change.

For the change in concentration of a binary mixture upon adsorption, the process is indicated in Fig. 1

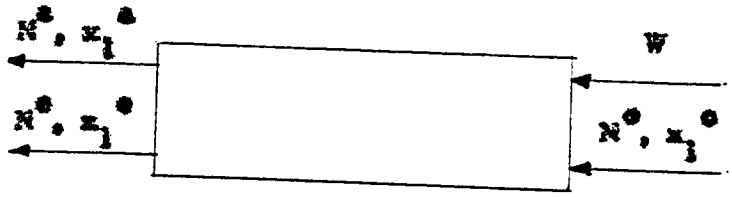


Fig. 1. Material balance of a solid-liquid batch adsorption process

where N^a is the number of moles adsorbed per gram of adsorbent;

N^e is the number of moles in the equilibrium mixture;

N^o is the number of moles in the initial mixture;

x_1^a is the mole fraction of component 1 on the surface;

x_1^o and x_1^e are the mole fractions of the mixtures before and after adsorption, respectively; and

W is the mass of adsorbent, in grams.

From the material balances

$$\frac{N^o}{W} = \frac{N^e}{W} + N^a \qquad (1)$$

and

$$\frac{N^{\circ} x_1^{\circ}}{W} = \frac{N^{e} x_1^{e}}{W} + N^{a} x_1^{a} \qquad (2)$$

the following expression is obtained

$$\frac{N^{\circ} (x_1^{\circ} - x_1^{e})}{W} = N^{a} (x_1^{a} - x_1^{e}) \qquad (3)$$

Thus, the change in concentration of a mixture on adsorption is related to the specific adsorption of both components from the bulk of the mixture onto the adsorbent.

Gipling (9) and others (1, 10) have shown that the change in concentration of the mixture is directly proportional to the Gibbs adsorption, i.e. the excess of a given substance in the bulk of the mixture.

The magnitude for the Gibbs adsorption depends on how the concentration in the mixture is expressed, and on the portion of mixture on the surface of the adsorbent and in the bulk being compared. If they are compared with respect to the number of moles

$$X_1^{(N)} = \frac{N^{\circ} (x_1^{\circ} - x_1^{e})}{W} \qquad (4)$$

If they are compared by weight

$$X_1^{(G)} = \frac{W^{\circ} (x_1^{\circ} - x_1^{e})}{W \cdot M_1} \qquad (5)$$

where W° is the weight of the initial mixture;

x_1° is the weight fraction of the initial mixture;

x_1^* is the weight fraction of the equilibrium mixture; and

M_1 is the molecular weight of component 1.

If they are compared by volume

$$\chi_1^{(V)} = \frac{V^\circ (\phi_1^\circ - \phi_1^*)}{W \cdot V_1} \tag{6}$$

where V° is the volume of the initial mixture;

ϕ_1° is the volume fraction of the initial mixture;

ϕ_1^* is the volume fraction of the equilibrium mixture; and

V_1 is the molar volume of component 1.

Since adsorbents differ in their surface area $\leq_s$, it is important to obtain the absolute magnitude of the adsorption, namely

$$\Gamma_1^{(N)} = \frac{\chi_1^N}{\leq_s} ; \Gamma_1^{(G)} = \frac{\chi_1^{(G)}}{\leq_s} ; \Gamma_1^{(V)} = \frac{\chi_1^{(V)}}{\leq_s} \tag{7}$$

The various sets of Γ_i are connected (11) by the following relation

$$\sum_i \Gamma_i^{(N)} = \sum_i \Gamma_i^{(G)} M_i = \sum_i \Gamma_i^{(V)} V_i = 0 \tag{8}$$

In a binary system

$$\Gamma_1^{(N)} = \Gamma_1^{(G)} \frac{\overline{M}}{M_2} = \Gamma_1^{(V)} \frac{\overline{V}}{V_2} \tag{9}$$

where $\overline{M}$ and $\overline{V}$ are the mean molecular weight and the mean molecular volume of the mixture, respectively.

Kiselev (12) studied the adsorption from mixtures of benzene with n-heptane on silica adsorbents. Some interesting conclusions in this paper were that the specific surface of the adsorbent as determined by liquid adsorption is not always in agreement with the value obtained by nitrogen adsorption and that a reduction in pore diameter causes an increase in the adsorption of benzene per unit surface area of the adsorbent. The effect of pore diameter was confirmed by Jones and Stuart (13) through measurements on the system benzene-cyclohexane with silica gels.

Kiselev (14) had also shown that decrease in the pore size in silica gels causes an increase in the adsorption of benzene and n-hexane vapors at low surface coverage.

Kiselev and Pavlova (15) studied the effect of surface hydration of silica gels on the adsorption of benzene- n-hexane mixtures. They found that the adsorption of benzene from solution in n-hexane diminishes in the following order: hydrated silica gel, dehydrated silica gel.

Jones and Stuart (13) and Kiselev (15) studied the effect of temperature on adsorption from solutions, on silicas. They found that the adsorption decreases with a rise in the temperature.

1. Individual adsorption isotherms

In order to resolve the composite adsorption isotherm to show the separate adsorption of each component, Bartell and Sloan (16) assumed that the individual adsorption isotherms of both components follow a Freundlich equation,

$$N_1^a = k_1 (x_1^e)^{\alpha} \; ; \text{ and } N_2^a = k_2 (x_2^e)^{\beta} \qquad (10)$$

where N_1^a and N_2^a are the number of moles of components 1 and 2 respectively, adsorbed per gram of adsorbent; and k_1, k_2, α and β are constants.

Bartell and Sloan obtained the following expression for the isotherm of concentration change,

$$\frac{N^o (x_1^o - x_1^e)}{W} = k_1 (x_1^e)^{\alpha} (1 - x_1^e) - k_2 (x_1^e)^{\beta} (1 - x_1^e) \qquad (11)$$

a. Monomolecular theory

Kipling and Tester (17), assumed that the individual adsorption isotherms followed a Langmuir equation

$$N_1^a = K_3 \frac{k_3 x_1^e}{1 + k_3 x_1^e} \; ; \text{ and } N_2^a = K_4 \frac{k_4 x_1^e}{1 + k_4 x_1^e} \qquad (12)$$

where K_3, K_4, k_3 and k_4 are constants. They obtained the following expression,

$$\frac{N^{\circ}(x_1^{\circ} - x_1^{e})}{W} = \frac{K_3 k^3 x_1^{e}(1 - x_1^{e})}{1 + k_3 x_1^{e}} - \frac{K_4 k_4 x_1^{e}(1 - x_1^{e})}{1 + k_4 (1 - x_1^{e})} \qquad (13)$$

Kipling and Tester (17) reported that the individual isotherms calculated from Equations 11 and 13 revealed a wide discrepancy.

Alternatively, the evaluation of N_1^{a} and N_2^{a} requires another equation, to be solved simultaneously with Equation 3.

Elton (18) and Kipling (17), postulated that the surface of the solid adsorbent is completely covered by a monolayer in adsorption from binary liquid mixtures. Then,

$$N_1^{a} \Phi_1 + N_2^{a} \Phi_2 = S \qquad (14)$$

where Φ_1 and Φ_2 are the areas occupied per mole of components 1 and 2 respectively, if they were adsorbed separately; and S is the surface area of 1 g. of adsorbent.

Equation 14 is valid only if the same area of surface is available to both components (19).

By solving Equations 3 and 14 for x_1^{a}, the following expression is obtained,

$$x_1^a = \frac{x_1^e + \frac{\Phi_2}{\leqslant_s} \cdot x_1^{(N)}}{1 + \frac{\Phi_2 - \Phi_1}{\leqslant_s} \cdot x_1^{(N)}} \qquad (15)$$

Nagy and Schay (20), proposed a graphical method to determine the adsorption capacities at monolayer coverage, $(N_1^a)_m$ and $(N_2^a)_m$, in systems where the composite adsorption isotherm has a linear section over a range of concentration. They assumed that $x_1^{(N)}$ is a linear function of x_1^e if N_1^a and N_2^a are constant over the concentration range corresponding to the linearity. Extrapolation of the linear section of the composite adsorption isotherm to $x_1^e = 0$ and $x_1^e = 1$ gives $(N_1^a)_m$ and $-(N_2^a)_m$, respectively.

In considering Nagy and Schay's analysis, Cornford, Ripling and Wright (21) pointed out that a constant concentration on the surface is only a particular case leading to

$$\frac{d^2 x_1^{(N)}}{d(x_1^e)^2} = 0 \qquad (16)$$

over a certain range of concentration in the equilibrium binary mixture. Although the method is strictly valid in exceptional cases, it gives approximate results of the thickness of the adsorbed layer.

The isotherms of adsorption from binary liquid mixtures were discussed by Schiessler and Rowe (22) on the basis of the concept of a constant relative adsorbability expressed in volumes.

$$K^{(V)} = \frac{\beta_1^a}{\beta_2^a} \cdot \frac{\beta_2^e}{\beta_1^e} \qquad (17)$$

From Equation 17 and a material balance for component 1 at equilibrium, they arrived at the expression

$$\beta_1^e = \frac{\beta_1^e \beta_2^e}{x_1^{(V)}} \left(\frac{1}{K^{(V)} - 1}\right) + V^a \qquad (18)$$

where V^a is the adsorptive capacity in cc/g.

Plots of $(\beta_1 \beta_2)^e / x_1^{(V)}$ against β_1^e resulted in straight lines from which V^a and $K^{(V)}$ were determined.

Siskova and Erdos (23) combined the expression for the separation factor expressed in moles, namely

$$K^{(N)} = \frac{x_1^a}{x_2^a} \cdot \frac{x_2^e}{x_1^e} \qquad (19)$$

with Equation 3 to yield

$$\frac{x_1^{(N)}}{1 - x_1^e} = -\frac{1}{K^{(N)}} \frac{x_1^{(N)}}{x_1^e} + N^a \left(\frac{K^{(N)} - 1}{K^{(N)}}\right) \qquad (20)$$

Plots of $x_1^{(N)}/(1 - x_1^e)$ against $x_1^{(N)}/x_1^e$ resulted in straight lines from which N^a and $K^{(N)}$ were determined.

Cleland (24) studied the adsorption of mixtures of benzene with cyclohexane, benzene with carbon tetrachloride, and carbon tetrachloride with cyclohexane, on porous (Vycor) glass. He examined the benzene - cyclohexane system in the light of Equation 20 using his data and those of others and found good agreement between the separation factor $K^{(N)}$ for silica gel and Vycor glass adsorbents. However, the molecular area of the adsorbate calculated using the nitrogen surface area varied from 230×10^3 m^2/mole for a silica gel to 430×10^3 m^2/mole for Vycor glass.

Everett (1) proposed an equation similar in form to Equation 18, but expressed in terms of moles, which he used to calculate the adsorptive capacity N^a and the separation factor $K^{(N)}$

$$\frac{x_1^{\bullet} x_2^{\bullet}}{X_1^{(N)}} = \frac{1}{N^a} \left(x_1^{\bullet} + \frac{1}{K^{(N)} - 1} \right) \qquad (21)$$

From values of N^a and the molar area of the adsorbate, the surface area of the adsorbent may be calculated.

The assumptions involved in the derivation of Equations 20 and 21 are: (a) monomolecular adsorption, (b) perfect solution-solid interface; (c) all adsorption sites have identical properties.

b. Multimolecular theory

Hansen (25) and Jones (26), supported an alternative mechanism for the adsorption from binary liquid mixtures using solid adsorbents. They assumed that the pores of the adsorbent are completely filled with adsorbed liquid and that the adsorption is not confined to a monomolecular layer. According to this analysis, the following relationship holds

$$N_1^a \tilde{V}_1 + N_2^a \tilde{V}_2 = V_p \qquad (22)$$

where $\tilde{V}_1$ and $\tilde{V}_2$ are the molal volumes of components 1 and 2; and V_p is the pore volume of the adsorbent.

The volumes that would be adsorbed if the adsorbent were immersed in components 1 and 2 are given by the expression

$$V_p = (N_1^a)_o \tilde{V}_1 = (N_2^a)_o \tilde{V}_2 \qquad (23)$$

where $(N_1^a)_o$ and $(N_2^a)_o$ are obtained in separate experiments. Solving equations 22 and 3 for x_1^a, the following expression is obtained

$$x_1^a = \frac{x_1^e + \frac{\tilde{V}_2}{V_p} \cdot x_1^{(N)}}{1 + \frac{(\tilde{V}_2 - \tilde{V}_1)}{V_p} \cdot x_1^{(N)}} \qquad (24)$$

Several workers (25, 26, 27) have presented experimental evidence supporting the view that adsorbents have a constant volume

available for adsorption, independent of the liquid used. It has been stated (25) that this would hold, provided that the pore diameters of adsorbents are larger than the molecular diameters of adsorbate components.

Three methods have been used in the determination of pore volumes:

1. The adsorbent was immersed in a liquid, the sample was then removed, dried externally with filter paper, and weighed (26, 27);
2. The adsorbent was saturated with the vapors of a pure liquid (26, 27), or with the vapors of a binary liquid mixture (27);
3. The vapor adsorption isotherm of a liquid was extrapolated to saturation vapor pressure (25, 26).

B. HEATS OF IMMERSION

The problem of obtaining thermodynamic data for the immersion of a solid in a liquid medium may be approached by studying the heat effect accompanying the process. The heat of immersion is the amount of heat liberated when a unit mass of the solid is immersed in a liquid medium.

1. Pure Liquids

The heat of immersion is currently explained in terms of surface energy changes that take place when a degassed inert

solid is immersed in a liquid, the solid-liquid interface replacing the solid surface.

The thermodynamic expression which governs the process of immersion of a solid in a pure liquid is given, by convention, as the difference between the final state and the initial state. Accordingly, the value of the heat of immersion is expressed by the following equation

$$h_I^o = h_{sL} - h_s \qquad (25)$$

where h_I^o is the heat of immersion of a unit surface area of the solid in a pure liquid; and

h_{sL} and h_s are the enthalpies of the unit area solid-liquid interface and degassed solid, respectively.

At constant pressure, the relationship between the change in enthalpy Δh and the change in internal energy $\Delta \epsilon$ is

$$\Delta h = \Delta \epsilon + P \Delta v \qquad (26)$$

the value of the volume change Δv is very small (28), hence

$$h \cong \epsilon \qquad (27)$$

and the change in enthalpy is equal to the change in internal energy.

a. Purity of materials

Several workers (2, 4, 28, 29) have pointed out the need for purity of adsorbates. Trace quantities of water in benzene, for instance, may double the heat of immersion of the adsorbent (4). Bartell and Suggitt (2) developed a technique for drying pure liquid adsorbates. They dispersed an amount of adsorbent, identical in preparation to the sample, in the pure liquid adsorbate prior to the actual determination. Trace amounts of water that could have diffused into the calorimeter vessel after it was loaded, and contaminated the adsorbate were thus eliminated.

Also, the adsorbent must be cleaned and prepared in a reproducible state. Culbertson and Winters (30) developed the technique of using samples sealed under vacuum. Rasouk (7) and La Porte (31) showed that the heat evolved using non-evacuated adsorbents is low, and that the need to displace air from the adsorbent surface increases the time required for the heat evolution and this in turn reduces the accuracy of the measurement.

b. Effect of degassing temperature

The role of degassing temperature on the heat of immersion is difficult to assess. There is experimental evidence to indicate a variation of the heat of immersion with degassing temperature, of a particular silica adsorbent in water (3, 32-35). In general, the heat

of immersion remains constant in the degassing temperature range between 20 and 110°C for some samples and between 20 and 180°C for others. Above this limit it increases, reaches a maximum, and then decreases. It has been suggested (3) that this variation is due to the summation of two processes: (a) water being lost reversibly during degassing and then regained during immersion; and (b) water being lost irreversibly from the point of view of the duration of a calorimetric measurement.

Similar data have been reported for the immersion of silica adsorbents in benzene (4, 36), n-hexane (37) and n-heptane (36).

Deviations from this general pattern have been presented for the immersion of some samples of quartz in water (34) and for silicas in cyclohexane (4), where the heats of immersion remain constant over wide ranges of degassing temperature.

c. Effect of particle size

Often, another factor, other than the degassing temperature, makes difficult the interpretation of heat of immersion data. Several workers (33, 35) list many contributors to experimental evidence showing that at a given degassing temperature, the heats of immersion of silica in water per unit of nitrogen surface area $h_I^o(N_2)$

apparently decrease with increasing nitrogen surface area $\leq_{s(N_2)}$. A similar effect has been reported for the immersion of silicas in n-hexane (37).

d. Effect of adsorbate

The activities of silica adsorbents in terms of heats of immersion in pure liquids have been determined by several workers (2, 4, 34, 36). The results showed that values for water were greater than those for benzene, which in turn were greater than values for n-alkanes.

2. Binary Liquid Mixtures

Bartell and Fu (38) studied the heats of immersion of a carbon of unspecified surface area in a series of binary mixtures. They postulated that "if both components are adsorbed from a binary mixture, the heat evolved must be due to the combined effect of both liquids".

The role of temperature on the heats of immersion of a charcoal adsorbent in aqueous solutions of n-propyl alcohol were studied by Runov and co-workers (39). They found no significant difference, within the accuracy of the measurements, between data obtained at 20° C and 50° C.

Young and co-workers (5) measured the heats of immersion of graphon in aqueous solutions of n-butyl alcohol. It was postulated that the heat of immersion of the solid adsorbent in the binary liquid mixture, h_I, may be considered as the results of two effects: (a) Heat of wetting, h_w, the energy changes that take place when the solid-liquid interface replaces the solid surface; and (b) Heat of dilution, $h_{dil.}$, due to the changes in concentration of the mixture. Thus, the expression for the heat of immersion is as follows

$$h_I = h_w + h_{dil.} \tag{28}$$

Young and co-workers (5) considered the surface of the adsorbent to be homogeneous and to be covered by a monolayer of adsorbed molecules; and that the "interaction between molecules in the bulk solution was the same as for the adsorbed layer and thus was not included in the heat of immersion". They derived an equation for the heat of immersion in a binary liquid mixture, which may be written as follows

$$H_I = \theta (H_I^{\circ})_1 + (1 - \theta) (H_I^{\circ})_2 + H_{dil.} \tag{29}$$

where θ is the fraction of the surface of the adsorbent covered with first layer of adsorbed molecules; and

$H_{dil.}$ is the heat of dilution effect in cal. per gram of adsorbent.

It was shown that there is good agreement between the experimental values of the heats of immersion of graphon in aqueous solutions of n-butyl alcohol and those calculated from Equation 29.

Smirnova et al, (40) measured the heats of immersion of aluminum oxide in mixtures of n-heptane with benzene, cyclohexane and cyclohexene. From these measurements and studies of the adsorption isotherms of vapors and mixtures of the pure components, the authors suggested a possible arrangement of the molecules of these hydrocarbons on the surface of the adsorbent and calculated their molecular characteristics.

Everett (1) considered the case of a perfect system, where

$$H_I = x_1^a (H_I^o)_1 + (1 - x_1^a)(H_I^o)_2 \qquad (30)$$

Combining with Equation 21, he obtained

$$H_I = x_1^e (H_I^o)_1 + x_2^e (H_I^o)_2 + \frac{x_1^e (1 - x_1^e)\left[(H_I^o)_1 - (H_I^o)_2\right]}{x_1^e + \frac{1}{K^{(N)} - 1}} \qquad (31)$$

Thus, the heat of immersion of an adsorbent in a binary liquid mixture may be readily determined from the heats of immersion in the two pure components and the separation factor $K^{(N)}$.

Equation 31 may be tested by arranging in the form

$$\theta_I = \frac{H_I - (H_I^\circ)_2}{(H_I^\circ)_1 - (H_I^\circ)_2} = \frac{K^{(N)} x_1^e}{1 + (K^{(N)} - 1) x_1^e} \qquad (32)$$

Recent measurements include those of Billet and co-workers (41) on the heats of immersion of a charcoal in mixtures of benzene with cyclohexane. They reported that the experimental values are in good agreement with those calculated from Equation 31.

3. Main Types of Calorimeters Used in the Determination of Heats of Immersion

Heats of immersion may be determined in calorimeters similar to those used for determining heats of mixing of liquids. Among the number of calorimeters previously used, suffice it to mention the main types, and the more important ones in chronological order.

Boyd and Jarkins (42), in 1942, used an 800-cc. Dewar flask provided with a 36-junction thermocouple for measuring the change of temperature on immersion. The adsorbent was contained in evacuated glass bulbs.

Hutchinson (43), in 1947, used a calorimeter similar in most respects to that used by Boyd and Harkins (42), except that a thermistor was incorporated to measure temperature changes.

Bartell and Suggitt (2), in 1954, used a twin metal calorimeter similar to that used by Dicker and co-workers (44), in 1939, in the study of heats of dilution of salt solutions.

Two methods have been used for contacting the solid sample with the liquid medium. The first consists of pouring the adsorbent into the liquid from an isolated container. The second consists in breaking a glass bulb containing the adsorbent under the liquid surface. Nowadays, heat of immersion calorimetry makes use, exclusively, of the technique of breaking a glass bulb containing the evacuated adsorbent, under the surface of the liquid.

EXPERIMENTAL DETAILS

A. MATERIALS

1. Gases

The nitrogen was of the "dry" grade with a minimum purity of 99.99%. The helium conformed to the specifications of the U.S. Bureau of Mines for grade "A" helium, the purity of which was 99.995%. They were passed through a column packed with activated silica gel in order to remove traces of water.

2. Adsorbents

The adsorbents were prepared from a commercial silica gel (20-[illegible]0 mesh, Davidson) obtained from Fisher Scientific Co., and from a Reagent grade silicic acid obtained from J. T. Baker Chemical Co.

a. Treatment of adsorbents with aqueous solutions of nitric acid

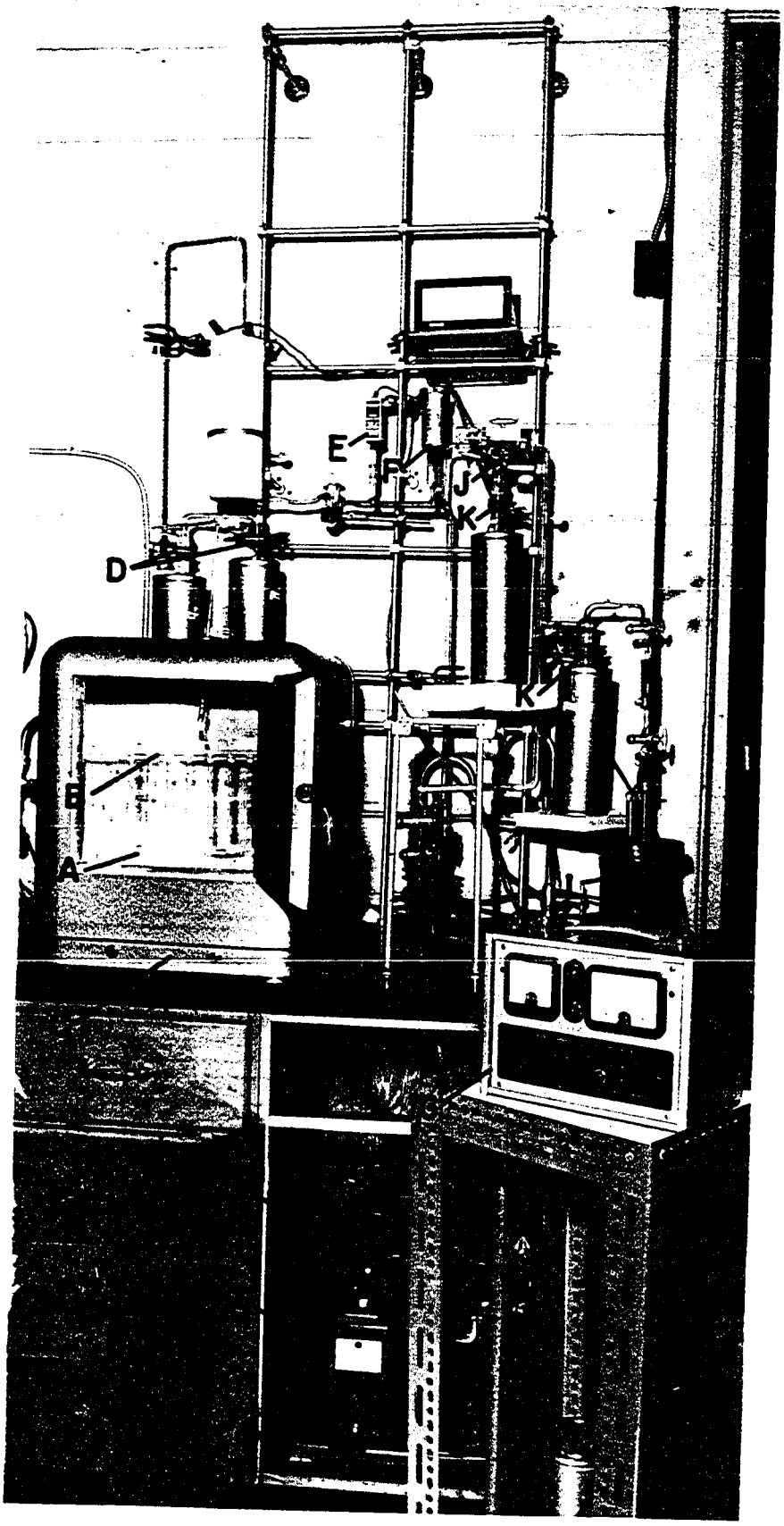
Samples of 20 to 30 grams of adsorbent were digested with nitric acid (d) 1:1 by volume, followed by an extraction with nitric acid 1:10 and then with four litres of distilled water per gram of sample. During the washing, which was done in a Buchner funnel, the adsorbents were always under water. Washing was followed by drying in an oven at 140° C for 24 hours.

Following this treatment, the silicic acid samples were ground into fine particles, in a glass mortar. The very finely divided particles were separated by sedimentation of the samples in 900 cc. of distilled water, using a one-liter graduated cylinder sitting vertically. The portion of the sample remaining in suspension after one minute was discarded; the residue was dried in the oven at 140° C.

b. Thermal degassing of the samples at reduced pressures

The apparatus for degassing adsorbents at reduced pressures is shown in Fig. 2 and schematically in Fig. 3.

The apparatus consists of glass ampoules (A) containing the adsorbent, a glass manifold (B) in the vacuum line, a temperature-controlled oven (C), two traps cooled by liquid nitrogen (D), a Pirani head (E), a Penning head (F), a Pirani-Penning type vacuum gauge (G),


E
F
J
K
D
K
B
A

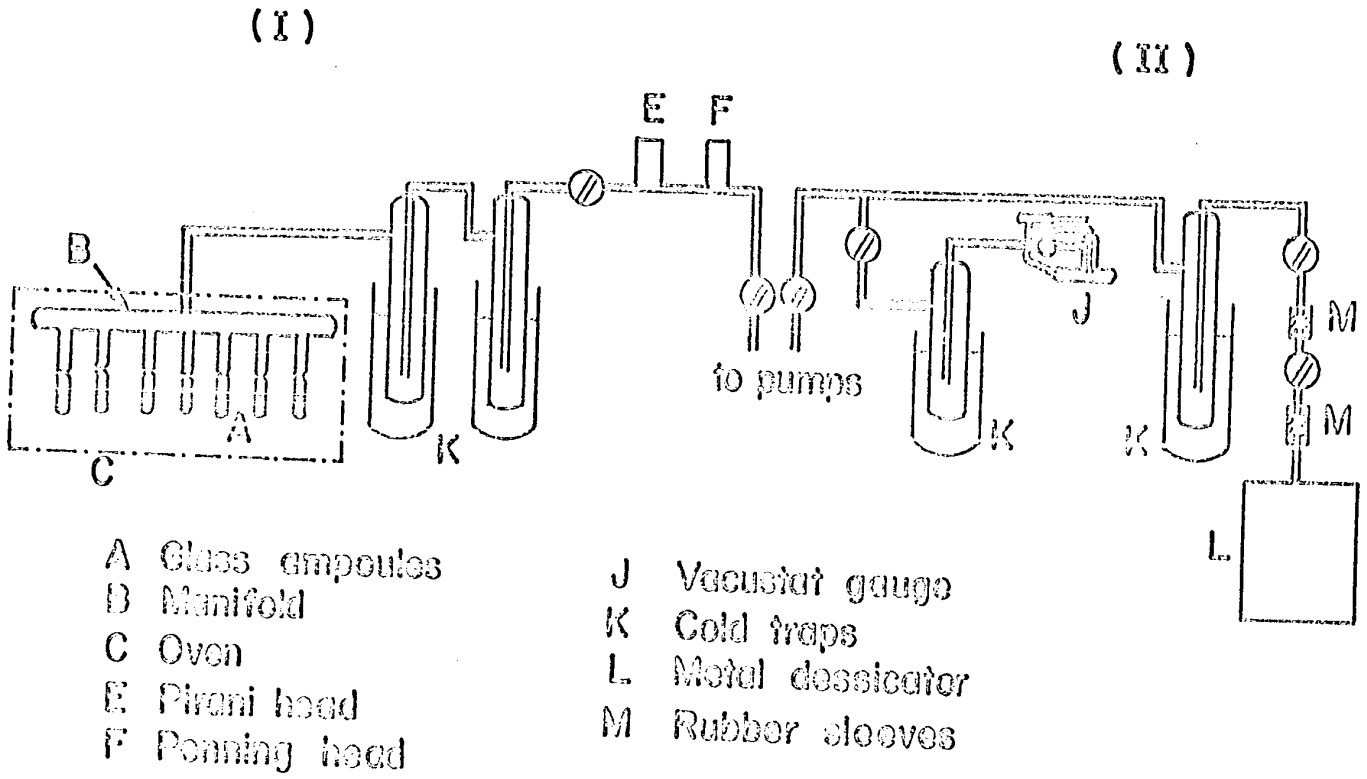


Fig. 3 Sketch of the degassing apparatus: (I) For adsorbents; (II) For mixing cells and auxiliary equipment

- 26 -

a vacuum pump (H), and suitable connections.

The traps served two purposes, namely, (1) condensing the water vapor resulting from the degassing of the adsorbent; and (2) trapping particles of the adsorbent blown off the glass ampoules during evacuation.

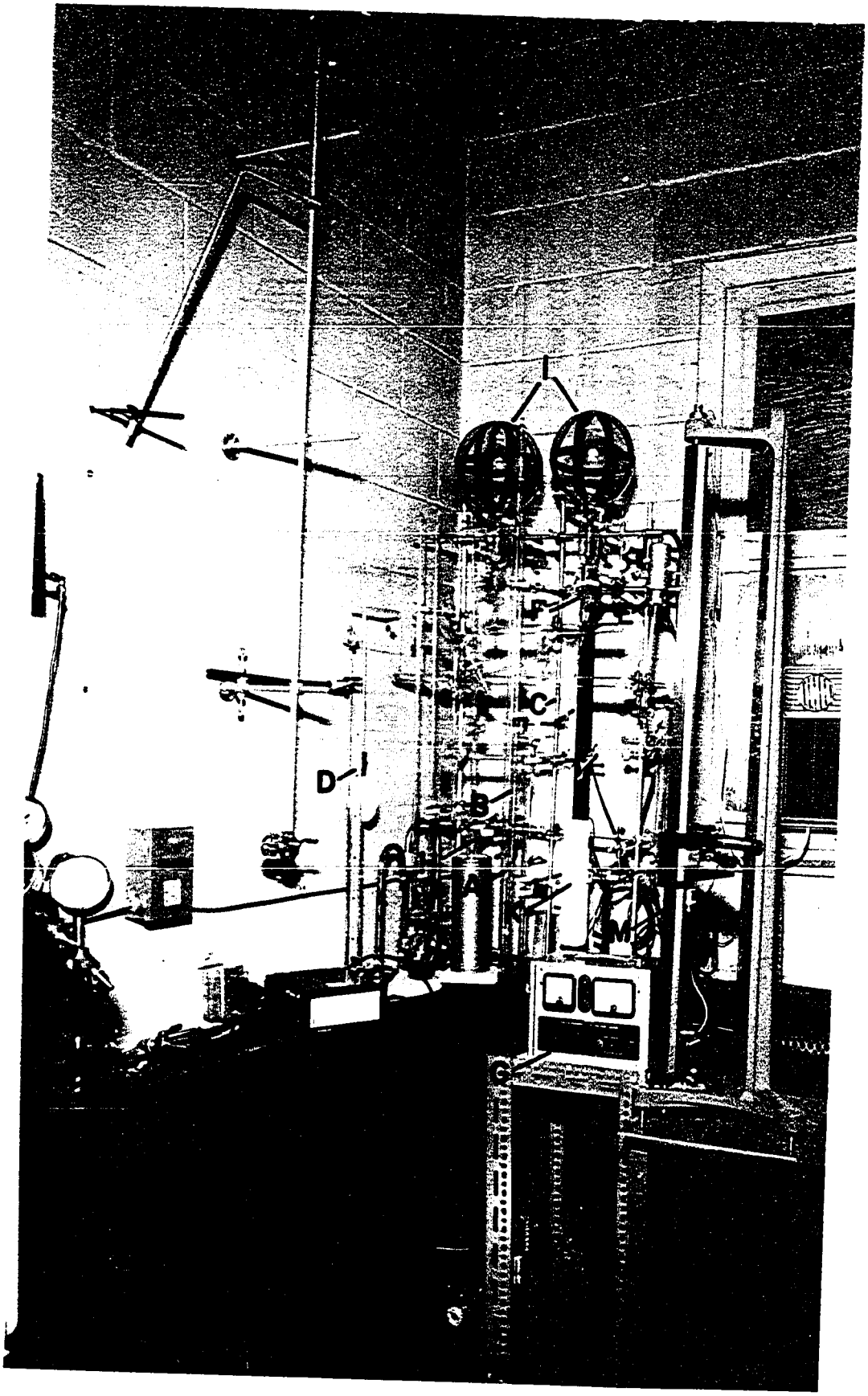
Portions of 0.8 gram of a batch of adsorbent were placed in pyrex-glass ampoules, which were then joined on to the glass manifold mounted inside the temperature-controlled oven. The adsorbent was degassed for at least 40 hours at 140° C and at a pressure of 3×10^{-5} mm. of mercury, after which period the ampoules were sealed off under vacuum with a blow torch. The ampoules were then stored in a desiccator with activated silica gel.

c. Surface area by B. E. T. method

Adsorption measurements were made by admitting nitrogen into an evacuated chamber containing the adsorbent; the amount adsorbed was determined gravimetrically with a McBain balance.

