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ADSORPTION OF GASES ON
HETEROGENEOUS SURFACE

by

Karan S. Gaur

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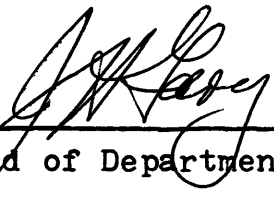
A Thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science in Chemical and Petroleum Refining Engineering.

Signed: 
Karan S. Gaur

Golden, Colorado

Date: may 19, 1971

Approved: 
Thesis Advisor


Head of Department

Golden, Colorado

Date: may 19, 1971

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A static system was used to measure the pure component isotherms of freon-21(CHFCl_2) and ethyl chloride. The measurements were made at 323°K and at pressure range from 0 to 695 mm of mercury. Binary mixture measurements were also made at the same temperature and at the system pressure of 560 mm of mercury. The simplified method of Kidnay and Myers was used to predict mixture isotherms using only the pure component isotherms.

Affectionately
to
my mother

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A C K N O W L E D G M E N T S

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I N T R O D U C T I O N

Adsorption has been an important method of commercial and laboratory separations. Solid adsorbents are commonly employed in industrial catalytic reactors. The surfaces of these adsorbents are heterogeneous with respect to their adsorption potential; that is the interaction energy between an adsorbed molecule and its surface site is not uniform over the surface. Homogeneous surfaces are of interest mainly for fundamental research and for theoretical purposes. These surfaces are of no commercial interest. Heterogeneity is of major importance in the monolayer region of adsorption, since it is in this region that molecules come in direct contact with the adsorbing surface.

Many studies have been made of physical adsorption of pure gases on solid surfaces, and attempts to extend such studies to gaseous mixtures have also received much attention. Only relatively few papers are to be found in literature which discuss mixture adsorption equilibria.

During the past, mixed gas adsorption calculations were mainly made by deriving a mixture adsorption isotherm by combining the constants from the isotherms for the pure components. This treatment is, of course, analogous to the method used in developing equations of state for gas mixtures. This approach to mixture adsorption, however, has been based on many untenable assumptions and on empirical arguments.

Recently, two major advances have been made in the theory of gas mixture adsorption; the first is due to Myers and Prausnitz (1) and the second is due to Hoory and Prausnitz (2). Myers and Prausnitz (1) present a thermodynamic analysis for gas mixture adsorption that is similar to that used for vapor-liquid equilibria. They define an ideal adsorbed solution, and develop equations for calculating the activity coefficients of the adsorbed phase. Attempts have been made by Kidnay and Myers (3) to modify the equations of Myers and Prausnitz (1). Henson and Kabel (4) further extended the development of Myers and Prausnitz (1) to include adsorption from a saturated vapor. Hoory and Prasnitz (2) generalize the equations developed by Ross and Oliver (5) for pure gases to the adsorption of gas mixtures. The development of Hoory and Prausnitz (2) differs from that of Myers and Prausnitz (1) in two respects: first they relate nonideality of mixing in the monolayer to constants in a two-dimensional equation of state, and second they introduce surface heterogeneity in an explicit manner through the use of distribution function.

The objective of this research was to make a series of measurements on the adsorption of selected pure gases and their binary mixtures on heterogeneous surfaces. The adsorbent selected was Linde Molecular Sieves 13 x, a highly porous material. The gases selected were freon-21 and ethyl chloride. The experimental data obtained provide a good comparison with the predicted mixed gas adsorption values.

THEORY OF ADSORPTION

Adsorption of gas on a solid particle can be described by a three step mechanism:

- 1) Diffusion of the component from the mainstream of the gas to the external surface of the adsorbent particle (external diffusion).
- 2) diffusion into the particle through pores (intraparticle diffusion), and
- 3) adsorption on the interface of the pore

The customary method of correlating adsorption equilibria involves isothermal treatment of the data. Many adsorption isotherms for single-component systems have been proposed over the years. Among the first was the Freundlich isotherm

$$N = KP^{1/n} \quad (1)$$

In recent years this form has been derived on theoretical grounds (6). The Langmuir isotherm (7) in its simplest form

$$N = \frac{aP}{1 + bP} \quad (2)$$

has been widely used to fit isothermal adsorption data and was originally derived from thermodynamic principles assuming adsorption in a single molecular layer. It has been rederived from kinetic(8) and statistical (9) considerations as well. The equation has also been derived by Schay (10) without resorting to the limitation of no molecular interaction present in the original derivations. If the adsorption is multilayer, the more general isotherm of Brunauer, Emmet and Teller (11) is a good starting point. More sophisticated approaches seem necessary when dealing with systems where Knudsen flow and internal molecular adsorption exist.

Adsorption of multicomponent mixtures has received less attention than pure-component adsorption; although industrial applications commonly deal with mixtures. Markham and Benton (12) extended Langmuir's isotherm to mixtures by deriving results in two equations which assume no interaction between the adsorbed components. Schay (13) has developed a similar equation which considers interaction of the components and gives a better prediction of adsorption from mixtures especially at higher partial pressures. In the model these interaction coefficients, β_i , are a complex function of the two-dimensional residual volumes of the components of the mixture, the maximum capacity of the adsorbent, and the adsorbent area. The resulting equation for multicomponent adsorption becomes

$$N_1 = \frac{A_1 P_1 / \beta_1}{1 + \sum_{j=1}^2 (b_j P_j / \beta_j)} \quad (3)$$

The potential theory of adsorption was first advanced and developed by Polanyi (14,15,16,17) and used by others, such as Lewis (8,18) and Dubinin (19). The theory, based on thermodynamic principles, states that enough work must be supplied to compress the gaseous molecules into their adsorbed state such that

$$E_i = \int_{P_0}^{P_a} v dP \quad (4)$$

where E_i is the work required to compress molecules from the gas phase to adsorbate in the i th layer. This work or adsorption potential varies from zero for the outer layer to some maximum at the solid-adsorbate interface. The adsorption potential E_i is a characteristic function of the amount of adsorbed material. A characteristic curve for a given adsorbate-adsorbent system may be established:

$$E = \varphi(v) \quad (5)$$

Once it has been determined for a temperature the curve will yield adsorption isotherms at any other temperature. This theory has been used to correlate adsorption data, but no critical test has been possible because the adsorbed phase density has never been evaluated or predicted successfully.

M A T E R I A L S

Adsorbent:

The adsorbent selected for this study was Linde Molecular Sieves 13x. The sieve used was in the form of 1/16" in. pellets.

The Linde sieve 13x is a Gaussian adsorbent, whose heterogeneity is described by a Gaussian distribution of adsorptive potentials. It is a synthetic Zeolite (Calcium substituted alumina silicate) based on the faujasite structural framework. It possesses high porosity, with pores (in reality, lattice vacancies) of uniform size and essentially molecular dimensions. It adsorbs small molecules only, is selective on molecular shape, and has a particular affinity for unsaturated and polar molecules. The opening into the cavity was about 5\AA in diameter.

Molecular sieves are used primarily in gas treatment but also are effective for drying organic liquids.

Adsorbates:

The gases selected for this investigation were freon-21

and ethyl chloride. The gases were of research grade, with purities of 99.95%. Freon-21 is colorless, non-flammable, non-toxic, and is mainly used as a refrigerent and as a solvent. Ethyl chloride is colorless, highly flammable and toxic. It is mainly used as refrigerent and solvent. Both the gases have approximately the same thermal conductivity.

EQUIPMENT AND PROCEDURE

In the first phase of the investigation, pure component measurements were made. The flow-diagram for the apparatus is shown in Figure 1. In the second phase of the investigation, the equipment was modified to allow mixture measurements to be made. The flow diagram for the mixture adsorption is shown in Figure 2. The pure gas data are tabulated in appendix 1 and the mixture data are tabulated in appendix 3.

Pure Component Measurements

The pure component measurements were made in three steps:

Measurement of the dead volume of the system,*

Reactivation of the adsorbent,

Measurement of the pure gas adsorption.

Measurement of the dead volume of the system: The step-wise procedure is as follows:

a. Keep valve 4 and 5 closed and start vacuum pump 1

* The adsorption system includes everything right of valve I to the reference point on the left leg of the manometer.

DESCRIPTION OF SYMBOLS
USED IN FLOW SHEET

1. Pure gas cylinder
 2. Helium gas cylinder
 3. 100 cc gas burette
 4. Constant temperature water bath
 5. Adsorbent cell
 6. Constant volume mercury manometer with 10 mm ID bore tubing.
 7. Mercury trap
 8. Molecular sieve column for pressure drops
 9. Mercury trap
 10. Molecular sieve column for pressure drops
- Valves 1 and 6 are 1/8" OD Whitey
- Valves 2 and 5 are 1/4" OD Whitey
- Valves I and IV are two way glass stopper
- Valves II and III are three way glass stopper
- Vacuum pump 1 and 2 are two vacuum pumps

