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MATTHEWS, Robert Ramage, 1933-
THEORY OF SOLUTIONS AND ION-SELECTIVE
MEMBRANE SYSTEMS.

The University of Oklahoma, Ph.D., 1963
Chemistry, physical

University Microfilms, Inc., Ann Arbor, Michigan

THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

THEORY OF SOLUTIONS AND ION-SELECTIVE MEMBRANE SYSTEMS

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

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Norman, Oklahoma

1962

THEORY OF SOLUTIONS AND ION-SELECTIVE MEMBRANE SYSTEMS

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PREFACE

The goal of this research was to extend the theoretical understanding of equilibrium and non-equilibrium properties of electrolyte solutions as an aid to the establishment of correct premises. The free volume model of pure liquids had been an effective interpretive tool for that class of substances. A considerable effort was expended in this research in an extension of the model to binary non-electrolyte solutions. The results of the treatment are interesting and useful, but they did not suggest profitable extension of the model to electrolytes. This dissertation appears in two distantly related parts, with the non-electrolyte contribution as Part II.

For practical reasons the electrolytes research was shifted from model interpretation of relatively simple systems to phenomenological description of complex systems. This contribution appears as Part I because it has required the greater effort and the results are regarded as the more significant.

The author wishes to express his gratitude to Dr. George W. Murphy who suggested and directed the present research. He is also indebted to the Office of Saline Waters, United States Department of the Interior, whose grant under Contract Number 14-01-001 - 191

made the research reported in Part I possible. The generosity and helpfulness of the staff of the University of Oklahoma Computer Laboratories was also greatly appreciated. Finally the author thanks the faculty, staff and fellow students of the Chemistry Department for their friendship and encouragement.

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THEORY OF SOLUTIONS AND ION SELECTIVE
MEMBRANE PROCESSES

PART I

NON-EQUILIBRIUM PROCESSES IN ELECTROLYTES
AND MEMBRANE SYSTEMS

CHAPTER I

NON-EQUILIBRIUM THERMODYNAMICS

A serious shortcoming of the method of classical thermodynamics is that its results are valid only for systems which are at equilibrium or are subjected to "reversible" processes. Unfortunately, no real system is ever completely at "equilibrium" nor is any real process "reversible." Hence, there is an obvious need for an extension of the theory of thermodynamics which will include irreversible processes.

During the last twenty years a rather complete system has been developed for a macroscopic theory of irreversible processes. Excellent reviews of the subject are given by Prigogine (1, 2), de Groot (3), and Denbigh (4); therefore, it is necessary here to present only a brief outline of the major principles of the discipline.

Phenomenological Equations

For a long time there have existed many phenomenological laws dealing with irreversible processes in the form of proportionalities. Familiar examples are Fick's law of diffusion relating a flux of a component in a mixture to its concentration gradient; Ohm's law, which relates the current flow to a potential gradient; and Fourier's law, relating the flow of heat to a temperature gradient.

The question naturally arises as to what is the effect of two or more such processes occurring simultaneously. Intuition suggests and experience proves that they will couple and interfere with one another. Again a number of examples could be given, such as the two reciprocal phenomena of the thermoelectricity arising from the interference of the conduction of heat and electricity, i.e. the Peltier effect and the so-called thermoelectric force. The mathematical laws describing such cross phenomena are truly "phenomenological" in the sense that they are verifiable by experiment and yet not included in the theory of reversible thermodynamics.

A systematic approach to the problems presented by irreversible processes is based on a theory published by Onsager (5) and a later refinement by Casimir (6). The methods presented by Onsager were soon used to formulate a systematic phenomenological description of the transport of heat and matter in systems departing from thermodynamic equilibrium (1, 3, 7, 8).

Irreversible processes can best be described in terms of generalized "fluxes" J_i (the flow of electric current, heat, matter, etc.) and generalized "forces" X_i (concentration and temperature gradients, etc.). DeDonder's term affinities for the quantities X_i is probably more appropriate than the term forces, but the latter has been adopted by most authors and will be used in the present paper. The quantities J_i and X_i are related in a set of phenomenological equations:

$$J_i = \sum_j L_{ij} X_j$$

Taking the clue from experience with many irreversible processes, it seems reasonable to assume that the coefficients L_{ij} will remain constant as long as the system remains not too far from equilibrium. This property of the L_{ij} 's can be demonstrated theoretically (4, 5, 6,) but mathematical complexity has thus far prevented a good answer to the question as to just how far from equilibrium is too far (7).

In order to demonstrate a very interesting and useful property of the coefficients L_{ij} , Onsager made use of the principle of microscopic reversibility. This principle, which is discussed in detail by Tolman (9) and Fowler and Guggenheim (10), postulates that, under equilibrium conditions, any molecular process and the reverse of that process will be taking place at the same rate. These authors show the principle to be on sound quantum theoretical ground. The apparent incompatibility of the principle of microscopic reversibility with the fact

of macroscopic irreversibility is discussed thoroughly by de Groot (3). Using the general methods of statistical mechanics and the principle of microscopic reversibility, Onsager (5) showed that the matrix of coefficients is symmetrical, i. e.

$$L_{ij} = L_{ji} \quad (1)$$

if forces X_i and fluxes J_i are chosen so that the rate of entropy production is given by

$$d\Delta S/dt = (1/T) \sum_i J_i X_i . \quad (2)$$

Many choices of the forces and fluxes are usually available which satisfy (2). However, some choices may be more suitable than others for bringing the phenomenological equations into terms of variables that are readily observable. Many problems which have proved quite difficult or impossible to solve using one set of forces and fluxes have readily yielded to solution once a suitable set has been found. The methods of transformation from one set of J_i 's and X_i 's to another is discussed in detail by Prigogine (1), de Groot (3), and Meixner (11). These authors state that in order to insure the thermodynamic equivalence of two sets of variables, it is necessary to insure that the entropy production rate remains invariant under the transformation, i. e.

$$T (d\Delta S/dt) = \sum_i J_i X_i = \sum_i J_i' X_i' , \quad (3)$$

where J_i' and X_i' are the new or transformed set of generalized fluxes and forces. The condition given by (3) is also sufficient if overall conservation of mass and energy are not violated by the transformation (1).

Entropy Production

Thus it is seen that the entropy production is of fundamental importance in the study of a system in which irreversible processes are taking place. Hence, it is not sufficient to discuss the entropy production qualitatively, but it will be necessary to derive quantitative expressions for $d\Delta S/dt$ in order to produce a mathematical description of non-equilibrium processes.

The entropy of a system, which is an extensive quantity relating to the system as a whole, can vary for two reasons and two reasons only: either by a transport of heat across the boundary of the system or by production of entropy by irreversible phenomena taking place within the system. If we denote by $d_e S$ the entropy being transported into a system during a specific time interval, and by $d_i S$ the entropy produced by irreversible processes within the system, then the total entropy change for the system is given by

$$dS = d_e S + d_i S. \quad (4)$$

The second law of thermodynamics states that

$$d_e S = dQ/T \text{ (reversible)}, \quad d_i S \geq 0. \quad (5)$$

This formulation of the second law is valid no matter what the specific conditions under which the process is carried out.

The flux of ions is the principal topic to be discussed in this paper. This phenomenon is found in several systems which are physically similar, namely solutions, cells with and without transference

and systems of solutions separated by membranes. We will consider the flux of ions in an electric field in some detail, for it will be seen that the results of such consideration can be applied with a little generalization to the remaining systems of interest.

Ion Flux in Solution with Electric Field

Figure 1 represents a differential volume element of a solution of some electrolyte.

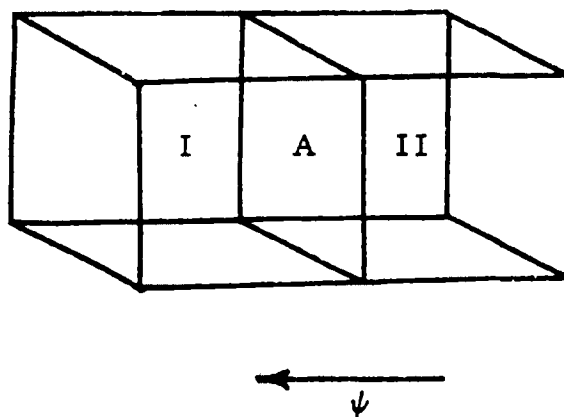


Figure 1

Let us conceive that the imaginary plane A separates the volume into two elements I and II which possess a difference in electrolyte concentration and a difference in electrical potential giving rise to an electric field whose component normal to plane A

is ψ . Writing a mass balance for the flux of ions across the plane A, we have

$$-dn_i^I = dn_i^{II} = d\xi_i, \quad (6)$$

where the function ξ_i is the so-called "degree of advancement." The total current I carried by the ions moving across A is given by

$$I = \sum_i z_i F d\xi_i / dt = \sum_i z_i F J_i, \quad (7)$$

if A is of unit area.

The first law of thermodynamics for this system has the form

$$dU = dQ - pdV + (\psi^I - \psi^{II}) I dt, \quad (8)$$

and the differential entropy change is given by the following formula due to Gibbs:

$$dS = \frac{1}{T} dU + \frac{p}{T} dV - \sum_i \left(\frac{\mu_i^I}{T} dn_i^I - \frac{\mu_i^{II}}{T} dn_i^{II} \right) \quad (9)$$

where μ_i^I and μ_i^{II} are the chemical potentials of the i^{th} ion in phases I and II respectively. (This formulation of dS is valid if we assume that S is a function of ψ , V , and n_i alone. This will be true in the absence of variation of polarization of matter (12).) Combining, we obtain

$$dS = \frac{dQ}{T} + \frac{1}{T} \sum \left[(z_i F \psi^I + \mu_i^I) - (z_i F \psi^{II} + \mu_i^{II}) \right] d\xi_i.$$

The combination of electric and chemical potentials, $z_i F \psi + \mu_i$, is referred to as the electrochemical potential and is symbolized $\bar{\mu}_i$. Thus,

$$dS = (dQ/T) + (1/T) \sum \Delta \bar{\mu}_i d\xi_i, \quad (10)$$

whence,

$$(dS/dt)_{\text{irreversible}} = (1/T) \sum \Delta \bar{\mu}_i J_i \quad (11)$$

Comparing (11) with (5) and (2) it is seen that $\Delta \bar{\mu}_i$ and J_i will serve as generalized forces and fluxes for formulation of this system in irreversible thermodynamics.