Adsorption Balance

A photograph (Fig. 4) shows the assembly used in the determination of surface area by nitrogen adsorption. The same assembly is shown schematically in Fig. 5. The solid adsorbent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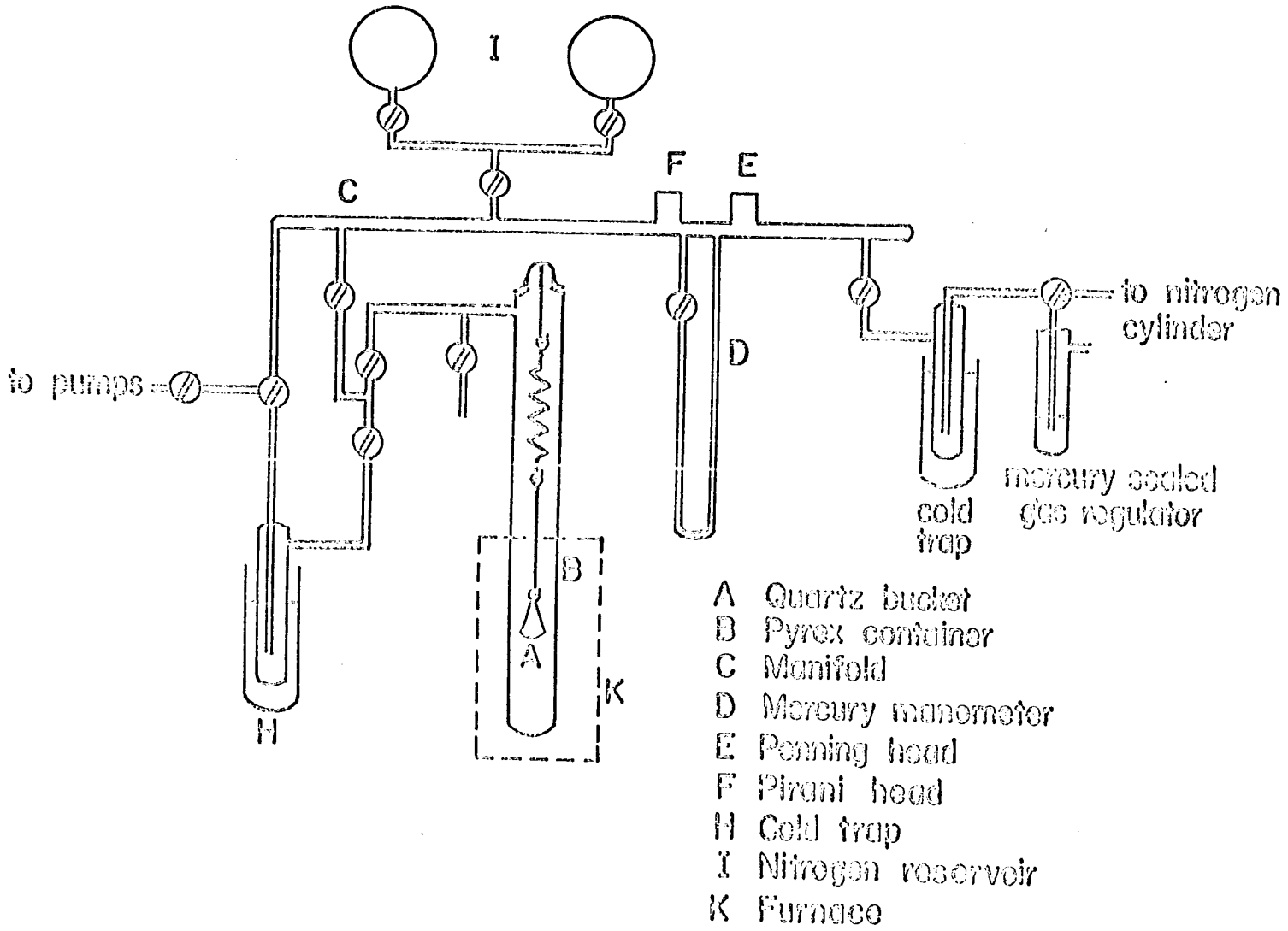


Fig. 5 Sketch of the nitrogen adsorption apparatus

- 29 -

was contained in a light quartz bucket (A), which was suspended from a calibrated quartz spring by a glass fibre. These parts were enclosed in a cylindrical Pyrex glass container (B) with an outside diameter of 1 1/4 in., an overall height of 54 in., with a conical tapered joint on top, for the purpose of loading and unloading the bucket.

The adsorption column was connected to a vacuum manifold (C) consisting of a mercury manometer (D), a Penning head (E), a Pirani head (F), a Pirani-Penning type vacuum gauge (G), a trap cooled by liquid nitrogen (H), two nitrogen-reservoir flasks (I), an oil diffusion pump (J), and suitable connections and stopcocks. Besides, the apparatus was equipped with an external furnace (K) connected to a temperature controller (L).

Degassing temperatures were measured using an iron-constantan thermocouple placed in contact with the external surface of the column and positioned between the bucket and the heater. Potential measurements were made with a K-3 potentiometer.

The balance had a sensitivity of about 1 mm. extension per mg. and a capacity of 400 mg. Spring extensions and mercury manometer pressure readings were readily determined to 0.01 mm. using a cathetometer (M). The accuracy of the reading was, however, of the order of 0.05 mm.

Procedure

A sample of the adsorbent, about 200 mg, was weighed in the calibrated bucket and degassed at a high temperature to an ultimate pressure of less than 10^{-4} mm. of mercury. The stopcocks connecting the systems to the vacuum pump were then closed and the furnace removed from around the column. As the column cooled down, it was immersed in liquid nitrogen to a height of about 5 inches above the pan. The reading of the spring extension was then recorded. Next, nitrogen was admitted into the column till the pressure was of a few mm. of mercury, and the manometer reading and spring extension reading were noted. These readings were made frequently until constancy was obtained. The time for obtaining equilibrium varied from 15 to 60 minutes, depending on the pressure, more time being required at higher pressures. Successive admissions of nitrogen were made till sufficient points for the isotherm had been obtained. The surface area was determined from 4 to five points on the isotherm in the relative pressure range P/P_o between 0.02 and 0.14, where P_o = 76.0 cm of mercury. A complete isotherm took about 10 additions of nitrogen. The results of these measurements are given in Appendix 1.

Calculations

The method of Brunauer, Emmet and Teller (B. E. T.) was used to evaluate the area of the adsorbents from the nitrogen adsorption data. The expression of the B. E. T. theory in terms of mass of adsorbate is

$$\frac{P/P_o}{W^a (1 - P/P_o)} = \frac{1}{W_m C} + \frac{C-1}{W_m C} \cdot \frac{P}{P_o} \qquad (33)$$

where W^a, in grams, is the mass of nitrogen adsorbed at an equilibrium pressure P and temperature T; and

W_m, in grams, is the mass of nitrogen adsorbed on W grams of adsorbent at monolayer coverage.

The terms W_m and C were evaluated from a plot of the left hand side of Equation 33 against the relative pressure P/P_o. The molecular area of the adsorbed nitrogen at -195° C was taken as $16.2 A^{o2}$ (28).

The area of the adsorbent $\leq_s$, in $m^2/g.$, is then

$$\leq_s = \frac{97.6 \times 10^3 \times W_m}{28.016 \times W} = 3481 \frac{W_m}{W} \qquad (34)$$

where 97.6×10^3 is the molar area of nitrogen in m^2/mole; and

28.016 is the molecular weight of nitrogen.

d. Total Pore Volume

The pore volume V_p in cc./g. was determined by extrapolating the isotherm $P/P_o = 1.0$. Thus,

$$V_p = \frac{(\text{Intercept})_{P/P_o = 1}}{\rho_g \times W} \qquad (35)$$

where ρ_g is the density of liquid nitrogen at -195° C., 0.808 g/cc.

e. Weight losses on degassing at reduced pressures

Weight losses of three adsorbents were determined gravimetrically with the McBain balance as a function of degassing temperature.

In separate experiments, two samples of silica gel and a sample of silicic acid were evacuated in the McBain balance for several hours at room temperature until constancy was obtained. Then the weight of the residue (W^o) was noted. Following this treatment, each sample was subjected to thermal degassing at various temperatures, the temperature range being between 22 and 500° C. Weight losses were calculated from the weight of the residue (W^1) at the temperature under study and the weight of the residue at 22° C., according to the expression

$$\text{losses (wt \%)} = \frac{100\,(W^o - W^1)}{W^o} \qquad (36)$$

f. Properties of adsorbents

The physical appearance of the samples of silica gel and of silicic acid varied considerably. Comparing the two silica surfaces, the silicic acid samples were very white whereas the silica gel samples were light grey in colour.

An optical microscopic examination of the adsorbents, Figs. 6a and 6b (same magnification), revealed that the silicic acid consisted of finely divided particles. In this connection it is worth mentioning that a great deal of care had to be taken in handling this sample in order to prevent it from spreading throughout the evacuating apparatus. The silica gel, on the other hand, consisted of particles with a large spread in their particle size.

A list of the adsorbents which have been studied is given in Table I along with the soaking period, the surface area (B. E. T.) and the pore volume. These values refer to samples which were degassed under vacuum in the temperature range between 140 and 275° C. Soaking the adsorbent in the presence of nitric acid solutions and distilled water prior to degassing decreased the surface area; the longer the period of soaking, the smaller the surface area. The effect of soaking on the pore volume was found to be almost nil. In the case of a silica soaked for a period of 40 days, the surface area was 560 m^2/g. and the pore volume was 0.38 cc./g. Soaking a silica for 7 months


(a)
1mm
(b)

Table 1

EFFECT OF SOAKING ON SURFACE AREA AND PORE VOLUME OF ADSORBENTS

Adsorbent	Soaking period days	Deg. Temp. °C	$S_{(N_2)}$ $m^2/g.$	V_p cc./g.
S. Gel A_o *	-	148	736	-
S. Gel A_o '*	-	200	666	0.36
S. Gel A_1 **	17	218	596	-
S. Gel A_2 **	28	260	587	-
S. Gel A_3 **	26	198	575	-
S. Gel A_4 **	40	148	560	0.38
S. Gel A_5 **	221	148	483	0.37
S. Acid B_1 ***	3	275	366	0.37
S. Acid B_2 **	20	196	348	-

* as received from supplier

** soaked in nitric acid solutions and in distilled water

*** soaked in distilled water only

decreased the surface area to 483 m^2/g. and the pore volume to 0.37 cc./g. The silica gel A_o^1, before digestion with nitric acid, had a pore volume of 0.36 cc./g.

The results of pore size analysis shown in Table 2 revealed that a large percentage of the volume of silicic acid adsorbent is in the macropore region, that is, in pores that have radii greater than 100 A^o, whereas in the silica gel adsorbents there are virtually no pores present with radii greater than 100 A^o and only a very small percentage between 20 and 100 A^o radius. Fig. 7 shows that the preferred micropore radius of silicic acid B_2 is about 40 A^o.

A summary of the results showing the effect of degassing temperature on the surface area of silica adsorbents, is given in Table 3. The results obtained indicate that the surface areas of the three adsorbents listed in Table 3, each one subjected to different treatment, did not vary significantly in the temperature range between 148 and 256° C. Between 256 - 481° C, the decrease in surface area varied over the narrow range of 4.2 to 6.6%.

Table 4 shows the results of weight loss analysis on three adsorbents ranging in surface area (B. E. T.) from 348 to 730 m^2/g. Fig. 8 shows a plot of weight loss of various adsorbents as a function of degassing temperature. The weight losses are seen to depend on

Table 2

POROSIMETRY DETERMINATION ON VARIOUS ADSORBENTS BY MERCURY INJECTION

Courtesy of the Bureau of Mines - Fuels Division

Adsorbent		A_4	A_5	A_5	B_2
$\Sigma_s(N_2)$, $m^2/g.$		560	482		348
(Deg. Temp.	200° C)		(in duplicate)		
Pressure Applied p.s.i.a.	Pore Radius A°	Cumulative Pore Volume cc/g.			
18	56,000	-	0	0	-
68	14,700	0	.01	.01	0
118	8,500	0	.02	.01	0
318	3,200	0	.02	.02	.01
1,000	1,000	0	.02	.02	.03
2,000	500	0	.02	.02	.05
3,000	330	-	-	-	-
4,000	250	-	-	-	-
5,000	200	0	.02	.02	.10
10,000	100	.01	.02	.03	.15
20,000	50	.01	.03	.03	.24
30,000	33	.03	.03	.06	.36
40,000	25	.03	.04	.06	.37
50,000	20	.05	.05	.05	.40

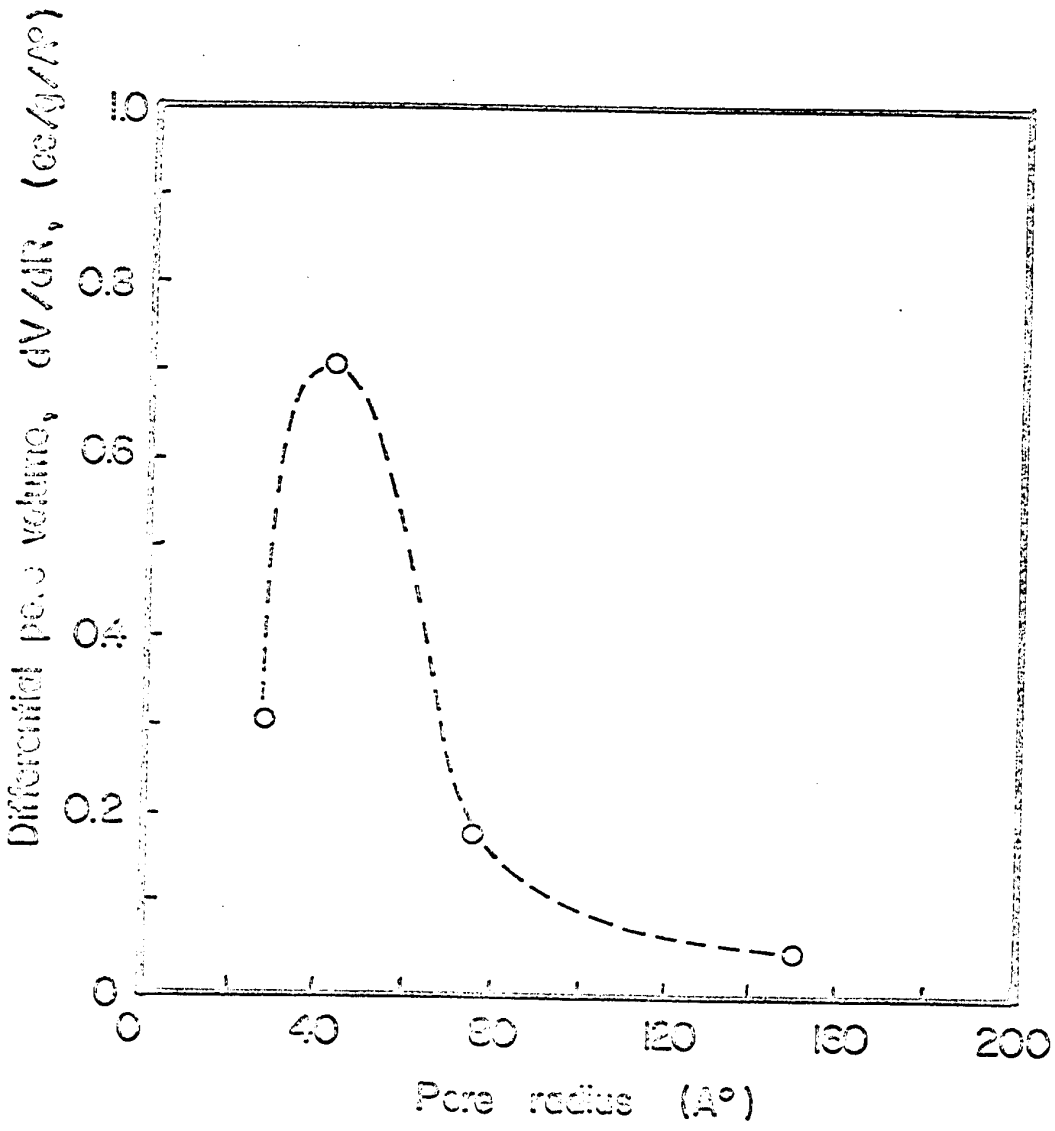


Fig. 7 Micropore size distribution in silicic acid B_2

Table 3

EFFECT OF DEGASSING TEMPERATURE ON SURFACE AREA OF VARIOUS ADSORBENTS

Adsorbent	A_o	A_1	B_1
Degassing Temp. °C		$\leq_{s(N_2)}$ $m^2/g.$	
148	736	-	-
218	-	596	-
256	731	-	-
266	-	600	-
275	-	-	365
429	691	-	-
438	-	579	-
471	-	-	345
476	686	-	-
481	-	572	-

EFFECT OF DEGASSING TEMPERATURE ON WEIGHT LOSSES OF VARIOUS ADSORBENTS

Adsorbent	A_o	A_1	B_1
$\leq s(N_2)$ $m^2/g.$	730	600	360
Degassing Temp. °C		weight losses (%)	
22	-	-	-
70	0.00	0.00	-
102	0.00	0.07	-
105	-	-	0.06
113	0.10	0.13	-
131	0.08	0.22	-
148	-	-	0.19
184	-	-	0.41
212	-	0.69	-
264	-	-	0.94
309	-	-	1.48
322	1.74	2.04	-
361	-	-	2.34
438	2.65	2.86	-
471	-	-	3.36
492	3.12	3.39	-

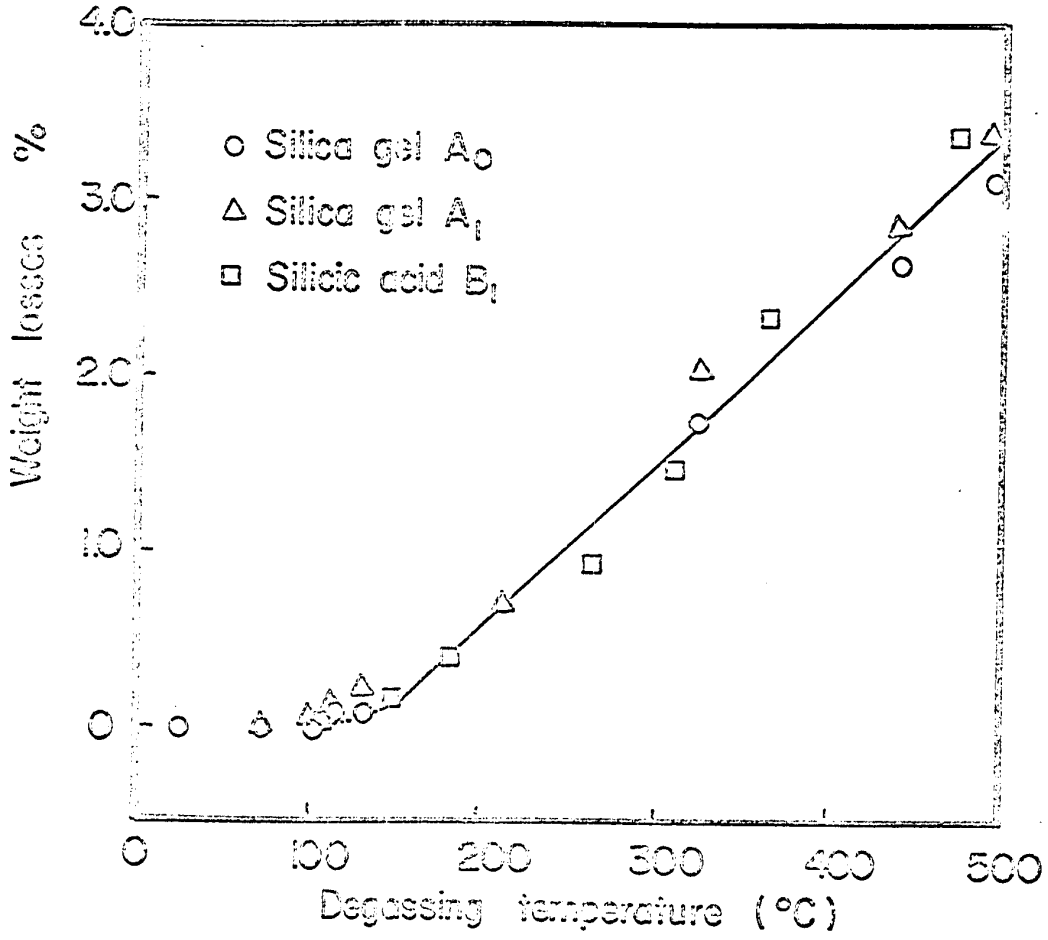


Fig. 8 *Effect of degassing temperature on weight losses of various adsorbents*

the degassing temperature, but show little variation from adsorbent to adsorbent. The magnitude of the weight losses (i.e. water losses) per 100° C in the interval 150 - 492° C is in good agreement with that calculated for a silica gel with a surface area (B.E.T.) of 200 - 250 m^2/g. in the interval 150 - 700° C (36), 0.94 and 0.82 g. water/100 g. adsorbent/100° C, respectively. Between 30 and about 150° C the weight losses did not exceed 0.2%.

3. Liquids

The list of pure liquids used in this study is given in Table 5 together with their grade, purity, and a comparison of measured and literature values of their refractive index at 25° C.

Table 5

PURE LIQUIDS

Compound **	Grade	Minimum* Purity (mole %)	Refractive Index at 25° C	
			Experimental	Lit. (45)
n-pentane	Pure	99	1.35478	1.35475
n-hexane	Research	99.9	1.37230	1.37226
n-heptane	Research	99.9	1.38525	1.38517
n-octane	Pure	99	1.39532	1.39505
n-decane	Pure	99	1.40975	1.40967
n-tridecane	Pure	99	1.42368	1.4235
Benzene	Spectrograde	99	1.49787	1.49790
Toluene	Research	99.9	1.49411	1.49413
Cyclohexane	Spectrograde	99	1.42333	1.42354
Methyl alcohol	Spectrograde	99	1.3267[a]	1.32669
Ethyl alcohol	Pure Absolute	99	1.35918	1.35914
Propanol-2	Spectrograde	99	1.37500	1.3749
Water	Redistilled		1.3325[a]	1.33250

a Determined with an Abbe-3L, Bausch and Lomb refractometer.

** The hydrocarbons were treated with activated silica gel to remove traces of water. The alcohols were used without further purification.

* supplier's data

a. Dehydration of hydrocarbons

Traces of water in pure hydrocarbons were removed under a dry-nitrogen atmosphere in a dry-box (46), by selective adsorption of water on activated silica gel.

About 3 grams of activated silica gel were added to a flask containing 50 cc. of a pure hydrocarbon, stirred vigorously for about 2 minutes, and then the liquid was decanted into another flask, the process being repeated three times. The hydrocarbon was transferred into a dried 50-cc. brass-storage vessel, which was then centrifuged for about 10 minutes, at 10,000 R.P.M., in order to separate the solid particles in suspension. Finally, the storage vessel was stored in a desiccator with activated silica gel.

The procedure used for drying a storage vessel is similar to that outlined for drying a mixing cell, on page 70.

b. Preparation of binary liquid mixtures

Under a nitrogen atmosphere in the dry box, a predetermined volume of the less volatile component was measured into a dried and preweighed weighing-vessel with the aid of a hypodermic syringe. The vessel with its contents was weighed before the addition of a calculated amount of the more volatile component. After this

the weight of the vessel with both components was recorded and the contents were mixed by shaking.

c. Analysis of mixtures

Mixtures were analyzed by measurement of their refractive indices in a Precision Refractometer, and values were determined to 0.00001. The accuracy of reading was, however, of the order of 0.00003. A precision temperature controller was used to keep the temperature of the instrument at 25.00 ± 0.02° C. in order to obtain the ultimate accuracy. The refractometer was located in a room where the temperature was controlled at 25 ± 0.5° C.

Prior to the determination of the composition of the mixture by means of the refractometer, calibration charts were obtained by determination of the refractive indices of mixtures of known composition. The composition of mixtures were determined analytically by weighing the samples to 0.1 mg. Tables in Appendix 2 show the composition-refractive indices of the calibrations.

d. Correlation of Refractive Index Data of Binary Systems

In order to obtain analytical expressions to represent the data, an empirical equation of the form proposed by Mrazek and

Van Ness (47) to represent heats of mixing data for alcohol-aromatic binary systems was used. In terms of refractive indices it is as follows

$$\frac{x_1 x_2}{n_D^E} = B + B' (x_1 - x_2) + \ldots \quad (37)$$

$$n_D^E = n_D - x_1 (n_D^o)_1 - x_2 (n_D^o)_2 \quad (38)$$

where x_1 and x_2 are the mole fractions of components 1 and 2, respectively;

B and B' are constants for the particular system considered, at 25° C; and

$(n_D^o)_1$ and $(n_D^o)_2$ are the refractive indices of pure components 1 and 2, respectively.

Figs. 9 and 10 show the plots of $x_1 x_2 / n_D^E$ versus x_1. It was found that only 2 constants were required for an adequate representation of the experimental data using Equation 37.

The series for the binary systems may be conveniently represented by

$$\frac{x_1 (1 - x_1)}{n_D^E} = B'' + B''' x_1 \quad (39)$$

where $B'' = B - B'$; and

$B''' = 2B'$

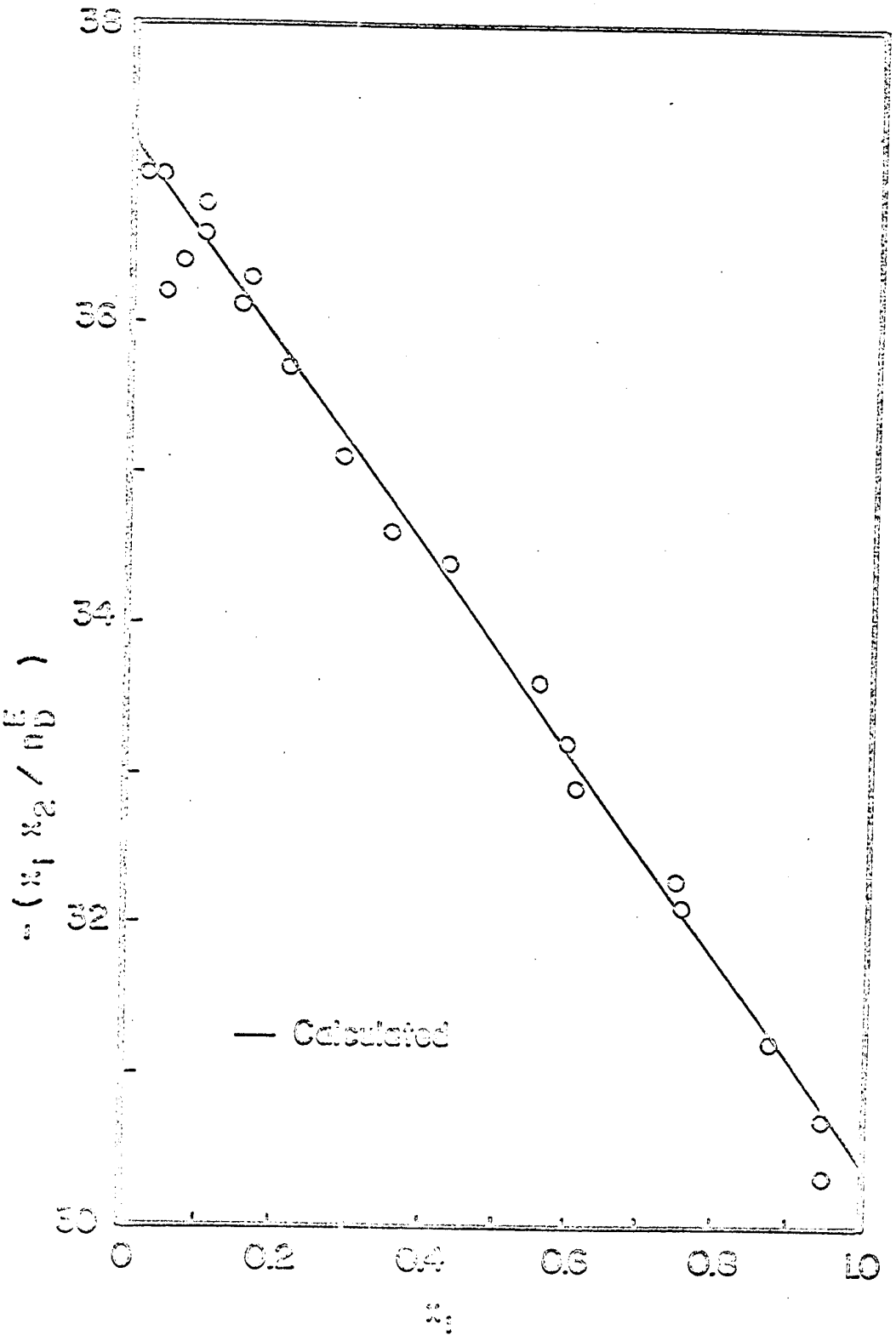


Fig. 9 Refractive Index correlation. System: Benzene - cyclohexane

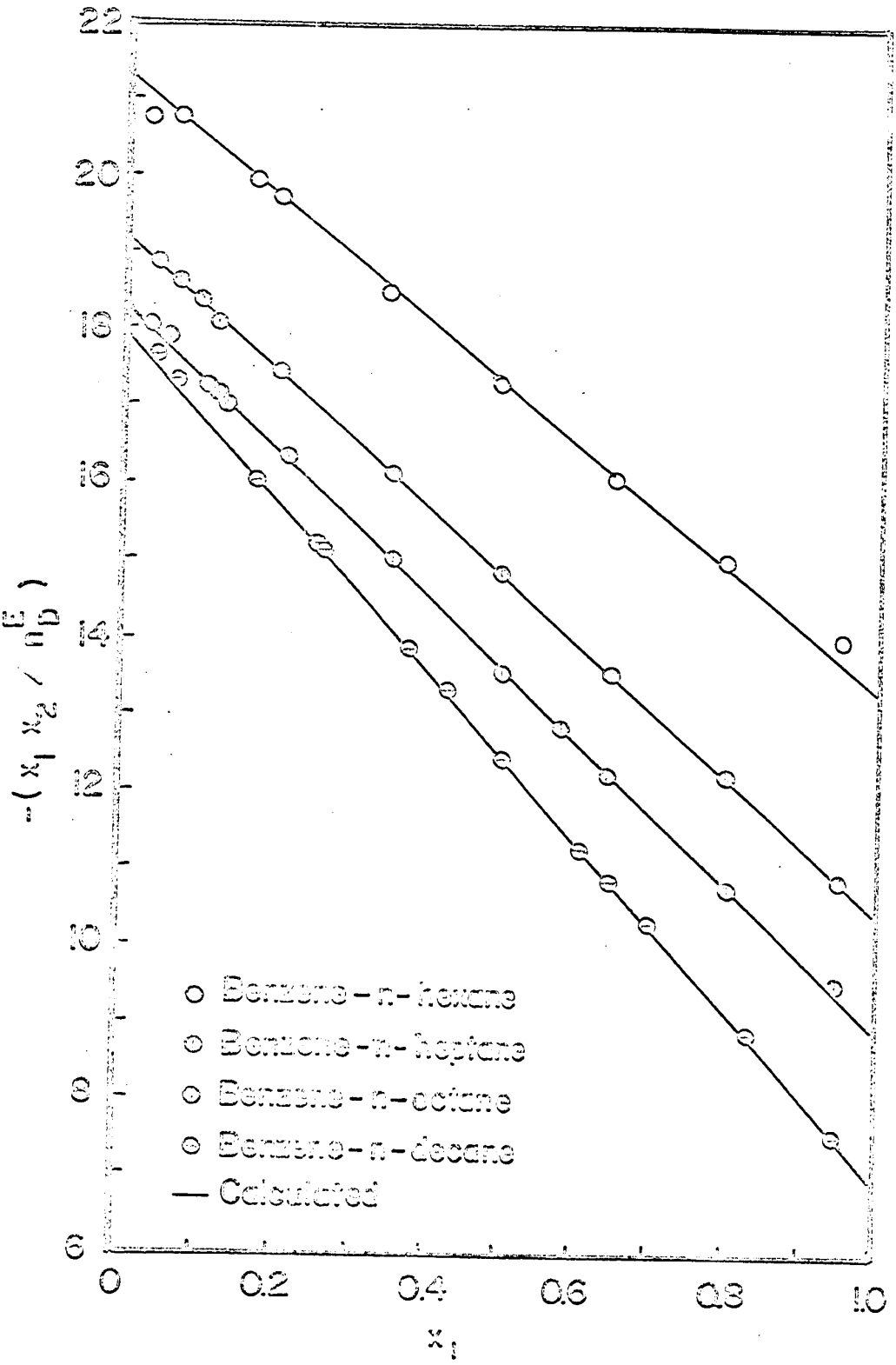


Fig. 10 Refractive Index correlation. Systems: Benzene - n-alkanes

Table 6 contains the values of the constants B'' and B''' determined by least square fittings of the systems studied.

An attempt was made to employ volume fraction ϕ_1 instead of mole fraction x_1, in Equation 39. Literature values indicate that the maximum deviation of the molecular volume of the mixture from the additivity rule is about 0.7% for the systems benzene-cyclohexane (48), benzene - normal hexane (15), and benzene - normal heptane (48). It is assumed in the calculation of ϕ_1 that the additivity rule holds in the case of binary mixtures of benzene with normal octane and benzene with normal decane.

It was found that for mixtures of benzene with cyclohexane, the following two constant equation may be used for representing the data

$$\frac{\phi_1 (1 - \phi_1)}{n_D - \phi_1 (n_D^\circ)_1 - (1 - \phi_1)(n_D^\circ)_2} = D + D_1 \phi_1 \qquad (40)$$

in which

$$\phi_1 = \frac{x_1 \tilde{V}_1}{x_1 \tilde{V}_1 + (1 - x_1) \tilde{V}_2} \qquad (41)$$

where $\tilde{V}_1$ and $\tilde{V}_2$ are the molar volumes of the pure components 1 and 2, respectively. The mixtures of benzene with normal alkanes require only one constant. The average difference between the calculated and experimental n_D values, using either Equation 39 or Equation 40, is of the same order of accuracy as the refractometer readings.

Table 6

CONSTANTS OF EQUATION 39 FOR THE REFRACTIVE INDICES OF MIXTURES OF BENZENE WITH n-ALKANES AND BENZENE WITH CYCLOHEXANE, AT 25°C.

Mixture (1)	(2)	-B''	B'''
Benzene-	n-Hexane	21.266	7.9218
Benzene-	n-Heptane	19.160	8.7143
Benzene	n-Octane	18.277	9.3491
Benzene	n-Decane	17.944	10.961
Benzene	n-Cyclohexane	37.200	6.8000

Table 7

CONSTANTS OF EQUATION 40 FOR THE REFRACTIVE INDICES OF MIXTURES OF BENZENE WITH n-ALKANES AND BENZENE WITH CYCLOHEXANE, AT 25°C.