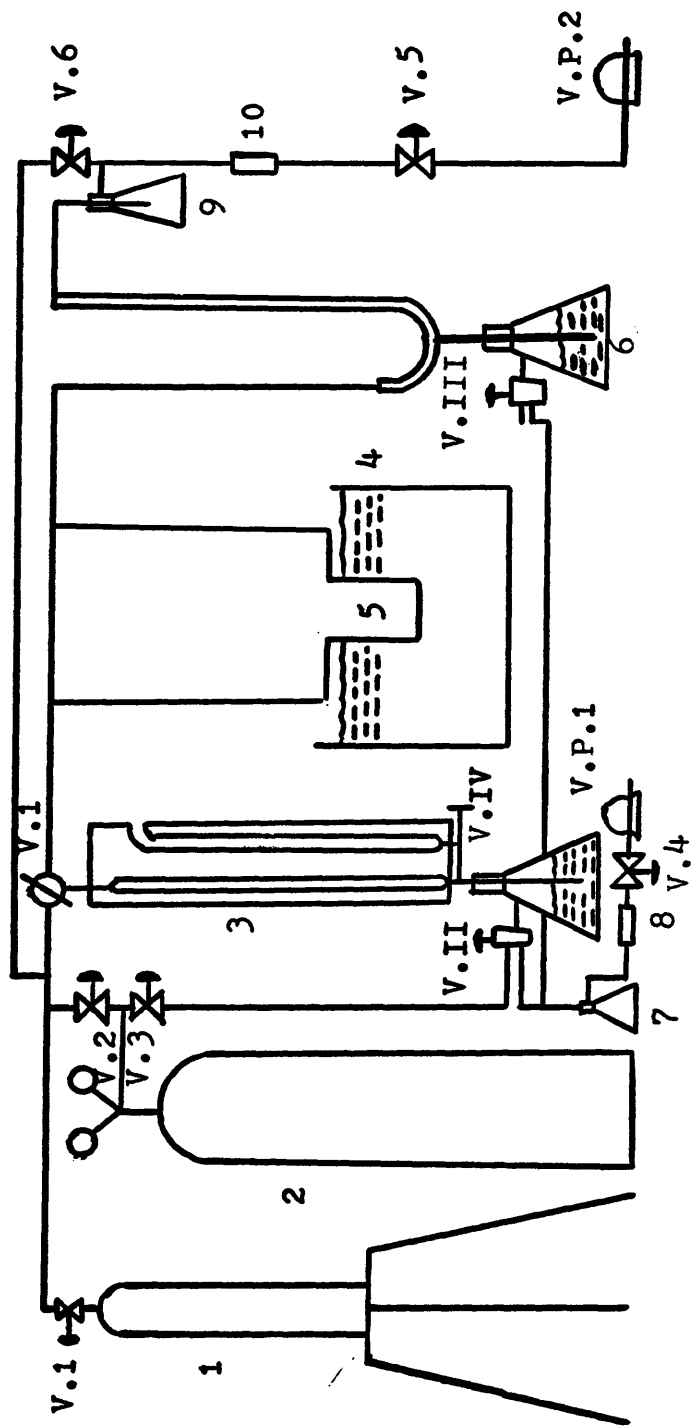


Figure 1 Flow diagram for pure component measurement

- and 2.
- b. Open valves 4 and 5 simultaneously so that mercury in reservoir under the manometer does not rise in the legs of manometer. Open valves 6 and I to pull a vacuum on the back line and gas-burette. Keep valves II and IV closed.
 - c. After about two hours, close valve 6 and open valve 2. Allow helium to flow in the burette by opening valve I.
 - d. Open valve IV and bring the gas-burette to atmospheric pressure with helium. Adjust the mercury in both arms of the burette to the same level by opening valve II to vacuum line or the pressure line. This is the initial reading of the burette.
 - e. Raise mercury in the manometer to isolate the adsorption system by opening valve III to the pressure line. Initially under good vacuum, the mercury in the manometer legs will be at the same level. Allow some helium to flow in the system by opening valve I to the system. Again bring the mercury in both arms of the burette to the same level. This will be the final burette reading.
 - f. Bring the mercury in the manometer to the reference point by adjusting valve III to the pressure line or the vacuum line. The mercury level at the reference point keeps the system volume constant. Read the system pressure i.e. difference in mercury-level in both legs

of manometer.

g. Note the following things:

Atmospheric pressure and temperature, initial and final burette readings, system pressure and room temperature. See appendix 2 for the calculation of the dead volume of the system.

h. Add more helium to increase the system pressure differentially to obtain some more readings.

Reactivation of Adsorbent: Repeat steps a and b of procedure I for about 24 hours while heating the adsorbent cell to about 380°F in a wax-bath and keeping valve 2 closed. The wax used for heating was petroleum wax with melting point range 112-124°F and flash point range 410-430°F. The wax was melted in a 500 ml beaker. The temperature was controlled by using a powerstat.

Measurement of the pure gas adsorption: The step-wise procedure is as follows:

- a. Close valves I and 6. Allow one of the gases to flow in the gas-burette by opening valves I and 1. Open valve IV to allow the gas in the burette to come to atmospheric pressure. Bring the mercury to the same level in both arms of the burette. This is the initial burette reading.
- b. Remove the wax bath from around the adsorbent cell and replace it with a water bath adjusted to maintain a temperature of 50°C.

c. Repeat steps e through g as in the case of dead volume measurements.

Repeat the steps above for another gas. See appendix 1 for tabulation of the pure gas measurements.

DESCRIPTION OF SYMBOLS
USED IN FLOW SHEET

1. Pure gas cylinder
 2. Helium gas cylinder
 3. 100 cc gas burette.
 4. Constant temperature water bath
 5. Adsorbent cell
 6. Constant volume mercury manometer with 10 mm ID bore tubing.
 7. Mercury trap
 8. Gas chromatograph
 9. Mercury trap
 10. Molecular sieve column for pressure drop
- Valves 1, 6 and 8 through 10 are 1/8" OD Whitey
Valves 2 through 5 and 7 are 1/4" OD Whitey
Valves I and IV are two way glass stopper
Valves II and III are three way glass stopper
V.P. 1 and 2 are two Vacuum pump
C.P. circulation pump.

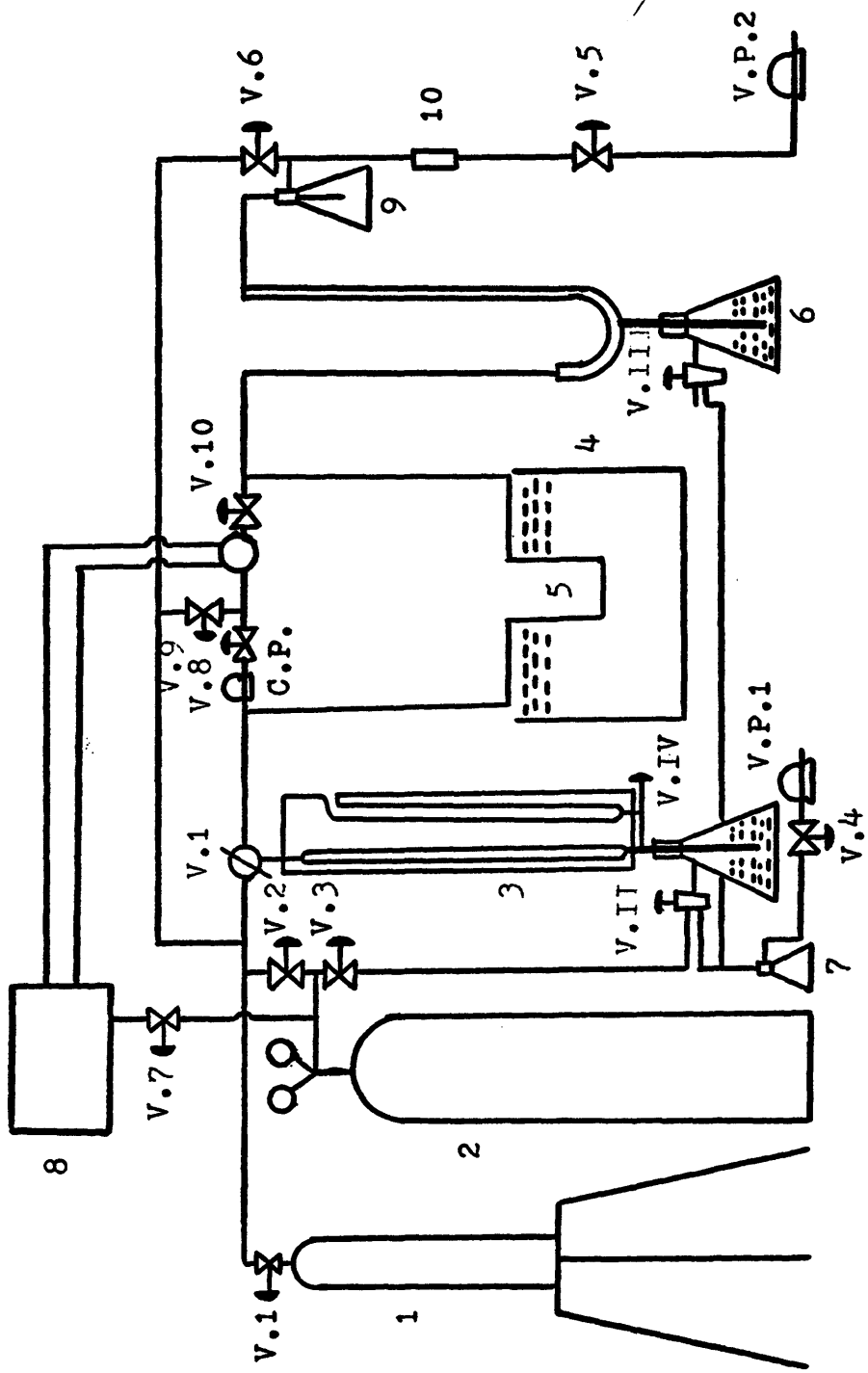


Figure 2 Flow diagram for binary mixture measurement

Procedure for Mixture Isotherm

Measurements for binary mixtures were made in 3 steps:

Reactivation of the adsorbent

Introduction of the gas mixtures

Chromatographic analysis of the gas-phase at equilibrium

Reactivation of adsorbent: First fill the system between valves 8,9 and 10 with helium. Close the valves 8,9 and 10 and reactivate the adsorbent as in step II of the procedure for pure component measurements. The reason for isolating part of the system is that the chromatograph sample valve is not entirely leak-proof. The rest of the system is leak-tight so at atmospheric system pressure we can make mixture measurements. After about 24 hours, remove the wax bath.

Introduction of the gas mixtures: The step-wise procedure is as follows:

- a. Close valve 6. Open valve 1 to let one of the pure gas into the burette. Close valve I and measure the volume of gas in the burette by opening valve IV and bringing the mercury to the same level in both arms of the burette. Note the reading. The volume of gas is the burette reading plus the uncalibrated volume of burette.
- b. Change the pure gas cylinder and evacuate the line from the gas-cylinder to valve 6 by opening valve 6. After half an hour, close valve 6 and open valve 1. Slowly open valve I and let the gas into the burette. Close

- valves I and 1. Bring the mercury to the same level and note the reading. The volume of gas introduced in this step is the difference between the two burette readings. These two volume gives the composition of the binary mixtures. Raise and lower mercury in burette few time by means of valve II to mix the gases.
- c. Raise the mercury in manometer legs by opening valve III to the pressure line, and open valve I to the adsorption system to let the gas mixture in the burette flow in. At the same time put the constant temperature water bath under the adsorbent and adjust it to maintain the bath temperature at 50°C. Note the volume of the mixture introduced.
- d. The system pressure does not reach atmospheric pressure and so another mixture of about the same composition is prepared and introduced into the system to bring the system pressure to about atmospheric pressure.
- e. Open valves 8 and 10. Keep valves 9 closed and switch on the circulation pump to circulate the mixture around the system. After about 26 to 30 hours switch-off the circulation pump and run the chromatographic analysis of the gas mixture in the sample loop. At this time read and note atmospheric pressure and temperature, the temperature of the water bath and the system pressure.

Chromatographic analysis of the gas-phase at equilibrium: The

step-wise procedure is as follows:

- a. Set the helium carrier gas flow through the chrom to-graph to about 10 psig. Switch on the recorder and thermal conductivity circuit and allow few minutes to stabilize the recorder.
- b. During the introduction of gas mixture, the sample valve remains in position 1 so that it is connected to the system. The sample valve is now switched to position two so that the equilibrium gas mixture in the loop will be carried to the chromatograph. Measure and record the peak heights. Since the thermal conductivities of the two gases are about same, the peak heights were used to get the compositions.

Repeat the above steps at various compositions at a fixed pressure and temperature for the system.

Analysis of Gases using Gas Chromotography:

Gas chromatographic technique was used in this study to determine the equilibrium composition of gases in a binary mixture.

Chromotography is a physical method of separation in which the components to be separated are distributed between two phases, one of which is a stationary bed of large area and the other, a fluid that percolates through the stationary bed.