CHAPTER II

SYSTEMS CONTAINING ION-PERMEABLE MEMBRANES

Donnan Equilibrium

If the imaginary plane A in Figure 1 is replaced by a membrane m, one has the situation represented in Figure 2. It occurred to Donnan (13) in 1911 that if such a membrane transmits certain kinds of ions but not others, then an unequal distribution of the ions that can pass through the membrane must be set up on either side at equilibrium, as a result of the requirement of electrical neutrality on both sides. If, for example, phases I and II are solutions of sodium chloride with different concentrations, and if the membrane permits the passage of sodium ions only, a flux of cations will take place from phase I to phase II (assuming the initial concentration of I to be higher than that of II). Of course, preservation of electrical neutrality of both sides must be maintained by use of electrodes ideally reversible to the anion which will furnish chloride ions to phase II and remove them from I.

The theoretical investigation of the Donnan membrane equilibrium (14, 15, 16, 17) has in the past outrun its experimental study,

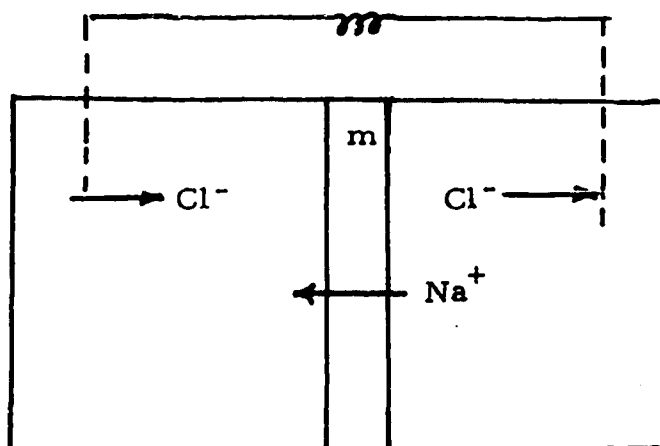


Figure 2

which was long confined to systems containing colloidal or semi-colloidal ions as nondiffusible ions, and to a few systems in which the ferrocyanide ion acted as the nondiffusible species in conjunction with a copper ferrocyanide membrane. Donnan equilibria in which small ions act as nondiffusible species could not be studied since suitable membranes were not available. Now, however, permselective membranes lend themselves admirably to this purpose.

Ion-Selective Membranes

These permselective membranes are composed of solid polyelectrolytes consisting of a hydrocarbon crosslinked skeleton to which polar groups are attached (18,19). The polar groups may be chemically

combined with the substance of the membrane. An example of the first type is provided by the anion-selective membranes of Sollner (20). These membranes are made by the adsorption of protamine cations on nitrocellulose membranes. The second type is exemplified by oxidized nitrocellulose membranes (21), where oxidation has produced carboxyl groups presumably on the sixth carbon atom of the glucose residues. In nuclear sulfonic cation-exchange resins the bound groups are the $-SO_3-$ anions. The counter ions, cations in these last two cases, may be considered dissociated from this skeleton. The small cations in the vicinity of the polyanion can move into an adjacent solution only to the extent determined by the relation between their thermal energy and electrostatic attraction. They can, however, move freely inside the resin.

The mechanism of ion transport within the membrane has received a great deal of theoretical attention (22 - 33). Qualitatively the principal ideas can be simply stated. Ions charged oppositely to the fixed charges on the membrane (gegenions) are free to move into and through the pores of the membrane, while ions of the same charge (nebenions) are restrained from entering the pores by electrostatic repulsion. If the pore size is small enough, nebenions are virtually excluded. Any membrane which is available at present must be assumed to be heteroporous, a mosaic of wider and narrower channels. The observable membrane effects are the gross result of the processes

which occur across the different pores and arise because of their interaction. Certain of the consequences of heteroposity were stressed by Sollner (34 - 37). Electrolyte leakage (simultaneous transport of nebenions and gegenions) will occur through the large pores. Multivalent ions are much more restricted in their permeation across the membrane than univalent ions because their high charge prevents them, by electric repulsion, from entering narrow pores which are accessible to univalent ions of the same size.

With increasing concentration of the outside electrolyte solutions, an increasing quantity of electrolyte, equivalent quantities of anions and cations, enters the pores. The specific influence of the membrane is thereby decreased. This explains why the ionic selectivity of a given membrane decreases if the concentration of the adjacent electrolyte solutions is increased.

At any rate, the virtual transportation of electricity across a permselective membrane is divided between anions and cations in a proportion which is different from the ratio of the transference number of these ions in free solution. If a membrane is exclusively permeable to cations, the transference number of the cation in the membrane is unity. This is ideal ionic selectivity. Furthermore, if a permselective membrane is interposed between two solutions of different concentration of the same electrolyte, an electromotive force arises which is different from that which would arise between

the same two solutions in the absence of a membrane, i. e. with free diffusion. The electromotive forces arising in such membrane concentration cells are referred to as "concentration potentials."

Membranes of very low porosity or with a high ratio of bound ions to pore volume will be nearly impermeable to the diffusion of salts and the concentration potential may reach the magnitude of the potential difference which would arise between two solutions if they were connected to each other through a pair of reversible electrodes specific for either the cations or the anions. This is the maximum possible value for the concentration potential; the lower limit is the liquid junction potential. Thus, it is seen that concentration cells with and without transference may be considered as special cases of membrane systems.

The theory of irreversible thermodynamics as applied to membrane processes has been studied by Spiegler (31). To explain transport processes in membranes, he used a simple frictional model which affords a relationship between the coefficients L_{ij} which supplements Onsager's reciprocal relations (1). This model and its theoretical consequences has been studied more extensively by Meares and coworkers (38 - 42).

The Osmionic Process

Consider the system of membranes depicted in Figure 3. It is constructed of four membranes, alternately cation- and anion-

selective, which enclose three compartments (S_1 , P, S_2) each containing an aqueous solution of an electrolyte. The entire cell is immersed in a brine (B) which is more concentrated than the solutions inside the cell.

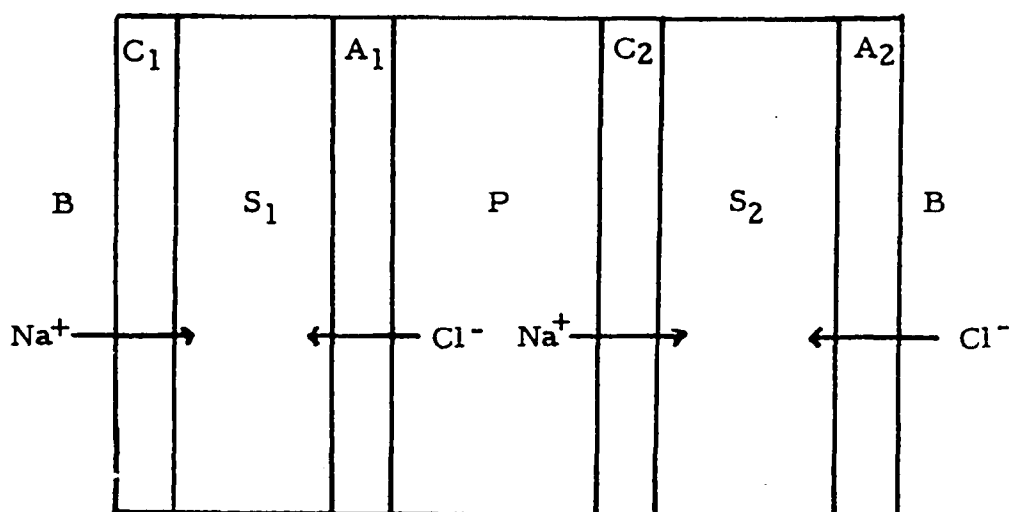


Figure 3

For simplicity of qualitative discussion let us say that sodium chloride is the only electrolyte present in the brine and in the solutions S_1 , P, and S_2 . Let us also assume perfect membrane selectivity.

The concentration gradient set up across membranes C_1 and A_2 will be responsible for a flux of sodium ions from the brine into solution S_1 and of chloride ions (in an equivalent amount) into solution S_2 . The maintenance of electrical neutrality in the S

compartments will require a simultaneous flux of cations from P to S₂ and of anions from P to S₁. Thus the S compartments will be concentrated and the P compartments will be demineralized. This process will continue until the Donnan equilibrium concentrations are attained.

Since the driving force for this process is a difference in concentration across membranes, it can be called osmotic; and since ionic transport in membranes is an essential feature, the overall process has been named osmionic (43, 44).

The use of this process for the demineralization of saline water was envisioned by Murphy (45). The process is similar to electrodyalysis, but has the advantage of requiring none of the conventional power sources, such as heat and electricity, except for pumps to move the fluid streams. The principle of the osmionic cell has been validated by Murphy and Taber (46) and a considerable amount of experimental work has been performed by the Southern Research Institute under contract 14-01-001-88 with the Office of Saline Water, United States Department of the Interior.

Figure 1 can be considered as a schematic diagram for a single effect osmionic cell. If an additional pair of membranes is added as in Figure 4, the driving force of the cell and hence the theoretical amount of demineralization in the P compartment will be increased. Such configuration of membranes is termed a double effect cell. Figure 5 is then schematic for a triple effect cell. This

multiplication of effects by the use of additional pairs of membranes can be continued indefinitely. Diagrams for other plausible membrane configurations are given by Murphy (47).