Mixture (1)	(2)	-D	D_1
Benzene-	n-Hexane	96.4	-
Benzene-	n-Heptane	75.2	-
Benzene-	n-Octane	67.6	-
Benzene-	n-Decane	59.9	-
Benzene-	Cyclohexane	60.4	-11.8

B. ADSORPTION FROM BINARY LIQUID MIXTURES

The measurements of adsorption from binary liquid mixtures on solid adsorbents were carried out in the following way: a previously prepared mixture of known composition was added to the adsorbent, weighed into a 12-cc brass adsorption cell. The cell was sealed, weighed again to obtain the weight of the mixture, and allowed to equilibrate in a constant temperature bath, controlled within 0.005° C at about 25° C. Mixing of the contents was effected by shaking the cell vigorously for one minute every half-hour, and after four hours, it was centrifuged and the equilibrium mixture analyzed. Pertinent details of the experimental procedure for drying and loading the adsorption cell, and for analyzing the equilibrium mixture are as described in pp. 70 and 77.

The refractive index of the sample of unknown composition was determined at 25° C. The composition of the mixture was calculated from equation 39 by substituting the experimentally determined value of n_D and then solving the equation for the positive square root of x_1.

The apparent adsorption per gram of adsorbent $x_1^{(N)}$ was obtained from the relation

$$X_1^{(N)} = \frac{N^\circ (x_1^\circ - x_1^e)}{W} \qquad (4)$$

and plotted against the equilibrium concentration of benzene.

The number of millimoles N^a adsorbed per gram of adsorbent, and the separation factor $\alpha^{(N)}$ were determined according to Equation 21 from plots of $x_1^e (1 - x_1^e)/X_1^{(N)}$ against the equilibrium concentration of benzene x_1^e, assuming a perfect system.

The surface areas per gram of adsorbent, determined from liquid adsorption data $\leqslant_{s(L)}$, were calculated assuming a value of $\phi_1 = \phi_2 = 241 \times 10^3$ m^2/mole for the benzene-cyclohexane system (1). The same molar area was assumed for the benzene-n-alkanes system.

C. CALORIMETER APPARATUS

The calorimeters reviewed in Section IX have been used primarily for the determination of heat of immersion of adsorbents in pure liquids. A serious shortcoming in these designs is the relatively large contribution, of the heat of breaking the bulb containing the adsorbent, to the total heat evolved. Although this problem seems to have been solved by the introduction of a new design of glass bulb (3) with a negligible heat effect on breaking, there still remains the problem that would be created by the possible contamination of a binary liquid mixture prior to the determination. Obviously, the technique of continuous drying prior to the determination as used for the pure components (4) is not satisfactory because the concentration of the mixture would change on adsorption. Besides, another problem of practical importance is the large volume of liquid required in most calorimeters for a single determination. This varied from 133 cc. (2) to 800 cc. (42).

The calorimeter described in this section has several unique advantages for the determination of heats of immersion of adsorbents in liquid mixtures; in order of importance, these are:

(1) The contamination of the adsorbate with water vapor prior to the determination is avoided.

(2) The heat associated with the breaking of the foil separating the compartments of the mixing cell is negligible.

Other desirable features of the calorimeter are:

(1) The design of the stirring mechanism makes it possible to accomodate several calorimeter jackets in the thermostatic bath.

(2) The brass jackets, unlike pyrex glass jackets, are easy to load and unload.

In addition to these, there are other advantages which are shared by other calorimeters:

(1) Mass losses to the outside are avoided.

(2) Small temperature changes may be measured accurately.

(3) Only small volumes of liquid are required for a determination.

On the other hand, the heat of immersion determination in this calorimeter has no apparent disadvantage that is not shared by other calorimeters. Of these common disadvantages, only one seems to be significant, namely, the time required for the adequate preparation of the mixing cell and the adsorbates.

1. General description

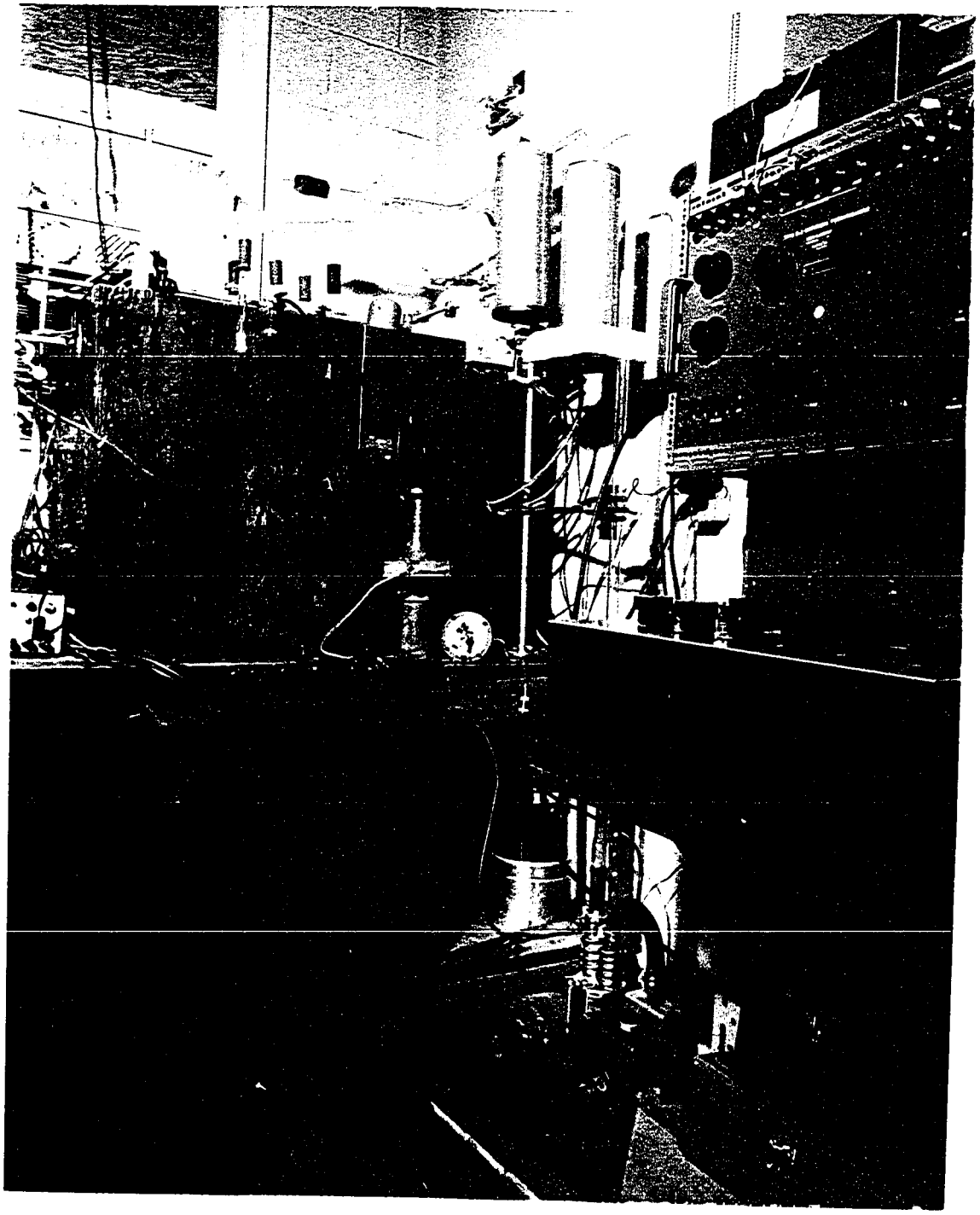
Before describing in detail each component of the calorimeter, a brief general description of the assembly, shown in Figs. 11 and 12, is given.

The calorimeter is similar in some respects to that used by Cheeseman and Whitaker (49) for the measurements of heats of mixing of binary liquid systems.

The apparatus consists essentially of a mixing cell in which the adsorbent and the adsorbate are isolated, from each other by a tin foil diaphragm, and from the surroundings by O-rings and plugs. A heater and a thermistor on the cell provide means of adding measured energy to the cell and contents, and of determining temperature changes, respectively. The mixing cell is placed in a brass jacket, and this in turn is submerged in a thermostatic bath controlled within 0.005° C., at about 25° C. The apparatus was located in a room where the temperature was controlled within 1° C at about 25° C.

An outlet tube on the jacket is provided for obtaining a high vacuum around the mixing cell. The electrical leads are brought out by means of a connector in the jacket.

The contents of the cell are brought into contact by the breaking of the diaphragm. The breaking of the diaphragm and the stirring of the cell are effected by a gold plated nail placed originally



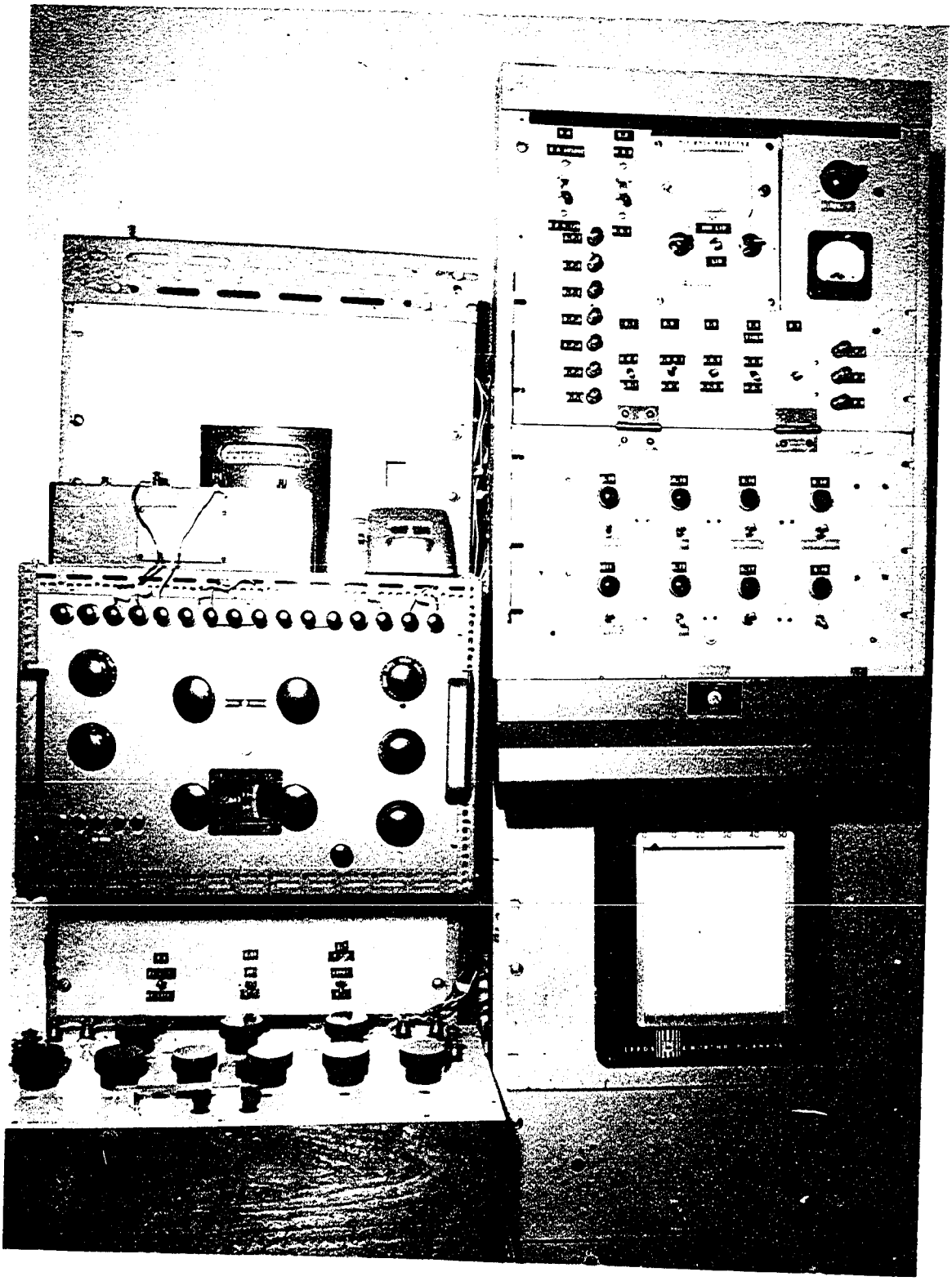


Fig. 12 Calorimeter assembly

in the larger compartment and which is made to operate under the influence of an external coil.

2. Construction details

a. Mixing Cell

A sketch of the cell is shown in Fig. 13.

The mixing cells were cylindrical brass vessels ranging from 8 to 15 ml. in total volume. Each cell had two compartments held together by a union; and isolated from each other by means of a 0.0015" tin foil diaphragm, placed between two 0.010" teflon gaskets. A filling opening was provided for each compartment and sealed by an O-ring and a brass plug. Several small compartments were made in order to vary the volume ratio in a cell.

The larger compartments of the mixing vessels were each provided with a thermistor temperature sensing element and with a heater. Thermistors (ranging in resistance from 550 ohms to 2200 ohms at 25°C) were cemented on to the external surface with Epoxy cement; and the heaters (ranging in resistance from 13 ohms to 21 ohms) were wound non-inductively from Manganin wire, on the external surface with Glyptal resin.

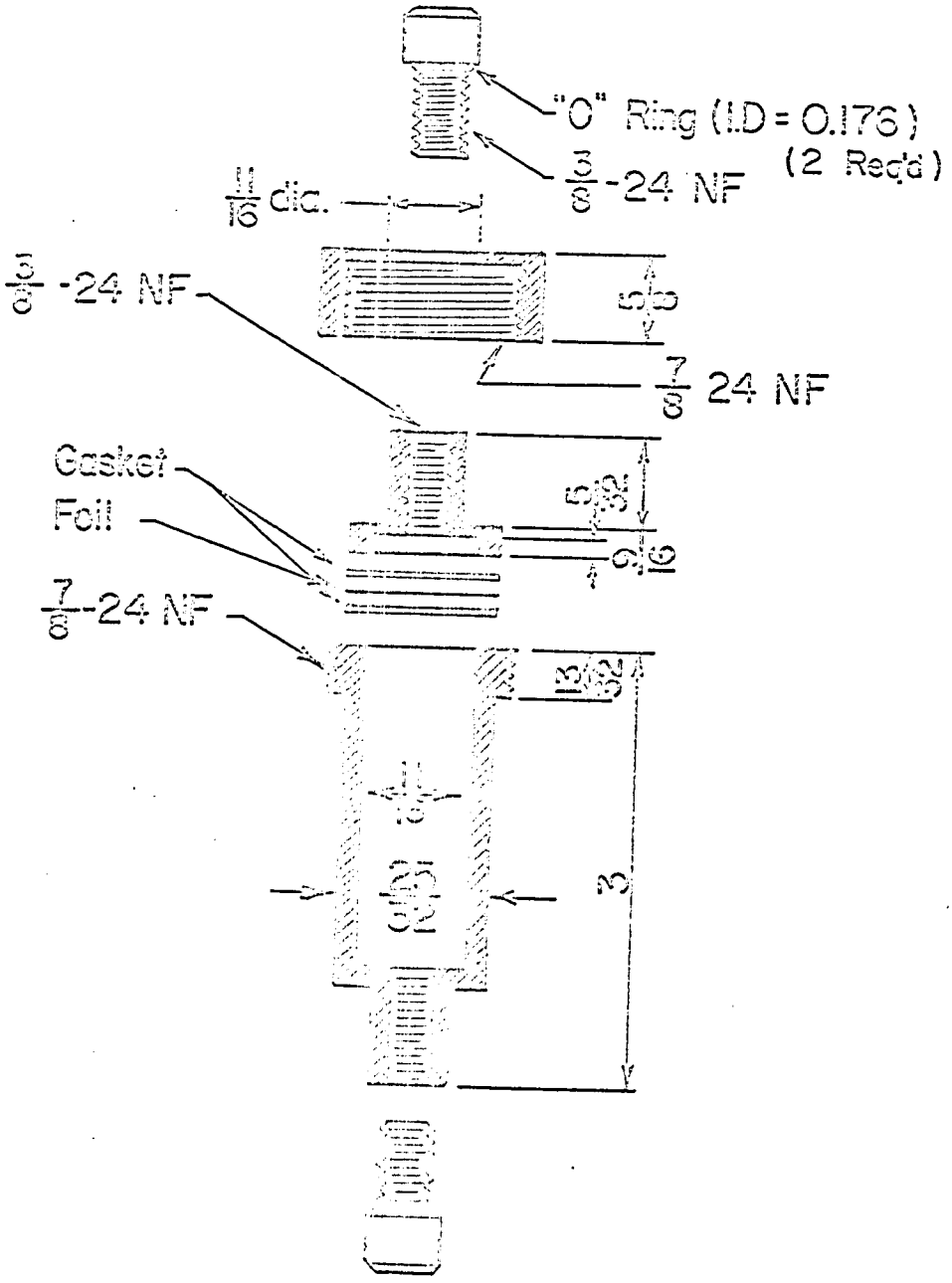


Fig. 13 Mixing cell

b. Jacket

A photograph of the calorimeter jacket is shown in Fig. 11. A sketch of the same jacket is shown in Fig. 14. It was constructed from 2 1/8" O.D. brass tube with a wall thickness of 1/8". The lower end of the tube was closed by a brass disk and the upper part of the tube was provided with a flange.

The lid of the jacket was provided with a flange. Two openings on the lid allowed connection of the jacket to the vacuum and to the electronic systems. The vacuum outlet was made of a 5/8" O.D. copper tube, about 4" long, soldered into an opening of the flange. A multiple point hermetic seal, containing 6 electrical leads was soldered into the other opening to allow electrical connections from the jacket to the outside. The electrical leads at the hermetic seal were electrically insulated with Glyptal resin, and isolated from the water bath by means of a 2 1/4" O.D. copper tube soldered concentric to the connector onto the lid.

The interior of the jacket was rendered air tight and water-proof by means of an O-ring, sitting on a rectangular groove made in the lower flange. Compression of the O-ring between upper and lower flanges was attained by applying a 10-pound torque on four sealing bolts.

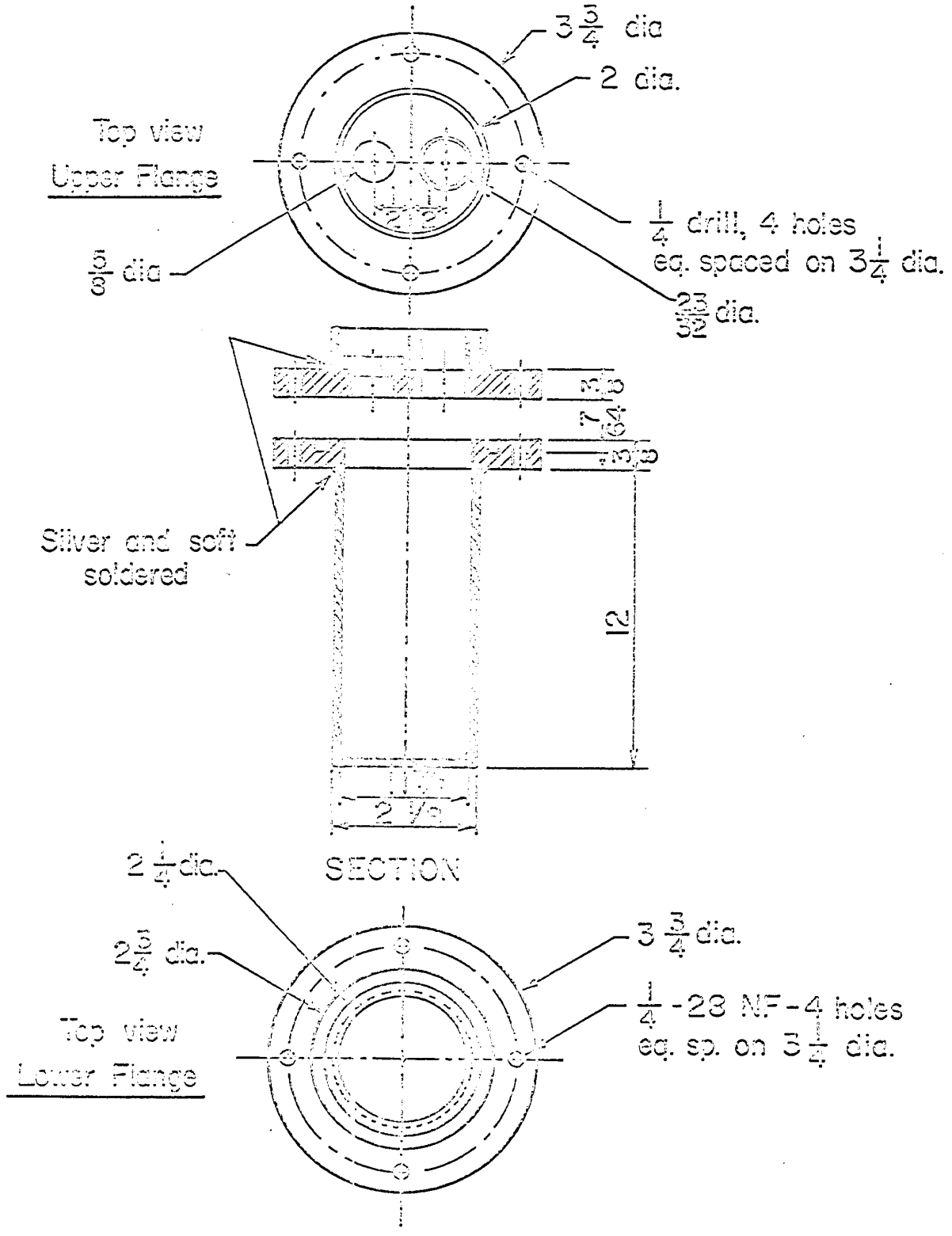


Fig. 14 Jacket

c. Coil

A sketch of the coil is presented in Fig. 15.

The coil was made of insulated copper wire No. 24B & S wound on a spool to give about 35 ohms. The spool was constructed of brass cylinder with plexiglass sides, and was waterproofed with Glyptal resin.

The coil was supported around the jacket by means of a brass ring bolted slightly onto the jacket, and was insulated from the supporting ring and from the jackets with styrofoam.

d. Water Bath

Fig. 11 shows the thermostatically controlled water bath.

It consisted of a 30" x 15" x 20" glass tank set in a wooden box with Styrofoam lagging between them. Temperature control was attained by a mercury glass regulator coupled with a "Transistor" Relay and was within 0.005°C. The temperature fluctuations in the bath were noted on a Beckman thermometer. Two stirrers provided efficient circulation throughout the bath to assure uniformity of temperature.

Heating was accomplished by means of two 120 volt, 750 watt immersion heaters. Cooling was effected by means of four cooling

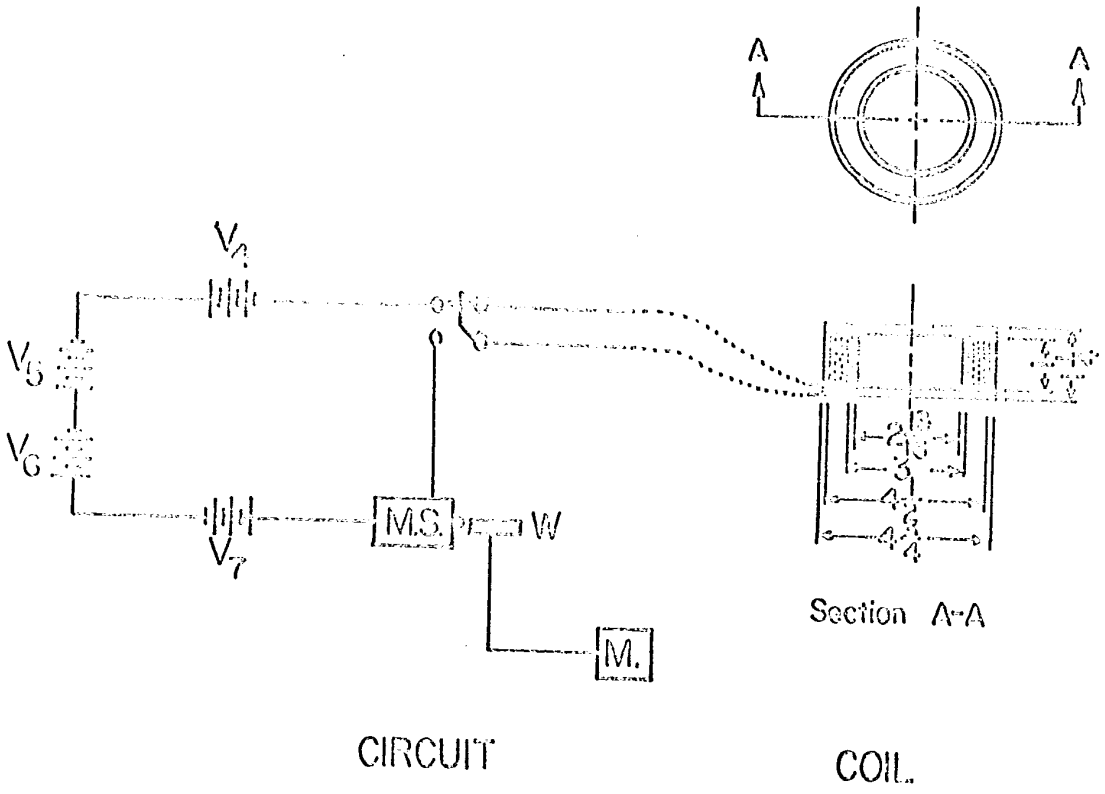


Fig. 15 Coil and its circuit

- 63 -

coils which were vertically mounted, two on either side of each stirrer, close to the corners of the tank.

The tank was also equipped with a brass supporting frame for the calorimeter jackets. It consisted of a 9" x 9" x 9" frame work on which were welded four 2 1/8" I.D. brass rings.

e. Vacuum system

A photograph of the calorimeter vacuum system is shown in Fig. 11.

Vacuum was attained by means of a high vacuum pump, mechanical and diffusion type, with a capacity of 600 litres per minute at 10^{-4} mm. of Hg. The Vacuum pump was connected to the pumping line through a metal to glass seal. The pumping line was provided with a Vacustat gauge, 2 traps cooled by liquid nitrogen, a four-outlet manifold and suitable connections. The traps were used to protect the system from mercury vapor and to condense vapors escaping during evacuation.

The calorimeter jackets were connected to the outlets of the manifold by means of rubber sleeves, 2.54 cm. O.D. and wall thickness of 0.82 cm.

f. Thermistor Circuit

The temperature measuring circuit is shown in Fig. 16.

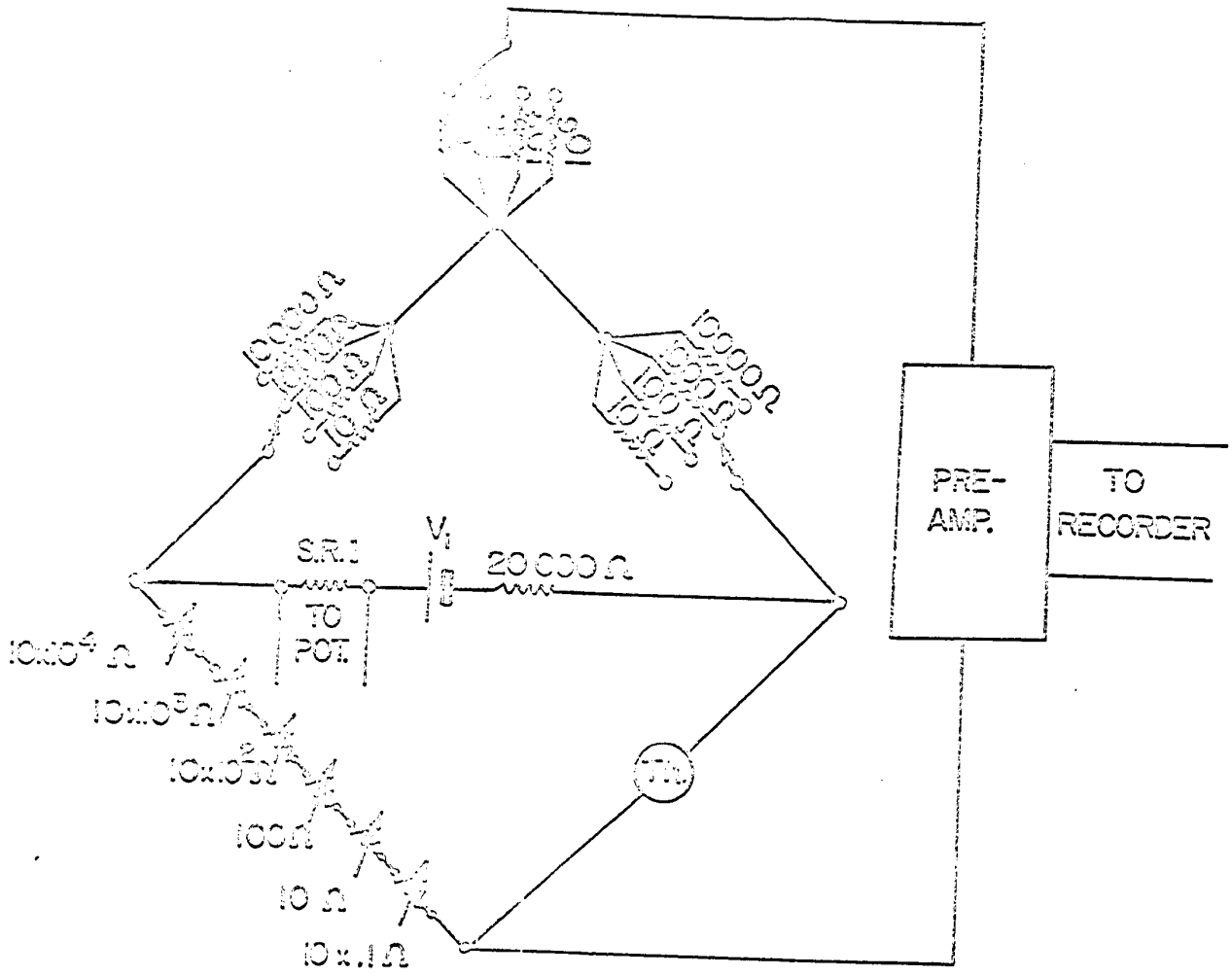


Fig. 16 Thermistor circuit

The temperature changes were measured with the aid of a Wheatstone bridge circuit, the thermistor (Th) being included in one of the arms of the bridge. A 2-volt, lead-acid (V_1) storage battery was used as the power supply for the bridge circuit. This arrangement included a resistance of 20,000 ohms connected in series with the power supply in order to keep the current flowing through the thermistor at about 30 μ amp., and thus prevent an undesirable dissipation of heat by the thermistor. A 40-ohm standard resistor SR1 in the circuit allowed the current flowing through the thermistor to be checked from time to time with a K-3 potentiometer.

When the resistance of the thermistor varied due to a change of temperature, the bridge equilibrium was disturbed. The output from the Wheatstone bridge was fed to the Electronic D-C Null-Detector shown in Fig. 12. The amplified D. C. voltage drove a 50 mv. recorder with a chart speed of one inch per minute. The sensitivity of the circuit is such that a change of 4 mv. corresponds to a change of temperature of about 0.001° C. The sensitivity of the system could be varied from about 0.2 to 4 mv. per 0.001° C. The heat effect was followed by the change of thermistor resistance with time, using the recorder as a null instrument.

g. Heater circuit

The circuit for measuring the electrical energy supplied to the calorimeter is shown in Fig. 17.

A 6-volt lead-acid storage battery (V_3) was used as the power supply for the heater circuit. A variable resistor (VR) allowed adjustment of the circuit potential. The current through the heater (R_H), of the order of 0.1 amperes, was calculated from the potential drop across a circuit with a standard resistor (SR 2). This potential drop was determined by measuring a portion of the potential from a volt box having a nominal ratio $R_1/(R_1 + R_2)$ of 1 to 10. The potential measurements were made with a K-3 potentiometer in conjunction with a high-sensitivity galvanometer. Provisions were made for measuring the resistance of the standard resistor on the Wheatstone bridge. The heater resistance which included 10 cm. of thermocouple wire No. 3c, was also measured on the Wheatstone bridge. The heating time was measured to $\pm$ 0.05 sec. by a Precision electric timer (T) operated from the power mains at a frequency of 60 cycles/sec. and synchronized with the calorimeter heater circuit.

During non-heating periods, the battery was discharged through a dummy resistor (D. R.) which had a resistance equivalent to that of the mixing cell heater plus leads. The working cell for the

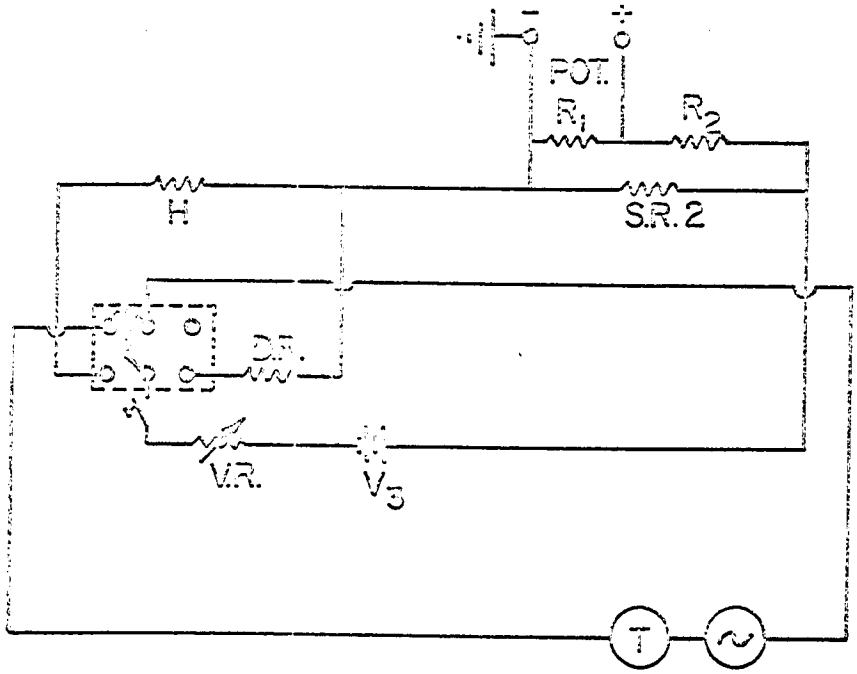


Fig. 17 Heater circuit

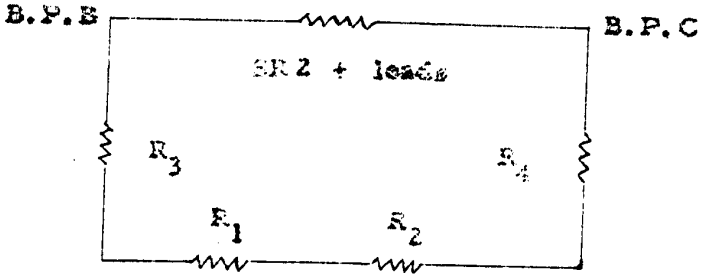
potentiometer was a 2-volt, lead-acid storage battery. The standard cell was certified by the Division of Applied Physics of the National Research Council of Canada.