The gas chromatograph utilized in this investigation was manufactured by Podbielniak Inc. It consists of a carrier gas system, gas and liquid injection system, column and detection system.

Gas Sampling:

Gas samples are usually injected either by a gas-tight syringe or a gas-sampling valve.

The gas-sampling valve used in this investigation was the Perkin-Elmer precision type. It is mainly a rotating stainless steel body and Teflon valve rotor. In one position a sample loop of known volume is filled at a known pressure and then swept into the column when the valve is rotated to the second position. Valves should permit reproducible injection to within 1/2 percent.

Chromotograph Column:

The preparation of a packed gas chromatograph column may be divided into five separate steps. The solid support must be obtained and subjected to particle-size grading. It

may also be treated with various chemicals to modify it in way. The stationary phase must be obtained or made. This is the material which is responsible for the separation, and may be a silicone fluid, a polyester or any number of relatively low-vapor-pressure materials; the stationary phase must be coated on the support. The next step is to pack the column with the coated packing. Finally the column must be conditioned prior to use.

The gas chromatograph column was manufactured by Beckman Corporation. Following are the data on this column:

Type:	GC-2A
Material:	Copper
Dimensions:	length - 12 feet OD - 1/4"
Partition liquid:	Dow Corning 200-500 (20% weight ratio)
Inert Support:	Chrom P (42/60 mesh size)
Maximum Recommended Temperature:	250°C
Maximum Usable Temperature:	275°C

Column Conditioning:

There are three reasons for conditioning columns prior to use:

1. To reduce background due to column bleed.
2. To ensure column stability at the operating temperature.

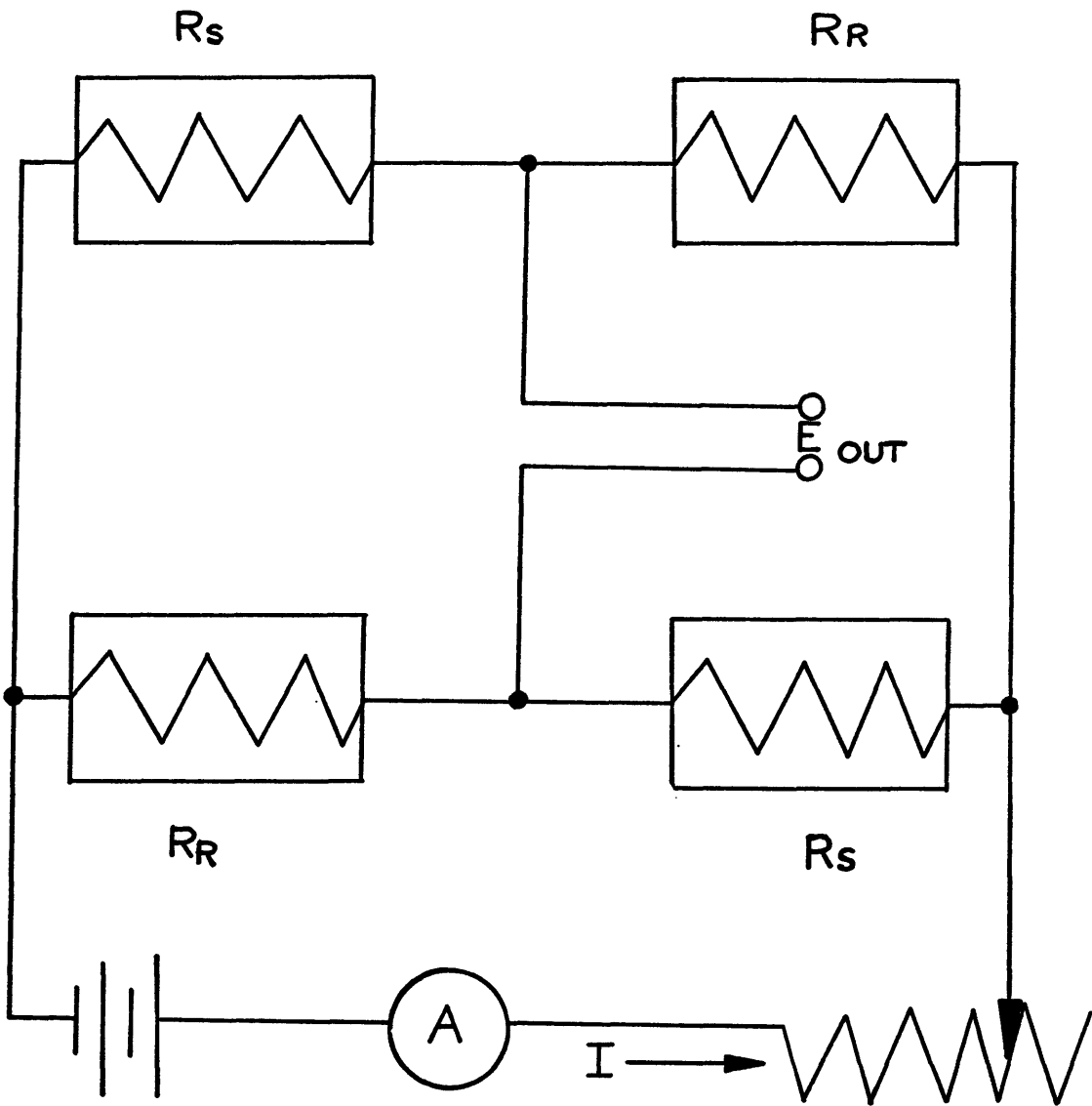
3. To avoid contamination of detectors, feed-throughs, etc. by partition liquid light ends.

The time and temperature for conditioning will vary with the type of partition liquid and the percentage coating, the sensitivity required for the analysis, whether temperature programming is to be used and to some extent on the column length, diameter and flow rate. The column outlet should be disconnected during the conditioning period to avoid accumulation of stationary phase or its decomposition products in the detector.

Chromotograph Detector:

The detector used in this instrument is of thermal conductivity type. The thermal conductivity unit has the advantage of being moderate in cost, and satisfactorily sensitive to any sample component having different conductivity than the carrier gas. This sensitivity arises from the fact that a thermal conductivity detector is basically a wheatstone bridge, which is among the most sensitive of the simple electrical measuring circuits .

The characteristic of thermal conductivity detectors which makes them responsive to changes in effluent gas composition also makes them responsive to a very small temperature changes due to other factors. An easy calculation, based on the equations in Fig. 3, will show that a temperature differential between the sensing resistance filaments of only 0.0005°C will



$$E_{OUT} = \frac{\Delta R I}{2}$$

$$(\Delta R = R_S - R_R)$$

$$I_{OUT} = \frac{E_{OUT}}{\frac{R_R + R_S}{2} + R_{INS} - R + R_{LEADS}}$$

Figure 3. TEMPERATURE - SENSING BRIDGE

produce an output of 5 v, or 0.5% full scale pen movement in a 1-mv recorder, with a detector current of 300 ma. With thermistor-sensing elements the same 5 v output will be caused by 0.00015°C change in one element of a detector at 200°C . Only a 0.00007°C change would cause a 5 v output from a detector at 25°C .

Such small temperature changes can be caused by variations in carrier gas flow, drafts on the instrument, line voltage variations on the heating element.

Other characteristics of test samples, such as specific heat and density as well as operational parameters of temperature, gas turbulence in the filament zones, and radiant and conductive heat exchange between detector body and filament also measurably influence the detector response to various sample vapors.

R E S U L T S

The results are discussed in two parts:

Pure component adsorption isotherms

Binary mixture adsorption isotherms

Pure Component Adsorption Isotherms

The isotherms of pure freon-21 and ethyl chloride are presented in figure 4, and the results are tabulated in Table 1. The results are reported as volume adsorbed at STP per gram of adsorbent as a function of equilibrium system pressure in mm of mercury.

Patel(32) has studied the adsorption of freon-21 and ethyl chloride on sterling FT-D5 carbon black (Homogeneous surface). The results are given in* Table 2.

Comparing the results obtained by him with the results of this study, it seems that the amount of the gases adsorbed at STP per gram of adsorbent is considerably higher in the case of molecular sieve. The probable reason for the higher adsorption in case of molecular sieve may be its high

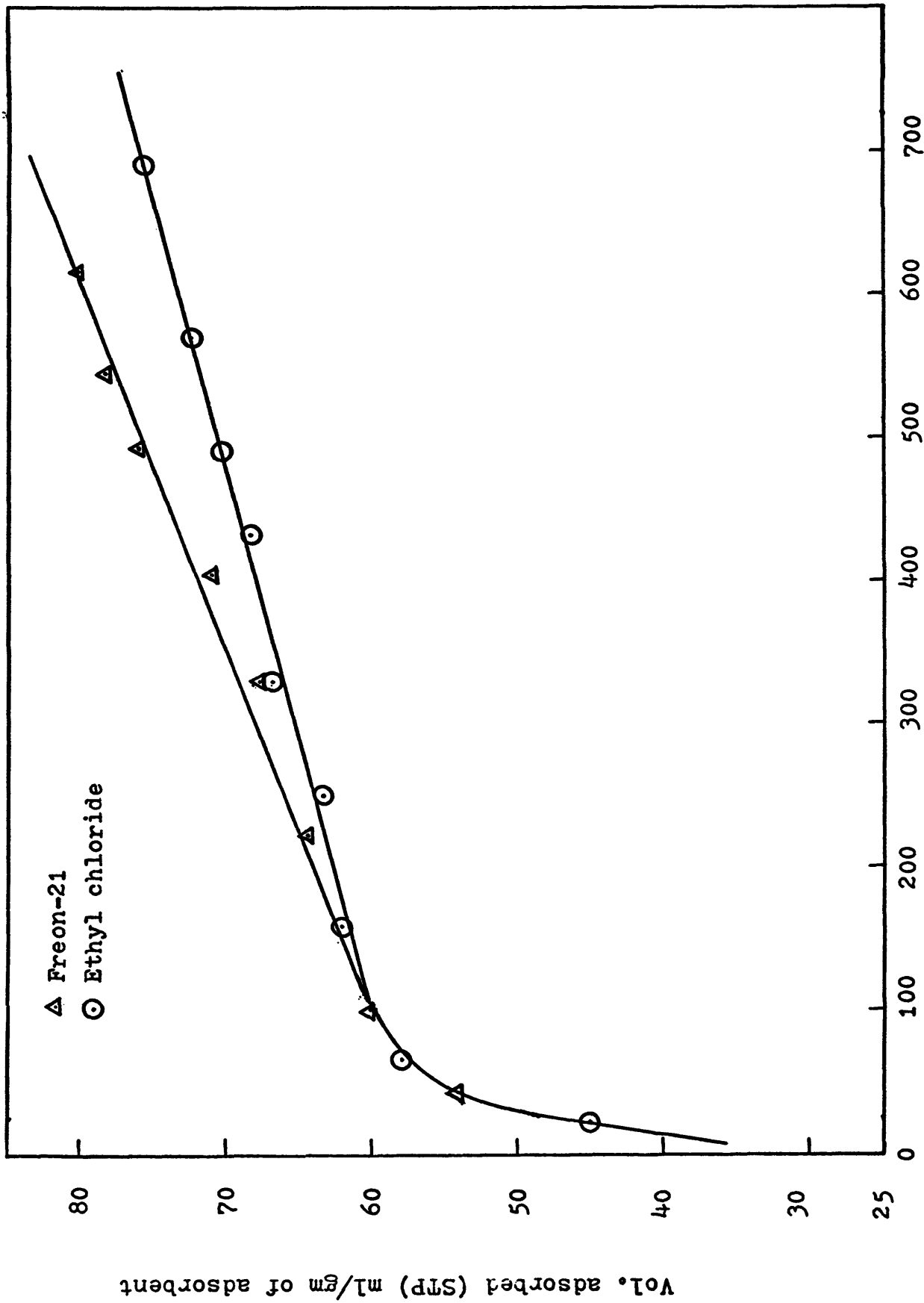


Figure 4. Adsorption of Freon-21 and Ethyl chloride on Linde Molecular Sieve 13x at 323°K