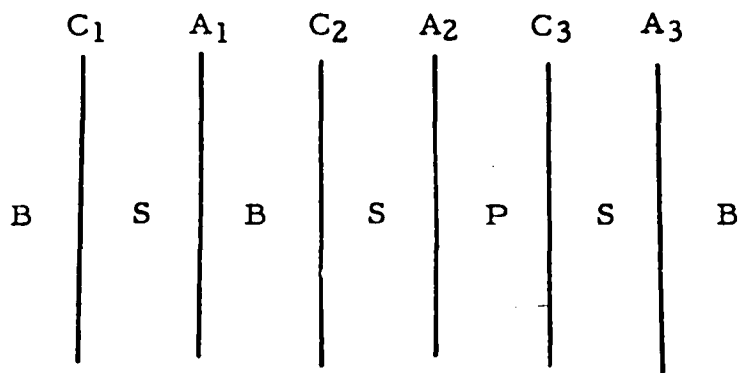


Figure 4

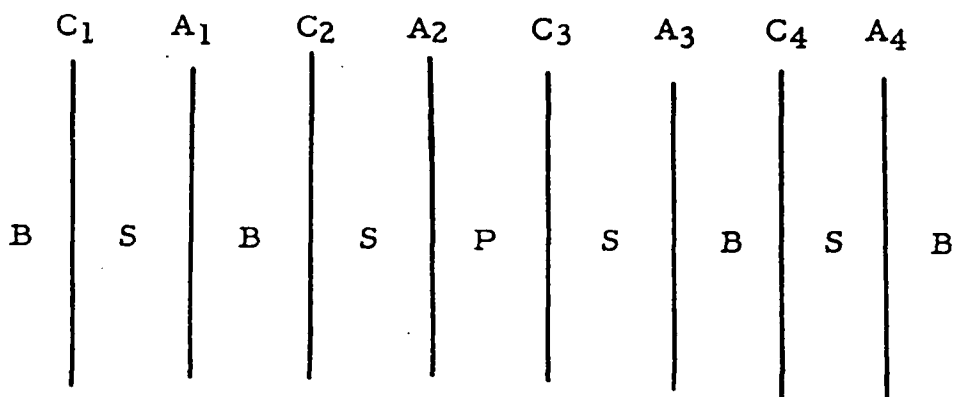


Figure 5

Theoretical expressions for the ionic fluxes arising in osmotic demineralization were derived by Murphy (47, 48) for the special case of one electrolyte. It is the purpose of the present research to extend Murphy's treatment to include any number of electrolytes. Also, membrane leakage, which was ignored in previous treatments, will be considered here.

CHAPTER III

THEORETICAL

The nomenclature used in the present treatment is the same as that used by Murphy and Taber (48) with a few exceptions. A summary of the symbols used in this paper is given in Table 1.

TABLE 1
SUMMARY OF SYMBOLS

A_i	symbol denoting anion permeable membrane
$[A]_{\alpha\beta}$	an element of the transformation matrix defined by (21)
$[A^{-1}]_{\alpha\beta}$	an element of the matrix inverse to A
B	symbol denoting brine compartment
$[B]$	matrix defined by equation (43)
\bar{C}_i^r	concentration of the i^{th} ion in region r
C_i	symbol denoting cation permeable membrane
C_{ij}^r	concentration of the ij^{th} electrolyte in region r

D^s	gap between membranes, cm
D^m	thickness of membrane m, cm
D	total gap between probe electrodes: $D = D^s + D^m$
E_i	potential of electrode reversible to i^{th} ion
F	Faraday constant: 96,494 coulomb/g - equivalent
G	Gibbs free energy
I_j	electric current density carried by j^{th} ion, coulombs/sec-cm ²
I	total current density
J_j	flux of the j^{th} ion, g-ion/cm ² -sec
P	compartment in osmionic cell being demineralized
R	gas constant
S_i	compartment in osmionic cell being enriched
T	absolute temperature
i, j	indices referring to ions of opposite polarity
k_j^s	specific ionic conductance of solution s: $k_j^s = \bar{C}_j^s \lambda_j^s$
k_j^m	specific ionic conductance of membrane m: $k_j^m = \bar{C}_j^m \lambda_j^m$
$k_j^{s,m}$	combined specific conductivity defined by (27)
$k^{s,m}$	function defined by (30)
m	superscript denoting general membrane
n_i, n_j	g-ion number of i^{th} and j^{th} ion respectively
n_{ij}	g-mol number of ij^{th} electrolyte

n'	number of species of ions of one polarity
n''	number of species of ions of the opposite polarity
n	total number of ionic species: $n = n' + n''$
r	an integer used in subscripts
s	symbol denoting general solution
v_s	velocity of the S_i streams, cm/sec
v_p	velocity of the P stream
z_i	charge of the i^{th} ion
α, β	subscripts denoting matrix elements
δ_{uv}	Kronecker delta: $\delta_{uv} = 0 (u \neq v)$; $\delta_{uv} = 1 (u = v)$
λ_i	equivalent conductivity of i^{th} ion
$\bar{\mu}_i$	electrochemical potential of the i^{th} ion
μ_{ij}	chemical potential of the ij^{th} electrolyte
$[\Delta\bar{\mu}], [\Delta\mu]$	matrices defined by (20) and (21)
ν_i^{ij}	number of g-ions of i^{th} ion liberated by complete dissociation of ij^{th} electrolyte
∇	derivative normal to a plane or membrane
Δ	difference
\sum_{α}	summation $1 \leq \alpha \leq n - 1$
\sum_{β}	summation $1 \leq \beta \leq n - 1$
\sum_i	summation $1 \leq i \leq n'$
\sum_j	summation $n' + 1 \leq j \leq n$

Ion Fluxes in Solutions of Electrolytes

Following Murphy and Taber (48), the basic equation relating the flux and the electrochemical potential gradient of the i^{th} ionic species is given by

$$J_i = -C_i \lambda_i \Delta \bar{\mu}_i / |z_i| F^2 . \quad (12)$$

In (48) the dependence of the flux of the i^{th} ion on the gradients of the electrochemical potentials of the other ionic species present has been neglected. Since this effect is small and would result in small correction terms which could not be applied to any of the practical applications contemplated here, this loss of generality seems justified (3, 48, 49, 50). Migration of the solvent, which would be an important effect only at very high concentration gradients (51) will also be neglected here.

The density of electric current carried by the i^{th} ion is related to the flux as

$$I_i = z_i F J_i , \quad (13)$$

and the total current density is given by

$$I = \sum_i I_i . \quad (14)$$

The Gibbs free energy of a phase containing electrolytes is given by

$$G = \sum_i n_i \bar{\mu}_i + \sum_j n_j \bar{\mu}_j . \quad (15)$$

The electrochemical potentials $\bar{\mu}_i$ and $\bar{\mu}_j$ appearing in (15) present themselves naturally as the "forces" to be used in a non-equilibrium thermodynamic description of ionic transport in solutions and through

membranes. However, these potentials, though they possess definite physical significance, are not the most convenient set of forces for the formulation of design equations. Murphy and Taber (48) met this difficulty by conceptually combining the ions into neutral compounds so that the chemical potentials of these compounds, which are measurable, could be substituted for the ionic electrochemical potentials.

It is a common technique for irreversible thermodynamics to substitute a thermodynamically equivalent system for the one actually under consideration (2). Though the concept of ionic association into neutral molecules is an artificial one, the equations resulting from this device correctly predict the ionic fluxes. This method has been used in the present formulation.

In the general case there will be a total of n' ionic species of one polarity and n'' species of the opposite polarity. (It will be stipulated that $n' \leq n''$.) These n ions can be combined into $n' \times n''$ neutral compounds, of which the ij^{th} compound is an association of ν_i^{ij} ions of charge z_i and ν_j^{ij} ions of charge z_j . The condition

$$z_i \nu_i^{ij} + z_j \nu_j^{ij} = 0 \quad (16)$$

is an obvious consequence. Electroneutrality of the system requires that

$$\begin{aligned} n_i &= \sum_j \nu_i^{ij} n_{ij} \\ n_j &= \sum_i \nu_j^{ij} n_{ij} \end{aligned} \quad (17)$$

Substitution of (17) in (15) gives

$$G = \sum_{ij} n_{ij} (\nu_i^{ij} \bar{\mu}_i + \nu_j^{ij} \bar{\mu}_j) \quad (18)$$

The chemical potentials of the neutral electrolytes can be defined as follows:

$$\mu_{ij} = \nu_i^{ij} \bar{\mu}_i + \nu_j^{ij} \bar{\mu}_j, \quad (19)$$

whence

$$G = \sum_{ij} n_{ij} \mu_{ij}. \quad (20)$$

As an example let us consider a system containing magnesium, sodium, and chloride ions (indicated by the subscripts 1, 2 and 3 respectively). In this case equations (19) become

$$\begin{aligned} \mu_{13} &= \bar{\mu}_1 + 2\bar{\mu}_3, \\ \mu_{23} &= \bar{\mu}_2 + \bar{\mu}_3. \end{aligned}$$

In the gradient form, (5) may be written

$$\nabla \mu_{ij} = \nu_i^{ij} \nabla \bar{\mu}_i + \nu_j^{ij} \nabla \bar{\mu}_j. \quad (19)$$

Equation (19) can be viewed as a rule for the transformation of the set of basis vectors $\nabla \bar{\mu}_i$ and $\nabla \bar{\mu}_j$ into the new basis vectors $\nabla \mu_{ij}$. The vectors $\nabla \bar{\mu}_i$ and $\nabla \bar{\mu}_j$ define an n-dimensional vector space; hence, of the n'x n'' vectors $\nabla \mu_{ij}$, only n of them can be linearly independent. The electrical potential gradient with respect to the nth ionic species, which can be measured by means of probe electrodes reversible to the nth ion, is to be used as one of the basis vectors in the new system. Hence, only n - 1 of the μ_{ij} 's may be taken for the set. The following is a convenient choice:

$$\begin{aligned} \nabla\mu_{mn''+r, n'+r}; & \quad 1 \leq r \leq n''; \quad 1 \leq mn''+r \leq n' \\ \nabla\mu_{n'+r, r+1}; & \quad 0 < r < n'' \end{aligned}$$

These two "subsets" will give a total of $n - 1$ linearly independent vectors, which, along with ∇E_n , completely define the vector space in the new system. From (19) it will be seen that $\nabla\mu_{ij} = \nabla\mu_{ji}$; i. e. the order in which the double subscript of $\nabla\mu$ is written is immaterial. The transformation law (19) can quite naturally be expressed in matrix notation:

$$\begin{bmatrix} \nabla\mu_{1, n'+1} \\ \vdots \\ \nabla\mu_n \\ Fz_n \bar{\nabla} E_n \end{bmatrix} = \begin{bmatrix} A_{\alpha\beta} \end{bmatrix} \begin{bmatrix} \bar{\nabla}\mu_1 \\ \vdots \\ \bar{\nabla}\mu_n \end{bmatrix} \quad (20)$$

where

$$\begin{aligned} A_{mn''+r, mn''+r} &= \nu_{mn''+r, n'+r} & 1 \leq r \leq n'' \\ A_{mn''+r, n'+r} &= \nu_{n'+r, mn''+r} & 1 \leq mn''+r \leq n' \\ A_{n'+r, n'+r} &= \nu_{n'+r, r+1} & 0 < r < n'' \\ A_{n'+r, r+1} &= \nu_{r+1, n'+r} \\ A_{n, n} &= 1 \end{aligned} \quad (21)$$

and all other $A_{ij} = 0$.