Connections made in the circuit, using binding posts BP, allowed the resistances of the standard resistor (SR 2), the leads, the switches, the volt box, and the equivalent of all these to be measured on the Wheatstone bridge. The equivalent resistance of this circuit, designated hereafter as standard resistor $(SR\,2)_c$, is given as follows

$$\frac{1}{(SR\,2)_c} = \frac{1}{(R_1 + R_2) + (R_3 + R_4)} + \frac{1}{SR\,2 + \text{leads}} \qquad (42)$$

$$\frac{1}{(SR\,2)_c} = \frac{1}{(300.00 + 2701.0) + 0.220} + \frac{1}{40.021}$$

$$(SR\,2)_c = 39.492 \text{ ohms}$$



where SR 2 + leads to binding posts B and C = 40.021 ohms;

$(R_1 + R_2)$ is the total resistance of the volt-box = (300.00 + 2701.0) ohms; and

$(R_3 + R_4)$ is the resistance of the leads and switches = 0.220 ohms

h. Coil circuit

The connections to the coil are schematically outlined in Fig. 15.

Four, twelve-volt, lead-acid storage batteries connected in series were used as the power supply for the coil. A motor with cam-actuated shaft, was used to operate a microswitch, which in turn opened and closed the circuit about 30 times per minute.

3. Preparation of the mixing cell and testing for leaks

The following procedure was adopted for preparing a calorimeter vessel and testing for leaks.

I) The mixing cell was carefully cleaned, assembled, and degassed for 10 hours at room temperature to 10^{-2} mm. Hg.

II) It was tested for leaks. This was accomplished by first filling the smaller compartment with petroleum ether and then sealing it, while the larger compartment was left open. The cell was then weighed, placed in a vacuum desiccator for 15 minutes at 10^{-1} mm. of Hg., and weighed again.

When the loss in weight on evacuating was greater than 3 or 4 mg., the evacuating process was repeated for 15 minutes. A further loss in weight of 3 to 4 mg. was indicative of a leaking cell. The cell was then re-assembled with new teflon gaskets,

new diaphragm and new O-rings, and the procedure was repeated. The larger compartment was tested for leaks by using a similar procedure, except that the petroleum ether was weighed in the larger compartment, leaving the smaller compartment open.

III) After testing for leaks, the mixing cell was dried, using the assembly shown on Figs. 2 and 3. This assembly consisted of a vacuum pump (I), a Vacustat gauge (J), two traps cooled by liquid nitrogen (K), a metal desiccator (L) and suitable connections. The cooled traps serve two purposes: they condense water and hydrocarbon vapors resulting from the drying of the cell, and protect the vacuum pump and the metal desiccator from the mercury vapor in the Vacustat gauge.

The cell was placed in the metal desiccator and this was evacuated to better than 10^{-3} mm. of Hg. for about 3 hours. At the end of this period, the cell was removed from the desiccator and the following weights were noted: the upper plug with O-ring; the lower plug with O-ring; the nail, and the rest. It was found that the components of the cell did not increase in weight in the time required for weighing.

IV) Next, the cell was placed again in the metal desiccator and evacuated at 10^{-3} mm. of Hg. for about 5 hours.

V) Subsequently, the ampoule containing the silica adsorbent and the containers holding the dehydrated hydrocarbon or the binary liquid mixture, to be used in the heat of immersion experiment, were placed in the dry box.

VI) Meanwhile, the dry box was conditioned by placing activated silica gel inside and allowing a stream of dry nitrogen to flow into and out of it. The stream of dry nitrogen was passed through towers packed with activated silica gel prior to and after its admission to the dry box.

VII) Following the evacuation, the brass desiccator was removed from the vacuum system, with the mixing cell in it under vacuum. This was accomplished by closing the stopcock in the line to the upper flange of the desiccator, and then sliding down the rubber sleeve which connected the desiccator to the vacuum system. Then, the dry box was opened and the desiccator placed in it. The dry box was closed, and nitrogen was allowed to flow for another 45 minutes. After this, the nitrogen stream was replaced by one of helium.

4. Loading the calorimeter

This operation comprised essentially three phases: the first one was the weighing of the adsorbate and the adsorbent in the

mixing cell, the second was the positioning of the cell in the jacket, and the third was the mounting of the calorimeter jacket with its contents in the water bath. The procedure was as follows:

The tip of the glass ampoule containing the adsorbent was cut off and part of the sample was quickly transferred into the smaller compartment of the cell, under a helium atmosphere in the dry box. The cell was then closed, withdrawn from the dry-box and weighed to 0.1 mg. Under similar conditions, a pure liquid or a binary liquid mixture was weighed into the larger compartment, which contained a gold-plated nail. Excess liquid was partially blown off with a stream of dry-nitrogen impinging on the sealing O-ring of the larger compartment, and the remainder was completely removed at a pressure of 10^{-2} mm. of Hg. The cell was re-weighed and this reading was the measure of the weight of the cell and its contents.

Afterwards, the cell was positioned in a brass jacket, with the smaller compartment facing downwards. This positioning was necessary in order to ensure the complete immersion of the sample of adsorbent in the liquid medium. A cell-holder made of 1 1/2" I.D. brass pipe, about 4 1/2" long, was used to support the mixing cell inside the jacket. Rings of Styrofoam and Plexi-glass were used to keep the cell-holder from touching either the cell or the calorimeter

jacket. Short circuiting was prevented by raising and rotating the cell-holder from its initial position until all leads were straight and clear from each other.

The jacket was closed, submerged in the constant temperature bath, and evacuated to a pressure of less than 10^{-3} mm. of Hg. The water bath was controlled to $\pm$ 0.005° C.

5. Heat effects

a. Immersion of a solid in a liquid medium

The experimental procedure used for measuring the heat of immersion was as follows:

The batteries in the thermistor and heater circuits were allowed to discharge for about 16 hours to ensure stable conditions at the beginning of the run. The batteries in the heater circuit were discharged through a dummy resistance until required for calibration.

The cell and its contents were allowed to reach thermal equilibrium with the bath. Due to the high vacuum inside the jacket, at least one night was required.

Before starting an experiment, the resistance of the thermistor was read at 30-minute intervals until either a negligible drift or no drift was obtained. Then the gold-plated nail, initially

placed in the larger compartment, was energized by the external solenoid at 48 volts, with about 30 on-off intervals per minute, to rupture the diaphragm and to stir the calorimeter vessel contents during the run. The change of thermistor resistance with time was recorded.

The sensitivity of the system could be varied from run to run and during the run, if necessary, from about 2 to 40 mv. per 0.01°C., on the recorder chart. During the electrical calibration, the variable resistances were used to rebalance the bridge continually using the recorder as a null instrument. This procedure allowed an expansion of the recorder scale and, in addition, minimized errors resulting from unbalancing (59).

A typical plot of thermistor resistance versus time is reproduced in Fig. 18, for the immersion of a sample of silica gel A_3 in a mixture of benzene and cyclohexane, mole fraction = x_1^o = 0.2478.

The tin foil diaphragm was broken at B. The evolution of heat, period BC, was completed in about 3 minutes. After the resistance of the thermistor had indicated a regular increase in its value, CD, the calorimeter was allowed, without stirring, to reach thermal equilibrium with the bath. The coil was then energized and the change of thermistor resistance with time due to the stirring effect

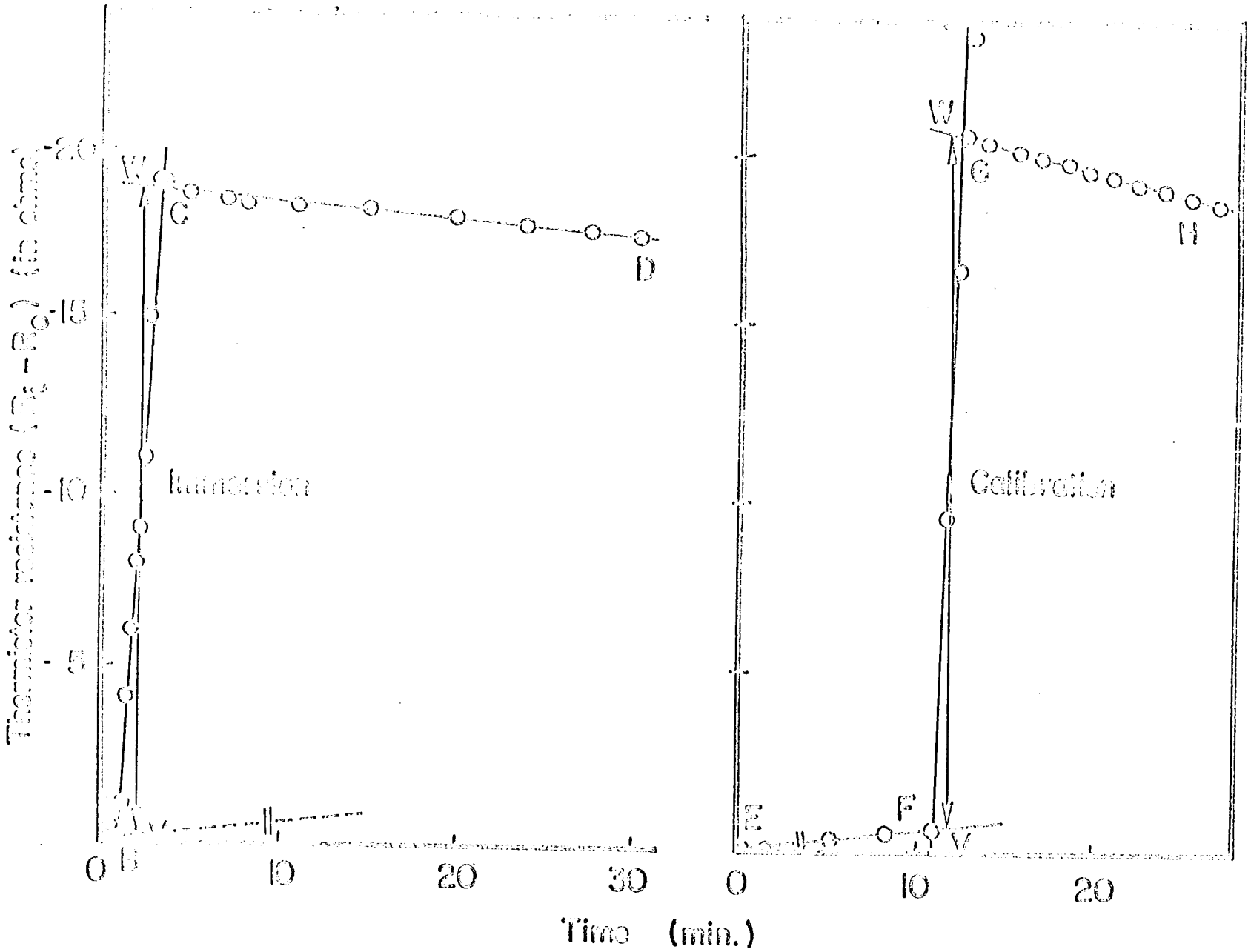


Fig. 18 Variation of thermistor resistance with time in a heat of immersion experiment

- 76 -

(minus any heat loss to the bath) was followed for about 10 minutes, shown as period EF. In general, this effect was found to be about 0.0005°C. per minute. Electrical energy was then supplied, FG, to duplicate the change of resistance that occurred during the immersion period.

During the heating period, the potential drop E across the standard resistor $(SR\ 2)_c$ was measured several times. After the heater was turned off, the mixing cell was allowed to come to a steady-state and the final rating period, GH, was established. The final rating period lasted about 15 minutes. The accumulated heating time within 0.05 sec. was read directly from the electric timer at the end of each calibration.

Next, the cell was removed from the bath and weighed to check for losses. Then, it was centrifuged at about 10,000 R.P.M., for about five minutes to remove the solids in suspension. It was found that the temperature rise on centrifuging, indicated by the thermistor resistance, was of the order of 1°C. Finally, the cell was placed again in the water bath for one hour in order to regain thermal equilibrium, and the equilibrium mixture was then analyzed with the refractometer.

The graphical method indicated in Fig. 18 was used to determine the quantity of heat Q_I released on immersion. The corrected temperature rise was obtained by the extrapolation of the intial and the final rating periods to the time when the resistance of the thermistor is equal to the average of the values, at the beginning and at the end of the immersion period (51). The vertical distance VW was selected as the quantity corresponding to the corrected temperature rise. The temperature rise for the majority of the experiments was of the order of 0.2 to 0.4° C. The pertinent data and complete set of calculations for this run are presented in Appendix 7.

The heat Q_I released on immersion of W grams of a solid adsorbent in N^o moles of a liquid of composition x_1^o and equilibrium composition x_1^e was calculated from the equation

$$Q_I = Q_c \frac{\Delta R_I}{\Delta R_c} \qquad (43)$$

where Q_c is the amount of electrical energy supplied to the calorimeter, in cal. ;

ΔR_I is the corrected change of thermistor resistance at the time of immersion, in ohms; and

ΔR_C is the corrected change in thermistor resistance during the electrical calibration, in ohms.

The amount of electrical energy supplied to the calorimeter, in calories, was found from Joule's equation

$$Q_c = \frac{I^2 R_H t}{J} \qquad (44)$$

where I is the current flowing through the heater of resistance R_H, in amperes;

t is the heating time, in sec.; and

J is the electrical equivalent of heat, (4.18 joules/cal.)

The heat of immersion, in cal./g. of adsorbent, is

$$H_I = \frac{Q_I}{W} \qquad (45)$$

b. Mixing of liquids

The procedure for loading the calorimeter, bringing about mixing, performing the electrical calibration of the system and calculating the total change of resistance of the thermistor on mixing, were essentially the same as that for the heats of immersion experiments. However, it should be mentioned that:

i) the alcohols and hydrocarbons were used without purification.

ii) the calorimeters were loaded under atmospheric conditions.

iii) whenever the mixing of liquids caused a temperature drop in the calorimeter, heat was supplied to the

calorimeter heater after a regular decrease of the thermistor resistance was indicated and until the thermistor resistance approached its original value.

The heat of mixing two pure liquids, ΔH^M, expressed in terms of calories per mole of mixture is given by the expression

$$\Delta H^M = \frac{Q^M}{N_1 + N_2} \tag{46}$$

where Q^M is the heat evolved or absorbed on mixing, in cal.;

N_1 is the number of moles of liquid 1; and

N_2 is the number of moles of liquid 2

When N° moles of a binary liquid mixture are mixed with one of the pure components, the heat of mixing per mole of the resulting binary mixture may be calculated by the equation

$$\Delta H^M = \frac{Q^M + (\Delta H^M)^\circ \times N^\circ}{N^\circ} \tag{47}$$

where $(\Delta H^M)^\circ$ is the heat of mixing of the binary mixture; and

N° is the number of moles of the resulting binary mixture.

D. CALORIMETER PERFORMANCE AND PRECISION: HEATS OF MIXING OF ALCOHOLS WITH WATER

Since much of this study was concerned with the experimental characteristics of the calorimeter, the first results obtained were measures of the precision and reproducibility of the results.

An indication of the reliability of the calorimeter was obtained, by comparing results on heats of mixing measurements of alcohols with water at 25° C., with results of previous investigators.

The heats of mixing values obtained for the following systems:

Methanol - water

Ethanol - water

Propanol-2- water

are given in Appendix 3. The data are compared with values available in the literature and presented graphically in Figs. 19-22. The results of these measurements have been presented and discussed elsewhere (52).

Vapor space in the calorimeter resulting from the contraction of volume during the mixing process was small, and maximum errors resulting from possible evaporation were estimated as follows:

Methanol	-	water 0.24%
Ethanol	-	water 0.66%
Propanol - 2	-	water 1.4 %

Errors due to heat exchange with the surroundings and to other measurements amounted to 1.1%.

Methanol-water: Heats of mixing of methanol and water have been previously reported in the literature. Bose (53) made his measurements at 0, 19.69 and 42.37° C; Ocon and Taboada (54), at 16.0, 35.4 and 53.5° C; and Katayama (55) at 5, 20, 35 and 50° C. Graphically interpolated values from these sets at 25° C are plotted in Figure 19. Recently, Benjamin and Benson (56) reported their measurements at 25° C which are also plotted in Fig. 19. The values obtained in this investigation are, in general, somewhat smaller than those of Benjamin and Benson but higher than those of Katayama.

Fig. 20 shows that there is good agreement between the experimental values obtained in this investigation and those recommended for this system at 25° C by th N. B. S. (57). The average deviation is of 1.4%.

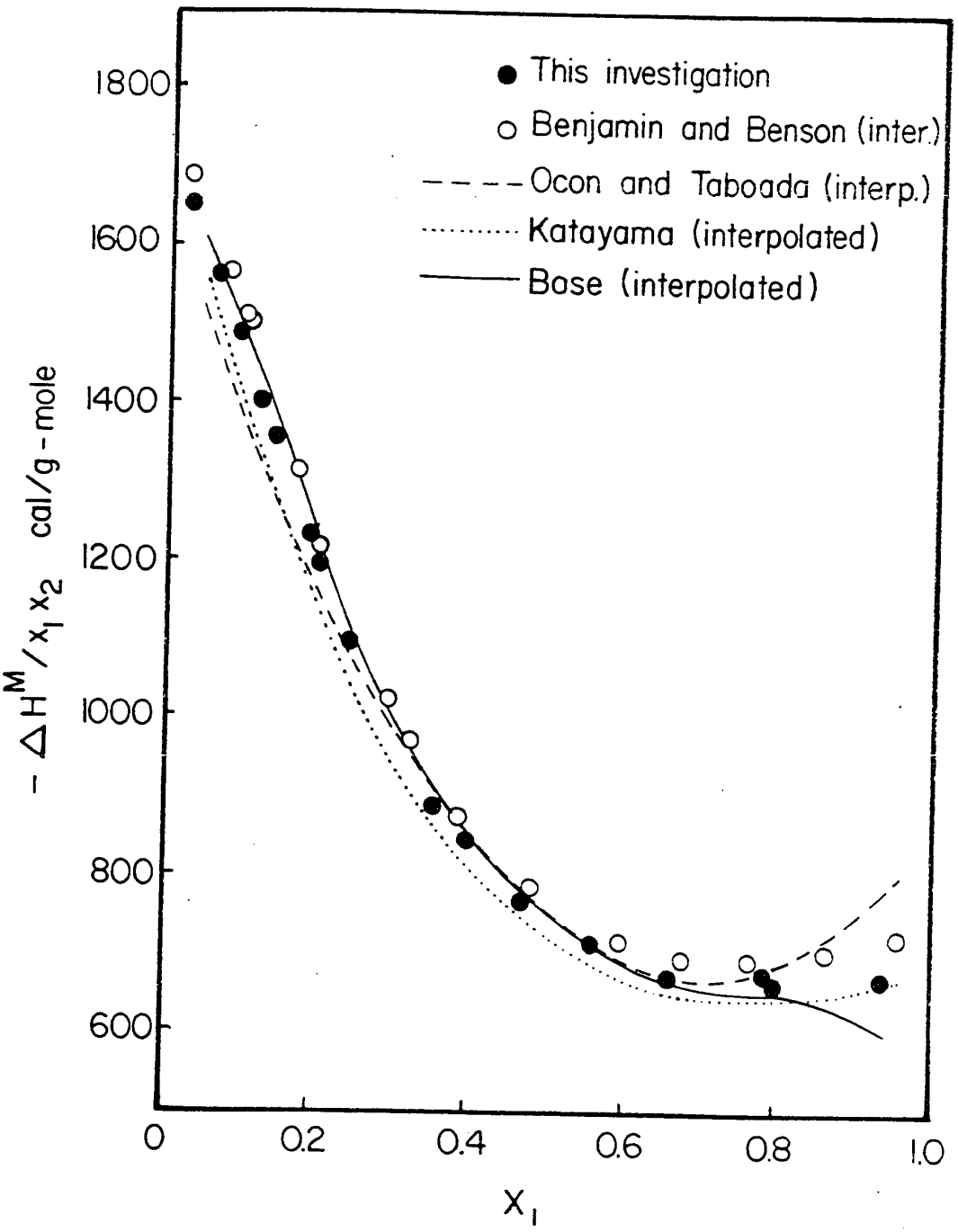


Fig. 19 Heats of mixing. System: Methyl alcohol - water at 25°C

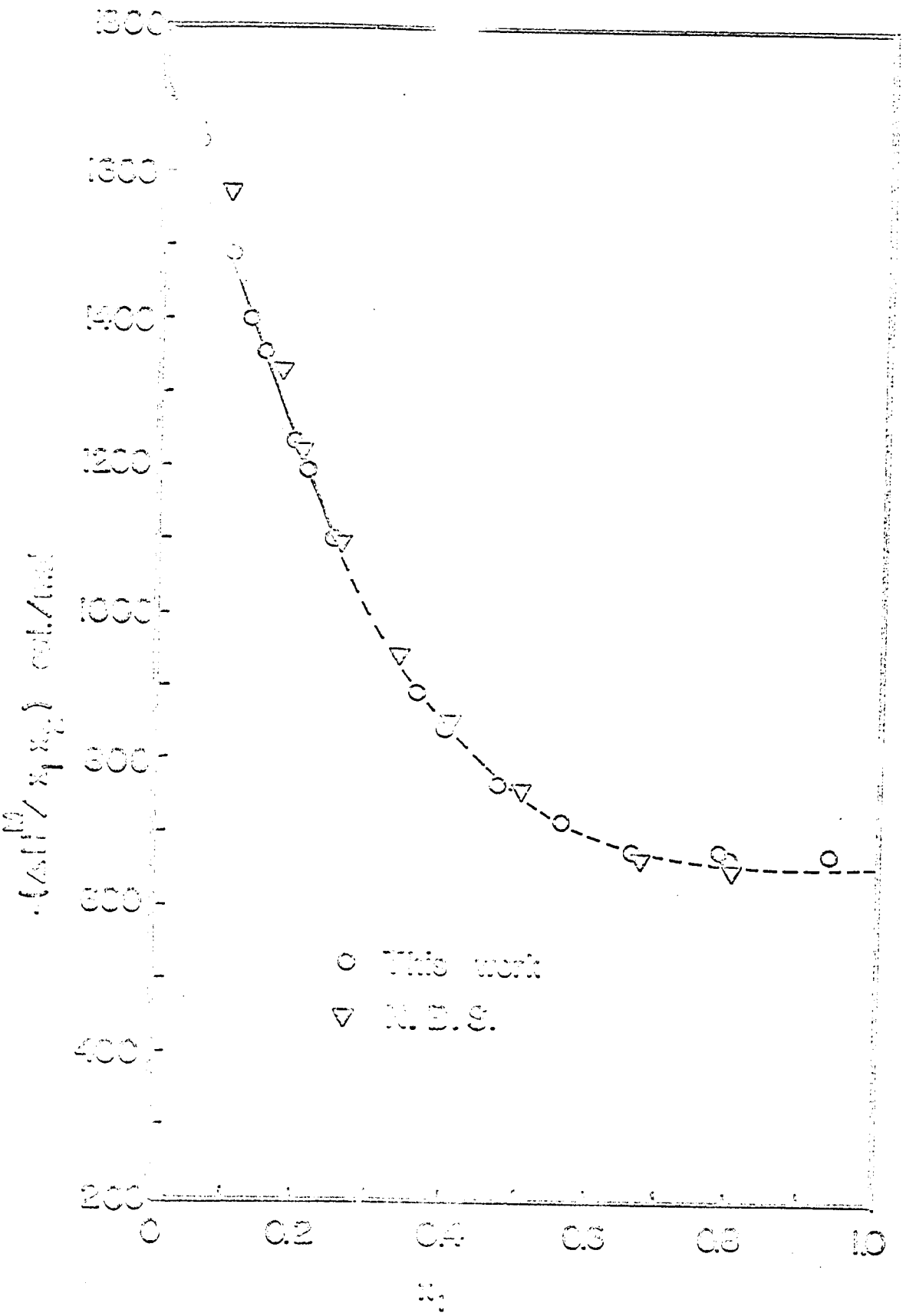


Fig. 20 Heats of mixing. System: Methyl alcohol - water at 25°C.

Ethanol-water: Bose (53) measured the heats of mixing of ethanol and water at 0, 17.33° and 42.05°C., and Bosjnakovic and Grumbt (58) reported values from 0 to 100°C at 10-degree intervals. Graphically interpolated values at 25°C from these two sets are compared with the values obtained in this investigation in Figure 21. At low mole fraction of alcohol, the values obtained in this study agree well with those of Bose, but at high mole fractions of alcohol, the values obtained in this investigation agree well with those of Bosjnakovic and Grumbt.

Propanol-2-water: Katayama (55) measured the heats of mixing of propanol-2 and water at 20°C and calculated heats of mixing values from 0 to 80°C at 10-degree intervals from the experimental heat capacity values for the system. Graphically interpolated values at 25°C are plotted in Fig. 22. Dimmling and Lange (59) determined the integral heats of dilution for the system at 25°C. These values were used to evaluate the heats of mixing values which are also plotted in Fig. 22. The values obtained in this study agree well with the interpolated values of Katayama.

The heats of mixing values for methanol and water can be represented by a third-order 4 constants Margules equation

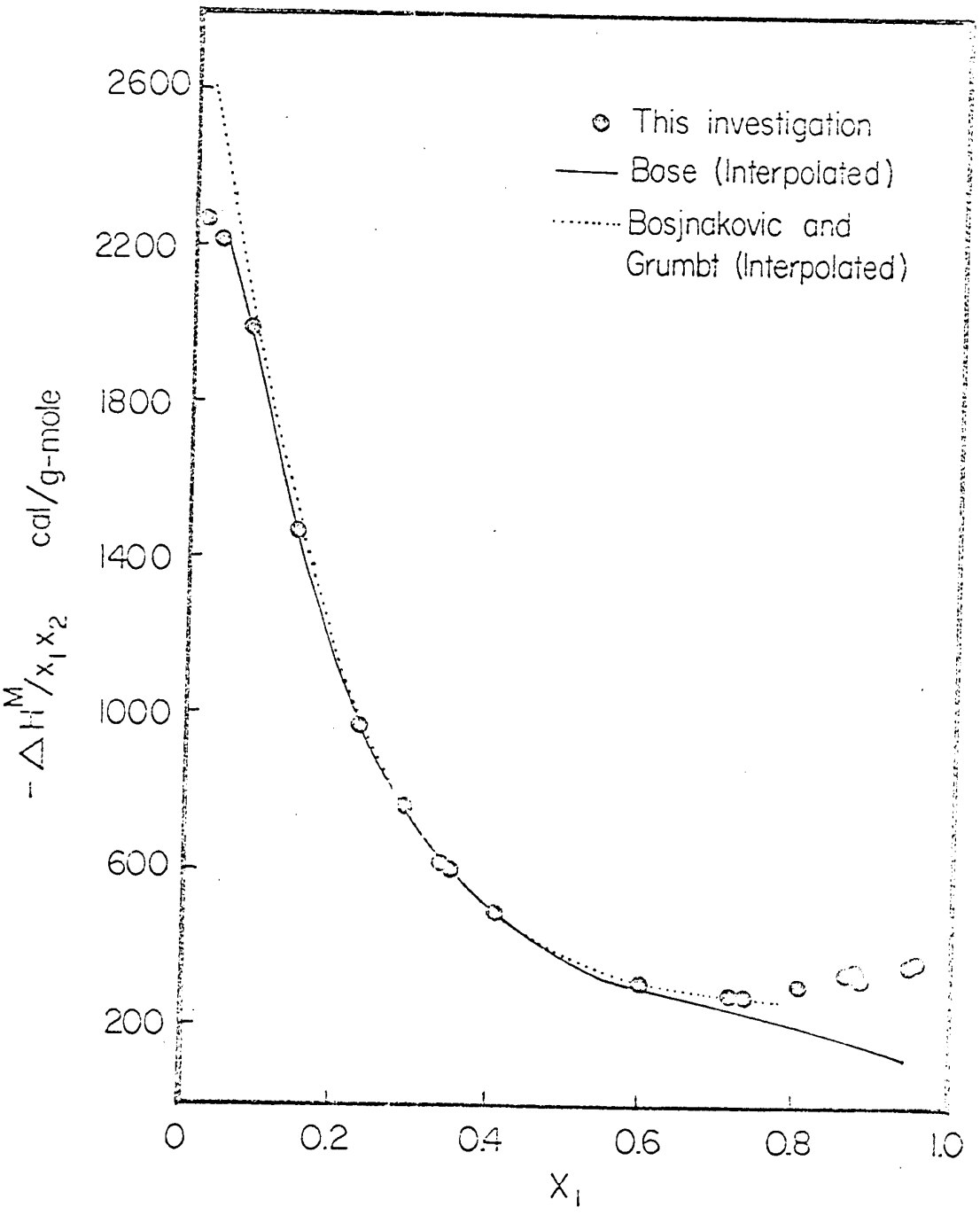


Fig. 21 Heats of mixing. System: Ethyl alcohol - water at 25° C.

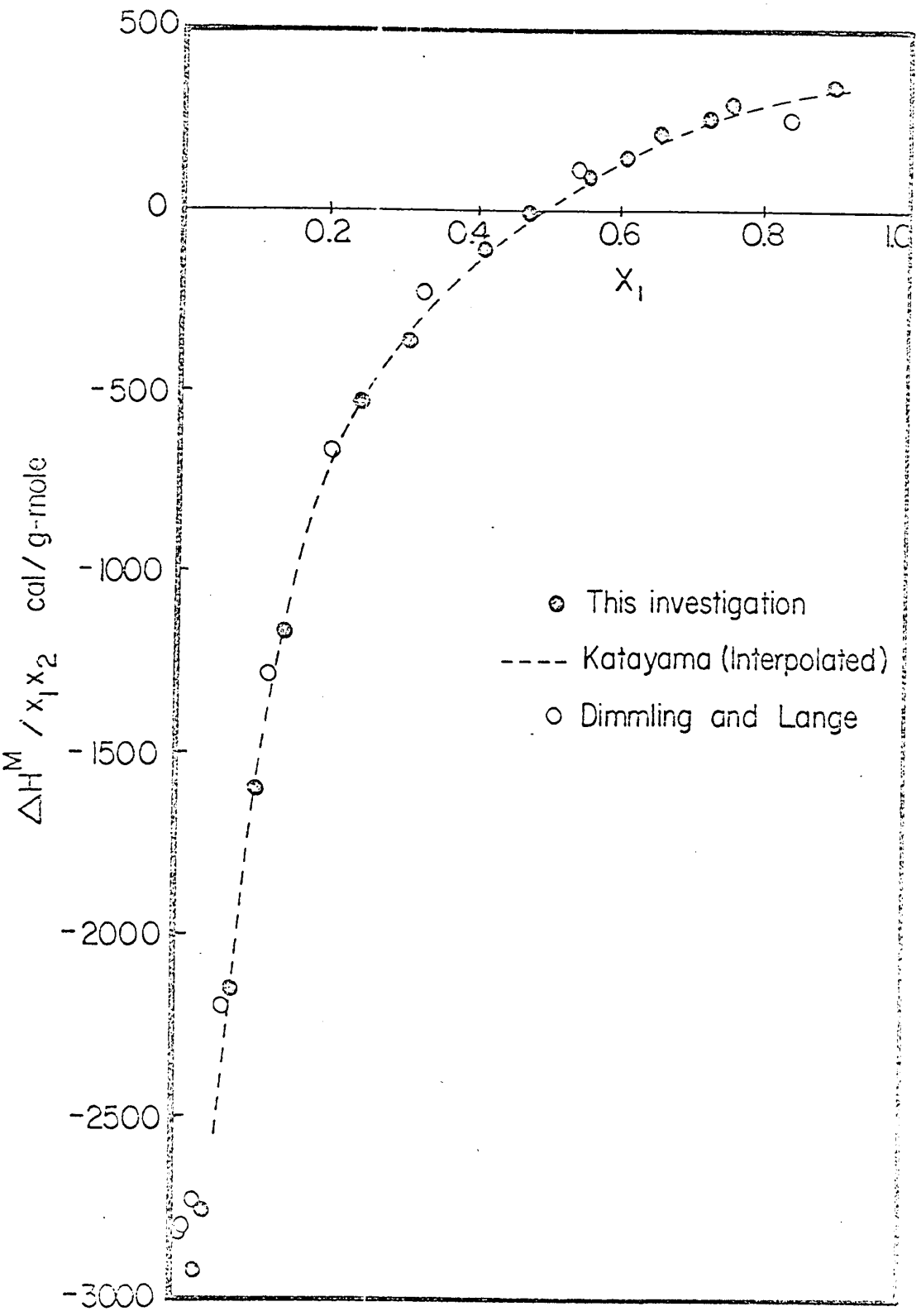


Fig. 22 Heats of mixing. System: Propyl alcohol - 2 - water at 25°C.

$$\frac{\Delta H^{M}}{x_1 x_2} = A + B\,(1 - 2x_1) + C\,(1 - 2x_1)^2 + D\,(1 - 2x_1)^3 \qquad (48$$

with values of -750.9, -401.3, -495.3, and -142.5 cal./mole for the constants A, B, C and D respectively. The heats of mixing data for ethanol and water and for propanol-2 and water cannot be represented as well by the Margules equation with the same number of constants.

The partial molal enthalpies of water in methanol, ethanol and propanol 2 at infinite dilution of water increase with the molecular weight of the alcohol and are -680, -400 and + 400 cal./mole, respectively. The partial molal enthalpies of alcohols in water at infinite dilution of alcohol decrease with the molecular weight of alcohols and are -1700, -2300 and -3200 cal./mole for methanol, ethanol and propanol-2, respectively. Recently, Aveyard and Lawrence (60) have reported values of -1750 and -2390 cal./mole for the partial molal enthalpies of methanol and ethanol in water at infinite dilution of alcohol, respectively.

XI RESULTS

The results are presented and discussed separately in two sections: A) The equilibrium adsorption; and B) The heats of immersion of adsorbents in pure liquids and in binary liquid mixtures.

An error analysis of the data is given in each section, immediately after the presentation of the results.

A. EQUILIBRIUM ADSORPTION DETERMINATIONS

1. Presentation of results

The results of the equilibrium adsorption determinations of binary mixtures on silica gel A_o and silicic acid B_1 are given in Appendix 4.

The temperature of 140° C was chosen for degassing since the adsorbents showed very slight decrease in weight below 150° C, suggesting that only physically adsorbed water is removed. This view finds support in findings, through measurements of water adsorption (61) and heats of immersion (35), of a lack of structural changes of some silicas between 20 and about 150° C.

The data were correlated according to Equation 21. Figs. 23-25 show the values of $x_1^e x_2^e / X_1^{(N)}$ against x_1^e for the various systems studied. The plots are all linear. The values of the constants in Equation 21 were determined by the method of least squares and are shown in Table 8. The average deviation between the experimental data and the calculated values of $x_1^e (1 - x_1^e)/X_1^{(N)}$ are given in column 3 of Table 8. Values of the apparent adsorption $X_1^{(N)}$, calculated from these equations at a number of mole fractions, were used to construct the curves in Fig. 26.