Table 1

Pure Component Isotherms (Linde Molecular Sieve 13X)

Freon-21, 323°K		Ethyl Chloride 323°K	
Pressure mm of Hg	Amount adsorbed cc(STP)/gm.	Pressure mm of Hg	Amount adsorbed cc(STP)/gm.
40.0	54.25	23.0	45.00
100.5	60.00	66.0	57.90
220.0	64.60	159.0	62.30
330.0	68.0	251.0	63.40
407.0	70.76	333.0	66.00
493.0	76.05	435.0	67.80
556.0	77.51	490.0	70.50
615.0	80.03	570.0	72.44
		695.0	75.73

*Table 2

Pure Component Isotherms (Sterling FT-D5 Carbon Black)

Freon-21, 323°K		Ethyl chloride, 323°K	
Pressure mm of Hg	Amount adsorbed cc(STP)/gram	Pressure mm of Hg	Amount adsorbed cc (STP)/gram
35.3	0.21	58.3	0.29
139.3	0.88	146.2	0.75
262.6	1.35	260.9	1.30
377.9	1.70	358.5	1.55
466.0	2.06	477.9	1.85
573.1	2.40	590.5	2.33

* Data taken from Patel(32) thesis

porosity and its molecular structure.

Binary Adsorption Isotherms

The isotherms for mixtures of freon-21 and ethyl chloride are shown in figure 5 and are tabulated in Table 3.

There are a number of techniques in the literature for predicting mixture adsorption isotherms using pure component isotherms and most of these are summarized by Young and Crowell(22). The simplified method of Kidnay and Myers (3) was used in this study.

A comparison of calculated and experimental values are shown in figure 5. Details of the calculations are in given in Appendix 5.

The results presented in Table 3 shows that the total amount adsorbed per gram of adsorbent is independent of the composition. The results obtained by Patel (32) for the adsorption of the mixture of freon-21 and ethyl chloride on carbon black (Sterling FT-D5) were in good agreement with the results by Kidnay and Myers simplified method. However, in the present study the results for the adsorption of the same gases on Linde Molecular Sieve 13X were in poor agreement and deviated considerably from those predicted by Kidnay and Myers simplified method. The disagreement between experimental and predicted results in this study may be mainly due to the non-ideality that exists in the adsorbed phase. It is quite likely also because of contamination of gas streams and the molecular sieve bed.

Figure 5

- △ Ethyl chloride
- Freon-21
- Experimental
- Predicted by Kidnay and Myers
simplified method

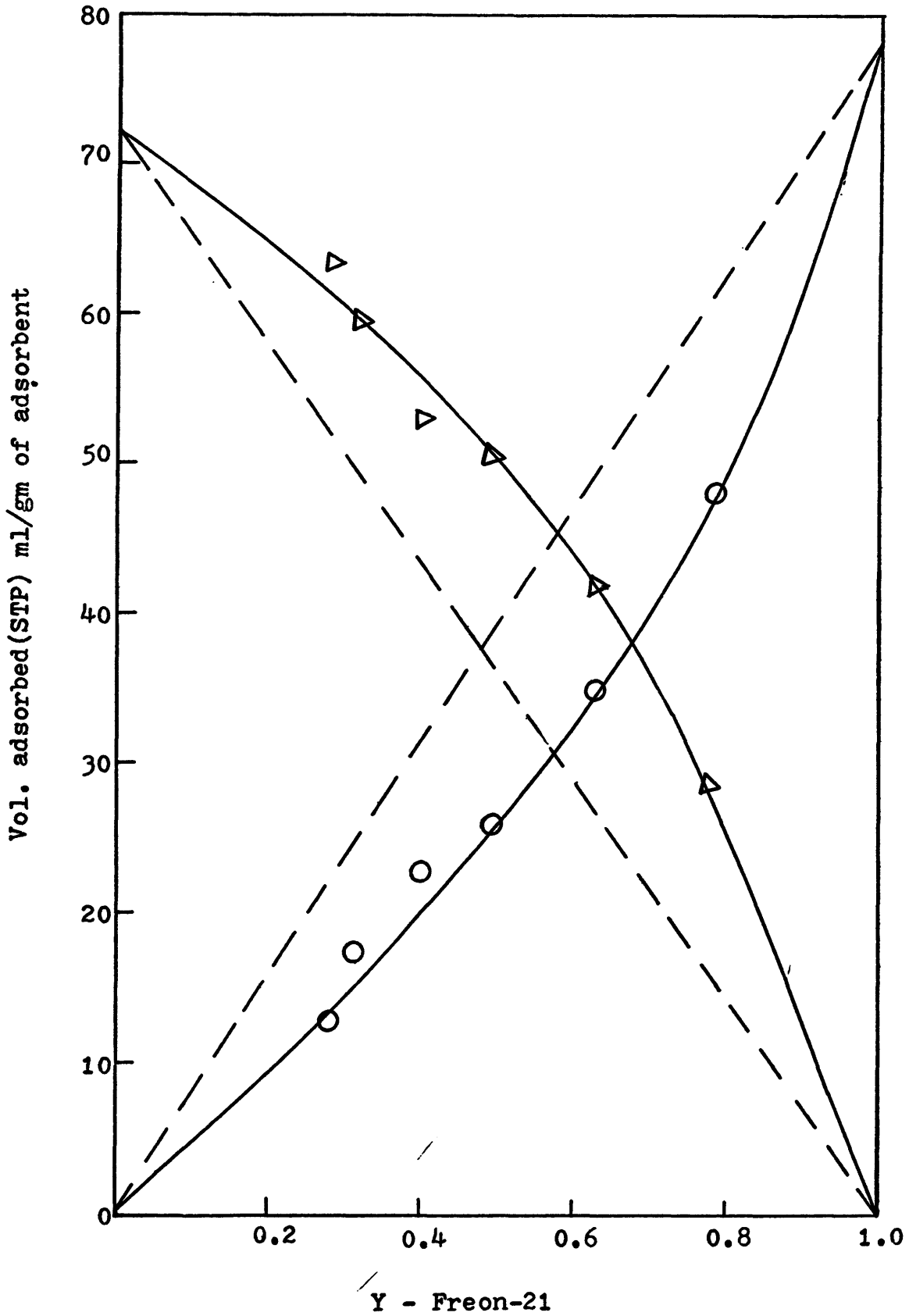


Figure 5. Freon-21 Ethyl chloride adsorption on Linde Molecular Sieve 13X, at 323°K

Table 3

Mixture Adsorption Isotherms

Run No.	Pressure mm of Hg	Amount Adsorbed cc(STP)/gm		Gas-phase Composition	
		Freon-21	Ethyl Chloride	Freon-21	Ethyl Chloride
1	556	48.02	28.05	78.5	21.50
2	566	22.88	52.97	40.00	60.00
3	558	26.08	50.50	48.80	51.20
4	574	17.30	59.68	31.70	68.30
5	567	12.81	63.57	28.10	71.90
6	539	34.84	41.94	63.00	37.00

Average Pressure = 560 mm of mercury

S U M M A R Y

The pure component isotherms of freon-21 and ethyl chloride were measured at 323°K and in the pressure range of 0 to 695 mm of mercury. Binary adsorption isotherms of mixtures at various compositions were measured at 323°K and at 560 mm of mercury. The adsorbent used was Linde Molecular Sieve 13x pellets. The experimental values are in poor agreement with the mixture values predicted by Kidnay and Myers method.

It is hoped that the results of this study may help to the basic understanding of the adsorption process and thereby aid in the development of quantitative design for industrial use.

NOTATION

.

a	Langmuir constant, mg. moles/atm. gm
A	constant, mg. moles/gm atm.
b	Langmuir constant, 1/atm
E	work of compression, adsorption potential; calories/gm mole
K	Freundlich constant, mg. moles
n	Freundlich exponential constant
N	mg. moles adsorbed/gm adsorbent
P	pressure, atm
R	gas constant
T	temperature, °K
T _{bath}	temperature of water bath
T _{atm}	atmospheric temperature
T _{mano}	temperature surrounding manometer
v	volume adsorbate, cc.
V	Volume cc.

/

Y mole fraction in gas phase

Greek letters

β Schay's interaction constant, dimensionless

σ density, mg. moles/cc.

ϱ function of

Subscripts

a adsorbate state

.g gaseous state

i ith layer

j jth layer

superscript o refers to temperature of 0°C

R E F E R E N C E S

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A P P E N D I X

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Table 1

Total dead volume measurements

P_{atm} mm of Hg	T_{atm} deg C	$V_{initial}$ ml	V_{final} ml	P_{system} mm of Hg	$T_{manometer}$ deg C
622.0	24.8	91.60	79.30	162.5	23.3
622.0	24.8	79.60	69.50	283.0	23.4
622.0	24.8	69.50	62.50	383.5	23.4
622.0	25.0	62.50	53.00	501.0	23.7
622.0	25.0	53.00	47.90	574.0	23.9
622.0	25.0	47.90	41.50	658.0	23.9

Table 2

Dead volume measurements of the
 system that remains at ambient
 conditions

P_{atm} mm of Hg	T_{atm} deg C	V_{initial} ml	V_{final} ml	P_{system} mm of Hg	$T_{\text{manometer}}$ deg C
615.2	23.4	83.90	83.20	83.0	22.0
615.2	23.4	83.20	76.00	178.0	22.0
615.2	23.4	76.00	67.50	290.0	22.0
615.0	23.4	67.50	58.90	405.0	22.0
615.2	23.4	58.90	47.50	560.0	22.0
615.2	23.4	47.50	41.20	636.5	22.0

Table 3

Pure ethyl chloride measurements

P_{atm} mm of Hg	T_{atm} deg C	V_{initial} ml	V_{final} ml	P_{system} mm of Hg	T_{bath} deg C	$T_{\text{manometer}}$ deg C
613.1	24.8	91.50	28.80	23.0	50.0	25.8
612.9	24.5	28.60	7.90	66.0	50.0	24.70
614.9	24.1	91.80	78.90	159.0	50.0	22.5
615.4	24.8	79.0	60.90	251.0	50.0	23.3
616.1	25.0	61.50	51.40	435.0	50.0	26.7
619.6	24.8	50.90	43.60	490.0	50.0	22.9
620.8	24.5	43.50	35.30	570.0	50.0	22.1
620.8	24.3	35.30	21.30	695.0	50.0	22.1