The relationship

$$\bar{\nabla}\mu_n = Fz_n \nabla E_n \quad (22)$$

has been used in the formulation of (20), which can now be written simply

$$[\nabla\mu] = [A] [\bar{\nabla}\mu] \quad (20a)$$

where $[\nabla\mu]$ and $[\bar{\nabla}\mu]$ are the $n \times 1$ -dimensional matrices of the chemical

and electrochemical potential gradients respectively, and $[A]$ is the transformation matrix. Now let us define $\nabla\mu_\alpha$ to be the element of the $[\nabla\mu]$ matrix whose first subscript is α , and $\nabla\bar{\mu}_\beta$ to be the β^{th} element of the $[\nabla\bar{\mu}]$ matrix; thus

$$\nabla\bar{\mu}_\beta = \sum_{\alpha=1}^{n-1} [A^{-1}]_{\beta\alpha} \nabla\mu_\alpha + [A^{-1}]_{\beta,n} F z_n \nabla E_n. \quad (21)$$

The coefficients L_{ij} in the phenomenological equations can now be determined by considering two special cases:

Case I: $\nabla\mu_\alpha = 0$ for all α

$$\nabla\bar{\mu}_\beta = [A^{-1}]_{\beta,n} F z_n \nabla E_n$$

$$J_\beta = -k_\beta [A^{-1}]_{\beta,n} z_n \nabla E_n / |z_\beta| F \quad (22)$$

$$I = -z_n \nabla E_n \sum_{\beta=1}^n z_\beta k_\beta [A^{-1}]_{\beta,n} / |z_\beta| \quad (23)$$

Case II: $\nabla E_n = 0, \nabla\mu_\alpha = 0$ for all $\alpha \neq \alpha'$

$$\nabla\bar{\mu}_\beta = [A^{-1}]_{\beta,\alpha'} \nabla\mu_{\alpha'}$$

$$J_\beta = -k_\beta [A^{-1}]_{\beta,\alpha'} \nabla\mu_{\alpha'} / |z_\beta| F^2 \quad (24)$$

$$I = -(\nabla\mu_{\alpha'} / F) \sum_{\beta} k_\beta [A^{-1}]_{\beta,\alpha'} z_\beta / |z_\beta| \quad (25)$$

We are now in a position to set up the equations desired:

$$J_i = \sum_j L_{ij} \nabla\mu_j + L_{in} \nabla\bar{\mu}_n$$

$$I = \sum_j L_{nj} \nabla\mu_j + L_{nn} \nabla\bar{\mu}_n,$$

for the coefficients L_{ij} can be obtained from (22) to (25) as follows:

$$L_{jj} = \left[\delta J_j / \delta \nabla\mu_j \right] \text{ (with } \nabla\bar{\mu}_n = \nabla\mu_i = 0 \text{ for } i \neq j)$$

$$L_{ij} = 0 \text{ for } i \neq j$$

$$\begin{aligned}
L_{in} &= \left[\delta J_i / \delta \nabla \bar{\mu}_n \right] \text{ (with } \nabla \bar{\mu}_n = \nabla \mu_i = 0 \text{ for all } i) \\
L_{nj} &= \left[\delta I / \delta \nabla \mu_j \right] \text{ (with } \nabla \mu_i = 0 \text{ for } i \neq j) \\
L_{nn} &= \left[\delta I / \delta \nabla \bar{\mu}_n \right] \text{ (with } \nabla \mu_i = 0 \text{ for all } i)
\end{aligned}$$

From the above it will be seen that the phenomenological equations will have the form:

$$I = -z_n \nabla E_n \sum_{\beta} z_{\beta} k_{\beta} [A^{-1}]_{\beta, n} / |z_{\beta}| \quad (26)$$

$$\begin{aligned}
& - (1/F) \sum_{\alpha} \sum_{\beta} z_{\beta} k_{\beta} [A^{-1}]_{\beta, \alpha} \nabla \mu_{\alpha} / |z_{\beta}| \\
J_{\beta} &= -k_{\beta} [A^{-1}]_{\beta, n} z_n \nabla E_n / |z_{\beta}| F \\
& - (k_{\beta} / |z_{\beta}| F^2) \sum_{\alpha} [A^{-1}]_{\beta, \alpha} \nabla \mu_{\alpha} \quad (27)
\end{aligned}$$

where $1 < \beta < n - 1$ and all summations are from 1 to $n - 1$. It can be seen that Onsager's reciprocal relations (1) are satisfied by equations (26) and (27). Let us take as an example a system containing two cations of valency +1 and +2 and one anion of valency -1. Equations (26) and (27) then become

$$J_1 = -(k_1 / F) (\nabla E_3 - \nabla \mu_{13} / F),$$

$$J_2 = -(k_2 / F) (\nabla E_3 - \nabla \mu_{23} / F),$$

$$\begin{aligned}
I &= -\nabla E_3 (k_1 + 2k_2 - k_3) \\
& - \frac{1}{F} (k_1 \nabla \mu_{13} + k_2 \nabla \mu_{23}).
\end{aligned}$$

It may be seen that the equation for J_1 is the same equation as would obtain if only ions 1 and 3 were present. The current, however, is seen to be an explicit function of all three ionic concentrations.

Ion Permeable Membrane Processes

Murphy and Taber's treatment (48) assumed that membrane resistance was negligible in comparison with solution resistance. A modification by Lacey (51) has shown how this assumption may be eliminated. He gives an equation of the form

$$D/k_i^{s,m} = (D/k_i)^s + (D/k_i)^m, \quad (27)$$

where the value of $k_i^{s,m}$ obtained from (29) is to be used in all the following equations to make them valid for membranes of non-zero resistance. Hence, in this respect, this treatment is more general than that in (48).

Single membrane cells. Consider a system in which an ion-selective membrane is placed between two solutions enclosed by a set of working electrodes reversible to the n^{th} ionic species. Probe electrodes, also reversible to the n^{th} species, are placed adjacent to the membrane for convenience in mathematical description. They are to be regarded as sufficiently porous to allow free passage of the solution. Equations analogous to (26) and (27) may be derived for the membrane, m :

$$J_{\beta}^m = -k_{\beta}^m [A^{-1}]_{\beta,n} z_n \Delta E_n^m / |z_{\beta}| \times F D^m \quad (28)$$

$$- (k^m / |z_{\beta}| F^2 D^m) \sum_{\alpha} [A^{-1}]_{\beta,\alpha} \Delta \mu_{\alpha}^m$$

$$I = (z_n \Delta E_n^m / D^m) \sum_{\beta} z_{\beta} k_{\beta}^m [A^{-1}]_{\beta,n} / |z_{\beta}| \quad (29)$$

$$- (1/D^m F) \sum_{\alpha} \sum_{\beta} z_{\beta} k_{\beta}^m [A^{-1}]_{\beta,\alpha} \Delta \mu_{\alpha}^m / |z_{\beta}|.$$

For convenience let us define

$$k^m = \sum_{\beta} z_{\beta} k_{\beta}^m [A^{-1}]_{\beta,n} / |z_{\beta}|. \quad (30)$$

Then (29) can be rewritten as follows:

$$\frac{z_n \Delta E_n^m}{D^m} = -\frac{I}{k^m} - \frac{1}{D^m F k^m} \sum_{\alpha} \sum_{\beta} \frac{z_{\beta} k_{\beta}^m [A^{-1}]_{\beta, \alpha} \Delta \mu_{\alpha}^m}{|z_{\beta}|} \quad (31)$$

Combination of (31) with (28) gives

$$J_{\beta}^m = \frac{k_{\beta}^m [A^{-1}]_{\beta, n}}{z_{\beta} F^2 k^m D^m} \left[F D^m I + \sum_{\alpha} \frac{z_{\beta} k_{\beta}^m [A^{-1}]_{\beta, \alpha} \Delta \mu_{\alpha}^m}{|z_{\beta}|} - \frac{k^m}{[A^{-1}]_{\beta, n}} \sum_{\alpha} [A^{-1}]_{\beta, \alpha} \Delta \mu_{\alpha}^m \right] \quad (32)$$

In the situation treated here we need only consider the components of $\Delta \mu^m$ and ΔE_n^m normal to the membrane which is considered to be planar. In (28) through (32) it is assumed that these components are linear across the membrane. Such is never actually the case when more than one salt is diffusing (52), but the assumption of linearity gives results surprisingly close to experiment (53).

This treatment also assumes that the distribution of ions at the membrane-solution interfaces during electromigration corresponds to the equilibrium distribution of ions which would exist without the flow of current, in the absence of any spontaneous net exchange across the membranes.

The question may arise as to whether or not the assumed ion exchange equilibrium is always maintained between the surfaces of the membrane and the layers of solution adjacent to it when two competing species of ions of the same charge are forced by the electric field into the pores of the membrane. It is conceivable that certain processes,

such as dehydration, associated with the transfer of the ions from solution to membrane might take place at different rates for different ions (54).

Ordinarily one distinguishes between two types of polarization. At the phase boundaries between two electrolytic conductors, such as a solution of electrolytes and an ionic membrane, chemical polarization which involves the discharge of ions obviously does not occur except under the most extreme conditions (55). However, as Nernst and Riesenfeld (56) have shown for the simple case of a univalent electrolyte distributed between two liquid phases, concentration polarization does take place if a current passes across the phase boundary unless the ratios of the transference numbers of cations and ions in the two phases are not the same. Now the ratios t_i^s/t_j^s and t_i^m/t_j^m will not be equal in general (57), therefore, on one side of the membrane, the diffusion layer will possess a concentration higher than the equilibrium value and there will be a corresponding lowering of the concentration on the other side of the membrane.

No fully satisfactory method seems to have been obtained for dealing mathematically with membrane polarization, but it can be safely assumed that at low current densities the effect will not be great. Lacey (58) has determined that polarization accounts for no more than a two per cent reduction in driving force per osmionic cell.