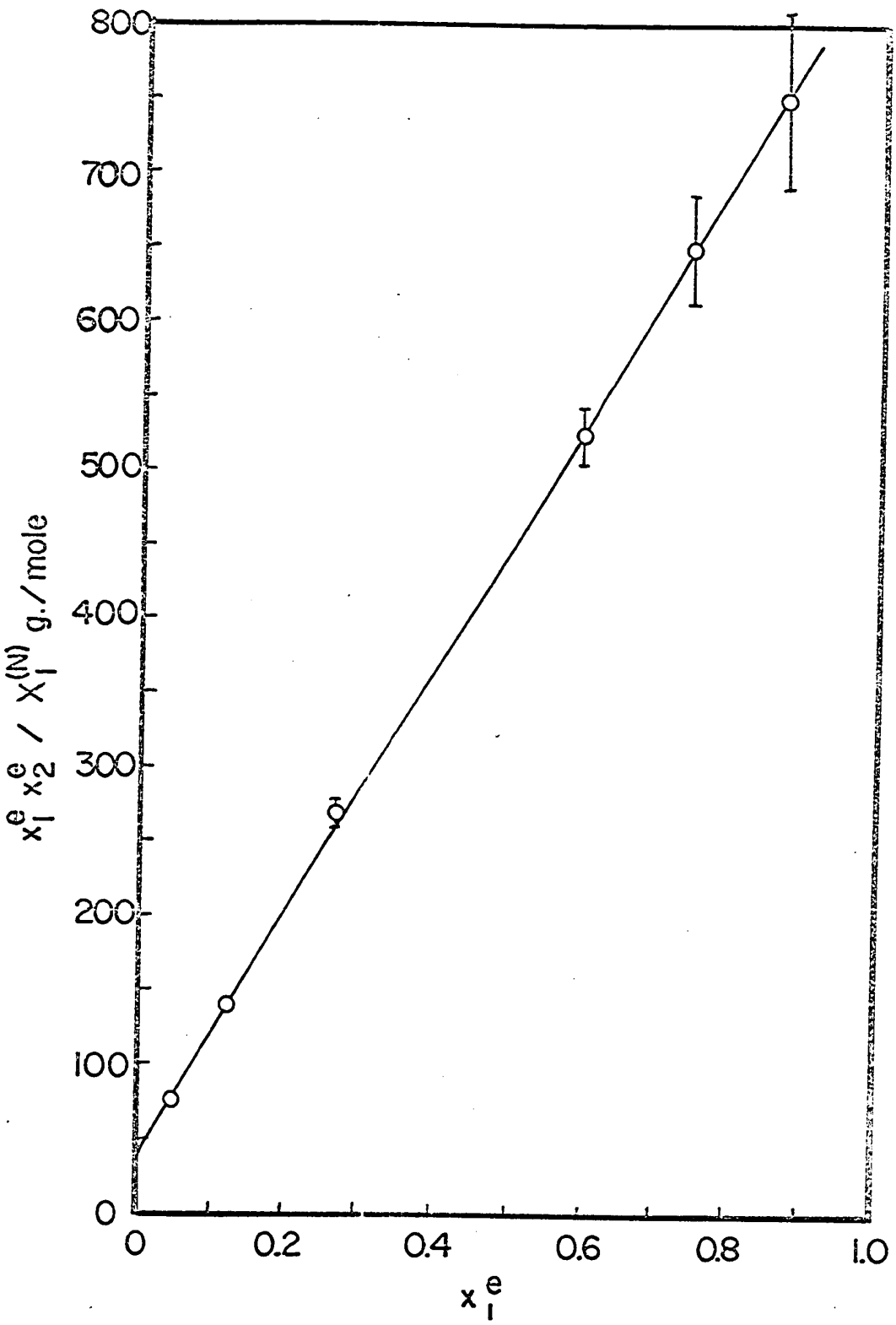


Fig. 23 Adsorption at 25° C. System: Benzene - cyclohexane - silicic acid B_1

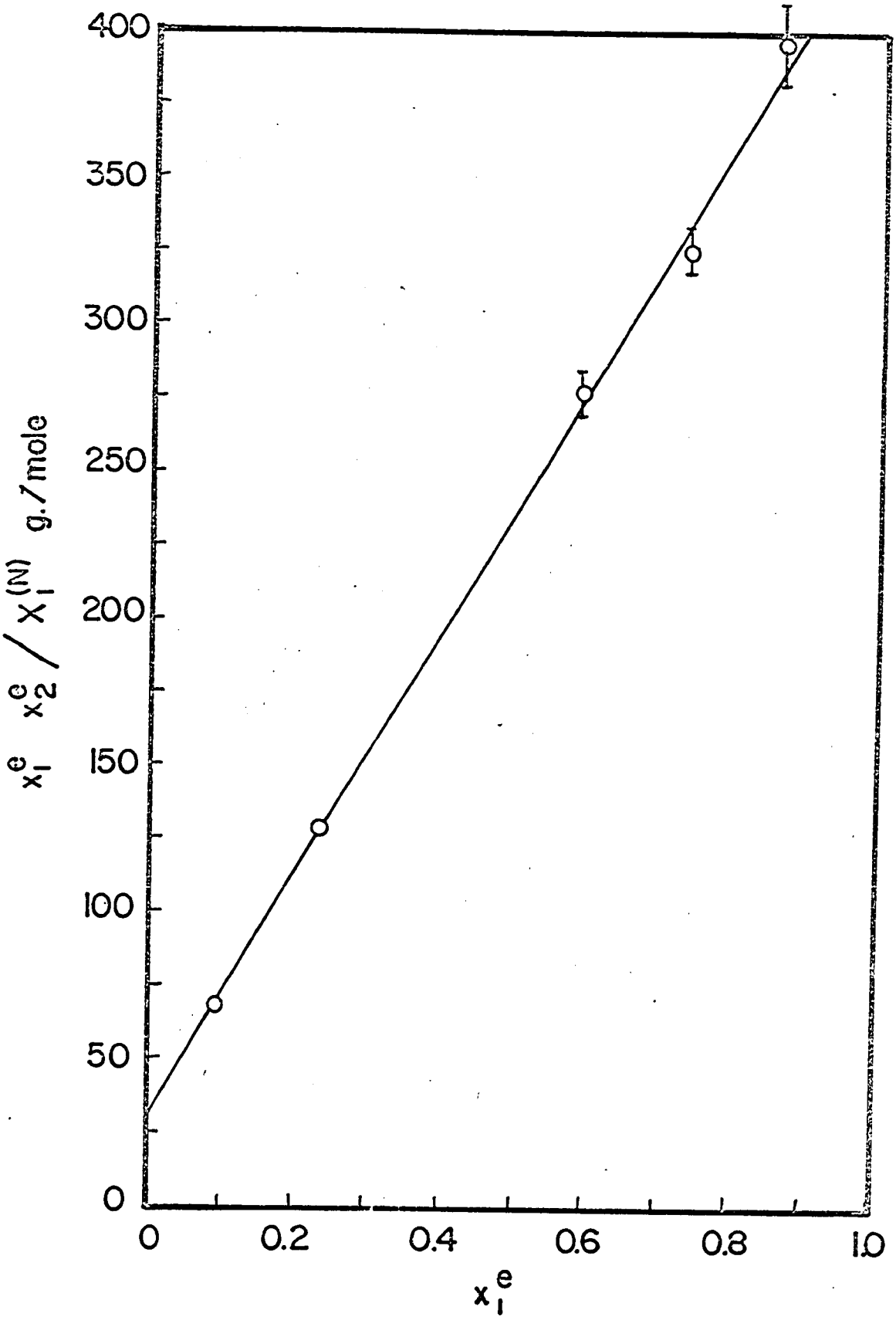


Fig. 24 Adsorption at 25° C. System: Benzene - cyclohexane - silica gel A_o'

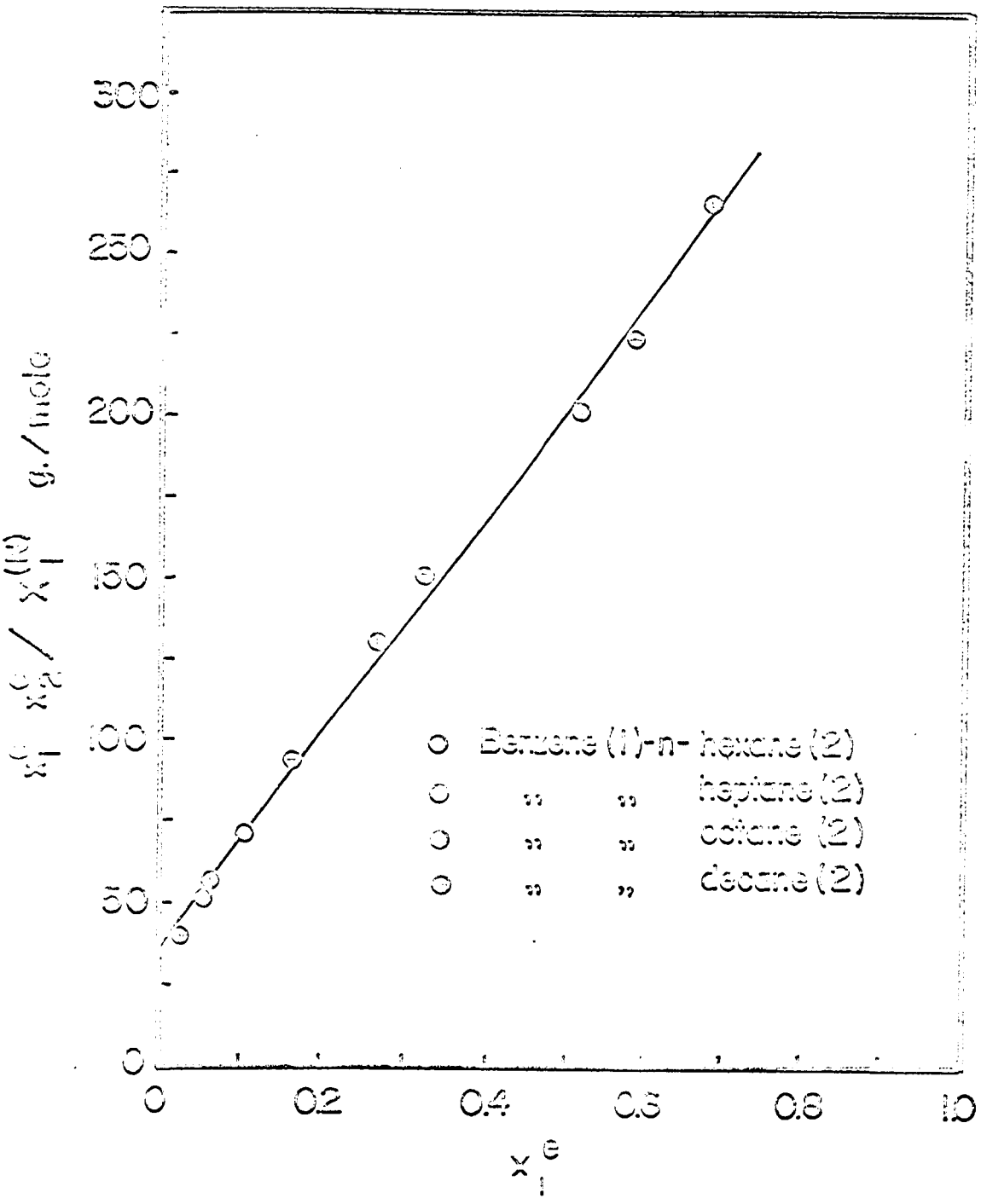


Fig. 25 Adsorption at 25°C. System: Benzene - n-alkanes - silica gel A_o'

Table 8

CONSTANTS OF EQUATION 21 FOR ADSORPTION FROM BINARY LIQUID MIXTURES ON SILICAS

Adsorbate	Adsorbent	Av. Deviation (%)	$1/N^a\,(K^{(N)} - 1)$ (mole^{-1}. g)	N^a (mole^{-1}. g)
Benzene- n-alkanes	Silica gel A_o'	3.5	36.9	328
Benzene - cyclohexane	Silica gel A_o'	1.9	30.9	410
Benzene - cyclohexane	Silicic acid B_1	0.93	42.4	809

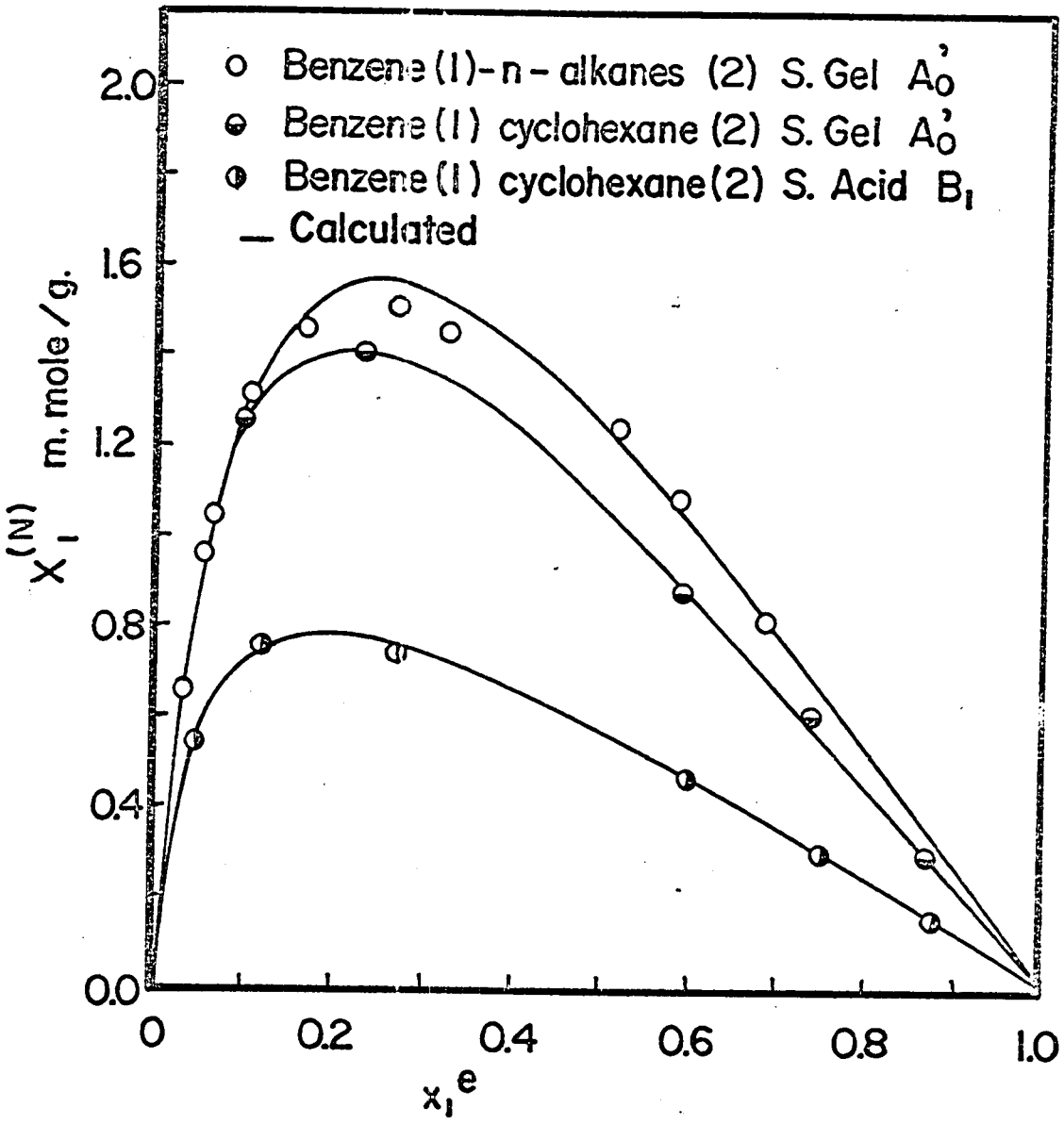


Fig. 26 Composite adsorption isotherms at 25° C.

The surface areas per gram of adsorbent, determined from liquid adsorption data $\leq_{s(L)}$, were calculated assuming a value of $\phi_1 = \phi_2 = 241 \times 10^3$ m^2/mole for the benzene-cyclohexane system (1). The same value was assumed for the benzene - n-alkane systems.

The separation factors and surface areas from liquid adsorption are shown in Table 9 together with the nitrogen surface area values. The values for the two binary systems studied here are given in Part I of the table. Part II gives values for mixtures, calculated from available data for mixtures of benzene with cyclohexane, on some silica adsorbents ranging in nitrogen surface area from 150 to 700 m^2/g.

It should be pointed out that one of the original assumptions in the derivation of Equation 21 is that the mixtures are ideal. This assumption has not been fully justified in this study because the measurements of the heats of mixing of benzene with cyclohexane and of benzene with n-alkanes presented in Appendix 6 indicate that the mixtures are non-ideal.

Fig. 27 shows the values of $\phi_1^e (1 - \phi_1^e)/x_1^{(V)}$ against ϕ_1^e for the various systems studied. The separation factors $\kappa^{(V)}$ and the monolayer volumes V^a are shown in Table 10 together with the total pore volume of the adsorbents as determined from adsorption of nitro-

Table 9

PARAMETERS OF EQUATION 21 FOR ADSORPTION FROM BINARY LIQUID MIXTURES ON SILICAS

Adsorbate	Adsorbent	$K^{(N)}$	N^a m. mole/g.	$\Sigma_{s(L)}$ $m^2/g.$	$\Sigma_{s(N_2)}$ $m^2/g.$	Ref.
		Part I				
Benzene-n-alkanes	Silica gel A_o'	9.9 ± 0.7	3.05	$736 \pm 4.3\%$	666	*
Benzene-cyclohexane	Silica gel A_o'	14.2 ± 0.6	2.44	$588 \pm 2.3\%$	666	*
Benzene-cyclohexane	Silicic acid B_1	20.0 ± 1.8	1.17	$286 \pm 5.0\%$	366	*
		Part II				
Benzene-cyclohexane	Porous glass	15	0.28	68	150	(24)
Benzene-cyclohexane	Silica gel	13	2.6	627	703**	(62)

* This work

** The nitrogen surface area was calculated from the reported butane surface area, using the correction factor $\Sigma_{s(N_2)} = 1.45\ \Sigma_{s\ (Butane)}$ (63)

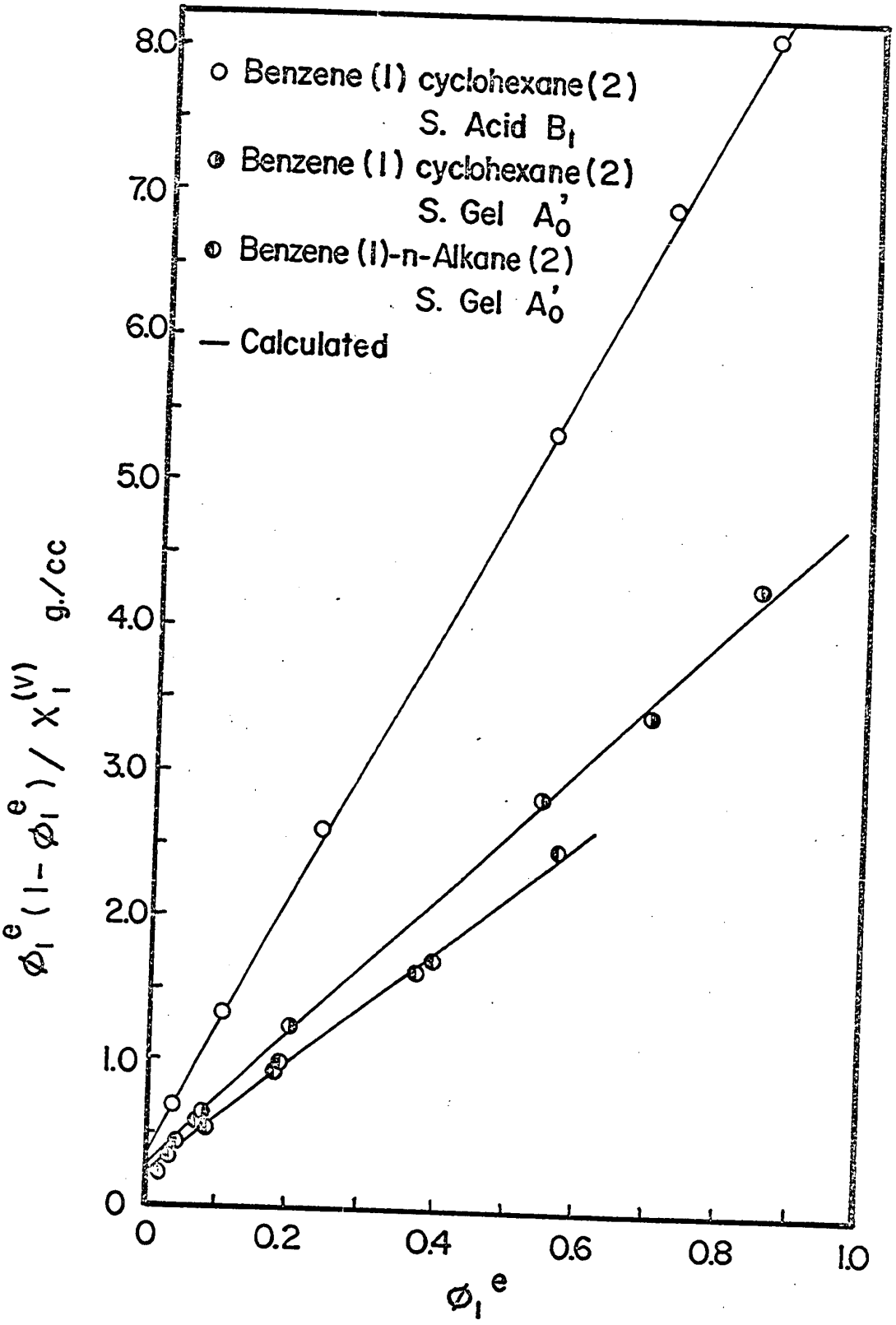


Fig. 27 Adsorption at 25° C.

Table 10

PARAMETERS OF EQUATION 18 FOR ADSORPTION FROM BINARY LIQUID MIXTURES ON SILICAS

Adsorbate	Adsorbent	Av. Deviation (%)	$K^{(V)}$	V^a (cc./g.)	V_p (cc./g.)
Benzene- n-alkanes	Silica gel A_o'	4.7	17.4	0.260	0.36
Benzene- cyclohexane	Silica gel A_o'	1.5	17.6	0.215	0.36
Benzene- cyclohexane	Silicic Acid B_1	1.2	24.7	0.109	0.37

gen. The average deviation between the experimental data and the calculated values of $\phi_1^e (1 - \phi^e)/X_1^V$ is given in column 3 of Table 10.

2. Error analysis

The accuracy of the presently reported values of $X_1^{(N)}$ is limited, primarily, by the experimental precision in the determination of the concentration of the equilibrium mixture.

The accuracy of the composition of binary liquid mixtures determined by measurement of the refractive index is given in Fig. 28 as a function of benzene mole fraction in the mixture. It is seen that the accuracy varies from system to system, according to the difference in the refractive indices of the pure components, and within the same system as a function of composition.

The accuracy of the values of $x_1 x_2/X_1^{(N)}$ were calculated and their magnitudes are indicated in the graphs of the composite adsorption isotherms. An example of calculation is presented below for the adsorption of mixtures of benzene with cyclohexane on silica gel A_o'

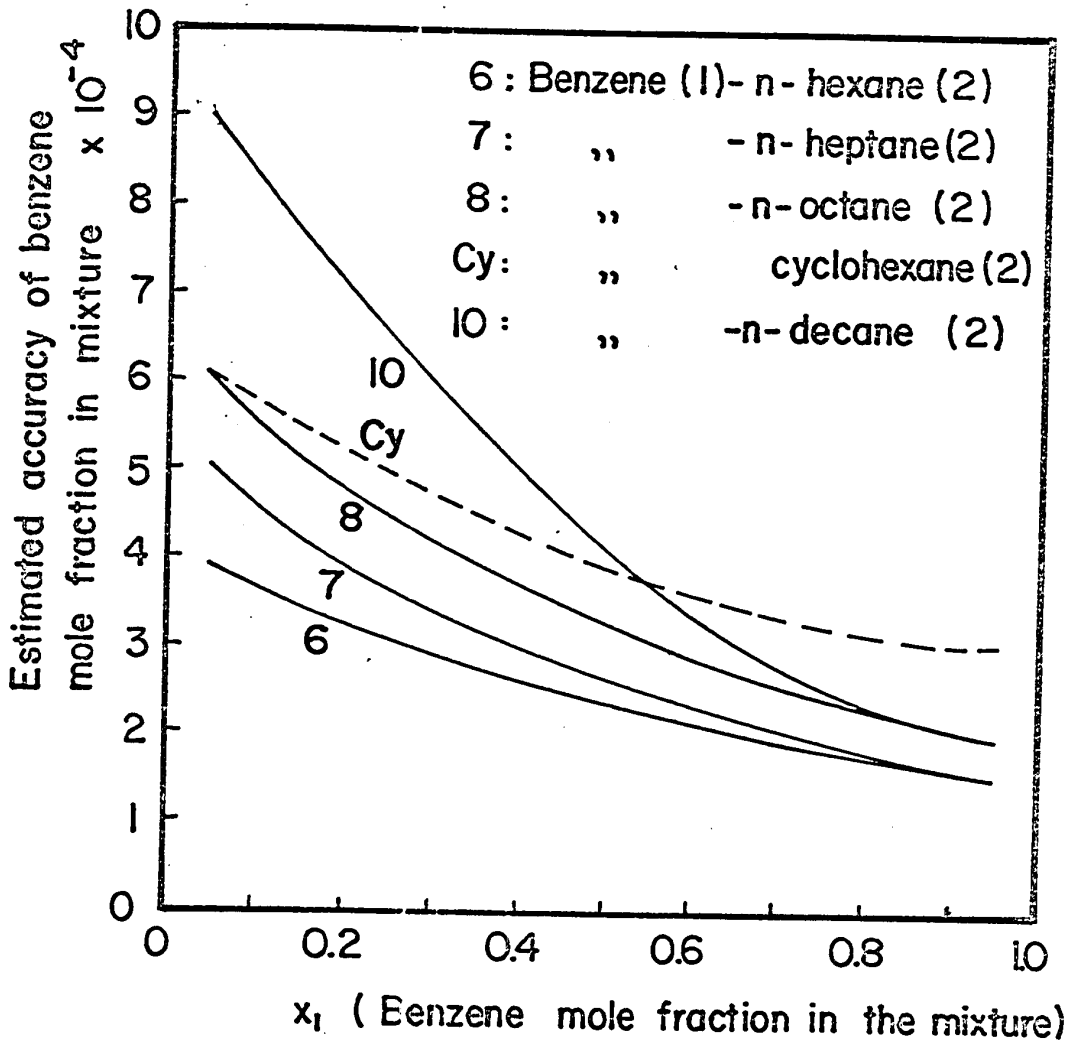


Fig. 28 Accuracy of liquid composition determination from Refractive index measurements

x_1^e	$x_1^e x_2^e / X_1^{(N)}$ (g./mole)	Weights
0.0953 (± 0.63%)	68.4 (± 2.0%)	2
0.2331 (± 0.21%)	128 (± 1.2%)	3
0.5901 (± 0.07%)	277 (± 2.4%)	2
0.7372 (± 0.04%)	325 (± 2.1%)	2
0.8659 (± 0.04%)	395 (± 3.6%)	1

In columns 1 and 2 of this table are given values of x_1^e and $x_1^e x_2^e / X_1^{(N)}$, respectively, with their corresponding uncertainties. In column 3 are presented the weights, for the different values of $x_1^e x_2^e / X_1^{(N)}$ with a weight of 1 assigned to $x_1^e x_2^e / X_1^{(N)}$ = 395.

The average deviation of the values of $x_1^e x_2^e / X_1^{(N)}$ is equal to the summation of the products of their uncertainties and their weights divided by the number of weighted observations:

$$\text{Av. D.} = \frac{2 \times 2.0 + 3 \times 1.2 + 2 \times 2.4 + 2 \times 2.1 + 1 \times 3.6}{10} = 2.0\% \qquad (49)$$

From the least square fitting, the following values were obtained for the constants of equation 21

$$1/N^a (K^{(N)} - 1) = D' = 30.9$$

$$1/N^a = D'' = 410$$

The accuracy of the values of N^a and $K^{(N)}$ was then calculated, assuming: a) that the chosen value of $\bar{\phi}_1 = \bar{\phi}_2 = 241 \times 10^3$ m^2/mole represents the true molar area of the different adsorbates on a monolayer; b) that the mixtures are ideal; and c) that the adsorbent has a homogeneous surface.

Then,

$$N^a = \frac{1}{410} = 0.00244\ (\pm\ 2.3\ \%)\ \frac{\text{mole}}{\text{g.}}$$

The surface area is:

$$\leqslant_{s(L)} = 0.00244 \times 241 \times 10^3 = 588\ (\pm\ 2.3\%)\ m^2/g.$$

For the separation factor,

$$K = 1 + \frac{410}{30.9} = 14.3\ (\pm\ 4.0\%)$$

In the system benzene- n-alkanes - silica gel A_o', the average deviation calculated from Equation 49, is smaller than that between the experimental values of $x_1^e (1 - x_1^e)/X_1^{(N)}$ and those calculated from Equation 21, 1.1 % and 3.5 %, respectively. Hence, the latter was used to estimate the uncertainties in $\leqslant_{s(L)}$ and $K^{(N)}$.

3. Discussion of Results

The investigation on the adsorption of binary liquid mixtures on the adsorbents may be interpreted to a first approximation from the viewpoint of the monomolecular model of liquid adsorption.

Figs. 23-27 show that the adsorption of benzene on both adsorbents is greater than that of the solvent, independent of the method chosen to express the magnitude of the apparent adsorption. When the apparent adsorption is plotted in terms of g./mole (Figs. 23-25), the equilibrium between the concentrations of the bulk and on the surface is shown to depend on the origin of the adsorbent. On the other hand, Fig. 25 shows that for n-alkanes in mixtures with benzene, the composite adsorption isotherm is quite insensitive to the solvent over the range of the experimental work covered in this study.

The data of part I in Table 9 indicate:

(i) A dependence of the separation factor on the adsorbate system for a given adsorbent. Thus, on silica gel A_c', the values of $K^{(N)}$ is lower for the system benzene- n-alkanes than for the system benzene - cyclohexane; and

(ii) A dependence of the separation factor on the source of the adsorbent for a given adsorbate system. Thus, for mixtures of benzene with cyclohexane, the value of $K^{(N)}$ is higher for silicic acid than for silica gel. It is possible, that differences in the structures of the adsorbents (33, 35) may have some bearing on the results obtained in adsorption from binary liquid mixtures.

A comparison of $K^{(N)}$ values for the benzene-cyclohexane system in silica gel A_o', and those in Part II in Table 9, indicate a satisfactory agreement for silica gel and porous glass; the differences in the values being attributed to the accuracy of the determinations and to different treatment of the adsorbents.

A consistent trend in the values of the surface area determined from the adsorption of mixtures of benzene with cyclohexane is observed, the B.E.T. values are about 80 m^2/g. larger than those from liquid adsorption. The relationship between $\leqslant_{s(L)}$ and $\leqslant_{s(N_2)}$ in m^2/g. may be written as follows

$$\text{Benzene - cyclohexane - silicas:} \quad \leqslant_{s(L)} = \leqslant_{s(N_2)} - 80 \tag{50}$$

On the other hand, the B.E.T. value for A_o' is smaller than that obtained from the adsorption of mixtures of benzene with n-alkanes, by about 70 m^2/g.

The discrepancy in the two sets of values obtained for the surface area determination from binary liquid adsorption data may arise from several causes, namely, the mixtures are not ideal in the bulk, and may not behave as ideal mixtures on the surface; the molecular areas on the surface of the adsorbents may not be 24.1×10^3

m^2/mole, and they may not be identical; the surface of the adsorbent may not be homogeneous; and finally, the adsorbed species may not be restricted to a single layer of molecules. All these effects will reflect changes in the calculated values of the surface area of adsorbents. In view of the nature of the assumptions involved and the general complexity of the phenomenon, the extent of the discrepancy is not very large in determinations of this type.

B. THE HEATS OF IMMERSION

1. Presentation of Results

a. Pure components

The heats of immersion of various silica adsorbents in nine pure adsorbates are shown in Table 11 along with their respective surface areas (B. E. T.).

All the adsorbents but two were degassed at 140° C and at reduced pressures. Sample A_{1a} was the same as A_1, but degassing was effected at 140° C and atmospheric pressure. Sample A_{1b} was obtained by deactivating A_1 with 3.8%, by weight, of water vapor.