Table 4
Pure Freon-21 measurements

P_{atm} mm of Hg	T_{atm} deg C	V_{initial} ml	V_{final} ml	P_{system} mm of Hg	T_{bath} deg C	$T_{\text{manometer}}$ deg C
610.4	25.0	99.10	22.00	40.0	50.0	22.9
610.8	25.0	21.80	9.00	100.5	50.0	22.7
611.0	25.0	98.60	81.00	220.0	50.0	22.5
616.9	24.4	80.90	69.90	330.0	50.0	22.4
619.1	24.6	69.60	59.60	407.0	50.0	22.0
622.6	24.0	60.00	47.50	493.0	50.0	21.6
623.2	24.0	47.40	40.90	556.0	50.0	22.3
623.4	24.9	40.70	32.40	615.0	50.0	21.0

A P P E N D I X II

Table 1
Pure component calculations

Dead volume of whole system		Dead volume of system at ambient condition	
P _{system} mm of Hg	Volume ml.	P _{system} mm of Hg	Volume ml.
162.5	47.20	83.0	45.40
283.0	47.00	178.0	46.00
383.5	47.20	290.0	46.20
501.0	47.20	405.0	46.00
574.0	47.40	560.0	46.00
658.0	47.30	636.5	46.20

Table 2

Pure ethyl chloride		Pure freon-21	
P_{system} mm of Hg.	Vol. ad(STP)/gm ml	P_{system} mm of Hg	Vol. ad(STP)/gm ml
23.0	45.00	40.0	54.25
66.0	57.90	100.5	60.00
159.0	62.30	220.0	64.60
251.0	63.40	330.0	68.00
333.0	66.00	407.0	70.76
433.0	67.80	493.0	76.05
490.0	70.50	556.0	77.51
570.0	72.44	615.0	80.03
695.0	75.73		

Sample calculation for total dead volume of the system:

$P_{\text{atm}} = 622.0$ mm of Hg at 24.8°C read from barometer.

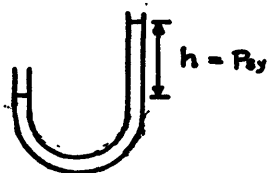
The above pressure reading is corrected to 0°C by taking manometric corrections from the Hand book of Chemistry by Lange, 10th edition p. 1696-7.

For the above pressure reading at 23.2°C , the correction is 2.5 mm of Hg.

Therefore P_{atm} at $0^{\circ}\text{C} = 619.5$ mm of Hg.

The system pressure is read from the manometer and is corrected for the temperature effect.

P_{system} at $T_{\text{manometer}} = 162.5$ mm of Hg at 23.3°C



Since area of leg of manometer is same then the differential height read at $T^{\circ}\text{C}$ should be corrected to 0°C as follows

$$\rho_{\text{Hg at } T^{\circ}\text{C}} \times A \times h_{\text{at } T^{\circ}\text{C}} = \rho_{\text{Hg at } 0^{\circ}\text{C}} \times A \times h_{\text{at } 0^{\circ}\text{C}}$$

Therefore

$$\begin{aligned} h_{\text{at } 0^{\circ}\text{C}} &= h_0 = P_{\text{system}} \\ &= \frac{h_{\text{at } T^{\circ}\text{C}} \times \rho_{\text{Hg at } T^{\circ}\text{C}}}{\rho_{\text{Hg at } 0^{\circ}\text{C}}} \\ &= \frac{P_{\text{system}} \times \rho_T}{\rho_0} \end{aligned}$$

where ρ_T = density of mercury at $T^\circ\text{C}$

and ρ_0 = density of mercury at 0°C

From Lange's handbook of chemistry (p.1119)

$$\text{at } 23.3^\circ\text{C } \rho_{\text{Hg}} = 13.538 \text{ gm/ml}$$

$$\text{and at } 0^\circ\text{C } \rho_{\text{Hg}} = 13.596 \text{ gm/ml}$$

Therefore

$$P_{\text{system at } 0^\circ\text{C}} = \frac{13.538}{13.596} \times 162.5 \text{ mm of Hg}$$

$$= 161.5 \text{ mm of Hg.}$$

Now the volume of Helium introduced into the system is equal to $91.60 - 79.30 = 12.30 \text{ ml}$.

The dead volume of the system is therefore

$$\begin{aligned} V_d = \text{dead volume} &= V_{\text{intro}} \times \frac{P_{\text{atm}}^0}{P_{\text{system}}^0} \\ &= \frac{12.30 \text{ ml} \times 619.5 \text{ mm of Hg}}{161.5 \text{ mm of Hg}} \\ &= 47.20 \text{ ml} \end{aligned}$$

The same procedure is followed in the case of the dead volume of the system at ambient condition.

Sample calculation for pure gas (freon-21)

Barometric pressure corrected to 0°C

$$P_{\text{atm}} = 610.4 \text{ mm of Hg at } 25.0^\circ\text{C}$$

Barometric correction is 2.5 mm of Hg

$$\begin{aligned} \text{Therefore } P_{\text{atm}}^0 &= 610.4 - 2.5 \\ &= 607.9 \text{ mm of Hg.} \end{aligned}$$

System pressure correction

$$P_{\text{system}} = 40.2 \text{ mm of Hg, } T_{\text{mano}} = 22.9^\circ\text{C}$$

$$\rho_{\text{Hg at } T_{\text{mano}}} = \rho_T = 13.539$$

$$p_{\text{Hg}} \text{ at } 0^{\circ}\text{C} = p_0 = 13.596$$

$$\begin{aligned} P_{\text{system at } 0^{\circ}\text{C}} &= P_{\text{system}}^0 = P_{\text{system}} \times p_T/p_0 \\ &= \frac{40.2 \times 13.539}{13.596} \\ &= 40.0 \text{ mm of Hg} \end{aligned}$$

Volume of gas introduced at atmospheric condition is corrected to 760.0 mm of Hg and 0°C (STP) using ideal gas equation.

Therefore,

$$\text{Volume introduced (STP)} = \frac{273.15}{T_{\text{atm}}} \times \frac{P_{\text{atm}}}{760.0} \times V_{\text{intro}}$$

Therefore,

$$\begin{aligned} \text{Volume introduced (STP)} &= \frac{273.15 \times 607.90}{298.15 \times 760.0} \times 77.10 \\ &= 56.50 \text{ ml} \end{aligned}$$

A part of adsorption system remains in air and part of the system remains in the constant temperature water bath.

dead volume of system = dead volume of system + dead volume
in the air of system in
water bath.

$$47.20 \text{ ml} = 46.00 \text{ ml} + 1.20 \text{ ml}$$

So for the system pressure of 40.0 mm of Hg 46.00 ml pure gas is at P_{sys}^0 and T_{mano} and 1.20 ml pure gas is at P_{sys}^0 and T_{bath} .

Therefore,

$$\begin{aligned} \text{Volume of gas(STP) in the system} &= \frac{46.0 \times 273.15 \times 40.0}{298.15 \times 760.0} \\ &= 2.20 \text{ ml} \end{aligned}$$

and volume of gas(STP) in the system

that remains in water bath. = 0.0534 ml

Therefore,

$$\begin{aligned}\text{Volume of freon-21 adsorbed (STP)} &= \text{Volume of gas introduced (STP)} \\ &\quad - \text{Volume of gas present} \\ &= 56.50 - (2.200 + 0.0534) \\ &= 54.25 \text{ ml}\end{aligned}$$

Therefore

$$\begin{aligned}\frac{\text{Volume of freon-21 adsorbed (STP)}}{\text{gm. of adsorbent}} &= \frac{54.25}{1.002 \text{ gm of adsorbent}} \\ &= 54.249 \text{ gm/ml.}\end{aligned}$$

The same procedure is applied in case of pure ethyl chloride.

A P P E N D I X III

Binary Mixture Adsorption Data

Run 1

$P_{atm} = 616.70$ mm of Hg. $T_{atm.} = 24.0^{\circ}C$, $T_{mano} = 22.0^{\circ}C$

Mixture I

Gas	Volume, ml	%
Freon-21	$29.40 + 6.75^*$ = 36.15	66.6
Ethyl chloride	$47.50 - 29.40$ = 18.10	33.4
Total	= 54.25	100.0

Amount introduced in the system = 54.25 ml.

Mixture II

$P_{atm} = 616.70$ mm of Hg, $T_{atm} = 24.3^{\circ}C$, $T_{mano} = 23.4^{\circ}C$

Gas	Volume, ml	%
Freon-21	$48.90 - 11.20$ = 37.70	67.7
Ethyl chloride	$11.20 + 6.75$ = 17.95	32.3
Total	= 55.65	100.0

Amount introduced in the system = 55.65 ml

* 6.75 is volume of uncaliberated part of burette.

Mixture III

$P_{\text{atm}} = 616.4$ mm of Hg. $T_{\text{atm.}} = 24.5^{\circ}\text{C}$, $T_{\text{mano}} = 23.9^{\circ}\text{C}$

Gas	Volume, ml	%
Freon-21 29.40 + 6.75	= 36.15	67.3
Ethyl Chloride 47.00 - 29.40	= 17.60	32.7
Total	= 53.75	100.0

Amount introduced = 6.70 ml

$P_{\text{atm}} = 616.4$ mm of Hg, $T_{\text{atm}} = 24.5^{\circ}\text{C}$, $T_{\text{mano}} = 23.9^{\circ}\text{C}$

Amount introduced = 4.20 ml

$P_{\text{atm.}} = 615.8$ mm of Hg, $T_{\text{atm}} = 24.0^{\circ}\text{C}$, $T_{\text{mano}} = 22.1^{\circ}\text{C}$

Amount introduced = 9.10 ml.