Polarization, however, is the main factor contributing to the formation of insoluble precipitates that ruin membranes in the osmionic and electro dialysis processes. In connection with their dialysis work Cowan and Brown (59) developed expressions that showed the lowest velocity that can be used without encountering difficulty from polarization. This velocity will usually--though not always--be exceeded in the practical cases considered here, hence the equations derived in this paper will make no account of concentration gradients in the liquid streams perpendicular to the direction of flow.

Osmionic demineralization. Figure 6 represents a schematic diagram for osmionic demineralization. Each of the internal compartments S₁, S₂, and P contains feed saline water initially. The solution P is demineralized during the process, while the S solutions are enriched. Compartment B contains a brine of constant composition. As before, probe electrodes reversible to the *n*th ionic species will be imagined adjacent to each of the membranes so that, in principle, *n* could be evaluated.

An expression for the current density in membrane C₂ can be deduced from the arguments which led to equation 32 in Murphy and Taber (48):

$$I = \frac{z_n \Delta E_n^{C_2, P, C_2}}{D C_2} - \frac{1}{D C_2 F} \sum_{\alpha, \beta} \frac{z_\beta k_\beta^{P, C_2} [A-1]_{\beta, \alpha} \Delta \mu_\alpha^{C_2}}{|z_\beta|} \quad (33)$$

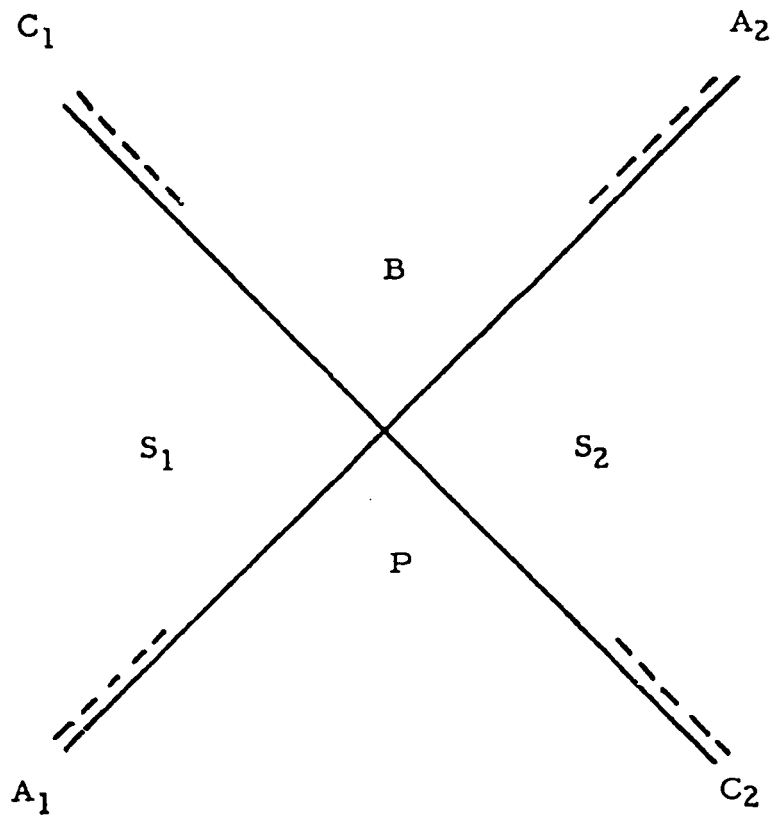


Figure 6

Three more similar equations can be written for the other membranes. This set of four equations can be used to eliminate ΔE_n , for by Kirchhof's second rule:

$$\sum_m E_n^m = 0,$$

Eliminating the $\Delta\bar{\mu}_n$'s gives:

$$\tau \left[\frac{DC_2}{k^{P,C_2}} + \frac{DA_2}{k^{S_2,A_2}} + \frac{DC_1}{k^{B,C_1}} + \frac{DA_1}{k^{S_1,A_1}} \right] = \left(\frac{1}{F} \right) \sum_{a,\beta} \frac{z_\beta [A^{-1}]_{\beta,a}}{|z|} \quad (34)$$

$$\left(\frac{k^{P,C_2} \Delta\mu_a^{C_2}}{k^{P,C_2}} + \frac{k^{B,C_1} \Delta\mu_a^{C_1}}{k^{B,C_1}} + \frac{k^{S_2,A_2} \Delta\mu_a^{A_2}}{k^{S_2,A_2}} + \frac{k^{S_1,A_1} \Delta\mu_a^{A_1}}{k^{S_1,A_1}} \right).$$

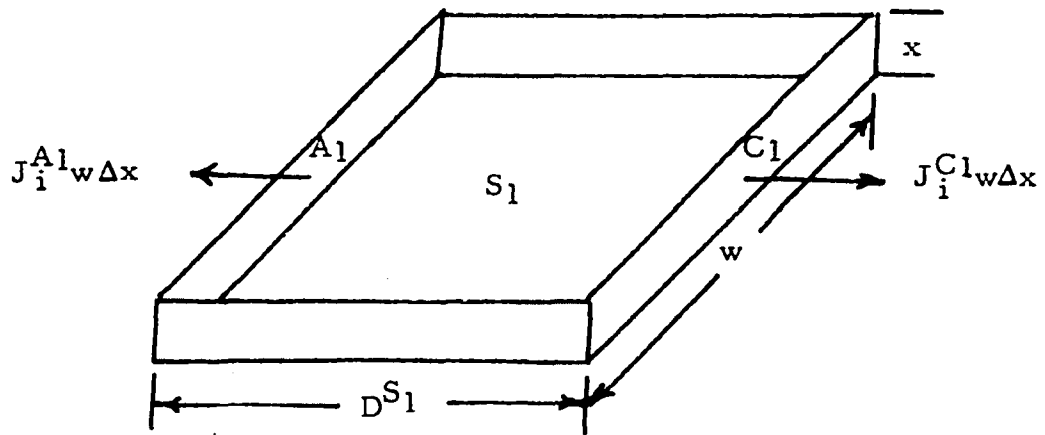


Figure 7

Figure 7 represents a segment of compartment S_1 of differential length Δx . D^{S_1} is the effective width of the compartment and w its height. The number of gram ions of the i^{th} species flowing into the differential volume per unit time is given by $v_s D^{S_1} w C_i^{S_1}(x)$, where v_s is the linear velocity of the S streams in cm/sec. A flux of electrolyte will also occur at the membranes as indicated in Figure 7. An electrolyte balance for the differential volume gives:

$$v_s D^{S_1} w C_i^{S_1}(x) = v_s D^{S_1} w C_i^{S_1}(x+\Delta x) + J_i^{C_1} w \Delta x - J_i^{A_1} w \Delta x,$$

whence

$$[C_i^{S_1}(x) - C_i^{S_1}(x+\Delta x)]/\Delta x = (J_i^{C_1} - J_i^{A_1})/v_s D^{S_1}, \quad (35)$$

or as $x \rightarrow 0$

$$dC_i^{S_1}/dx = J_i^{S_1}/v_s D^{S_1}, \quad (36a)$$

where

$$J_i^{S_1} = J_i^{C_1} - J_i^{A_1},$$

Similarly,

$$dC_i^{S_2}/dx = J_i^{S_2}/v_s D^{S_2}, \quad (36b)$$

$$dC_i^P/dx = J_i^P/v_p D^P, \quad (36c)$$

Where

$$J_i^{S_2} = J_i^{C_2} - J_i^{A_2} \text{ and } J_i^P = J_i^{A_1} - J_i^{C_2}.$$

The values of I obtained from (34) may be used in (32) for the determination of the individual fluxes, which in turn may be used for the solution of equations (36).

The $3n - 3$ simultaneous differential equations (36) give the variation with x of the ionic concentrations of the S and P streams. Since the fluxes J_i are complicated functions of all the C_i^S 's, the equations must be solved by numerical methods. Thus even for simple cases it is a practical necessity to solve the equations by means of a high speed computer.

Evaluation of specific ionic conductivity in solution. The dependence of the right hand sides of equation (36) on the ionic concentrations in the various streams must be made explicit if the equations are to be solved. This requirement necessitates a method for relating specific ionic conductivities to concentration.

An hypothesis advanced by Van Rysselberghe (60) states that the mobilities of the various ions in a solution of mixed electrolytes are proportional to their values in a solution of the same salts alone having the same concentration as the total concentration of the mixture, i. e.,

$$\Omega_i = g_i \Omega_i^0, \quad (37)$$

where Ω_i is the mobility of the i^{th} ionic species in a solution of mixed electrolytes, and Ω_i^0 is the mobility of the i^{th} ion in a solution of some single electrolyte (yielding the i^{th} ion on dissociation) at a concentration equal to the total concentration ($C = \sum_j C_j$) of the solution of mixed electrolytes, and g_i is a constant of proportionality.

The formula established by MacInnes (61) for the evaluation of transference numbers in mixed electrolytes can be shown to follow from this hypothesis and has been found to agree with experimental results up to a total concentration of 5N for mixtures of alkali halides (62 to 67). The hypothesis does not give such good agreement with experiment for mixtures of electrolytes containing polyvalent forms because of the incomplete dissociation of such salts.

The use of this hypothesis leads to an approximate method for relating specific conductivities in a solution of mixed electrolytes to the concentrations. It is customary to express mobility as

$$\Omega_i = \Omega_i / |z_i| F^2, \quad (38)$$

This formula coupled with (37) gives

$$\lambda_i(C_i) = g_i \lambda_i(C) \quad (39)$$

or

$$k_i(C_i) = g_i k_i(C) C_i / C. \quad (40)$$

Thus we see that

$$g_i = |z_i|$$

will fulfill the conditions that $k_i = 0$ when $C_i = 0$ and $k_i(C_i) =$ when $|z_i| C_i = C$. This method for finding the specific ionic conductivity of ions in solution is, of course, exact if only two ions are present. It is admittedly approximate for more general systems but gives results good at least to two significant figures. Since the data presently available for conductivity of membranes are no better, (40) with $g_i = |z_i|$ may be used in a computer solution of equations (36).

The formula to be used for finding λ_i^S as a function of C_i^S is:

$$\log (\lambda_i^O - \lambda_i^S) = A_i + B_i \log C_i^S \quad (41)$$

which fits experimental data very well in the concentration range of practical interest.