The heats of immersion per unit surface area, i.e.

$$h_{I(N_2)}^{\circ} = \frac{H_I^{\circ}}{\leqslant_{s(N_2)}} \quad ; \quad \text{and} \quad h_{I(L)}^{\circ} = \frac{H_I^{\circ}}{\leqslant_{s(L)}} \qquad (51)$$

are compared in Table 12. The figures in parentheses refer to values of h_I° calculated from surface areas determined by adsorption of binary liquid mixtures of benzene and cyclohexane. The relationship between the nitrogen surface area $\leqslant_{s(N_2)}$ and the benzene - cyclohexane surface area $\leqslant_{s(L)}$, in $m^2/g.$, being

$$\leqslant_{s(L)} = \leqslant_{s(N_2)} - 80 \qquad (50)$$

Table 11

HEATS OF IMMERSION OF SILICAS (cal./g.) IN PURE LIQUIDS, AT 25° C

Adsorbent	A_1	A_{1a}	A_{1b}	A_2	A_3	A_{4a}	A_{4b}	A_5	B_2
$\leqslant_s(N_2)$, $m^2/g.$	596	-	-	588	575	560		483	348
				H_I^o (cal./g.)					
Ethanol	30.1	-	-	-	28.8	-	-	-	-
Water	27.4	23.8	18.4	-	26.2	25.3	-	-	20.8
Toluene	-	-	-	14.2	13.8	13.4	-	-	-
Benzene	14.0	13.4	11.5	13.7	13.3	12.9	13.0	11.3	7.6
Cyclohexane	6.5	6.1	6.0	-	6.3	-	-	5.2	3.5
N-hexane	7.8	-	-	7.8	-	-	-	-	-
N-heptane	-	-	-	7.8	-	-	-	-	-
N-octane	-	-	-	-	-	7.1	-	-	-
N-decane	-	-	-	7.8	-	-	7.2	-	-

- 108 -

Table 12

HEATS OF IMMERSION PER UNIT SURFACE AREA OF EVACUATED ADSORBENTS IN PURE LIQUIDS, AT 25°C

Adsorbent	A_1	A_2	A_3	A_{4a}	A_{4b}	A_5	B_2
$\leq s(N_2)$, m^2/g	596	588	575	560		483	348
$\leq s(L)$, m^2/g	(516)	(508)	(495)	(480)		(403)	(268)
				h_I^o (cal./m^2) $\times 10^3$			
Ethanol	50.5	-----	50.1	-----	-----	-----	-----
	(58.3)	-----	(58.2)	-----	-----	-----	-----
Water	46.0	-----	45.6	45.2	-----	-----	59.8
	(53.1)	-----	(52.9)	(52.7)	-----	-----	(77.6)
Toluene	-----	24.2	24.0	23.9	-----	-----	-----
	-----	(28.0)	(27.9)	(27.9)	-----	-----	-----
Benzene	23.5	23.3	23.1	23.0	23.2	23.4	(21.8)
	(27.1)	(27.0)	(26.9)	(26.9)	(27.0)	(28.0)	(28.3)
Cyclohexane	10.9	-----	11.0	-----	-----	10.8	10.1
	(12.6)	-----	(12.7)	-----	-----	(12.9)	(13.1)

Table 12 (Continued)

Adsorbent	A_1	A_2	A_3	A_{4a}	A_{4b}	A_5	B_2
$\leq s(N_2)$, m^2/g	596	588	575	560		483	348
$\leq s(L)$, m^2/g	(516)	(508)	(495)	(480)		(403)	(268)
				h_l^o (cal./m^2) x 10^3			
N-hexane	13.1	13.3	-----	-----	-----	-----	-----
	(15.1)	(15.4)	-----	-----	-----	-----	-----
N-heptane	-----	13.3	-----	-----	-----	-----	-----
	-----	(15.4)	-----	-----	-----	-----	-----
N-octane	-----	-----	-----	12.7	-----	-----	-----
	-----	-----	-----	(14.8)	-----	-----	-----
N-decane	-----	13.3	-----	-----	12.9	-----	-----
	-----	(15.4)	-----	-----	(15.0)	-----	-----

b. Binary mixtures

A total of five binary systems in nine adsorbents were made at the following conditions: degassing temperature of 140° C., calorimeter temperature of 25 ± 0.2° C., adsorbate to adsorbent ratio of 0.066 to 0.777 moles/g. Under these conditions the corrected temperature rise in the calorimeter varied between 0.1 and 0.6 of a degree centigrade, and in the majority of the experiments $x_1^e \approx x_1^o$.

Two adsorbents from different sources have been studied, namely, (i) a Commerical Silica gel, and (ii) Silicic acid. In addition, data have been obtained with deactivated samples of silica gel.

Five binary liquid mixtures have been studied, namely, (a) Benzene-cyclohexane; (b) Benzene- n-hexane; (c) Benzene- n-heptane; (d) Benzene- n-octane and (e) Benzene- n-decane.

The systems tested are summarized in Table 13.

A preliminary experiment on the heat of immersion of silica gel A_2 in a mixture of n-hexane with n-decane (n-hexane mole fraction = 0.4971) has shown identical results for the mixture as for the pure components.

Table 13

SUMMARY OF BINARY SYSTEMS TESTED IN HEATS OF IMMERSION MEASUREMENTS

Adsorbent		State of the adsorbent	Adsorbate
Silicic Acid	B_2	degassed under vacuum	Benzene-cyclohexane
Silica Gel	A_3	degassed under vacuum	Benzene-cyclohexane
Silica Gel	A_5	degassed under vacuum	Benzene-cyclohexane
Silica Gel	A_{1a}	degassed in the oven at 140°C	Benzene-cyclohexane
Silica Gel	A_{1b}	containing 3.8% of H_2O	Benzene-cyclohexane
Silica Gel	A_1, A_2, A_{4b}	degassed under vacuum	Benzene- n-hexane
Silica Gel	A_2	degassed under vacuum	Benzene- n-heptane
Silica Gel	A_2, A_{4a}	degassed under vacuum	Benzene- n-octane
Silica Gel	A_{4b}	degassed under vacuum	Benzene- n-decane

A typical heat of immersion isotherm is shown in Fig. 29 for the system benzene-cyclohexane-silica gel A_3. The isotherm exhibits a steep rise in the diluted benzene region, then the slope of the curve decreases rapidly, and ultimately the curve tends to flatten off.

The data collected in these determinations are shown in Appendix 5. The results obtained on the heats of immersion of various adsorbents in binary liquid mixtures were compared by defining a relative heat of immersion θ_I, as follows,

$$\theta_I = \frac{H_I - (H_I^\circ)_2}{(H_I^\circ)_1 - (H_I^\circ)_2} \qquad (52)$$

From the tabulated data, the relative heat of immersion θ_I values were obtained and plotted as a function of x_1° in Figs. 30 - 33. The values of θ_I calculated from Equation 32 are shown in broken lines.

2. Error analysis

The sources of error in heat of immersion calorimetry are: a) The uncertainty in the correction for the heat evolved in breaking and piercing the diaphragm; b) The contamination of the adsorbate; c) The vaporization of volatile liquid; d) Others. These sources of error will be discussed individually in the following paragraphs.

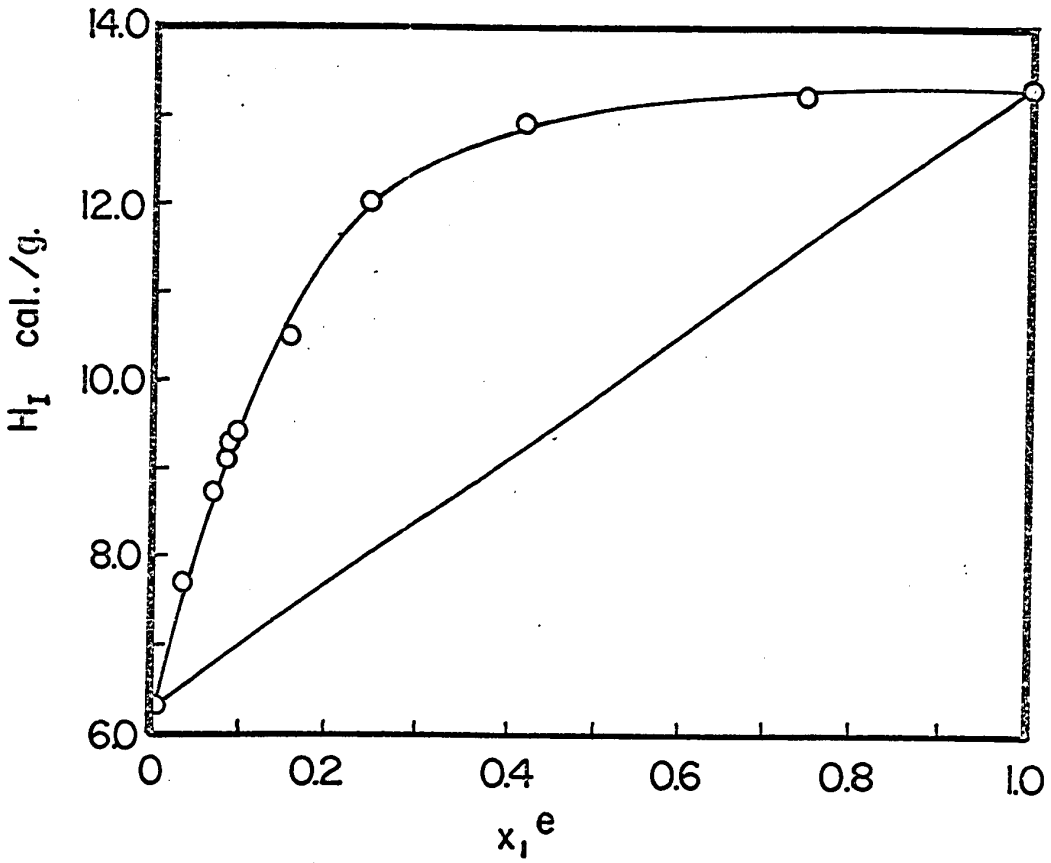


Fig. 29 Isotherm of heats of immersion at 25° C. System: Benzene - cyclohexane - silica gel A_3

a. Heat of breaking and piercing the diaphragm

When foils were broken in blank tests using the same liquid in both compartments of the mixing cell, no heat effect due to this action was detected.

b. Contamination of the adsorbate

The effect of traces of water in the adsorbate on heats of immersion of silica gel A_3 in benzene is shown in Table 14.

The results indicate that the heats of immersion of silica gel A_3 are appreciably larger in the adsorbate containing traces of water than in the dry sample. Thus, while the value for benzene "as received" was 13.8 cal./g., successive immersions of several portions of silica gel in the sample of benzene resulting from the first immersion gave essentially the same value, namely, 13.3 cal./g. When the dry benzene resulting from the fourth immersion was saturated in the presence of water vapor, and then contacted with silica gel, the heat of immersion was of 16.5 cal./g. Hence, it can be concluded that the adsorbate may be dehydrated by using activated silica gel as a drying agent.

In the course of this investigation, it was found also, that the presence of traces of water in benzene increased the time required for the heat evolution, hence, the accuracy of the measurements was reduced.

Table 14

EFFECT OF TRACES OF WATER IN THE ADSORBATE ON HEATS OF IMMERSION OF SILICA GEL A_3 IN BENZENE

Adsorbate	$-H_I^\circ$ (cal./g.)
First immersion ("as received")	13.8
Second immersion	13.3
Third immersion	13.3
Fourth immersion	13.4
Fifth immersion (saturated with water)	16.5

c. Vaporization of volatile liquid

In order to be reasonably certain of the accuracy of the data, measurements were taken with different ratios of N°/W for pure liquids. Since the magnitude of the error involved on immersion is a function of the vapor space, it should be possible to estimate the approximate error if several void spaces were used. If the results using two or more ratios of N°/W were within experimental reproducibility, it could be safely assumed that no corrections are necessary. In Table 15, data are given for the heat of immersion of a silica gel A_{1a} in water, in benzene and in cyclohexane as a function of N°/W. The data show that the heat of immersion obtained using different ratios of N°/W are essentially the same for each adsorbate. Therefore, it can be concluded that the correction for the vaporization of the adsorbate inside the mixing cell is negligible.

d. Other errors

		%
Voltage measurements	±	0.05
Resistance measurements	±	0.01
Time measurements	±	0.06
Mass measurements	±	0.02
Heat transfer to surroundings	±	1.00
Vaporization and condensation effects		nil
Total	±	1.14%

Table 15

HEATS OF IMMERSION OF SILICA GEL A_{1a} IN PURE LIQUIDS AS A FUNCTION OF N°/W

W (g.)	N° (moles)	N°/W (moles/g.)	$-H_1^{\circ}$ (cal/g.)	Adsorbate
0.9435	0.78468	0.8317	24.1	Water
0.4571	0.78810	1.724	23.8	Water
0.2364	0.55696	2.356	23.8	Water
1.5861	0.089011	0.05612	13.4	Benzene
0.6323	0.093710	0.1482	13.2	Benzene
0.3062	0.13181	0.4305	13.4	Benzene
1.5861	0.079125	0.04989	6.1	Cyclohexane
0.5901	0.078543	0.1331	6.1	Cyclohexane

The uncertainty in the measured heats of immersion is then about 1.1%.

3. Heat of dilution on immersion

This effect would arise out of the non-ideal behaviour of the binary mixtures used in this investigation. From an enthalpy balance,

$$H_{dil.} = \frac{N^o}{W}\left[(\Delta H^M)^e - (\Delta H^M)^o \right] + N^a \left[(\Delta H^M)^a - (\Delta H^M)^e \right] \quad (53)$$

where $H_{dil.}$ is the heat of dilution on immersion, in cal. per gram of adsorbent;

$(\Delta H^M)^e$ is the molal enthalpy of the equilibrium mixture, in cal./mole;

$(\Delta H^M)^o$ that for the initial mixture, in cal./mole; and

$(\Delta H^M)^a$ that for the mixture on the surface, in cal./mole.

Equation 53 has three unknowns: $H_{dil.}$, N^a and $(\Delta H^M)^a$. This implies that in order to estimate a value of $H_{dil.}$ it is necessary to assume a mechanism for the adsorption process.

Calculations of $H_{dil.}$ from Equation 53 using the monolayer and the multimolecular models of adsorption are presented in Table 16 for the immersion of silica gel A_3 in mixtures of benzene with cyclohexane. A sample of calculations is given in Appendix 7.

Table 16

HEAT OF DILUTION ON IMMERSION

SYSTEM: BENZENE - CYCLOHEXANE - SILICA GEL A_3

x_1^e	N^o/W	$-H_I$ (cal./g.)	Monolayer model. N^* based on: $s(N_2)$	$s(L)$	Multilayer model. N^* based on: V_p = 0.37 cc/g.
			$(H_{dil.}/H_I) \times 100$		
0.0000	0.3756	6.3	-	-	-
0.0320	0.3150	7.7	1.7	2.3	1.9
0.0650	0.5457	8.7	3.3	3.9	2.8
0.0825	0.06633	9.1	3.1	3.5	2.0
0.0873	0.1079	9.3	3.2	3.7	2.2
0.0942	0.3301	9.4	3.4	3.8	2.2
0.1550	0.4016	10.5	4.3	4.5	2.5
0.2443	0.3496	12.0	4.2	4.2	2.2
0.4115	0.2066	12.9	3.3	2.9	1.2
0.7470	0.4421	13.2	1.3	1.0	1.2
1.0000	0.5167	13.3	-	-	-
	Average uncertainty %:		3.1	3.3	1.9

- 119 -

The average uncertainty introduced by the heat of dilution, in the values of the heat of wetting, may be expressed as follows,

$$\sum_{i} (H_{dil.}/H_{I})_{i}/n \qquad (54)$$

where n is the number of observations.

According to the three sets of calculations presented in Table 16, the average uncertainty is of the order of 1.9 to 3.3%, with a maximum uncertainty of 4.5%. These calculations, however, must be taken with caution, in view of the assumptions involved in their estimation.

The various errors in the determination of the heat of immersion combine with the uncertainty due to the heat of dilution on immersion, to produce an estimated error in the heats of wetting values of the order of -0.8 to -4.3%.

3. Discussion of Results

a. Heats of immersion of silicas in pure liquids

A comparison of the results presented in Table 11 shows that the heats of immersion of a given adsorbent in ethanol and in water are higher than in hydrocarbons, the values for the n-alkanes being independent of chain length. Determination of the effect of

adsorbent activity on heats of immersion revealed: (a) that in a given liquid, values for the evacuated adsorbents were greater than those for the adsorbents containing small quantities of water; and (b) that the decrease in the heats of immersion of deactivated adsorbents with respect to the evacuated adsorbents diminish in the sequence: water, benzene, cyclohexane.

The data of Table 12 show good agreement for the absolute heat of immersion h_I° of silica gel in pure components. In the case of silicic acid B_2, the values of $h_{I\,(N_2)}^\circ$ in benzene and in cyclohexane are only about 8% lower than those of the silica gel adsorbents but the corresponding value of $h_{I\,(N_2)}^\circ$ in water is about 32% higher for silicic acid. This difference may be attributed to different origins of the adsorbents and may be connected with differences in the structure (33, 35) of the samples under investigation.

Comparing the results obtained on the absolute heats of immersion of different adsorbents in a particular adsorbate, it seems that the values based on the surface area determined from adsorption of binary liquid mixtures of benzene with cyclohexane $h_{I\,(L)}^\circ$ form a more consistent set than those calculated from the nitrogen surface area, for example, the value of $h_{I\,(N_2)}^\circ$ for silica gel in benzene is 7.8% larger than that of silicic acid whereas the difference

in h_I^o (L) values for these adsorbents in the same adsorbate is only 4.4%.

b. Heats of immersion of silicas in mixtures of benzene with cyclohexane

Comparison of the relative heats of immersion for the four fine-pore samples of silica gel in Fig. 30 shows that there is no noticeable difference between activated and deactivated adsorbent data. In the region where $x_1^e > 0.2$ the values of θ_I are in agreement with those predicted from Equation 32 with a separation factor $K^{(N)} = 14.2$, but for values of $x_1^e < 0.2$, the experimental values of θ_I fall below the predicted values. In this region, results may be approximated by Equation 32 with a value of $K^{(N)} = 8$.

On the basis of these results it is tempting to conclude that the deviations of the experimental data from the predicted values may be attributed mainly to the non-ideal behaviour of the binary liquid system. However, Fig. 31 shows that the data for the sample of silicic acid is in excellent agreement with the predicted values using a separation factor $K^{(N)} = 20$, over the entire concentration range.

The different adsorptive behaviour of silica gel and silicic acid with mixtures of benzene and cyclohexane is emphasized in Fig. 32. It is observed from the isotherms of relative heats of immersion

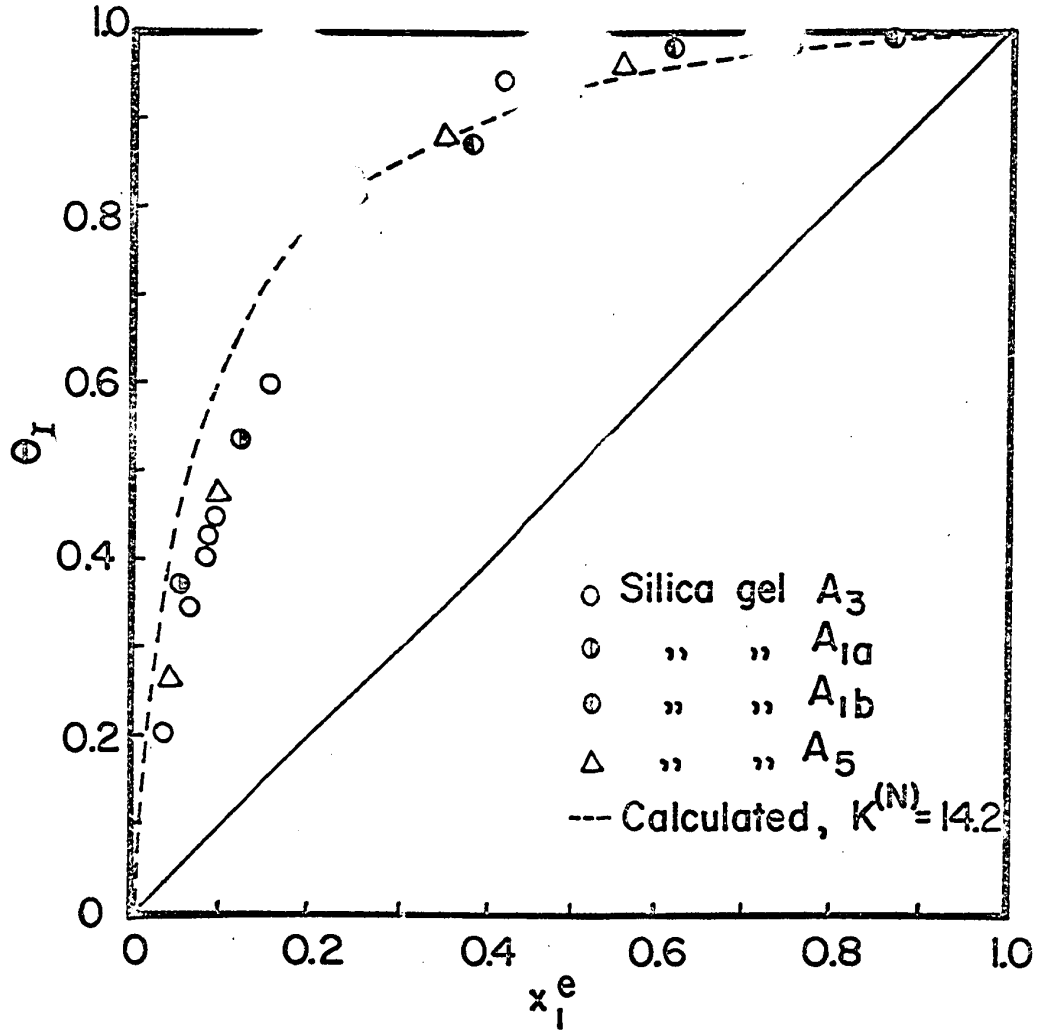


Fig. 30 Relative heats of immersion at 25° C. System: Benzene - cyclohexane - silica gel

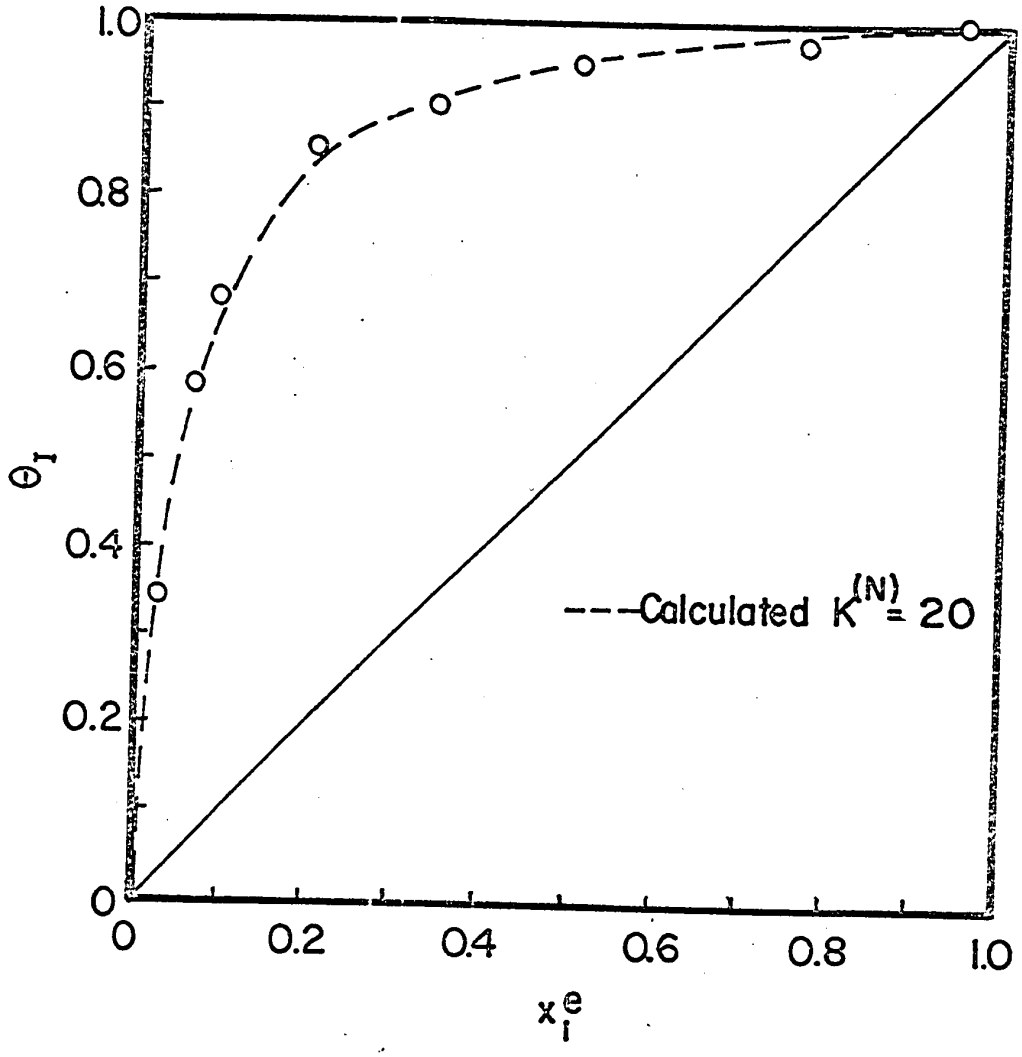


Fig. 31 Relative heats of immersion at 25° C. System: Benzene - cyclohexane - silicic acid B_2

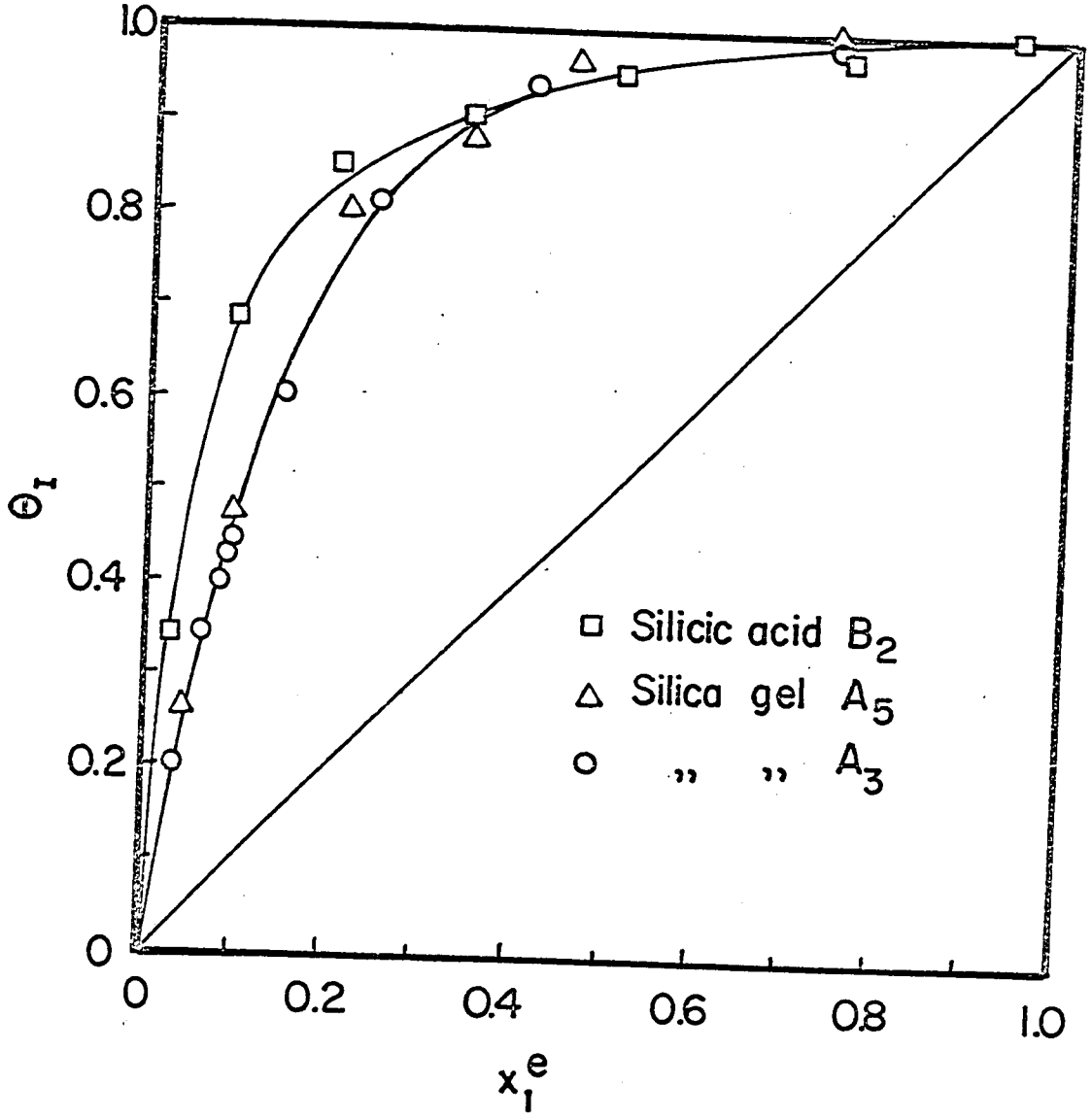


Fig. 32 Relative heats of immersion at 25° C. System: Benzene - cyclohexane - silica adsorbents (degassed)

of the evacuated adsorbents, that at a given value of x_1^e, the relative heat of immersion for silicic acid is higher than for silica gel. The difference between the two isotherms is more evident in the region where x_1^e 0.4, thus, at x_1^e = 0.05, values of θ_1 for silica gel and for silicic acid are 0.28 and 0.52, respectively, whereas, at x_1^e 0.4, the difference between the determined values of θ_1 for both adsorbents is negligible.

c. Heats of immersion of silica gel in mixtures of benzene with n-alkanes

The heats of immersion of silica gel in mixtures of benzene with n-alkanes may give some information as to the effect of the chain length when considered in the light of the monolayer theory of adsorption for perfect systems, wherein H_1 is given by Equation 31.

The homologous series of n-alkanes in mixtures with benzene form an interesting group for the following reasons:

i. The heats of immersion of silica gel in n-alkanes are essentially the same;

ii. A preliminary experiment on the heat of immersion of silica gel in a mixture of n-hexane with n-decane (n-hexane mole fraction of 0.4971) has shown identical results for the mixture as for the pure components; and

iii. The equilibrium adsorption data for the mixtures of benzene with n-alkanes may be represented by Equation 21 with a constant separation factor.

Thus, it may be expected that the heats of immersion of silica gel in the four binaries would not depend on the n-alkane solvent.

Fig. 33 is a plot of θ_1 against x_1^e for the systems studied. It is evident that there is a significant variation of the isotherm of the heat of immersion with the solvent. At corresponding mole fractions of benzene in the equilibrium mixtures, the relative heats of immersion are higher, the smaller the molecule of the solvent n-alkane, this effect being more pronounced at lower values of x_1^e.

It is not possible to offer a very plausible explanation of the dependence of θ_1 on the solvent and hence, of the failure of Equation 32 to give an adequate representation of the data. Of course, it is likely that the assumptions of a constant separation factor $K^{(N)}$ and monolayer coverage may not be true for these binary systems, adsorbed on the silica gel used in this study. It seems that a satisfactory explanation of the effect of the solvent in liquid phase adsorption will be forthcoming only with a more detailed study aimed specially at this problem.

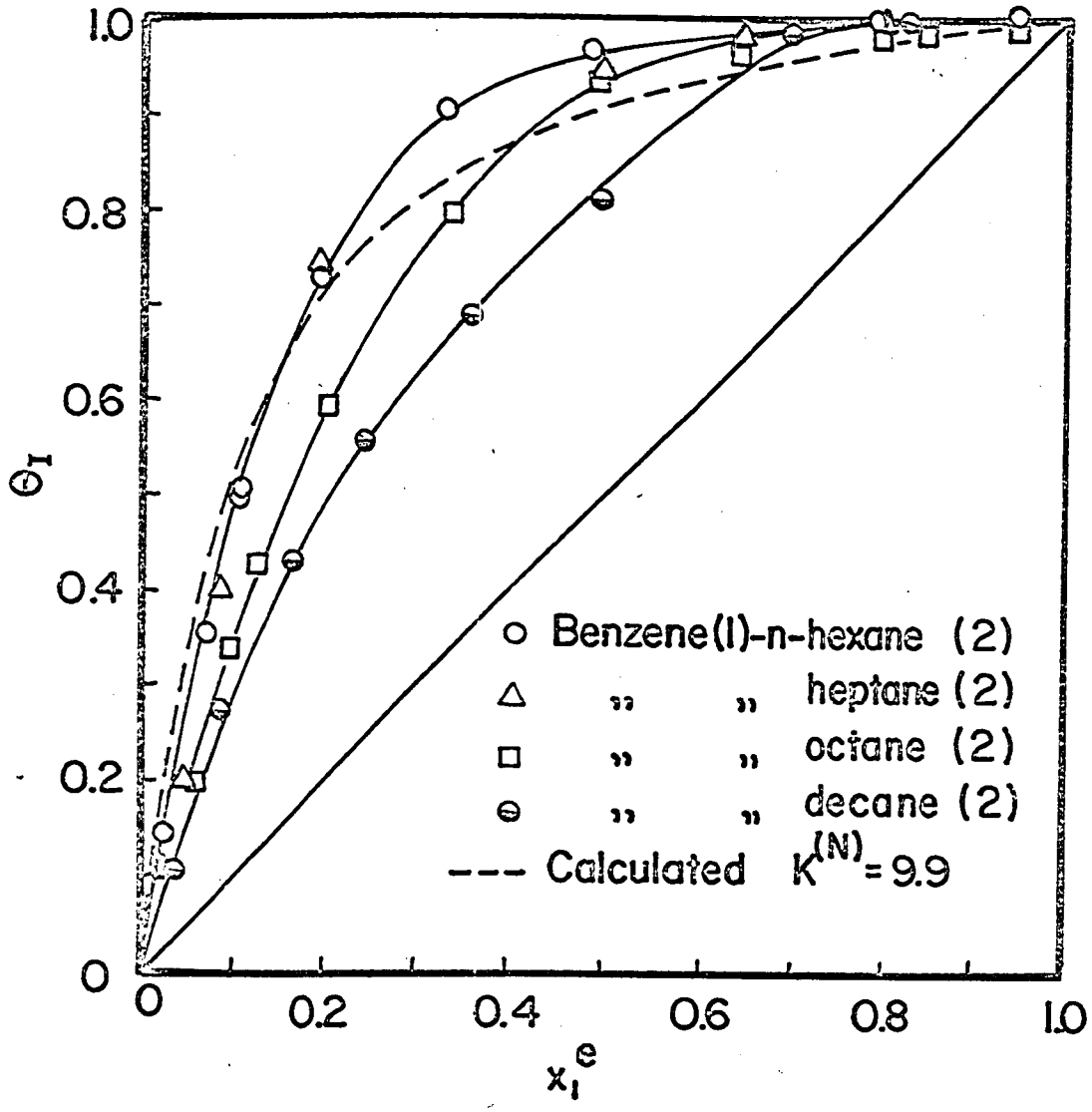


Fig. 33 Relative heats of immersion at 25° C. System: Benzene - n-alkanes - silica gel

d. Semi-empirical correlating criteria

In the remaining part of this discussion are shown the results of several efforts aimed at correlating the heat of immersion data of silica gel in binary liquid systems using equations of the Langmuir type.

The fact that the heats of immersion of silica gel in mixtures of benzene with n-alkane decrease with increasing molecular volume of the solvent suggests that an alternative correlation is possible between θ_I and the concentration of the equilibrium mixture expressed in terms of volume fraction. This plot is shown in Fig. 34. Evidently, there is a general upward displacement of the isotherms; the effect of using volume fractions ϕ to express the concentration of the equilibrium mixture being to bring the isotherms closer together.