$P_{\text{atm}} = 615.3$ mm of Hg, $T_{\text{atm}} = 24.7^{\circ}\text{C}$, $T_{\text{mano}} = 20.5^{\circ}\text{C}$

Amount introduced = 5.40 ml

$P_{\text{atm}} = 612.1$ mm of Hg, $T_{\text{atm}} = 24.0^{\circ}\text{C}$, $T_{\text{mano}} = 20.4^{\circ}\text{C}$

Amount introduced = 3.80 ml

$P_{\text{atm}} = 611.1$ mm of Hg, $T_{\text{atm}} = 24.10^{\circ}\text{C}$, $T_{\text{mano}} = 21.0^{\circ}\text{C}$

Amount introduced = 11.70 ml

$P_{\text{atm}} = 610.1$ mm of Hg, $T_{\text{atm}} = 23.8^{\circ}\text{C}$, $T_{\text{mano}} = 20.4^{\circ}\text{C}$

Chromatographic Analysis:

Helium flow at 10 psig $T_{\text{atm}} = 24.3^{\circ}\text{C}$

Attenuation = 2.0 $T_{\text{mano}} = 21.4^{\circ}\text{C}$

P_{atm} = 610.2 mm of Hg

T_{bath} = 50.0°C

P_{sys} = 637.0 mm of Hg

Freon-21 peak height = 25.5/32.0"

Ethyl chloride peak height = 7/32"

Run 2

$P_{\text{atm}} = 623.60$ mm of Hg, $T_{\text{atm}} = 24.0^{\circ}\text{C}$, $T_{\text{mano}} = 21.4$

Mixture I

Gas	Volume, ml	%
Freon-21	$48.10 - 30.20 = 17.90$	32.60
Ethyl chloride	$30.20 + 6.75 = 36.95$	67.40
Total	$= 54.85$	100.00

Amount introduced in the system = 54.85 ml

Mixture II

$P_{\text{atm}} = 623.70$ mm of Hg, $T_{\text{atm}} = 23.9^{\circ}\text{C}$, $T_{\text{mano}} = 21.0^{\circ}\text{C}$

Gas	Volume, ml	%
Freon-21	$11.60 + 6.75 = 18.35$	32.90
Ethyl chloride	$49.10 - 11.60 = 37.50$	67.10
Total	$= 55.85$	100.00

Amount introduced in the system = 55.85 ml

Mixture III

$P_{\text{atm}} = 623.6$ mm of Hg, $T_{\text{atm}} = 23.9^{\circ}\text{C}$, $T_{\text{mano}} = 22.0^{\circ}\text{C}$.

Gas	Volume, ml	%
Freon-21	$47.50 - 29.60 = 17.90$	33.00
Ethyl chloride	$29.60 + 6.75 = 36.35$	67.00
Total	$= 54.25$	100.00

Amount introduced = 5.80ml

$P_{\text{atm}} = 623.6$ mm of Hg, $T_{\text{atm}} = 23.9^{\circ}\text{C}$, $T_{\text{mano}} = 22.2^{\circ}\text{C}$

Amount introduced = 1.80 ml

$P_{atm} = 622.9$ mm of Hg, $T_{atm} = 23.7^{\circ}C$, $T_{mano} = 22.2^{\circ}C$

Amount introduced = 2.60 ml

$P_{atm} = 622.5$ mm of Hg, $T_{atm} = 23.8^{\circ}C$, $T_{mano} = 23.1^{\circ}C$

Amount introduced = 3.0 ml

$P_{atm} = 622.5$ mm of Hg, $T_{atm} = 23.1^{\circ}C$, $T_{mano} = 21.1^{\circ}C$

Amount introduced = 8.50 ml

$P_{atm} = 622.0$ mm of Hg, $T_{atm} = 23.2^{\circ}C$, $T_{mano} = 20.6^{\circ}C$

Amount introduced = 6.70 ml

$P_{atm} = 620$ mm of Hg, $T_{atm} = 23.0^{\circ}C$, $T_{mano} = 20.8^{\circ}C$

Amount introduced = 8.70 ml

$P_{atm} = 618.5$ mm of Hg, $T_{atm} = 23.4^{\circ}C$, $T_{mano} = 19.6^{\circ}C$

Amount introduced = 3.20 ml

$P_{atm} = 618.5$ mm of Hg, $T_{atm} = 23.6^{\circ}C$, $T_{mano} = 20.1^{\circ}C$

Chromatographic Analysis:

Helium flow at 10 psig $T_{atm} = 24.0^{\circ}C$

Attenuation = 2.0 $T_{mano} = 24.3^{\circ}C$

$P_{atm} = 616.0$ mm of Hg $T_{bath} = 50.0^{\circ}C$

$P_{sys} = 650.0$ mm of Hg

Freon-21 peak height = 19/32"

Ethyl chloride peak height = 28/32"

Run 3Mixture I

$$P_{\text{atm}} = 611.40 \text{ mm of Hg}, \quad T_{\text{atm}} = 23.4^{\circ}\text{C}, \quad T_{\text{mano}} = 23.5^{\circ}\text{C}$$

Gas	Volume, ml	%
Freon-21 15.30 + 6.75	= 22.05	40.0
Ethyl chloride 48.40 - 15.30	= 33.10	60.0
Total	= 55.15	100.0

Amount introduced in the system = 55.15 ml

Mixture II

$$P_{\text{atm}} = 611.30 \text{ mm of Hg}, \quad T_{\text{atm}} = 23.5^{\circ}\text{C}, \quad T_{\text{mano}} = 23.3^{\circ}\text{C}$$

Gas	Volume, ml	%
Freon-21 50.80 - 26.70	= 24.10	41.85
Ethyl chloride 26.70 + 6.75	= 33.45	58.15
Total	= 57.55	100.00

Amount introduced in the system = 55.80 ml

Mixture III

$$P_{\text{atm}} = 611.10 \text{ mm of Hg}, \quad T_{\text{atm}} = 23.6^{\circ}\text{C}, \quad T_{\text{mano}} = 23.6^{\circ}\text{C}$$

Gas	Volume, ml	%
Freon-21 14.00 + 6.75	= 20.75	36.85
Ethyl chloride 49.60 - 14.00	= 35.60	63.15
Total	56.35	100.00

Amount added = 7.50 ml

$$P_{\text{atm}} = 611.1 \text{ mm of Hg}, \quad T_{\text{atm}} = 23.8^{\circ}\text{C}, \quad T_{\text{mano}} = 23.7^{\circ}\text{C}$$

Amount added = 6.30 ml

$$P_{\text{atm}} = 612.2 \text{ mm of Hg}, \quad T_{\text{atm}} = 23.9^{\circ}\text{C}, \quad T_{\text{mano}} = 23.2^{\circ}\text{C}$$

Amount added = 8.50 ml

$P_{\text{atm}} = 614.7$ mm of Hg, $T_{\text{atm}} = 24.1^{\circ}\text{C}$, $T_{\text{mano}} = 22.4^{\circ}\text{C}$

Amount added = 8.70 ml

$P_{\text{atm}} = 617.8$ mm of Hg, $T_{\text{atm}} = 24.0^{\circ}\text{C}$, $T_{\text{mano}} = 21.8^{\circ}\text{C}$

Amount added = 9.00 ml

$P_{\text{atm}} = 619.4$ mm of Hg, $T_{\text{atm}} = 23.7^{\circ}\text{C}$, $T_{\text{mano}} = 21.1^{\circ}\text{C}$

Amount added = 1.40 ml

$P_{\text{atm}} = 621.9$ mm of Hg, $T_{\text{atm}} = 23.0^{\circ}\text{C}$, $T_{\text{mano}} = 21.0^{\circ}\text{C}$

Chromatographic Analysis:

Helium flow at 10.0 psig

$T_{\text{atm}} = 23.5^{\circ}\text{C}$

Attenuation = 2.0

$T_{\text{mano}} = 22.8^{\circ}\text{C}$

$P_{\text{atm}} = 623.0$ mm of Hg

$T_{\text{bath}} = 50.5^{\circ}\text{C}$

$P_{\text{sys}} = 639.0$ mm of Hg

Freon-21 peak height = 21/32"

Ethyl chloride peak height = 22/32"

Run 4Mixture I

$P_{\text{atm}} = 614.0$ mm of Hg,	$T_{\text{atm}} = 24.4^{\circ}\text{C}$,	$T_{\text{mano}} = 22.7^{\circ}\text{C}$
Gas	Volume, ml	%
Freon-21 12.20 + 6.75	= 18.95	24.70
Ethyl chloride 69.80 - 12.20	= 57.60	75.30
Total	= 76.55	100.00

Amount introduced in the system = 76.55 ml

Mixture II

$P_{\text{atm}} = 613.80$ mm of Hg,	$T_{\text{atm}} = 24.0^{\circ}\text{C}$	$T_{\text{mano}} = 22.0^{\circ}\text{C}$
Gas	Volume, ml	%
Freon-21 56.90 - 40.20	= 16.70	26.20
Ethyl chloride 40.20 + 6.75	= 46.95	73.80
Total	= 63.65	100.00

Amount introduced in the system = 41.90 ml

Mixture III

$P_{\text{atm}} = 613.8$ mm of Hg,	$T_{\text{atm}} = 24.1^{\circ}\text{C}$,	$T_{\text{mano}} = 23.0^{\circ}\text{C}$
Gas	Volume, ml	%
Freon-21 9.20 + 6.75	= 15.95	23.90
Ethyl chloride 59.90 - 9.20	= 50.70	76.10
Total	= 66.65	100.00

Amount introduced = 6.30 ml

$P_{\text{atm}} = 615.1$ mm of Hg,	$T_{\text{atm}} = 24.0^{\circ}\text{C}$,	$T_{\text{mano}} = 24.2^{\circ}\text{C}$
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Amount introduced = 3.80 ml

$P_{\text{atm}} = 615.8$ mm of Hg,	$T_{\text{atm}} = 24.4^{\circ}\text{C}$,	$T_{\text{mano}} = 23.6^{\circ}\text{C}$
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Amount introduced = 7.00 ml

$P_{\text{atm}} = 616.4$ mm of Hg, $T_{\text{atm}} = 24.3^{\circ}\text{C}$, $T_{\text{mano}} = 22.9^{\circ}\text{C}$

Amount introduced = 5.10 ml

$P_{\text{atm}} = 616.4$ mm of Hg, $T_{\text{atm}} = 24.5^{\circ}\text{C}$, $T_{\text{mano}} = 22.4^{\circ}\text{C}$

Amount introduced = 8.30 ml

$P_{\text{atm}} = 617.7$ mm of Hg, $T_{\text{atm}} = 24.1^{\circ}\text{C}$, $T_{\text{mano}} = 20.1^{\circ}\text{C}$

Chromatographic Analysis:

Helium flow at 10 psig

$T_{\text{atm}} = 24.5^{\circ}\text{C}$

Attenuation = 2.0

$T_{\text{mano}} = 24.2^{\circ}\text{C}$

$P_{\text{atm}} = 618.30$ mm of Hg

$T_{\text{bath}} = 50.0^{\circ}\text{C}$

$P_{\text{sys}} = 659.0$ mm of Hg

Freon-21 peak height = 13.5/32"

Ethyl chloride peak height = 29/32"

Run 5Mixture I

$P_{\text{atm}} = 615.90$ mm of Hg,	$T_{\text{atm}} = 24.2^{\circ}\text{C}$,	$T_{\text{mano}} = 22.6^{\circ}\text{C}$
Gas	Volume, ml	%
Freon-21	$47.40 - 36.80 = 10.60$	19.50
Ethyl chloride	$36.80 + 6.75 = 43.55$	80.50
Total	$= 54.15$	100.00

Amount introduced in the system = 54.15 ml

Mixture II

$P_{\text{atm}} = 616.0$ mm of Hg,	$T_{\text{atm}} = 24.3^{\circ}\text{C}$,	$T_{\text{mano}} = 22.8^{\circ}\text{C}$
Gas	Volume, ml	%
Freon-21	$4.85 + 6.75 = 11.60$	20.0
Ethyl chloride	$51.10 - 4.85 = 46.25$	80.0
Total	$= 57.85$	100.0

Amount introduced in the system = 45.30 ml.