Evaluation of membrane conductivity. Data taken by Lacey (68) for the transference numbers of ions in permselective membranes and for the resistance of these membranes when equilibrated in electrolyte solutions can be used to obtain the dependence of k_i^m on C_i^m

If data concerning transference numbers and resistance are available for the membranes in the system under consideration, the specific ionic conductivities of the membrane can be calculated, since

$$t_i^m / R_{ij}^m = C_i^m \lambda_i^m / D^m = k_i^m / D^m .$$

The data taken by Lacey give the following results for AMF membranes by the "solution method":

C_{NaCl}^m	$(k_{Na^+}/D)^C$	$(k_{Na^+}/D)^A$	$(k_{Cl^-}/D)^C$	$(k_{Cl^-}/D)^A$
0.01	0.256	0.0	0.0053	0.127
0.4	0.241	0.0013	0.0153	0.130
2.0	0.202	0.0172	0.0404	0.138

A plot of $(k_{Na^+}/D)^m$ versus concentration is linear for the four cases above so that the following equation can be written in general:

$$(k_i/D)^m = F_i^m + G_i^m C_i^m \quad (42)$$

The constants F_i^m and G_i^m are to be determined from the best transference number and resistance data available for the membranes under consideration.

Evaluation of $\Delta\mu_{ij}$. The function $\Delta\mu_{ij}$ is customarily understood to be given by $RT \ln C_{ij}^{(1)}/C_{ij}^{(2)}$, where the superscripts indicate the regions in which the concentrations are measured, but in the general case, the quantities C_{ij} are not uniquely defined. A set of $n-1$ ion balances can be written as follows:

$$(a) \quad \bar{C}_i = \sum_{j=1}^{n'} v_i^{ij} C_{ij} \quad n'+1 \leq i \leq n-1$$

$$(b) \quad \bar{C}_j = \sum_{i=n'+1}^n v_j^{ij} C_{ij} \quad 1 \leq j \leq n'.$$

The index i is not allowed to take the value n in (a) because C_n is functionally dependent on the other C_i 's, i.e.

$$\bar{C}_n = -(z_i \bar{C}_i + z_j \bar{C}_j) / z_n$$

Equations (a) and (b) can be solved for $n-1$ of the C_{ij} 's in terms of the \bar{C}_i 's, \bar{C}_j 's and the remainder of the $n' \times n''$ C_{ij} 's. The latter can take on any arbitrary values and equations (a) and (b) will define unique values of the C_{ij} 's chosen to be non-arbitrary. It is convenient to take the $n-1$ non-arbitrary C_{ij} 's to have the same subscripts as the set μ_{ij} which is chosen for the basis vectors in the transformed system. The remaining C_{ij} 's can all be set equal to zero. A convenient matrix formulation of equations (a) and (b) is then

$$[\bar{C}] = [B] [C] \quad (43)$$

where $[\bar{C}]$ is the matrix of ionic concentrations:

$$\begin{pmatrix} \bar{C}_1 \\ \vdots \\ \bar{C}_i \\ \vdots \\ \bar{C}_{n-1} \end{pmatrix}$$

and [C] is the matrix of non-arbitrary electrolyte concentrations:

$$\begin{pmatrix} C_{1, n' - 1} \\ \dot{C}_a \\ \dot{C}_{n-1, n''} \end{pmatrix}$$

and [B] is the $(n-1)^2$ transformation matrix. Thus

$$[C] = [B^{-1}][\bar{C}]$$

and

$$\Delta\mu_a = RT \left(\ln \sum_{\beta} [B^{-1}]_{\alpha\beta} C_{\beta}^{(1)} - \ln \sum_{\beta} [B^{-1}]_{\alpha\beta} C_{\beta}^{(2)} \right) \quad (44)$$

A special case. The special case $n'' = 1$ (corresponding to a system with n' cations and one anion or vice versa) is of interest because of the simplification which can be effected. Let us assume that there is only one anion which will be indicated by the subscript a .

$$\nabla\mu_{ia} = \nu_i^{ia} \nabla\bar{\mu}_i + \nu_a^{ia} \nabla\bar{\mu}_a \quad (19')$$

$$\begin{bmatrix} \nabla\mu_{ia} \\ \cdot \\ \nabla\mu_{n'a} \\ \text{Fz}_a \text{ E}_a \end{bmatrix} = \begin{bmatrix} \nu_1^{1a} & 0 & 0 & \cdot & \cdot & \nu_a^{1a} \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & 0 & \nu_{n'}^{n'a} & \nu_a^{n'a} & \cdot \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \nabla\bar{\mu}_1 \\ \cdot \\ \nabla\bar{\mu}_{n'} \\ \nabla\bar{\mu}_a \end{bmatrix} \quad (20')$$

Since $n'' = 1$, r in (21) may have only the value 1 and m may take all values from 0 to $n'-1$. Since there are no integers such that $0 < r < 1$, the second set in (21) makes no contribution to the A matrix. Hence (21) becomes

$$\begin{aligned} A_{m+1, m+1} &= \nu_{m+1}^{m+1, a} \\ A_{m+1, n'+1} &= \nu_a^{m+1, a} & 0 \leq m \leq n'-1 \\ A_{n'+a, n'+a} &= 1 \end{aligned} \quad (21')$$

It can be shown that the elements of $[A^{-1}]$ are

$$[A^{-1}]_{\alpha} = \delta_{\alpha} / \nu_{\alpha}^{aa} : 1 < \beta < n'; 1 < \alpha < n'$$

$$[A^{-1}]_{\alpha} = z_{\alpha} / z_a : \beta = n'+1 ; 1 < \alpha < n'+1 .$$

The current density and the ionic fluxes can be had from (28) and (29):

$$J^m = - (k_{\beta}^m / FD^m) (\Delta E_a^m + \Delta \mu_{\beta a}^m / |z_{\beta}| F \nu_{\beta}^{\beta a}) \quad (28')$$

$$I = - (\Delta E_a^m / D^m) \sum_{\beta} z_{\beta} k_{\beta}^m - (1 / D^m F) \sum_{\beta} k_{\beta}^m \Delta \mu_{\beta a}^m / \nu_{\beta}^{\beta a} . \quad (29')$$

The case of a system containing two cations of valency 1 and

2 and one anion of valency -1 would then be given by

$$J_1^m = - (k_1^m / FD^m) (\Delta E_3^m + \Delta \mu_{13}^m / F) ,$$

$$J_2^m = - (k_2^m / FD^m) (\Delta E_3^m + \Delta \mu_{23}^m / 2F) ,$$

$$I = - (\Delta E_3^m / D^m) (k_1^m + 2k_2^m) \\ - (1 / D^m F) (k_1^m \Delta \mu_{13}^m + k_2^m \Delta \mu_{23}^m) .$$

CHAPTER IV

CALCULATIONS

The set of simultaneous first order differential equations (36) cannot be solved analytically and a numerical solution would be too lengthy to undertake other than by use of a high speed computer. Therefore, the program for computer solution of equations (36) which appears in the appendix was written. This program will solve the equations for any system containing only one anion (or only one cation) with not more than four ionic species of the opposite polarity and not more than six membranes.

A total of five such solutions was obtained on the computer in order to determine the relative effects of the experimentally independent variables.

In all cases data used for the resistance and transference numbers in membranes were taken from Lacey's findings (68) for American Machine and Foundry membranes. Data for specific ionic conductivities were taken from Robinson and Stokes (106).

Four calculations were made for one double effect cell containing sodium chloride only. The membrane thickness used was 0.015 cm.

A fifth calculation was made for simultaneous demineralization of sodium and magnesium chloride. The calculated concentration of the P stream (the stream being demineralized) as a function of linear distance in the cell is presented graphically in Figures 8 and 9.

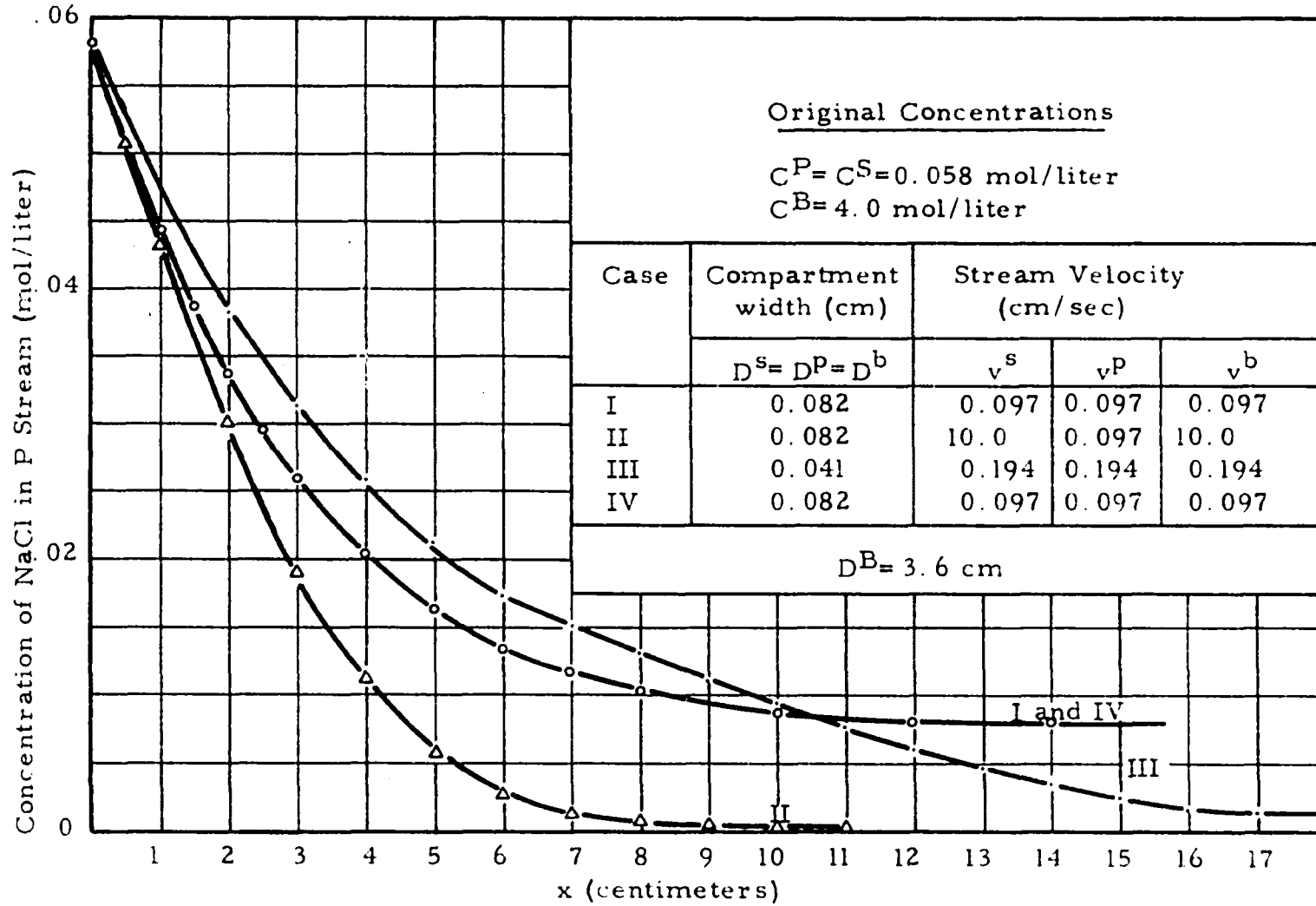
The calculated results show that an increase in the velocity of the internal brine has no appreciable effect on the demineralization of the P compartment, while an increase in the velocity of the S streams to an essentially infinite value gives a marked improvement in the rate of demineralization. It can also be seen that a reduction in the distance between membranes by one-half, while leaving the volumetric flow rates the same, results in a decreased rate of demineralization. The ultimate percentage of sodium chloride removed, however, is greater since a reduction in the cell dimensions entails a reduction in the resistance of the cell; hence an increased driving force results.