When the comparison of the heats of immersion for mixtures of benzene with n-alkanes is made in terms of θ_I', where

$$\theta_I' = \frac{\theta_I \tilde{V}_2}{\theta_I \tilde{V}_2 + (1 - \theta_I) \tilde{V}_1}$$

it is seen in Fig. 35 that, at a given value of ϕ_1^e, θ_I' is a constant for all the systems studied. An expression analogous to a Langmuir equation may be used to represent adequately the combined isotherm,

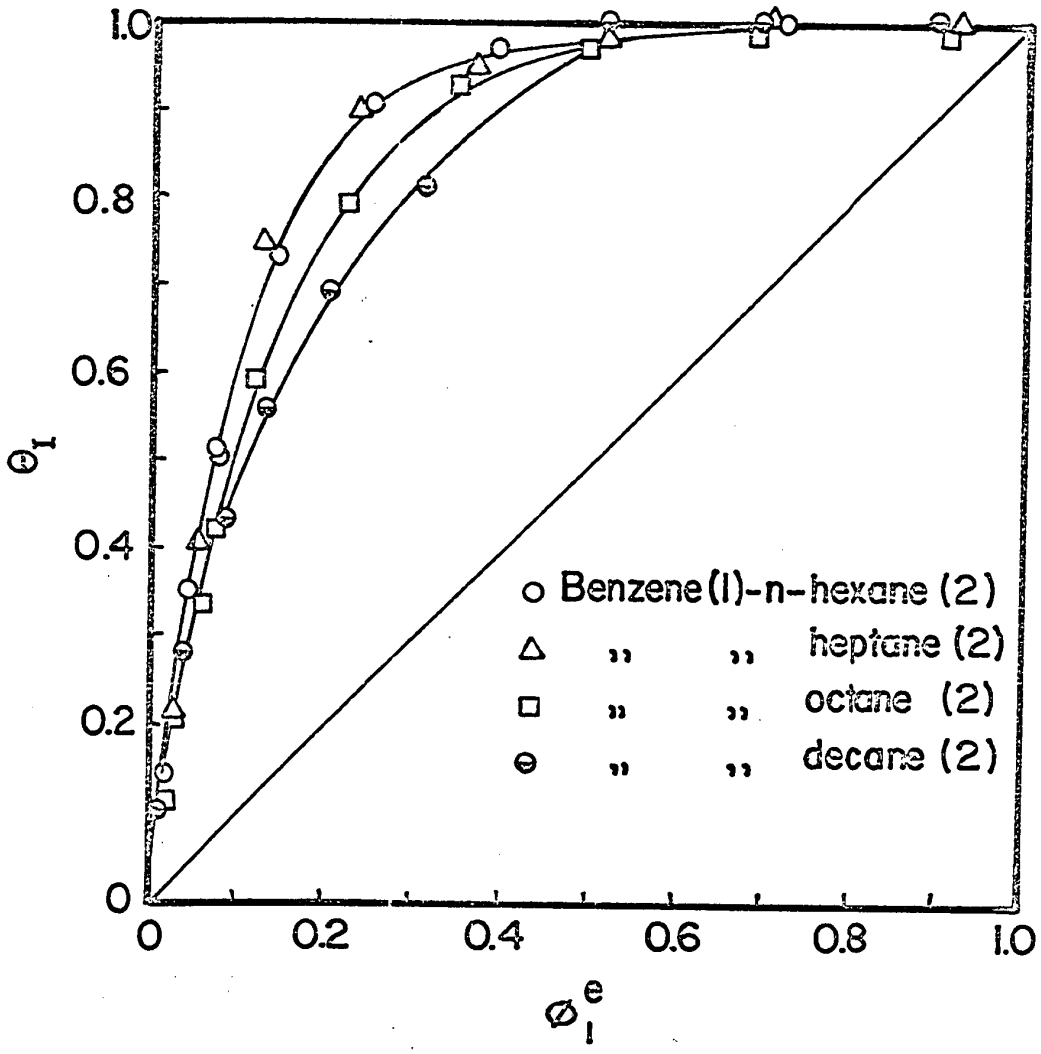


Fig. 34 Relative heats of immersion at 25° C. System: Benzene - n-alkanes - silica gel

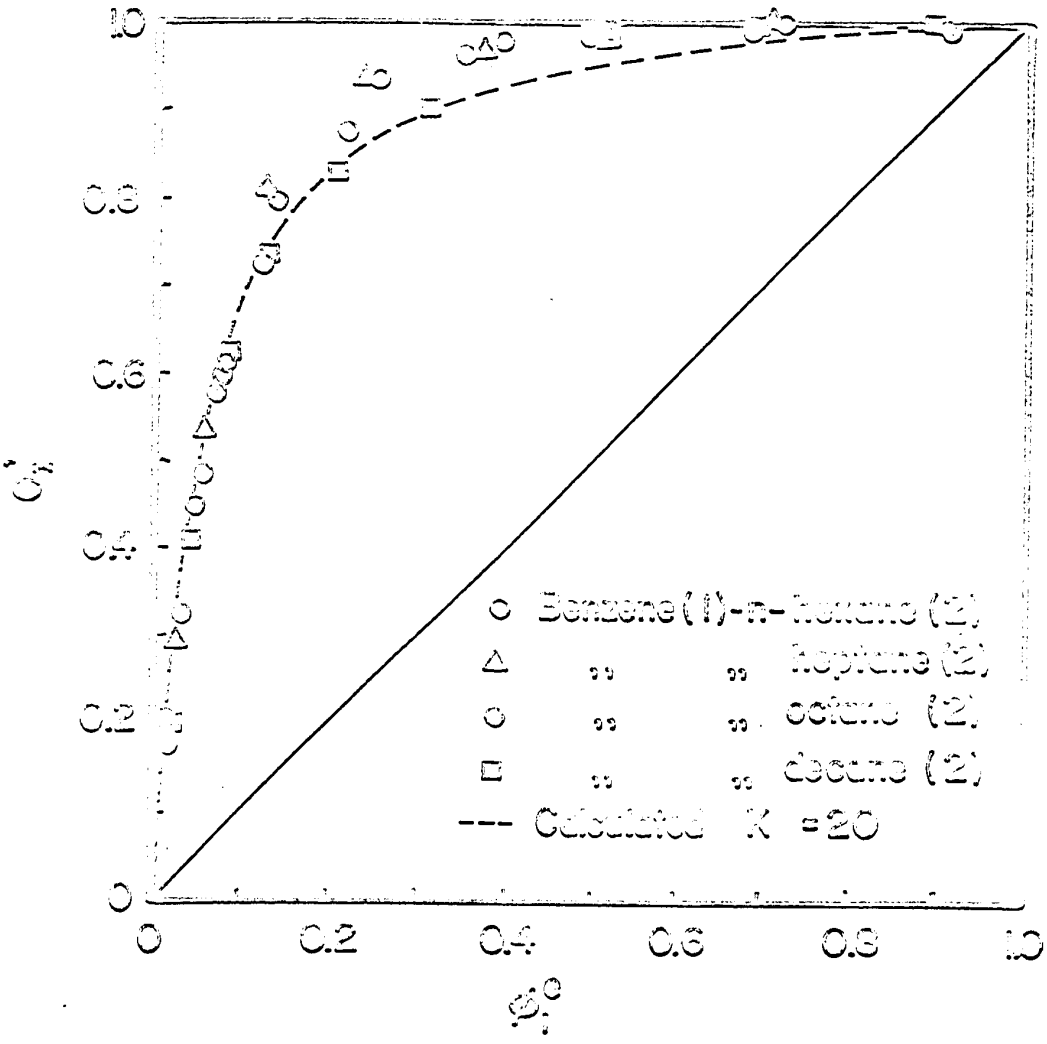


Fig. 35 Corrected relative heats of immersion at 25° C. System: Benzene - n-alkanes - silica gel

$$\frac{\theta_I'}{1 - \theta_I'} = K \frac{\phi_1^e}{1 - \phi_1^e} \qquad (55)$$

In terms of θ_I, Equation 55 becomes

$$\frac{\theta_I}{1 - \theta_I} = K \cdot \frac{\tilde{V}_1}{\tilde{V}_2} \cdot \frac{\phi_1^e}{1 - \phi^e} \qquad (56)$$

where $K = 20$.

Solving Equation 56 for H_I gives,

$$H_I = H_2^o + \frac{20\, \tilde{V}_1/\tilde{V}_2 \left[(H_I^o)_1 - (H_I^o)_2 \right] \phi_1^e}{1 + (20\, \tilde{V}_1/\tilde{V}_2 - 1)\, \phi_1^e} \qquad (57)$$

Upon comparing the experimental data in Appendix 5 with the values of H_I calculated using Equation 57, it is found that this latter represents the heats of immersion within 3%.

The possibility that, increasing hindrance in the pores of the adsorbent is partly responsible for the decrease in heats of immersion of silica gel in binary liquid mixtures of benzene with n-alkanes, as the solute ascends the homologous series, has been considered. A plot is given in Fig. 36 of θ_I/ϕ_1^e against θ_I for the evacuated adsorbents immersed in binary liquid mixtures, including the system benzene-cyclohexane - silica gel. Linear relations, except at high values of θ_I,

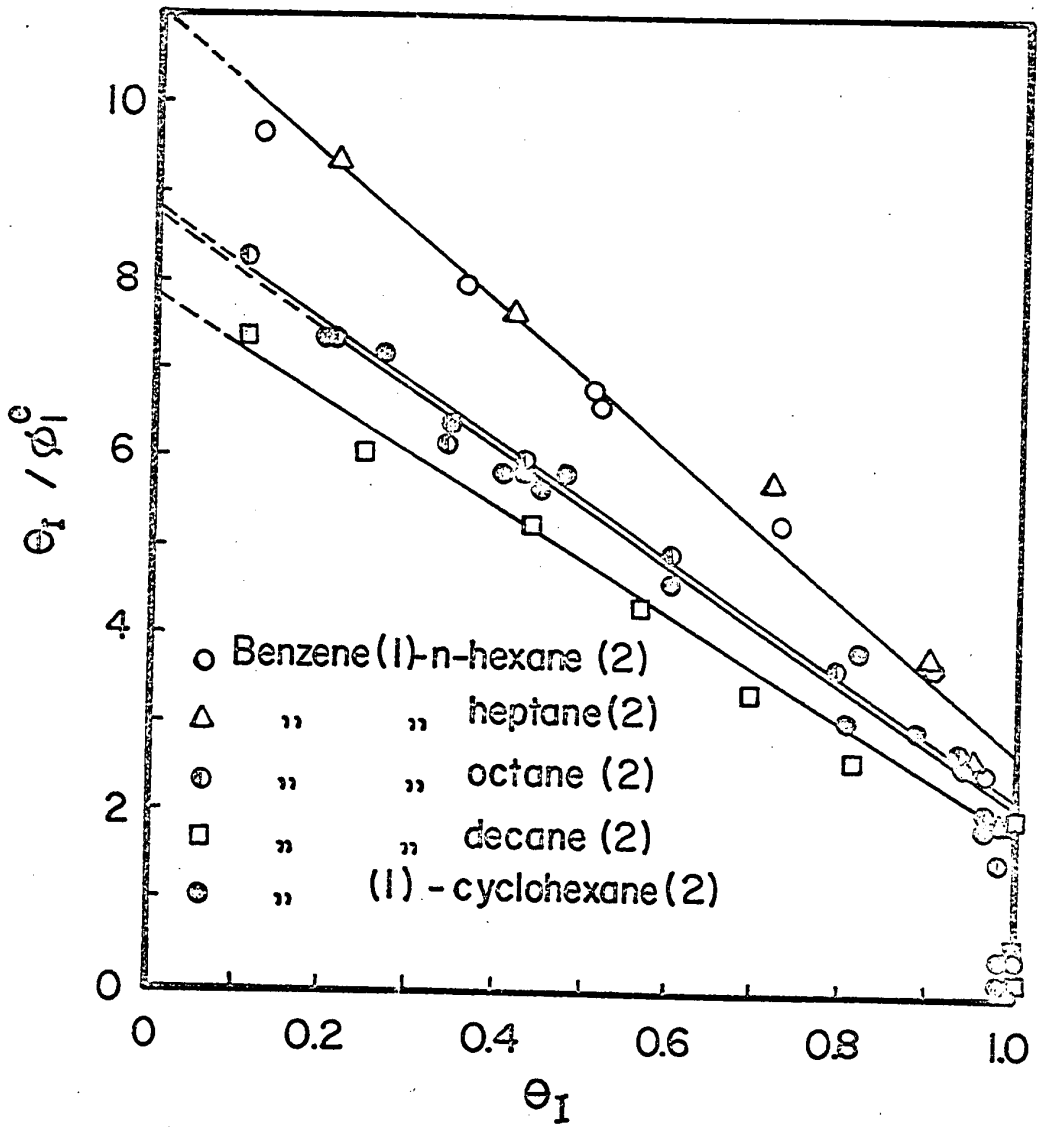


Fig. 36 θ_1/ϕ_1^e vs. θ_1. Systems: Benzene - n-alkanes - silica gel; and Benzene - cyclohexane - silica gel, at 25° C.

are obtained for each system. Extrapolation of the lines in Fig. 36 to $\theta_I = 1$ reveals that the value of ϕ_1^e at which the maximum value of the heat of immersion occurs $(\phi_1^e)_c$ will vary depending on the nature of the solvent.

The values of $(\phi_1^e)_c$ for the different binary adsorbate systems are given below.

Adsorbate system	$(\phi_1^e)_c$
Benzene - cyclohexane	0.45
Benzene - n-hexane	0.37
Benzene - n-heptane	0.37
Benzene - n-octane	0.45
Benzene - n-decane	0.56

In Fig. 37 there have been plotted values of $\theta_I (\phi_1^e)_c / \phi_1^e$ against θ_I for all the heat of immersion data of evacuated silica gel in binary mixtures, in the range of ϕ_1^e between 0.01 and $(\phi_1^e)_c$. When the points near $\theta_I = 1.0$ are disregarded, the data of Fig. 37 may be considered to fall on a straight line, the equation of which is

$$\frac{\theta_I (\phi_1^e)_c}{\phi_1^e} = K' - (K' - 1)\, \theta_I \qquad (58)$$

where $K' = 4.1$.

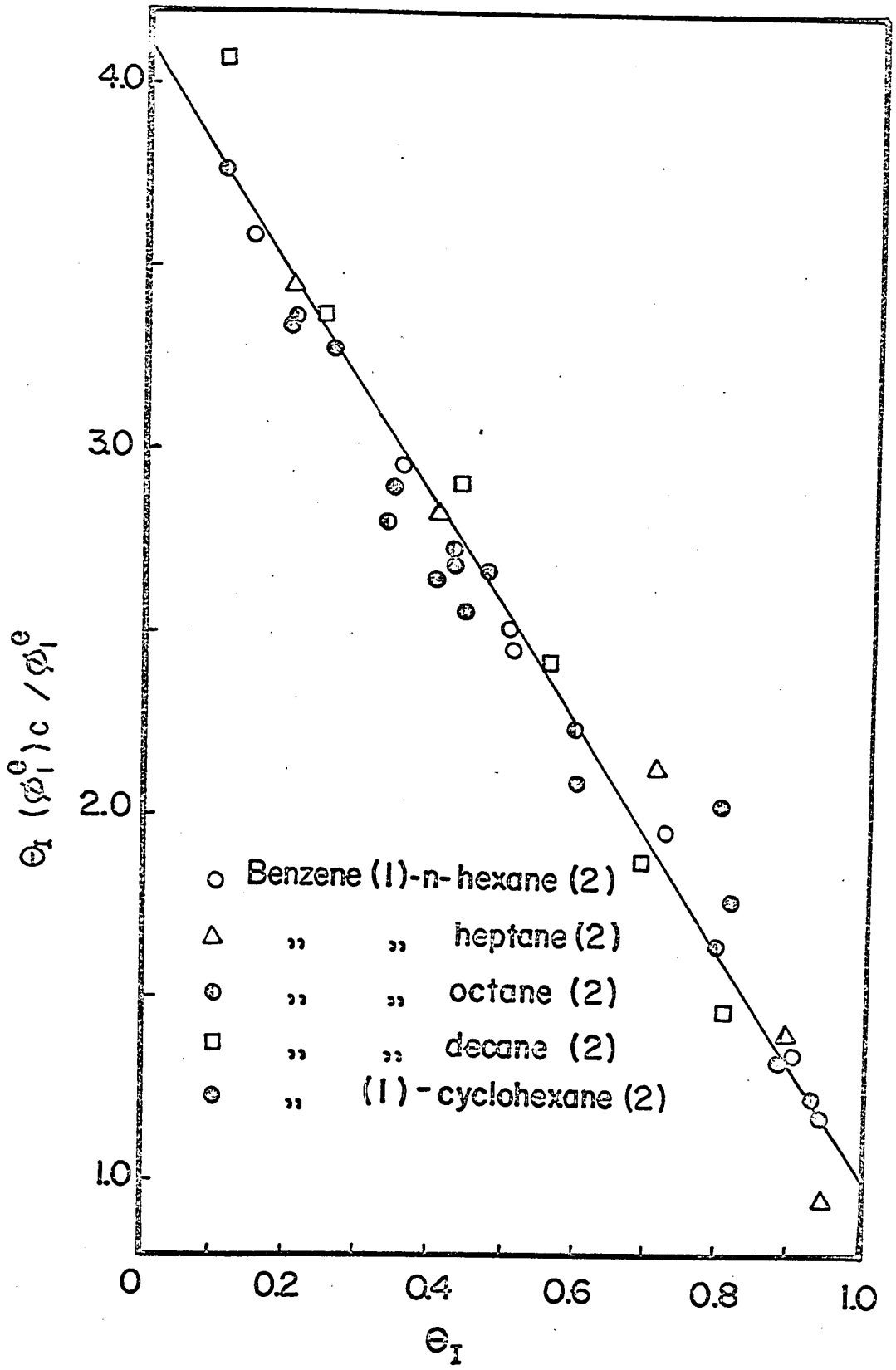


Fig. 37 $\theta_I (\phi_1^e)_c / \phi_1^e$ vs. θ_I. Systems: Benzene - n-alkanes - silica gel; and Benzene - cyclohexane - silica gel, at 25° C

Rearranging Equation 58 and solving for θ_1 gives:

$$\theta_1 = \frac{K_1' \phi_1^e}{(\phi_1^e)_c + (K' - 1)\phi_1^e} \qquad (59)$$

It is found that for the immersion of silica gel in the various binary systems studied, the values of H_1 calculated from Equation 59 are within 2 % of the experimentally determined data, over the range of ϕ_1^e between 0.01 and $(\phi_1^e)_c$.

VII CONCLUSIONS

A. EQUILIBRIUM ADSORPTION

1. The data taken show that the separation factor $K^{(N)}$ in the adsorption of benzene from mixtures with cyclohexane diminishes in the following order:

Adsorbent	$K^{(N)}$	$\leq s(N_2)/m^2/g.$	Preferred Micropore Radius, A^o
silicic acid	20.6	348	40
silica gel	14.2	666	20

The difference in the adsorption properties of the adsorbents used in this investigation may be attributed to different origins of the samples.

2. In the adsorption of mixtures of benzene with n-alkanes on silica gel, the solvent has no effect on the separation factor $K^{(N)}$.

3. The separation factor $K^{(N)}$ for the adsorption from binary liquid mixtures on silica gel diminishes in the following order: benzene-cyclohexane, benzene- n-alkanes.

4. The surface area of adsorbents calculated from the adsorption data for mixtures of benzene with cyclohexane are 80 $m^2/g.$ lower than the surface area determined by nitrogen adsorption.

5. The surface area of a sample of silica gel calculated from the adsorption data for mixtures of benzene with n-alkanes is 70 m^2/g. higher than the surface area determined by nitrogen adsorption.

B. HEATS OF IMMERSION

1. A calorimeter has been constructed and put into operation successfully for the measurements of heats of immersion of silica adsorbents in pure components and in liquid mixtures.
2. Heats of immersion for silica gel containing small quantities of water are markedly lower than those of the evacuated adsorbent in pure components.
3. Absolute heats of immersion of silica and silicic acid are found to be in good agreement for benzene and cyclohexane. In water, however, the value for the silicic acid is 32% higher than that of silica gel.
4. Among the systems investigated only that of benzene - cyclohexane - silicic acid yield values, in agreement with those predicted by Equation 31 for perfect systems.
5. The relative heats of immersion in mixtures of benzene with cyclohexane show no observable difference, within the concentration investigated, between activated and deactivated adsorbents.

6. In mixtures of benzene with cyclohexane, the relative heats of immersion of silicic acid are greater than those of silica gel.

7. The relative heats of immersion of silica gel in mixtures of benzene with n-alkanes decrease with increasing length of the n-alkane chain.

8. Semi-empirical correlations have been obtained for the heats of immersion of silica gel in binary liquid mixtures.

C. OTHERS

1. Correlations are presented for the refractive index of mixtures of hydrocarbons.

2. The heats of mixing of water with methyl alcohol, ethyl alcohol, and isopropyl alcohol at 25° C, were determined as part of the program for testing the reliability of the calorimeter.

3. The heats of mixing of benzene with n-pentane, n-decane, and n-tridecane at 25° C, were determined, in an effort to secure information about the behaviour of mixtures of benzene with n-alkanes.

4. Correlations are presented for the heats of mixing of benzene with n-alkanes and benzene with cyclohexane.

XIII SUGGESTIONS FOR FURTHER WORK

1. The heats of immersion of silicic acid in mixtures of benzene with n-alkanes should be studied to extend the measurements of silica gel in these binary systems. In this way the effect of increased pore diameter on the heats of immersion could be deduced.
2. It is suggested that the effect of degassing temperature on the heats of immersion of silicas in binary liquid mixtures be studied. In this manner the validity of the monomolecular model could be tested further.
3. It is suggested that the effect of temperature on the heats of immersion of silica adsorbents in binary liquid mixtures be studied.
4. Work also should be undertaken in the vapor adsorption of hydrocarbons on silica adsorbents to ascertain the feasibility of calculating the molecular areas of the adsorbates on the surface of the adsorbents.

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XVII APPENDICES

Appendix 1

Adsorption of Nitrogen on Adsorbents

Table 17

Sample: Silica gel A_o

Amount of sample = 224.1 mg.

Degassing temp. 148 °C

P cm.	W^s mg.
0.75	30.9
5.30	47.0
7.45	49.9
10.60	53.4
13.80	56.6

Sample: Silica gel A_o

Amount of sample = 183.0 mg.

Degassing temp. 256 °C

P cm.	W^s mg.
0.54	24.5
3.15	33.8
7.84	40.2
12.35	43.9

Sample: Silica gel A_o

Amount of sample = 204.2 mg.

Degassing temp. 429 °C

P cm.	W^s mg.
0.51	25.8
2.00	33.5
5.10	39.5
7.65	41.4
10.45	45.0
13.00	47.4

Sample: Silica gel A_o

Amount of sample = 256.0 mg.

Degassing temp. 476 °C

P cm.	W^s mg.
0.54	28.4
3.15	41.8
7.84	51.0
12.35	56.5

Table 17 (Continued)

Sample: Silica gel A_0'		Sample: Silica gel A_1	
Amount of sample = 269.5 mg.		Amount of sample = 246.0 mg.	
Degassing temp. 200 °C		Degassing temp. 218 °C	
P cm.	W^B mg.	P cm.	W^B mg.
2.84	45.3	0.51	28.2
6.04	51.6	2.00	35.3
9.67	56.4	5.10	41.4
13.77	59.7	7.65	44.3
17.75	63.3	10.45	47.1
23.77	67.9	13.00	49.3
32.51	72.8		
43.69	76.8		
53.02	78.4		
65.45	79.0		
68.62	79.0		

Table 17 (Continued)

Sample: Silica gel A_1

Amount of sample = 244.7 mg.

Degassing temp. 266 °C

P cm.	W^s mg.
0.54	28.1
3.15	37.7
7.84	43.9
12.35	48.4

Sample: Silica gel A_1

Amount of sample = 283.5 mg.

Degassing temp. 438 °C

P cm.	W^s mg.
0.51	30.8
2.00	49.5
5.10	46.2
7.65	49.6
10.45	52.8
13.00	55.4

Sample: Silica gel A_1

Amount of sample = 250.4 mg.

Degassing temp. 481 °C

P cm.	W^s mg.
0.54	23.2
3.15	33.2
7.84	40.9
12.35	46.0

Sample: Silica gel A_2

Amount of sample = 195.0 mg.

Degassing temp. 198 °C

P cm.	W^s mg.
1.15	25.8
6.18	33.1
9.95	36.8
13.36	38.9

Table 17 (Continued)

Sample: Silica gel A_3		Sample: Silica gel A_4	
Amount of sample = 248.8 mg.		Amount of sample = 242.6 mg.	
Degassing temp. 260 °C		Degassing temp. 148 °C	
P cm.	W^s mg.	P cm.	W^s mg.
1.61	33.2	1.31	31.2
4.42	38.8	5.64	39.2
8.05	43.9	9.60	43.3
10.90	46.4	13.03	46.4
13.28	48.5	21.72	53.1
		33.85	63.5
		40.50	68.1
		58.42	74.8
		71.53	75.0

Table 17 (Continued)

Sample: Silica gel A_5		Sample: Silicic acid B_1	
Amount of sample = 286.0 mg.		Amount of sample = 212.1 mg.	
Degassing temp. 148 °C		Degassing temp. 275 °C	
p cm.	W^s mg.	p cm.	W^s mg.
1.45	30.1	1.84	19.0
4.26	37.9	5.36	22.2
6.82	41.5	9.06	23.8
10.16	44.1	12.70	25.8
16.59	48.9	17.32	27.5
25.10	55.3	24.25	29.8
30.70	59.7	33.29	32.7
40.00	66.7	43.51	35.7
49.57	75.4	52.49	39.2
60.14	84.0	57.94	45.1
69.72	85.9	62.86	49.3
72.90	86.1	66.35	52.6

Table 17 (Continued)

Sample: Silicic acid B_1		Sample: Silicic acid B_2	
Amount of sample = 175.5 mg.		Amount of sample = 274.2 mg.	
Degassing temp. 471 °C		Degassing temp. 196 °C	
P cm.	W^s mg.	P cm.	W^s mg.
2.54	15.5	1.46	23.0
5.12	17.3	5.47	27.1
7.73	19.1	9.05	30.2
11.26	19.7	13.89	32.8

Appendix 2

Refractive Index of binary mixtures

Table 18

CALIBRATION OF REFRACTOMETER

Benzene (1)- Cyclohexane (2)

x_1	n_D^{25}
0.0150	1.42405
0.0352	1.42503
0.0479	1.42564
0.0667	1.42659
0.0967	1.42814
0.0974	1.42820
0.1433	1.43061
0.1580	1.43144
0.2098	1.43433
0.2884	1.43899
0.3503	1.44287
0.4295	1.44822
0.5586	1.45763
0.5970	1.46059
0.6081	1.46141
0.7483	1.47328
0.7553	1.47388
0.8749	1.48504
0.9474	1.49233
0.9500	1.49258

Table 1d (Continued)

CALIBRATION OF REFRACTOMETER

Benzene (1)-n-hexane (2)		Benzene (1)-n-heptane (2)	
x_1	n_D^{25}	x_1	n_D^{25}
0.0245	1.37423	0.0366	1.38750
0.0663	1.37765	0.0632	1.38918
0.1616	1.38581	0.0925	1.39109
0.1943	1.38878	0.1193	1.39288
0.3386	1.40272	0.1920	1.39799
0.4894	1.41935	0.3452	1.41014
0.6482	1.43954	0.4932	1.42400
0.7926	1.46090	0.6420	1.44061
0.9500	1.48821	0.7994	1.46214
		0.9501	1.48789

Table 18 (Continued)

CALIBRATION OF REFRACTOMETER

Benzene (1)-n-octane (2)		Benzene (1)-n-decane (2)	
x_1	n_D^{25}	x_1	n_D^{25}
0.0294	1.39676	0.0384	1.41105
0.0531	1.39796	0.0648	1.41196
0.1031	1.40053	0.1698	1.41591
0.1175	1.40132	0.2426	1.41910
0.1296	1.40200	0.2527	1.41956
0.2087	1.40662	0.3683	1.42545
0.3450	1.41565	0.4232	1.42873
0.4990	1.42808	0.5000	1.43376
0.5770	1.43552	0.6059	1.44198
0.6405	1.44223	0.6461	1.44562
0.8004	1.46257	0.6995	1.45098
0.9468	1.48711	0.8305	1.46703
		0.9484	1.48684

Appendix 3

Heats of mixing data

Systems: Alcohols with water

Table 19

HEATS OF MIXING DATA AT 25° C

Methanol-water
(1) (2)

x_1	ΔH^M cal./mole
0.0287	-46.0
0.0492	-76.8
0.0495	-77.3
0.0674	-98.1
0.0973	-130.6
0.1253	-155.3
0.1463	-169.4
0.1903	-189.6
0.2041	-193.7
0.2463	-202.9
0.3562	-203.7
0.3953	-201.9
0.4689	-191.5
0.5563	-175.4
0.6598	-151.6
0.7883	-114.7
0.7990	-106.8
0.9348	-40.8

Table 19 (Continued)

HEATS OF MIXING DATA AT 25° C

Ethanol-water
(1) (2)

x_1	ΔH^M cal./mole
0.0132	-29.5
0.0172	-38.4
0.0367	-78.5
0.0772	-141.4
0.1442	-181.9
0.2288	-172.0
0.2861	-165.9
0.3366	-138.3
0.3468	-138.2
0.4018	-123.6
0.6008	-77.8
0.7180	-59.6
0.7314	-55.6
0.8070	-49.6
0.8684	-38.4
0.8774	-38.0
0.8807	-35.4
0.9487	-18.1
0.9596	-14.8

Table 19 (Continued)

HEATS OF MIXING DATA AT 25° C

Propanol-2-water
(1) (2)

x_1	ΔH^M cal./mole
0.0275	-78.0
0.0398	-104.8
0.0767	-152.4
0.1090	-155.9
0.1446	-144.4
0.2474	-99.8
0.3079	-72.8
0.4092	-25.9
0.4689	-2.75
0.5525	22.8
0.6074	35.1
0.6529	48.8
0.7224	50.7
0.7559	51.8
0.8988	29.6

Appendix 4

Adsorption on silicas from binary liquid mixtures

Table 20

ADSORPTION ON SILICIC ACID B_1 FROM BINARY LIQUID MIXTURES AT 25°C

Benzene (1) - Cyclohexane (2)

x_1^o	x_1^e	N^o (moles)	W (g.)	$x_1^{(s)}$ (moles/g.) x 10^3
0.0515	0.0425	0.08478	1.3776	0.54
0.1433	0.1211	0.07526	2.1837	0.76
0.2884	0.2724	0.07028	1.5132	0.74
0.6081	0.5967	0.08155	2.0206	0.46
0.7553	0.7483	0.09001	2.1941	0.29
0.8749	0.8710	0.08844	2.2966	0.15

Table 21

ADSORPTION ON SILICA GEL A_o' FROM BINARY LIQUID MIXTURES AT 25°C

Benzene (1)-Cyclohexane (2)

x_1^o	x_1^e	N^o (moles)	W (g.)	$\Lambda_1^{(N)}$ (moles/g.) x 10^3
0.1433	0.0953	0.07447	2.8480	1.26
0.2884	0.2331	0.06807	2.6838	1.40
0.6081	0.5901	0.10020	2.0655	0.87
0.7553	0.7372	0.08998	2.7278	0.60
0.8749	0.8659	0.08874	2.7159	0.29

Table 22

ADSORPTION ON SILICA GEL A_o' FROM BINARY LIQUID MIXTURES AT 25° C

Benzene (1)-n-alkanes (2)

x_1^o	x_1^e	N^o (moles)	W (g.)	$z_1^{(N)}$ (moles/g.) x 10^3	carbons in n-alkane
0.0648	0.0266	0.04767	2.7701	0.65	10
0.1175	0.0513	0.04072	2.8253	0.95	8
0.1193	0.0636	0.05364	2.8775	1.04	7
0.1616	0.1030	0.06450	2.8935	1.31	6
0.2527	0.1632	0.04690	2.8710	1.46	10
0.3383	0.2672	0.06234	2.9349	1.51	7
0.4232	0.3210	0.04276	3.0103	1.45	10
0.5770	0.5179	0.05932	2.8247	1.24	8
0.6461	0.5884	0.06419	3.4379	1.08	10
0.7154	0.6849	0.08572	3.2356	0.81	7

Appendix 5

Heats of Immersion of adsorbents

in

binary liquid mixtures

Table 23

HEATS OF IMMERSION DATA AT 25°C

System: Benzene (1)-Cyclohexane (2)-Silicic Acid B_2

x_1^o	x_1^e	N^o (moles)	W (g.)	$-H_I$ (cal./g.)
0.0000	0.0000	0.07673	0.5500	3.5
0.0293	0.0270	0.06351	0.3985	4.9
0.0607	0.0592	0.06607	0.1917	5.9
0.1008	0.0964	0.06697	0.4181	6.3
0.2038	0.2022	0.11754	0.2271	7.0
0.3435	0.3416	0.11639	0.3044	7.2
0.5044	0.5032	0.12165	0.2381	7.4
0.7637	0.7632	0.12670	0.2049	7.5
0.9474	0.9474	0.15194	0.1955	7.6
1.0000	1.0000	0.15277	0.2532	7.6

Table 24

HEATS OF IMMERSION DATA AT 25°C

System: Benzene (1)-Cyclohexane (2)-Silica Gel A_5

x_1^o	x_1^e	N^o (moles)	W (g.)	$-H_I$ (cal./g.)
0.0000	0.0000	0.07978	0.3351	5.2
0.0453	0.0441	0.13062	0.2783	6.8
0.0990	0.0969	0.12836	0.3118	8.1
0.2132	0.2114	0.11639	0.2158	10.1
0.3503	0.3475	0.12080	0.3669	10.6
0.5586	0.5536	0.08777	0.6550	11.1
0.7478	0.7470	0.12551	0.4117	11.3
1.0000	1.0000	0.15767	0.2605	11.3

Table 25

HEATS OF IMMERSION DATA AT 25°C

System: Benzene (1) - Cyclohexane (2) - Silica Gel A_3

x_1^o	x_1^e	M^o (moles)	W (g.)	$-H_I$ (cal./g.)
0.0000	0.0000	0.12434	0.3310	6.3
0.0352	0.0330	0.11388	0.3615	7.7
0.0667	0.0649	0.12700	0.2327	8.7
0.0974	0.0825	0.06308	0.9510	9.1
0.0967	0.0873	0.06689	0.6197	9.3
0.0976	0.0942	0.11280	0.3417	9.4
0.1580	0.1550	0.13494	0.3310	10.5
0.2478	0.2443	0.11422	0.3467	12.0
0.4166	0.4115	0.07140	0.3455	12.9
0.7483	0.7475	0.12969	0.2933	13.2
1.0000	1.0000	0.13514	0.2616	13.3

Table 26

HEATS OF IMMERSION DATA AT 25°C

System: Benzene-Cyclohexane-Silica Gel

x_1^o	x_1^e (calcd.)*	N^o (moles)	W (g.)	$-H_I$ (cal./g.)
A_{1a}				
0.0000	0.0000	0.10887	0.2932	6.1
0.0627	0.0549	0.06564	0.6274	8.8
0.1251	0.1204	0.07945	0.3325	10.0
0.2300	0.2424	0.07033	0.4388	12.2
0.7502	0.7474	0.14961	0.8513	13.4
1.0000	1.0000	0.13181	0.3062	13.4
A_{1b}				
0.0000	0.0000	0.07930	0.6532	6.0
0.3779	0.3720	0.06603	0.3465	10.8
0.4984	0.4922	0.07349	0.4816	11.1
0.6176	0.6138	0.07547	0.3934	11.4
0.8707	0.8689	0.07207	0.5053	11.4
1.0000	1.0000	0.09575	0.7574	11.5

* Equilibrium mixtures were analyzed in an Abbe 3L, Bausch and Lomb refractometer. Presently reported values of x_1^e were calculated from Equation 21, assuming the following:

$$\bar{\sigma}_{s(L)} = 516 \ m^2/g., \text{ and}$$

$$K^{(N)} = 14.2$$

Table 27

HEATS OF IMMERSION DATA AT 25° C

System: Benzene (1)-n-Hexane (2) - Silica Gel

x_1^o	x_1^e	N^o (moles)	W (g.)	$-H_I$ (cal./g.)
A_1				
0.0000	0.0000	0.05536	0.4548	7.8
0.0345	0.0220	0.06580	0.3785	8.7
0.0663	0.0642	0.09967	0.2298	10.0
0.1943	0.1906	0.11290	0.3189	12.3
0.3386	0.3286	0.06040	0.4598	13.4
0.4894	0.4828	0.06364	0.3801	13.8
0.7926	0.7904	0.07331	0.3259	14.0
1.0000	1.0000	0.13743	0.4585	14.0
A_{4b}				
0.0000	0.0000	0.04813	0.5013	7.2*
0.1080	0.1052	0.10680	0.2834	10.1
1.0000	1.0000	0.13790	0.2876	13.0
A_2				
0.0000	0.0000	0.10880	0.2882	7.8
0.1185	0.1095	0.05742	0.4545	10.8
1.0000	1.0000	0.15280	0.4389	13.7

* n-decane value

Table 28

HEATS OF IMMERSION DATA AT 25° C

System: Benzene (1)-n-Heptane (2)-Silica Gel A_2

x_1^o	x_1^e	N^o (moles)	W (g.)	$-H_I$ (cal./g.)
0.0000	0.0000	0.04803	0.3487	7.8
0.0366	0.0354	0.09160	0.2061	9.0
0.0925	0.0848	0.05049	0.3854	10.2
0.1920	0.1889	0.10333	0.2430	12.0
0.3452	0.3387	0.06506	0.3239	13.1
0.4932	0.4915	0.10260	0.1626	13.4
0.6420	0.6402	0.11183	0.2569	13.6
0.7994	0.7958	0.13390	0.1791	13.7
1.0000	1.0000	0.09502	0.3802	13.7

Table 27

HEATS OF IMMERSION DATA AT 25° C

System: Benzene (1)-n-Octane (2)-Silica Gel

x_1^o	x_1^e	N^o (moles)	W (g.)	$-H_1$ (cal./g.)
A_{4a}				
0.0000	0.0000	0.04370	0.2622	7.1
0.0282	0.0226	0.04276	0.5874	7.7
0.0531	0.0502	0.07697	0.3182	8.3
0.3450	0.3392	0.09571	0.4487	11.7
0.4990	0.4934	0.09443	0.5282	12.5
0.6405	0.6378	0.11490	0.4015	12.7
0.8004	0.7980	0.06774	0.3627	12.8
0.9468	0.9466	0.13070	0.2349	12.8
1.0000	1.0000	0.09197	0.5279	12.9
A_2				
0.0000	0.0000	0.10880	0.2882	7.8*
0.1031	0.0964	0.04578	0.3380	7.8
0.1296	0.1222	0.07926	0.4298	10.3
0.2087	0.2009	0.05736	0.3361	11.3
1.0000	1.0000	0.15280	0.4989	13.7

* n-hexane value

Table 33

HEATS OF IMMERSION DATA AT 25°C

System: Benzene (1)-n-Decane (2)-Silica Gel

x_1^o	x_1^e	N^o (moles)	W (g.)	$-H_I$ (cal./g.)
A_{4b}				
0.0000	0.0000	0.04813	0.5013	7.2
0.0867	0.0833	0.07600	0.2707	8.6
0.1698	0.1645	0.07960	0.3429	9.7
0.3693	0.3611	0.07550	0.4489	11.2
0.5000	0.4953	0.09417	0.4363	11.9
0.6995	0.6973	0.10050	0.3475	13.0
0.8395	0.8293	0.12530	0.3739	13.2
0.9484	0.9478	0.14280	0.3475	13.0
1.0000	1.0000	0.15790	0.2876	13.0
A_2				
0.0000	0.0000	0.04344	0.5420	7.8
0.0384	0.0299	0.03680	0.4834	8.4
0.2527	0.2451	0.06971	0.3906	11.1
1.0000	1.0000	0.15280	0.4989	13.7

Appendix 6

Heats of mixing of benzene

with

n-alkanes

HEATS OF MIXING, AT 25° C

Benzene with n-alkanes

Data on heats of mixing of the following systems (64)

Benzene- n-Pentane

Benzene- n-Decane

Benzene- n-Tridecane

were critically reviewed and are given in Tables 31-33.