Mixture III

$P_{\text{atm}} = 616.0$ mm of Hg,	$T_{\text{atm}} = 24.5^{\circ}\text{C}$,	$T_{\text{mano}} = 23.2^{\circ}\text{C}$
Gas	Volume, ml	%
Freon-21	$8.60 + 6.75 = 15.35$	20.00
Ethyl chloride	$70.00 - 8.60 = 61.40$	80.00
Total	$= 76.75$	100.00

Amount added = 17.30 ml

$P_{\text{atm}} = 616.0$ mm of Hg,	$T_{\text{atm}} = 24.5^{\circ}\text{C}$,	$T_{\text{mano}} = 23.2^{\circ}\text{C}$
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Amount added = 1.90 ml

$P_{\text{atm}} = 615.3$ mm of Hg,	$T_{\text{atm}} = 24.3^{\circ}\text{C}$	$T_{\text{mano}} = 23.1^{\circ}\text{C}$
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Amount added = 4.40 ml

$P_{atm} = 615.5$ mm of Hg,

$T_{atm} = 24.1^{\circ}C$,

$T_{mano} = 23.8^{\circ}C$

Amount added = 3.40 ml

$P_{atm} = 617.0$ mm of Hg,

$T_{atm} = 24.0^{\circ}C$,

$T_{mano} = 23.8^{\circ}C$

Amount added = 6.60 ml

$P_{atm} = 617.9$ mm of Hg,

$T_{atm} = 23.0^{\circ}C$,

$T_{mano} = 23.5^{\circ}C$

Amount added = 2.40 ml

$P_{atm} = 616.9$ mm of Hg,

$T_{atm} = 24.0^{\circ}C$,

$T_{mano} = 24.3^{\circ}C$

Amount added = 11.80 ml

$P_{atm} = 616.5$ mm of Hg,

$T_{atm} = 23.7^{\circ}C$

$T_{mano} = 24.4^{\circ}C$

Amount added = 9.00 ml

$P_{atm} = 616.7$ mm of Hg,

$T_{atm} = 24.0^{\circ}C$.

$T_{mano} = 24.4^{\circ}C$

Chromotographic Analysis:

Helium flow at 10 psig

$T_{atm} = 23.8^{\circ}C$

Attenuation = 2.0

$T_{mano} = 24.5^{\circ}C$

$\bar{P}_{atm} = 616.6$ mm of Hg

$T_{bath} = 50.1^{\circ}C$

$P_{sys} = 639.0$ mm of Hg

Freon-21 peak height = 5/32"

Ethyl chloride peak height = 11/32"

Run 6Mixture I

$P_{atm} = 615.0$ mm of Hg,	$T_{atm} = 24.6^{\circ}C$,	$T_{mano} = 24.4^{\circ}C$
Gas	Volume, ml	%
Freon-21 24.90 + 6.75	= 31.65	50.0
Ethyl chloride 56.60 - 24.90	= 31.70	50.0
Total	= 63.35	100.0

Amount introduced in the system = 63.35 ml

Mixture II

$P_{atm} = 615.1$ mm of Hg,	$T_{atm} = 24.8^{\circ}C$	$T_{mano} = 24.2^{\circ}C$
Gas	Volume, ml	%
Freon-21 47.30 - 20.30	= 27.00	50.0
Ethyl chloride 20.30 + 6.75	= 27.05	50.0
Total	= 54.05	100.0

Amount introduced in the system = 47.25 ml

Mixture III

$P_{atm} = 615.2$ mm of Hg	$T_{atm} = 24.8^{\circ}C$	$T_{mano} = 24.8^{\circ}C$
Gas	Volume, ml	%
Freon-21 24.50 + 6.75	= 31.25	50.0
Ethyl chloride 55.70 - 24.50	= 31.20	50.0
Total	= 62.45	100.0

Amount added = 11.10 ml

$P_{atm} = 615.2$ mm of Hg,	$T_{atm} = 24.8^{\circ}C$	$T_{mano} = 24.1^{\circ}C$
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Amount added = 3.70 ml

$P_{atm} = 615.8$ mm of Hg,	$T_{atm} = 24.5^{\circ}C$	$T_{mano} = 23.1^{\circ}C$
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Amount added = 8.00 ml

$P_{atm} = 616.4$ mm Hg, $T_{atm} = 24.2^{\circ}C$, $T_{mano} = 22.4^{\circ}C$

Amount added = 4.30 ml

$P_{atm} = 618.6$ mm of Hg, $T_{atm} = 24.6^{\circ}C$, $T_{mano} = 22.3^{\circ}C$

Amount added = 4.10 ml

$P_{atm} = 615.9$ mm of Hg, $T_{atm} = 24.5^{\circ}C$, $T_{mano} = 23.8^{\circ}C$

Amount added = 2.50 ml

$P_{atm} = 616.2^{\circ}$ mm of Hg, $T_{atm} = 24.8^{\circ}C$, $T_{mano} = 23.2^{\circ}C$

Amount added = 3.40 ml

$P_{atm} = 618.5$ mm of Hg, $T_{atm} = 24.8^{\circ}C$, $T_{mano} = 24.0^{\circ}C$

Amount added = 1.50 ml

$P_{atm} = 621.4$ mm of Hg, $T_{atm} = 23.5^{\circ}C$, $T_{mano} = 24.3^{\circ}C$

Amount added = 1.50 ml

$P_{atm} = 621.8$ mm of Hg, $T_{atm} = 23.6^{\circ}C$, $T_{mano} = 24.3^{\circ}C$

Chromatographic Analysis:

Helium flow at 10 psig

$T_{atm} = 24.0^{\circ}C$

Attenuation = 2.0

$T_{mano} = 24.0^{\circ}C$

$P_{atm} = 621.0$ mm of Hg

$T_{bath} = 50.0^{\circ}C$

$P_{sys} = 618.0$ mm of Hg

Freon-21 peak height = 11/32"

Ethyl chloride peak height = 6.5/32"

A P P E N D I X I VBinary Mixture Sample Calculation for Run No.2:

The following steps are involved in the calculation

- 1) Calculate the exact composition of feed and the volume of each gas introduced at STP
- 2) Calculate the equilibrium composition of the gaseous mixture in the system.
- 3) Calculate the volume of each gas adsorbed at STP.

Step 1

In the calculation of the feed composition, the volume of the uncaliberated part of gas-burette is needed and was determined in the previous investigation (32) as

Volume of uncaliberated part = 6.75 ml

For mixture I

Freon-21 Volume = 17.90 ml

Ethyl chloride volume = 36.95 ml

Total gas volume = 54.85 ml

Therefore

$$\begin{aligned} \text{Percent freon-21 in the mixture} &= \frac{17.90 \times 100}{54.85} \\ &= 32.6 \% \end{aligned}$$

$$\text{Similarly ethyl chloride} = 67.4 \%$$

Similarly for mixture II

$$\begin{aligned} \text{Percent freon-21} &= 32.90 \% \\ \text{and Percent ethyl chloride} &= 67.10 \% \end{aligned}$$

and for mixture III

$$\begin{aligned} \text{Percent freon-21} &= 33.0 \% \\ \text{and \% ethyl chloride} &= 67.0 \% \end{aligned}$$

Therefore

$$\begin{aligned} \text{average percent of ethyl} \\ \text{chloride in the system} &= \frac{67.40 + 67.10 + 67.00}{3} \\ &= 67.17\% \end{aligned}$$

$$\begin{aligned} \text{and average percent of freon-21} \\ \text{in the system} &= 32.83\% \end{aligned}$$

for mixture I

$$\text{amount introduced} = 54.85 \text{ ml}$$

$$P_{\text{atm}} = 623.60 \text{ mm of Hg.}, T_{\text{atm}} = 24.0^{\circ}\text{C}$$

$$\text{Barometer reading correction to } 0^{\circ}\text{C} = 2.40 \text{ mm of Hg.}$$

$$\begin{aligned} \text{Therefore } P_{\text{atm}}^{\circ} &= 623.60 - 2.40 \\ &= 621.20 \text{ mm of Hg.} \end{aligned}$$

so volume introduced at STP

$$\begin{aligned} &= \frac{54.85 \times 273.15 \times 621.20}{297.15 \times 760.0} \\ &= 41.20 \text{ ml.} \end{aligned}$$

for mixture II

$$\text{amount introduced} = 55.85 \text{ ml}$$

$$P_{\text{atm}} = 623.7 \text{ mm of Hg.}, T_{\text{atm}} = 23.9^{\circ}\text{C}$$

Barometer reading correction = 2.40 mm of Hg.

$$\begin{aligned} \text{Therefore } P_{\text{atm}}^{\circ} &= 623.70 - 2.40 \\ &= 621.40 \text{ mm of Hg} \end{aligned}$$

So volume introduced at STP

$$\begin{aligned} &= \frac{55.85 \times 273.15 \times 621.30}{297.05 \times 760.0} \\ &= 41.90 \text{ ml} \end{aligned}$$

for mixture III

(i) amount introduced = 5.8 ml

$$P_{\text{atm}} = 623.6 \text{ mm of Hg, } T_{\text{atm}} = 23.9^{\circ}\text{C}$$

Barometer reading correction = 2.40 mm of Hg

$$\begin{aligned} \text{Therefore } P_{\text{atm}}^{\circ} &= 623.60 - 2.40 \\ &= 621.20 \text{ mm of Hg} \end{aligned}$$

So volume introduced at STP

$$\begin{aligned} &= \frac{5.8 \times 273.15 \times 621.20}{297.05 \times 760.0} \\ &= 4.36 \text{ ml} \end{aligned}$$

(ii) amount added = 1.80 ml

$$P_{\text{atm}} = 622.9 \text{ mm of Hg, } T_{\text{atm}} = 23.7^{\circ}\text{C}$$

Barometer reading correction = 2.40 mm of Hg

$$\text{Therefore } P_{\text{atm}}^{\circ} = 620.5 \text{ mm of Hg}$$

So volume introduced at STP

$$\begin{aligned} &= \frac{1.80 \times 273.15 \times 620.50}{296.85 \times 760.0} \\ &= 1.35 \text{ ml} \end{aligned}$$

(iii) volume introduced = 2.60 ml

$$P_{\text{atm}} = 622.50 \text{ mm of Hg, } T_{\text{atm}} = 23.8^{\circ}\text{C}$$

Barometer reading correction = 2.42 mm of Hg

$$\text{Therefore } P_{\text{atm}}^{\circ} = 622.5 - 2.42 = 620.08 \text{ mm of Hg}$$

So volume introduced at STP

$$= \frac{2.60 \times 273.15 \times 620.08}{296.95}$$

$$= 1.95 \text{ ml}$$

(iv) Volume introduced = 3.0 mls

$$P_{\text{atm}} = 622.50 \text{ mm of Hg, } T_{\text{atm}} = 23.1^{\circ}\text{C}$$