Figure 9 shows that the use of a predominately sodium chloride brine for the simultaneous demineralization of sodium chloride and magnesium chloride results in a good total reduction in the concentration of both cations in the P stream.

It was desired to perform another sample calculation involving a three ion system. The removal of the computer from the campus, however, prevented this.

Figure 8

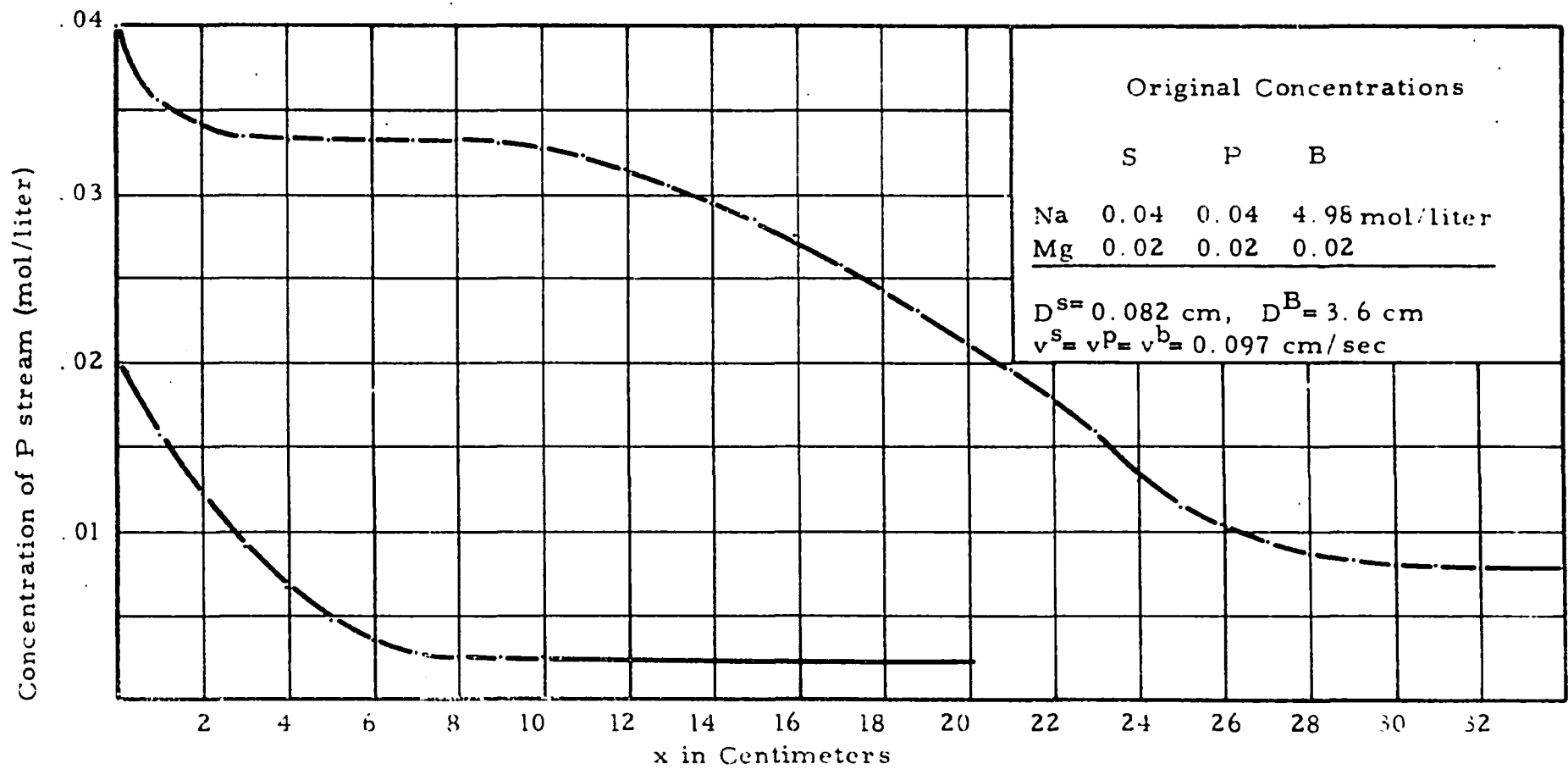
CONCENTRATION OF P STREAM VERSUS DISTANCE



14

Figure 9

SIMULTANEOUS DEMINERALIZATION OF $MgCl_2$ AND $NaCl$



PART II

FREE VOLUME CONCEPT APPLIED TO BINARY NON-ELECTROLYTE SOLUTIONS

CHAPTER I

HISTORICAL AND THEORETICAL

Free Volume

Van der Waal's familiar equation of state is based on the idea that molecules are incompressible spheres moving in a potential energy field which is an explicit function of V , the volume of a phase. This assumption enabled him to derive the concept of an "empty" or "forbidden" volume ($V-b$), where b was considered to be the invariant volume of the molecules. Van der Waal's formulation has the advantage of conceptual and mathematical simplicity and, for limited ranges of pressure and temperature, accounts well for properties of most compounds in the gaseous state. Applied to liquids and thermodynamic processes such as vaporization, however, it is less successful.

The contribution of Jäger (69) in 1896, though frequently unacknowledged, forms the basis for nearly all the subsequent elaborations

of the free space concept. It occurred to this author that the volume of a phase can be considered as a potential energy field with infinite discontinuities at the sites of the molecules. Hence the remaining sites are not all equally available for fluctuations of the molecules. This line of reasoning leads to a new conception of "free" volume: $V-B(V, P, T)$, where B is no longer a constant, as in van der Waal's equation, but an undetermined function of the phase volume, pressure and temperature.

Jäger also presented a justification for the use of the statistics of Maxwell and Boltzmann for the treatment of the liquid state. His work therefore made obsolete the erroneous and misleading concept of empty space left over from hard spheres. As stated by Moelwyn-Hughes (70):

Free volume is the Lebensraum for which the molecules must struggle against the prevailing forces.

Defined mathematically, the free volume of a single molecule is the integral of that part of the molecular potential energy which is due to thermal displacements of the centers of gravity of the molecules from their equilibrium positions (71), i. e.

$$V_f = 4\pi \int_0^{\infty} r^2 \exp \{ -\psi(r) + \psi(0) / kt \} dr.$$

Evaluation of the integral defined above is rather a mathematical impasse. Hence later authors have assumed that the molecules are constrained to move about in spherical "cages" (72, 73, 74). Though this assumption is open to valid criticism (75), it has led to useful and interesting

conclusions, some of which will be discussed below. More recently, the free volume concept has been placed on sounder footing by statistical mechanical formulations involving clearly defined assumptions not including theoretical molecular models (76, 77).

Free Volume and the Entropy of Vaporization

If the van der Waal's equation is accepted, it can be shown (78) that the entropy of vaporization is given by

$$\Delta S^V = R \ln (V^G - b) / (V^L - b) , \quad (1)$$

where V^G and V^L are the molar volumes of the gas and liquid respectively. If V^G is sufficiently larger than b and $(V^L - b)$ is taken to be the free volume of the liquid, the entropy of vaporization becomes

$$\Delta S^V = R \ln V^G / v^{f'} . \quad (2)$$

$v^{f'}$ in equation (2) is a composite free volume which Bondi (79) calls the "fluctuation volume."

According to the "cage" model, the change in entropy from any state 1 to a state 2 may be expressed as (72, 73, 74).

$$\Delta S = S_2 - S_1 = R \ln \frac{v_2^{f'}}{v_1^{f'}} + RT \frac{\partial}{\partial T} \ln \frac{v_2^{f'}}{v_1^{f'}} . \quad (3)$$

Hence, if the second term is ignored, equation (3) is the same as equation (2). If the vapor is ideal (i. e. $V^G = RT/p$), (3) becomes

$$v^{f'} = (RT/p) e^{-\Delta S^V / R} = (RT/p) e^{-\Delta H^V / RT} . \quad (4)$$

Equation (4) may also be developed from Jäger's treatment and

from statistical mechanics by setting the free energy of the gas equal to that of the liquid and assuming that the rotational and vibrational partition functions are the same in both the liquid and gas phases (74).