The following equation

$$\frac{x_1 x_2}{\Delta H^{E}} = A + A' x_1 \qquad (60)$$

was used successfully to correlate this data for the systems studied. This equation was also found to be applicable to the fitting of published data on the heats of mixing of a series of binary mixtures of benzene with normal alkanes and of benzene with cyclohexane. The values of the constants and the average deviations are given in Table 34.

Heats of mixing calculated, at a number of mole fractions, from these equations were used to construct the curves in Fig. 38. The calculated values of $x_1 x_2/\Delta H^{E}$ were plotted as a function of x_1 in Fig. 39 for mixtures of benzene with n-alkanes, where the experimental points have been omitted for the sake of clarity.

It is observed that the partial molal heats of dilution at infinite dilution of benzene are the same for all the mixtures of benzene

Table 31

HEATS OF MIXING DATA AT 25° C

Benzene (1)-n-pentane (2)

x_1	ΔH^M cal./mole
0.1516	94.8
0.2447	143.0
0.3985	193.1
0.5632	211.7
0.9668	31.1

Table 32

HEATS OF MIXING DATA AT 25° C

Benzene (1)-n-decane (2)

x_1	ΔH^M cal./mole
0.2283	141.5
0.3663	207.8
0.4835	251.2
0.6831	249.5
0.6913	248.4
0.8088	202.3
0.8340	188.5
0.9567	62.7

Table 33

HEATS OF MIXING DATA AT 25° C

Benzene (1)-n-tridecane (2)

x_1	ΔH^M cal./mole
0.2609	161.4
0.2881	177.9
0.3896	232.2
0.4153	243.5
0.5968	286.3
0.8353	214.6
0.8644	192.4
0.9643	65.8
0.9649	64.7

Table 34

CONSTANTS OF EQUATION 60 FOR THE HEATS OF MIXING OF BENZENE WITH NORMAL-ALKANES AND BENZENE WITH CYCLOHEXANE, AT 25° C

Mixture (1)	(2)	Ref.	$A \times 10^3$	$-A' \times 10^4$	Av.D., %**	Max.D., %***
Benzene-	n-Pentane	(*)	1.393	3.844	1.0	1.2
Benzene-	n-Hexane	(65)	1.400	4.758	1.3	3.4
Benzene-	n-Hexane	(66)	1.370	4.488	1.6	4.2
Benzene-	n-Heptane	(66)	1.397	5.422	1.1	2.8
Benzene-	n-Heptane	(67)	1.377	5.139	0.6	1.4
Benzene-	n-Octane	(66)	1.452	6.955	0.3	1.0
Benzene-	n-Nonane	(66)	1.404	7.127	0.4	1.1
Benzene-	n-Decane	(*)	1.409	7.973	1.1	3.0
Benzene-	n-Tridecane	(*)	1.403	9.166	1.6	2.6
Benzene-	n-Hexadecane	(67)	1.265	8.258	0.6	2.4
Benzene -	Cyclohexane	(66)	1.385	1.420	1.3	3.0
Benzene -	Cyclohexane	(68)	1.409	0.977	1.3	2.4
Benzene -	Cyclohexane	(69)	1.439	1.852	1.6	5.6
Benzene -	Cyclohexane	(67)	1.375	1.467	0.7	1.2

* This work

** Av.D. = $\leq$ (d)/n, average deviation; where d is the difference (without sign) between the observed value and the calculated value of a single observation and n is the number of observations.

*** Max.D. = Maximum deviation (without sign) of any one value within a set of data for a binary system.

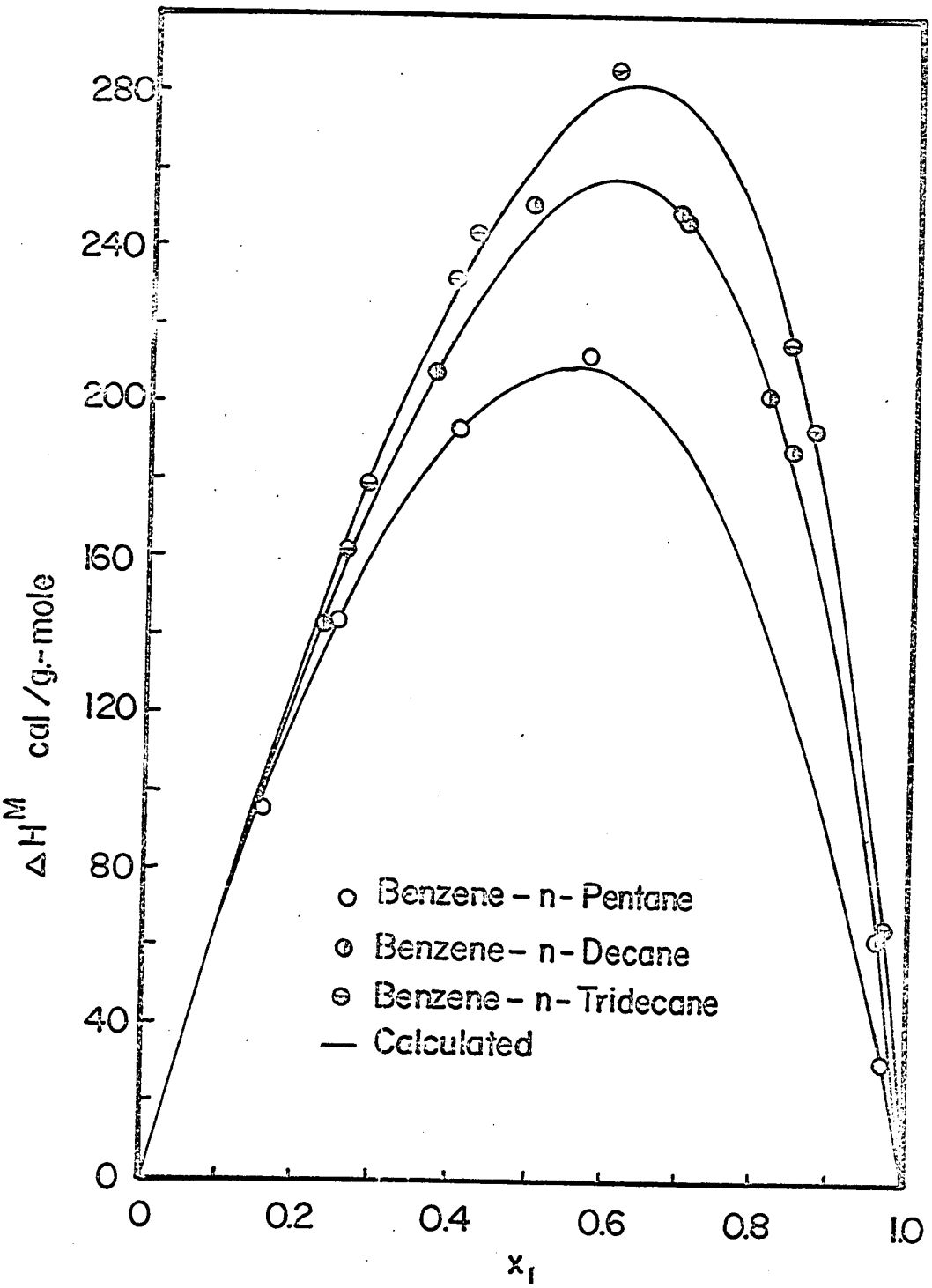

Fig. 38 Heats of mixing at 25°C. Systems: Benzene - n-pentane; benzene - n-decane; and benzene - n-tridecane

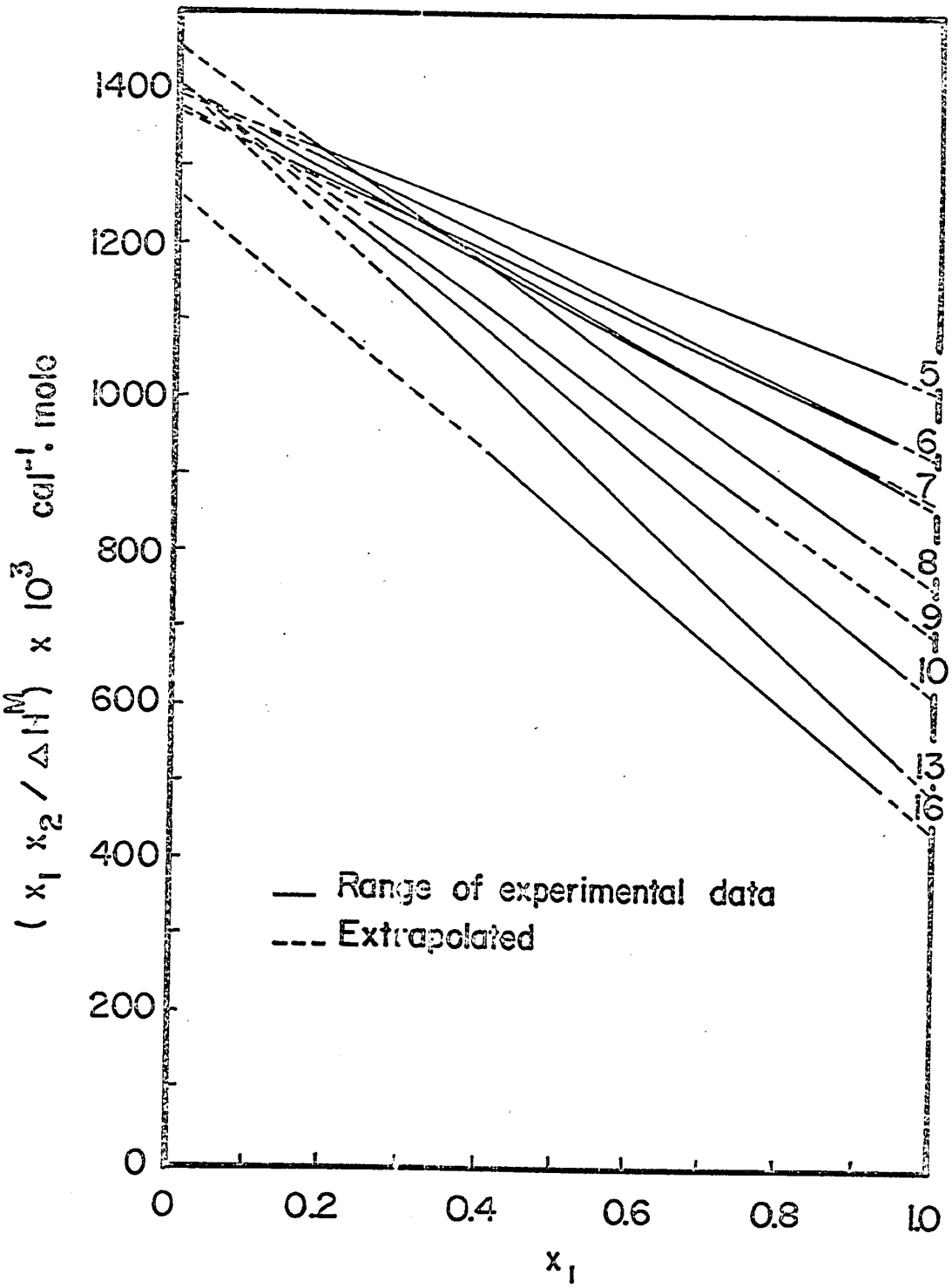

Fig. 39 Heats of mixing at 25° C. Systems: Benzene - n-alkanes

with n-alkanes having a chain length ranging from 5 to 13 carbons, namely, $1/1.400 \times 10^{-3} = 714$ cal./mole. The average deviation is 1.1%.

The partial molal heats of dilution at infinite dilution of n-Alkane increases as the chain length increases, from 990 cal./mole for n-pentane to 1630 cal./mole for n-tridecane.

A similar behavior of the partial molal quantities at infinite dilution has been reported by Otterstedt and Missen (70) for binary mixtures of n-alcohols with carbon tetrachloride. They found that the partial molal heat of dilution at infinite dilution of carbon tetrachloride is 5 K cal./mole and that the partial molal heat of dilution at infinite dilution of alcohol increases as the chain length increases. These authors regard carbon tetrachloride as "inert" solvent for the alcohols at infinite dilution.

An attempt was made to use volume fraction instead of mole fraction in Equation (60). It was found that for all the mixtures of benzene with n-alkanes and benzene with cyclohexane, the following one constant equation may be used for representing the data

$$\frac{\phi_1 \phi_2}{\Delta H^{M}} = A'' \qquad (61)$$

The A'' values obtained are listed in Table 35. The average deviation for a system varied from 0.5% to 2.2%.

Table 35

CONSTANTS OF EQUATION 61 FOR THE HEATS OF MIXING OF BENZENE WITH N-ALKANES AND BENZENE WITH CYCLOHEXANE, AT 25°C

Mixture (1) (2)	Ref.	A''	Av.D., %	Max.D., %
Benzene- n-Pentane	(*)	0.1216	1.7	3.2
Benzene- n-Hexane	(65)	0.1238	1.5	4.6
Benzene- n-Hexane	(66)	0.1218	1.7	4.1
Benzene- n-Heptane	(66)	0.1255	1.1	2.9
Benzene- n-Heptane	(67)	0.1252	0.8	1.5
Benzene- n-Octane	(66)	0.1272	0.9	3.0
Benzene- n-Nonane	(66)	0.1250	0.5	1.2
Benzene- n-Decane	(*)	0.1232	1.2	3.2
Benzene- n-Tridecane	(*)	0.1226	1.6	4.3
Benzene- n-Hexadecane	(67)	0.1209	2.2	4.7
Benzene - Cyclohexane	(66)	0.1295	2.5	6.7
Benzene - Cyclohexane	(68)	0.1342	1.7	5.4
Benzene - Cyclohexane	(67)	0.1323	1.7	4.7
Benzene - Cyclohexane	(67)	0.1289	1.4	4.4

* this work

The heats of mixing for benzene with n-alkanes may be represented by the universal constant 0.1236 cc/cal. or 8.09 cal./cc. obtained by averaging the values of A''. The average deviation for a system varied from 1.2 to 3.0%, as shown in Table 36.

Table 36

ACCURACY OF HEATS OF MIXING OF BENZENE WITH N-ALKANES, USING EQUATION 61 WITH A_{12} = 0.1236

Mixture (1) (2)	Ref.	Av. D., %	Max. D., %
Benzene- n-Pentane	(*)	2.2	4.6
Benzene- n-Hexane	(65)	1.4	4.7
Benzene- n-Hexane	(66)	1.7	5.7
Benzene- n-Heptane	(66)	1.6	4.3
Benzene- n-Heptane	(67)	1.4	2.5
Benzene- n-Octane	(66)	2.8	4.3
Benzene- n-Nonane	(66)	1.2	1.8
Benzene- n-Decane	(*)	1.5	2.8
Benzene- n-Tridecane	(*)	2.1	3.5
Benzene- n-Hexadecane	(67)	3.0	7.8

* this work

Appendix 7

SAMPLE CALCULATION FOR

HEAT OF IMMERSION

A sample calculation for heat of immersion is given for the immersion of 0.4834 grams of silica gel A_3 in a binary mixture of benzene and cyclohexane of concentration 0.2478 mole fraction benzene, at 25° C.

1. *Weighings*

a.	weight of mixing cell	99.3649	g.
b.	weight of mixing cell + silica gel (in small compartment)	99.6919	g.
c.	weight of mixing cell + silica gel + binary mixture (in large compartment)	109.1346	g.
d.	weight W of silica gel	0.3267	g.
e.	weight of binary mixture	9.4427	g.
f.	average molecular weight of the binary mixture	82.672	g./mole
g.	binary mixture in cell	0.11422	moles

2. Estimation of the change of temperature on immersion

a.	thermistor resistance prior to the rupture of the diaphragm	1705.5	ohms
b.	resistance change of the thermistor on immersion, corrected for heat exchange with the surroundings and for stirring	18.8	ohms
c.	corrected final resistance of the thermistor = (1705.5 - 18.8) ohms=	1686.7	ohms
d.	average resistance = (1705.5 + 1686.7)/2 ohms =	1696.1	ohms

e.	slope of the thermistor in ohms/°C, at the value of the average resistance	63.45	ohms/°C
f.	temperature change on immersion = 18.8/63.45°C	0.296	°C

3. Electrical calibration of mixing cell and contents

a.	thermistor resistance prior to energizing the coil	1711.2	ohms
b.	thermistor resistance at the beginning of the electrical calibration period	1710.6	ohms
c.	resistance change of the thermistor on calibrating, corrected for heat exchange with the surroundings and for stirring	20.0	ohms
d.	corrected final resistance of the thermistor	1690.6	ohms
e.	average resistance = (1710.6 + 1690.6)/2 ohms =	1700.6	ohms
f.	slope of the thermistor in ohms/°C at the value of the average resistance	63.73	ohms/°C
g.	temperature change on calibrating (20.0/63.73)°C	0.314	°C
h.	potential drop (E) across the standard resistor $(SR\,2)_c$	3.4685	volts
i.	resistance (R_H) of the calorimeter heater	20.899	ohms
j.	heating time (t)	108.4	sec.
k.	electrical energy input = $\frac{I^2 \times R_H \times t}{4.184}$ =	4.177	cal.
l.	heat capacity of the mixing cell and contents = (4.177/0.314) cal./°C	13.30	cal./°C

4. Heat evolved on immersion Q_I

a. $-Q_I$ = (0.296 x 13.30) cal. = 3.937 cal.

b. also, the heat effect on immersion may be calculated directly from the corrected changes of resistance of the thermistor on immersion and on calibrating, and from the electrical energy input

$$-Q_I = 18.8 \text{ ohms} \times \frac{4.177 \text{ cal.}}{20.0 \text{ ohms}} = 3.926 \text{ cal.}$$

c. the difference between the values of Q_I calculated by these methods is 0.28 %

d. Heat of immersion, in calories per gram of adsorbent,

$$-H_I = \frac{Q_I}{W} = \frac{3.926}{0.3267} = 12.0 \text{ cal./g.}$$

5. Determination of the equilibrium concentration of the binary mixture

weight of calorimeter + contents (at the end of the experiment) 109.1415 g.

losses nil

refractive index (n_L) of the equilibrium mixture 1.43635

the concentration of the equilibrium mixture was obtained by solving the following equation for the positive square root of x_1

$$\frac{x_1^e \; x_2^e}{n_D - x_1^e(n_D^o)_1 - x_2^e(n_D^o)_2} = -37.200 + 6.8000 \; x_1^e$$

$$x_1^e = 0.2443$$

6. **Heat of dilution effect**

$$H_{dil.} = \left[(\Delta H^M)^e - (\Delta H^M)^o\right]\frac{N^o}{W} + \left[(\Delta H^M)^a - (\Delta H^M)^e\right] N^a$$

at $x_1^o = 0.2478$

The heats of mixing were calculated from data for this system (67) fitted into Equation 64, as shown in Appendix 6.

$$(\Delta H^M)^o = \frac{0.2478 \times 0.7522}{0.001375 - 0.0001467 \times 0.2478} = 139.2 \text{ cal./mole}$$

at $x_1^e = 0.2443$ $\qquad (\Delta H^M)^e = 137.9$ cal./mole

a. **Monomolecular model**

$$x_1^a = \frac{\kappa^{(N)} x_1^e / x_2^e}{1 + \kappa^{(N)} \frac{x_1^e}{x_2^e}} = \frac{14.2 \times 0.2443 / 0.7557}{1 + 14.2 \times \frac{0.2443}{0.7557}}$$

$x_1^a = 0.821$

at $x_1^a = 0.821$ $\qquad (\Delta H^M)^a = 117.1$ cal./mole

$$\leq_{s(L)} = \leq_{s(N_2)} - 80 = 575 - 80 = 495 \text{ m}^2/\text{g}.$$

$$N^a = \frac{\leq_{s(L)}}{\phi} = \frac{495}{241 \times 10^3} = 0.00205 \text{ mole/g}.$$

$$H_{dil.} = (137.9 - 139.2) \times \frac{0.11422}{0.3267} + (117.1 - 137.9) \times 0.00205$$

$$H_{dil.} = -0.50 \text{ cal./g}.$$

$$\frac{H_{dil.}}{H_1} \times 100 = \frac{0.50}{12.0} \times 100 = 4.2\%$$

Similarly, when

$$N^a = \frac{\leqslant_{s(N_2)}}{241 \times 10^3} \; ; \; \frac{H_{dil.}}{H_I} \times 100 = 4.2\%$$

b. Multimolecular model

$$x_1^a = \frac{x_1^e + \frac{\tilde{V}_2}{V_p} \times X_1^{(N)}}{1 + \frac{(V_2 - V_1)}{V_p} \times X_1^{(N)}}$$

The value of $X_1^{(N)}$ was calculated from Equation 21 for silica gel A_o' in mixtures of benzene with cyclohexane corrected for the differences in surface area of samples A_o' and A_3

$$x_1^{(N)} = \frac{x_1^e (1 - x_1^e)}{30.9 + 410\, x_1^e} \times \frac{495}{586}$$

where 495 and 586 are the $\leqslant_{s(L)}$ of samples A_3 and A_1', respectively

$$X_1^{(N)} = \frac{0.2443 \times 0.7557}{30.9 + 410 \times 0.2443} \times \frac{495}{586} = 0.00119 \quad \text{mole/g.}$$

$$X_1^a = \frac{0.2443 + \frac{108.744}{0.37} \times 0.00119}{1 + \frac{(108.744 - 89.401)}{0.37} \times 0.00119} = 0.559$$

at $x_1^a = 0.559$ $\quad (\Delta H^{1/4})^a = 190.3$ cal./mole

$$H_{dil.} = (137.9 - 139.2) \times \frac{0.11422}{0.3267} + (196.3 - 137.9) \times 0.00378$$

$$H_{dil.} = -0.26 \text{ cal./g.}$$

$$\frac{H_{dil.}}{H_I} \times 100 = \frac{0.26}{12.0} \times 100 = 2.2\%$$

Appendix 8

THERMISTORS

Thermistors are thermally sensitive resistors whose resistance decreases exponentially with increased temperature,

$$\frac{R}{R^{o}} = e^{\beta (1/T - 1/T^{o})} \tag{62}$$

where R is the thermistor resistance, in ohms, at temperature T °K;

R^{o} is the thermistor resistance, in ohms, at temperature T^{o} °K; and

β is the work function, in °K.

Over a limited temperature range, β may be considered constant and may be used in Equation 62 for interpolation purposes.

An important distinction between thermistors and other resistance materials is the extreme sensitivity of thermistors to relative minute changes of temperature. The change of thermistor resistance with temperature is obtained by differentiating Equation 62 with respect to T,

$$\frac{dR}{dT} = \frac{\beta \times R}{(T)^{2}} \tag{63}$$

The temperature coefficient of resistance (α) is the ratio of dR/dT to the resistance of the thermistor at a specified temperature,

$$\alpha = \frac{1}{R} \cdot \frac{dR}{dT} = \frac{\beta}{T^{2}} \tag{64}$$

Table 37 shows the values of β determined by the least square technique from calibrations of thermistor resistance as a function of temperature, in the temperature range between 24 and 29° C in steps of about 1° C. Also shown on the same table are the values of α at 25° C.

Table 37

THERMISTOR CHARACTERISTICS

Thermistor No.	Resistance at 25° C ohms	β °K	α ohms/100 ohms/° C
1	978.0	3402	3.827
2	1036.6	3019	3.396
3	2090.1	3503	3.940
4	1836.2	3446	3.876
5	1935.2	3439	3.868
6	1889.8	3400	3.885
7	1024.1	3449	3.880
8	1987.5	3258	3.665
9	1052.1	3460	3.892

Appendix 9

List of

Equipment items

and

Manufacturer or Supplier

ITEM		MANUFACTURER OR SUPPLIER
1.	**Chemicals**	
a.	Silica gel, Davidson 28-200 mesh.	Fisher Scientific Co., Ltd., Fair Lawn, N.J.
b.	Silicic acid, 'Baker Analyzed' Reagent.	Baker Chemical Co., Phillipsburg, N.J.
c.	Gases	Union Carbide Ltd., Linde Gases Division, Ottawa, Ontario.
d.	Benzene, Cyclohexane, Methyl alcohol, Isopropyl alcohol, Spectroquality Reagent, 99 mole %.	Matheson, Coleman and Bell, Norwood (Cincinnati), Ohio.
e.	Ethyl alcohol, 'Pure Absolute', 99 mole %.	Consolidated Alcohols Ltd., P.O. Box 372, Terminal "A", Toronto, Ontario.
f.	n-Pentane, n-Octane, n-Decane, n-Tridecane, 'Pure Grade', 99 mole %.	Phillips Petroleum Co., Special Products Division, Bartlesville, Oklahoma.
g.	n-Hexane, n-Heptane, Toluene, Research Grade, 99.9 mole %.	Phillips Petroleum Co., Special Products Division, Bartlesville, Oklahoma.
h.	Nitric Acid, Reagent.	The McArthur Chemical Co., Ltd., Montreal, Quebec.
2.	**Thermal degassing of adsorbents**	
a.	Oven, temperature controlled within 2° C., Cat. No. 13-245-1.	Fisher Scientific Co., Ltd.
b.	Pirani and Penning heads.	Edwards High Vacuum Canada Ltd., P.O. Box 15, Burlington, Ontario.
c.	Vacuum pump, High Vacuum, Mechanical and Diffusion Type, Two stage, Welch Duo-Seal. Cat. No. 1-102V1	Fisher Scientific Co., Ltd.

ITEM		MANUFACTURER OR SUPPLIER
3. Surface Area Measurements		
a.	Quartz springs and quartz pans.	Worden Laboratory, 695 Rocky River, Huston 27, Texas.
b.	Pirani and Penning heads.	Edwards High Vacuum.
c.	Pirani-Penning Type, Gauge Model 2.	Edwards High Vacuum.
d.	Vacuum pump Cat. No. 1-102. V1.	Fisher Scientific Co., Ltd.
e.	Temperature Controller Type PT 4004 RE/52C.	Phillips Electronics Equipment Ltd., 5800 Cote de Liesse Road, Montreal, Quebec.
f.	Cathetometer Cat. No. 2207.	Wild of Canada Ltd., 881 Lady Ellen Place, Ottawa, Ontario.
4. Refractive Index Measurements		
a.	Precision Refractometer, Cat. No. 33-45-03.	Bausch and Lomb, Optical Company, Rochester 2, N. Y.
b.	Haake Ultratherm Pump, Cat. No. 13-874-110.	Fisher Scientific Co., Ltd.
c.	Centrifuge, International Clinical Model, Cat. No. 5-101.	Fisher Scientific Co., Ltd.
d.	Balance Gramatic, precision of $\pm$ 0.1 mg., Cat. No. 1-910-4 X 3.	Fisher Scientific Co., Ltd.
5. Mixing Cells		
a.	O-rings.	Precision Rubber Product Co., Ste Therese de Blainville, Quebec.
b.	Tin foil and teflon.	Camus Equipment Ltd., 340 Gladstone Ave., Ottawa 2, Ontario.

ITEM	MANUFACTURER OR SUPPLIER
5. Mixing Cells (Continued)	
c. Thermistors, Veco, Cat. No. 32A12, 31A2, 32A75.	Rocke International Corp., 13 East 40th Street, New York 16, N. Y.
d. Manganin wire, size 26, about 1.1 ohms/foot.	Hawkesbury Wire Co., Ltd., Hawkesbury, Ontario.
6. Jackets	
a. Hermetic seals, Cat. No. 406/8/C.	Quality Hermetics Ltd., 45 Hollinger Rd., Toronto, Ontario.
7. Thermostatic Bath	
a. Thermoregulator, Rotostat, Differential, Cat. No. 15-180-15.	Fisher Scientific Co., Ltd.
b. Transistor Relay, Cat. No. 13-991-80-V2.	Fisher Scientific Co., Ltd.
c. Stirrers, heavy duty, variable speed, non-sparking.	Canadian Laboratory Supplies, Ltd., Toronto, Ontario.
d. Heaters, Immersion, 750 watts, Cat. No. 11-463-5V4.	Fisher Scientific Co., Ltd.
8. Calorimeter Vacuum System	
a. Vacuum pump.	Fisher Scientific Co., Ltd.
b. Metal to glass seal.	The C. H. Johns Glass Co., Ltd., 219 Broadview Avenue, Toronto 8, Ontario.
c. Vacustat 2G, range 1 to 10^{-3} mm/Hg.	Edwards High Vacuum, Canada Ltd.

ITEM	MANUFACTURER OR SUPPLIER
9. Thermistor Circuit	
a. Wheatstone bridge S.K. 4970.	Tinsley Instruments, Smith Falls, Ontario.
b. 2-volt batteries, 'Exide Type', Cat. No. 52819.	Keyes Supplies Co., Ltd., 80 Bayview Road, Ottawa, Ontario.
c. K - 3 Potentiometer.	Leeds and Northrup Canada Ltd., 465 Victoria Avenue, St. Lamber, Montreal, Quebec.
d. Electronic D.C. Null Detector, Cat. No. 9834-1.	Leeds and Northrup of Canada Ltd.
e. Recorder, Speedomax H, response time: 1 sec., chart speed: 60 in./hr.	Leeds and Northrup of Canada Ltd.
10. Heater Circuit	
a. Volt box, Cat. No. 83417	Central Scientific Co. of Canada Ltd., Ottawa, Ontario.
b. Galvanometer, type SR4, sensitivity: 200 mm/μa.	Tinsley Instruments Ltd., Smith Falls, Ontario.
c. Precision electric timer.	Precision Scientific Co., Chicago, Ill.
d. Standard cell, saturated type 1149.	Tinsley Instruments Ltd.
e. Connectors.	Cesco Electronics Ltd., 1300 Carling Avenue, Ottawa, Ontario.
11. Coil circuit	
a. Bodine Motor, type M NYC 13R.	Foxboro Co., Foxboro, Mass.
b. Microswitch, 10A 125/250 VAC, Licom 11-204.	Licon, Chicago, Ill.