Barometer reading correction = 2.25 mm of Hg

$$\text{Therefore } P_{\text{atm}}^{\circ} = 622.50 - 2.25$$

$$= 620.25 \text{ mm of Hg.}$$

So volume introduced at STP

$$= \frac{3.0 \times 273.15 \times 620.25}{296.25 \times 760.0}$$

$$= 2.26 \text{ ml.}$$

(v) Volume introduced = 8.50 ml

$$P_{\text{atm}} = 622.0 \text{ mm of Hg, } T_{\text{atm}} = 23.2^{\circ}\text{C}$$

Barometer reading correction = 2.30 mm of Hg.

$$\text{Therefore } P_{\text{atm}}^{\circ} = 622.0 - 2.30$$

$$= 619.70 \text{ mm of Hg.}$$

So volume introduced at STP

$$= \frac{8.50 \times 273.15 \times 619.70}{296.35 \times 760.0}$$

$$= 6.38 \text{ ml}$$

(vi) Volume introduced = 6.70 ml

$$P_{\text{atm}} = 620.6 \text{ mm of Hg, } T_{\text{atm}} = 23.0^{\circ}\text{C}$$

Barometer reading correction = 2.30 mm of Hg.

$$\text{Therefore } P_{\text{atm}}^{\circ} = 620.60 - 2.30$$

$$= 618.30 \text{ mm of Hg.}$$

So volume introduced at STP

$$= \frac{6.70 \times 273.15 \times 618.30}{296.15 \times 760.0}$$

$$= 5.25 \text{ ml}$$

(vii) Volume introduced = 8.70 ml

$$P_{\text{atm}} = 618.50 \text{ mm of Hg}, \quad T_{\text{atm}} = 23.4^{\circ}\text{C}$$

Barometer reading correction = 2.35 mm of Hg.

$$\begin{aligned} \text{Therefore } P_{\text{atm}}^{\circ} &= 618.50 - 2.35 \\ &= 616.15 \text{ mm of Hg.} \end{aligned}$$

So volume introduced at STP

$$\begin{aligned} &= \frac{8.70 \times 273.15 \times 616.15}{296.45 \times 760.0} \\ &= 6.49 \text{ ml} \end{aligned}$$

(viii) Volume introduced = 3.20 ml

$$P_{\text{atm}} = 618.50 \text{ mm of Hg}, \quad T_{\text{atm}} = 23.6^{\circ}\text{C}$$

Barometer reading correction = 2.35 mm of Hg.

$$\begin{aligned} \text{Therefore } P_{\text{atm}}^{\circ} &= 618.50 - 2.35 \\ &= 616.15 \text{ mm of Hg.} \end{aligned}$$

So volume introduced at STP

$$\begin{aligned} &= \frac{3.20 \times 273.15 \times 616.15}{296.75 \times 760.0} \\ &= 2.39 \text{ ml} \end{aligned}$$

So Total volume introduced at STP

$$= 111.60 \text{ ml.}$$

Therefore volume of freon-21 introduced (STP)

$$\begin{aligned} &= 111.60 \times 0.3283 \\ &= 36.60 \text{ ml} \end{aligned}$$

and volume of ethyl chloride introduced (STP)

$$= 75.00 \text{ ml.}$$

Step 2

Calculation of equilibrium composition of gases

Since there was very little separation of peaks and it

was difficult to obtain calibration curves for the pure gases due to leak in sample valve on the chromatograph, a peak ratio was the means used to get the composition. This approximation is valid since there is not much difference in thermal conductivity of both the gases.

$$\text{Freon-21 peak height} = 19/32''$$

$$\begin{aligned} \text{Ethyl chloride peak} \\ \text{height} &= 28/32'' \end{aligned}$$

Therefore

$$\begin{aligned} \% \text{ of Freon-21} &= \frac{(19/32)}{(19 + 28/32)} \times 100 \\ &= 40\% \end{aligned}$$

and percent of Ethyl chloride = 60.0%

Step 3

The sample valve on chromatograph is included in the system and since it is not leakproof, the sample loop was first filled with helium at atmospheric pressure, and so that much helium is mixed with the feed. The volume of that loop is 5.05 ml determined as follows:

1/8" OD Cu-tubing, 37.64 in long with volume = 2.03 ml

1/4" OD Cu-tubing, 6.50 in long with volume = 3.02 ml

Therefore

$$\text{Total volume} = 5.05 \text{ ml.}$$

Also due to a mixing problem in the system,

part of the system will be at the feed composition.

This volume is as follows:

left leg of manometer, 38.25 in long with 0.3 cm ID

$$\text{Volume} = 6.83 \text{ ml}$$

Burette's top valve to tee near circulation pump

$$3.50 \text{ in. Cu-tubing, with } 0.4 \text{ cm ID, Vol.} = 1.12 \text{ ml.}$$

$$1.75 \text{ in Cu-tubing, with } 1.00 \text{ cm ID, Vol.} = 3.40 \text{ ml}$$

$$12.00 \text{ in Cu-tubing, with } 0.065 \text{ in ID, Vol} = 0.65 \text{ ml}$$

Therefore

$$\text{Total volume at feed composition} = 12.10 \text{ ml}$$

Thus we have for the system

$$12.10 \text{ ml at feed composition, } P_{\text{sys}} \text{ and } T_{\text{mano}}$$

$$38.95 \text{ ml at equilibrium composition, } P_{\text{sys}} \text{ and } T_{\text{mano}}$$

$$\text{and } 1.20 \text{ ml at equilibrium composition, } P_{\text{sys}} \text{ and } T_{\text{bath}}.$$

The effective system pressure will be the system pressure less the partial pressure of the helium which is mixed with the gases.

Therefore

$$\begin{aligned} P_{\text{sys}}(\text{effective}) &= P_{\text{sys}} - P_{\text{sys}} \times \text{vol \% helium} \\ &= 650 \text{ mm of Hg} - 650.0 \text{ mm of Hg} \times \frac{5.05}{40.15} \\ &= 650.0 - 80.9 \\ &= 569.10 \text{ mm of Hg.} \end{aligned}$$

$$\begin{aligned} P_{\text{sys}}^{\circ}(\text{effective}) &= 569.10 \text{ mm of Hg} \times \frac{\text{Hg at } T_{\text{mano}}}{\text{Hg at } 0^{\circ}\text{C}} \\ &= 569.10 \text{ mm of Hg} \times \frac{13.5362}{13.5955} \\ &= 566.0 \text{ mm of Hg.} \end{aligned}$$

The volume of gas mixture present at STP will be

$$\frac{12.10 \times 566.0 \times 273.15}{760.0 \times 297.15}$$

$$= 8.30 \text{ ml at feed composition}$$

$$\frac{38.95 \times 566.0 \times 273.15}{760.0 \times 297.15}$$

$$= 26.70 \text{ ml at equilibrium composition}$$

$$\text{and } \frac{1.20 \times 566.0 \times 273.15}{760.0 \times 323.15}$$

= 0.757 ml at equilibrium composition

Volume of mixture present ml (STP)	Freon-21		Ethyl chloride	
	%	Vol. present	%	Vol. present
8.300	32.83	2.725	67.17	5.575
26.700	40.00	10.695	60.00	16.005
0.757	40.00	0.303	60.00	0.454
Total		13.723		22.034

Gas	Volume into (STP) ml	Volume present (STP) ml	Volume adsorbed pergram ml
Freon-21	36.60	13.723	22.877
Ethyl chloride	75.00	22.034	52.966
Total	111.60	35.757	75.843

A P P E N D I X V

Prediction of mixture isotherm

The procedure for calculating mixture adsorption from the pure component isotherms is as follows:

1. Select the value of P_{sy}^0 (on pure gas isotherms),
560 mm of Hg.
2. Select a value n_t lying between $n_1(P_{sy}^0)$ and $n_2(P_{sy}^0)$,
where subscript 1 refers to freon-21 and 2 refers to
ethyl chloride
3. From the pure gas isotherms obtain $P_{sy1}^0(n_t)$ and
 $P_{sy2}^0(n_t)$
4. Calculate x_1 using

$$P_{sy}^0 = P_{sy1}^0 \cdot x_1 + P_{sy2}^0 \cdot x_2$$

$$x_2 = 1 - x_1$$

5. Calculate y_1 using

$$y_1 = \frac{P_{sy1}^0 \cdot x_1}{P_{sy}^0}$$

$$y_2 = 1 - y_1$$

6. Calculate volume (STP) adsorbed/gm of adsorbent
using

$$n_1 = x_1 \cdot n_t$$

$$n_2 = (1 - x_1) \cdot n_t$$

$$n_t = n_1 + n_2$$

y_1 and y_2 = Gas-phase equilibrium composition for component
1 and 2

x_1 and x_2 = adsorbed - phase composition for component 1 and 2.

Table

$P_{sy}^0 = 560$ mm of Hg

$n_1(P_{sy}^0) = 78.00$ ml

$n_2(P_{sy}^0) = 72.00$ ml

n_t	$P_{sy1}^0(n_t)$	$P_{sy2}^0(n_t)$	x_1	x_2	y_1	y_2	n_1	n_2
72.00	420.0	560.0	0.000	1.000	0.000	1.000	0.000	72.00
73.00	435.0	585.0	0.166	0.834	0.129	0.871	12.10	60.90
74.00	465.0	610.0	0.345	0.655	0.287	0.713	25.50	48.50
75.00	485.0	650.0	0.545	0.455	0.471	0.529	40.80	34.20
76.00	500.0	670.0	0.645	0.354	0.575	0.424	49.00	27.00
77.00	535.0	730.0	0.870	0.130	0.831	0.169	66.00	11.00
78.00	560.0	800.0	1.000	0.000	1.000	0.000	78.00	0.00

APPENDIX VI.

ERROR ESTIMATION

Error in the results may be caused by errors made in various measurements during the experimental investigation. Following are the possible sources of error in measurements.

1. Burette: Volume of the calibrated part = 100.0 cc.
Magnitude of smallest division = 0.2 cc.
Possible error in reading the
the volume = ± 0.1 cc

2. Mercury Manometer: Scale is from 0 mm of Hg to 990
mm of Hg.
Magnitude of smallest division = 1 mm.
of Hg.
Possible error in reading the
pressure = ± 0.5 mm of Hg.

3. Peak Heights on the Chromotograph Chart:
Peak heights were measured by scale 1:32
Possible error in measuring the peak height = $\pm 1/64$ in

4. Gas Sampling Valve: Possible error could be caused by the difference in sample volume of different samples introduced to the chromatograph. But, as the sensitivity of the detector depends on the concentration of the gases in the sample mixture rather than the volume of the sample, it is less likely to be the source of error in the results.
5. Flow of the carrier gas in the chromatograph: The constant flow of the helium gas is maintained in each run indirectly by maintaining the constant 10 psig pressure of helium in the chromatograph.
6. Dead Volume Measurement: The accuracy of the data may be dependent on the accuracy of the dead volume measurement of the system.