The Entropy of Mixing

If equation (3) is considered as applying to the mixing process, reasoning by analogy with the behavior of ideal gases, mixing can be thought of as the sum of two expansions, one for each component. The first component has, before mixing, only its own free volume available, but after mixing, the free volume of component two is also available. Hence,

$$\Delta S^M = -R \left[x_1 \ln \frac{x_1 V_1^{\text{of}'}}{v_f'} + x_2 \ln \frac{x_2 V_2^{\text{of}'}}{v_f'} \right] . \quad (5)$$

Where x_1 and x_2 are mole fractions of components 1 and 2, $V_1^{\text{of}'}$ and $V_2^{\text{of}'}$ are the free volume of the pure components from equation (4), and v_f' is the free volume of the resulting mixture (80). This equation may be solved for v_f' , giving

$$v_f' = e^{-\Delta S^M/R} (x_1 V_1^{\text{of}'})^{x_1} (x_2 V_2^{\text{of}'})^{x_2} . \quad (6)$$

Translational and Rotational Contributions to the

Entropy of Vaporization

Both equations (6) and (4) are based on analogy with the behavior of ideal gases in which only translational motions of the molecules contribute to the thermodynamic behavior of the system. In the liquid state,

such a simplification is unsatisfactory because rotation of the molecules as well as electronic and vibrational effects may contribute significantly to the total entropy. Therefore, it is necessary to generalize this approach by writing the entropy of a state as a sum of terms:

$$S_{\text{total}} = S_{\text{translational}} + S_{\text{rotational}} + S_{\text{vibrational}} + S_{\text{electronic}}. \quad (7)$$

The difference in the entropy of two states can then be expressed as

$$S_{12} = S_2 - S_1 = (S_2 - S_1)_{\text{translational}} \\ (S_2 - S_1)_{\text{rotational}}, \text{ etc.} \quad (8)$$

For the case of vaporization or mixing of metals, the electronic contribution in equation (8) will be of sufficient magnitude as to necessitate its inclusion, but for nonelectrolytes and solutions of nonelectrolytes, the electronic term may be safely ignored. The difference between excitations of vibrational states in the liquid and the gas is also apparently of a very small order of magnitude in most cases (81) and may be ignored. The case for rotation, of course, is quite different. Restriction of rotation in the liquid state due to association of the molecules or to steric hindrance to free rotation is certain to cause a lowering of the entropy of the liquid and a corresponding increase in the entropy of vaporization (82, 83, 84). The dilution of a highly hindered compound with one less highly hindered is also going to give rise to rotational effects which cannot be disregarded in a theoretical treatment of the thermodynamics of binary solutions.

The Free Angle Ratio

Eyring and co-workers (73, 74, 75) found it convenient to define a new quantity, the free angle, which is the total integral of angular displacement of a molecule about its center of mass from its equilibrium position. The free angle ratio δ is given by the ratio of the partition functions for the restricted rotation of the molecule in the liquid and its free rotation in the gas phase. Thus δ will vary from a lower value (greater than zero) to unity, depending on the magnitude of the potential barrier restricting free rotation in the liquid. In equation (4), the right-hand side is the product of the free volume and the free angle ratio, which will always be smaller than the free volume. Thus equation (4) must be modified to

$$\delta V^f = (RT/p)e^{-\Delta H^V/RT} \quad (4a)$$

Equation (7), as it applies to vaporization can be written

$$\Delta S^V = \Delta S_{\text{translational}}^V + \Delta S_{\text{rotational}}^V$$

The translational term is given by equation (2), that is

$$\Delta S^V = R \ln(V^G/V^f) + \Delta S_{\text{rotational}}^V$$

whence,

$$\delta V^f \exp \left\{ -\Delta S_{\text{rotational}}^V/R \right\} = (RT/p) \exp \left\{ -\Delta H^V/RT \right\} \quad (9)$$

if δ is set equal to $e^{-S_{\text{rotational}}^V/R}$, equation (9) is seen to be equivalent to equation (4a).

Empirical Methods for the Determination of the Rotational
Contribution to the Entropy of Vaporization

Hildebrand's rule (35), which states that liquids vaporizing to states with equal vapor volumes should have the same entropy of vaporization, gives one a means of determining the value of δ for various systems, because it implies that the internal degrees of freedom are the same in the liquid and vapor phases. For this work, in keeping with precedent (86), mercury was chosen as a compound for which there is no restriction of rotation in the liquid. The difference in the entropy of vaporization of a liquid and that of mercury, such that both expand to equal vapor volumes, should give an indication of the amount of entropy lowering in the liquid due to restriction of rotation, i. e.

$$\Delta S^V - \Delta S_{\text{Hg}}^V = \Delta S_{\text{rot}}^V. \quad \text{Thus one is able to obtain the free angle ratio:}$$

$$\delta = e^{-\Delta S_{\text{rot}}^V / R} \quad (10)$$

Objections to the use of mercury as a reference liquid will be discussed later.

All attempts at deriving Hildebrand's rule on theoretical basis (74, 87) result in Pitzer's rule (88), i. e., liquids vaporizing to the same ratio of vapor volume to liquid volume should have the same entropy of vaporization. This rule can also be used to determine the rotational entropy of a liquid. The inert gases are used as a basis for no restriction of rotation in the liquid. From the data given by Pitzer (88), it can be seen that for the inert gases, a plot of $\log (V^G/V^L)$ versus S^V is linear.

If values of the translational contribution to the entropy of vaporization are taken from this plot, equation (10) may be used for the calculation of δ , and equation (4a) for the calculation of V^f .

There is some question as to whether Hildebrand's or Pitzer's rule is superior for the determination of translational contributions to the entropy of vaporization (86, 89). The critics of Pitzer's rule point out that it is not obeyed by a large class of compounds. However, the identification of the discrepancies shown by certain compounds from Pitzer's rule with the rotational entropy is not new (86, 88). Furthermore, the fact that inert gases, in which it would be difficult to invoke restricted rotation, obey Pitzer's rule has induced reliance upon it rather than upon Hildebrand's rule for the present work.

CHAPTER II

CALCULATIONS AND DISCUSSION OF RESULTS

Entropy of Vaporization and Pitzer's Rule

Since no calculations (using Pitzer's rule) of the rotational and translational contributions to the entropy of vaporization for many pure compounds of interest are reported in the literature, it was desired to perform such calculations, as the results are needed for the evaluation of V^f for these compounds.

The inert gases argon, krypton and xenon were used as reference substances for no rotational contribution to the entropy of vaporization. For a compound at a particular temperature the gas-liquid volume ratio V_G/V_L was calculated. The value of ΔS^V (from Pitzer's data (88) for the inert gases) corresponding to the calculated value of V_G/V_L was taken to be the translational contribution to the entropy of vaporization, ΔS_{trans}^V . This value subtracted from the actual entropy of vaporization ΔS^V gives then the rotational contribution ΔS_{rot}^V . The results of the calculations are given in Table 2.

The negative value for the $\Delta S_{rotational}^V$ of mercury deserves

TABLE 2

 ROTATIONAL CONTRIBUTION TO THE ENTROPY OF
 VAPORIZATION BASED ON PITZER'S RULE

Compound	T°C	vG/vL	ΔS^V	$\Delta S^V_{\text{trans}}$	ΔS^V_{rot}
Ethyl Acetate	70	327	22.41 ^a	18.57	3.84
	80	236	21.38	17.55	3.83
	100	129	19.38	15.61	3.77
Ethyl Ether	0	890	25.48	21.77	3.71
	30	262	20.78	17.90	2.88
	40	185	19.57	16.75	2.82
	100	32.7	13.56	12.19	1.36
Ethanol	0	24,432	38.55		
	40	2,451	32.12	25.15	6.97
	60	954	29.48	22.00	7.48
	70	626	28.15	20.63	7.52
	80	422	26.87	19.43	7.44
	100	204	24.31	17.16	7.15
	120	105	21.54	14.96	6.58
Ethyl Formate	50	362	22.40	18.92	3.48
	60	258	21.28	17.85	3.43
Ethyl Pro- pionate	90	302	22.65	18.35	3.30
	100	222	21.75	17.35	3.40
Benzene	40	1,072	25.07	22.35	2.72
	100	168	19.11	16.48	2.63
Chloro- benzene	130	291	20.71	18.11	2.60
	140	225	19.99	17.38	2.61
Fluoro- benzene	80	329	21.77	18.60	3.17
	90	243	20.79	17.65	3.14
Iodo- benzene	180	333	21.01	18.65	2.36
	190	265	20.55	17.92	2.53

TABLE 2 -- Continued

Compound	T°C	VG/VL	ΔS^V	$\Delta S^V_{\text{trans}}$	ΔS^V_{rot}
Diisobutyl	90	283	22.00	18.15	3.85
	100	207	20.85	17.16	3.69
Diisopropyl	50	246	20.76	17.65	3.11
	60	179	19.69	16.65	3.04
n-Heptane	90	230	21.45	17.46	3.99
	100	170	19.86	16.50	3.36
n-Hexane	60	250	20.89	17.72	3.17
	70	181	19.87	16.60	3.27
Methyl	50	404	22.99	19.25	3.74
	60	286	21.91	18.15	3.76
Methanol	60	751	25.90	21.23	4.77
	70	509	24.68	19.97	4.71
	100	179	21.12	16.67	4.45
Methyl Chloride	0	159	18.23	16.19	2.05
n-Octane	120	188	20.73	16.85	3.88
	130	144	19.82	15.97	3.85
n-Pentane	30	252	20.42	17.77	2.65
	40	180	19.41	16.68	2.73
n-Propyl Alcohol	90	476	27.90	19.78	8.12
	100	324	26.40	18.57	7.83
CCl ₄	70	323	21.02	18.54	2.48
	80	241	20.03	17.61	2.42
	90	182	19.15	16.70	2.45
	100	140	18.23	15.86	2.38

TABLE 2 -- Continued

Compound	T°C	V _G /V _L	ΔS ^V	ΔS _{trans} ^V	ΔS _{rot} ^V
Mercury	200	111,591	30.45 ^b	37.03	-6.58
	260	22,327	26.85	32.05	-5.20
	320	6,288	23.98	27.93	-3.95
	360	3,109	22.36	25.72	-3.36
Water	0	206,267	39.36 ^c	38.96	0.40
	50	11,901	31.69	29.94	1.75
	100	1,603	26.00	23.66	2.34
	150	360	21.47	18.89	2.58
	200	110	17.62	15.11	2.51
	250	40.0	14.09	12.58	1.51
	CCl ₂ F ₂	-40	370	21.17 ^b	18.99
	-23.33	183	19.06	16.78	2.28
	- 1.11	81.9	16.50	14.15	2.35
	10.00	57.2	15.31	13.26	2.05
	26.67	40.7	13.56	12.61	0.95

^aData for V_G/V_L and ΔS^V taken from Landolt-Bornstein.

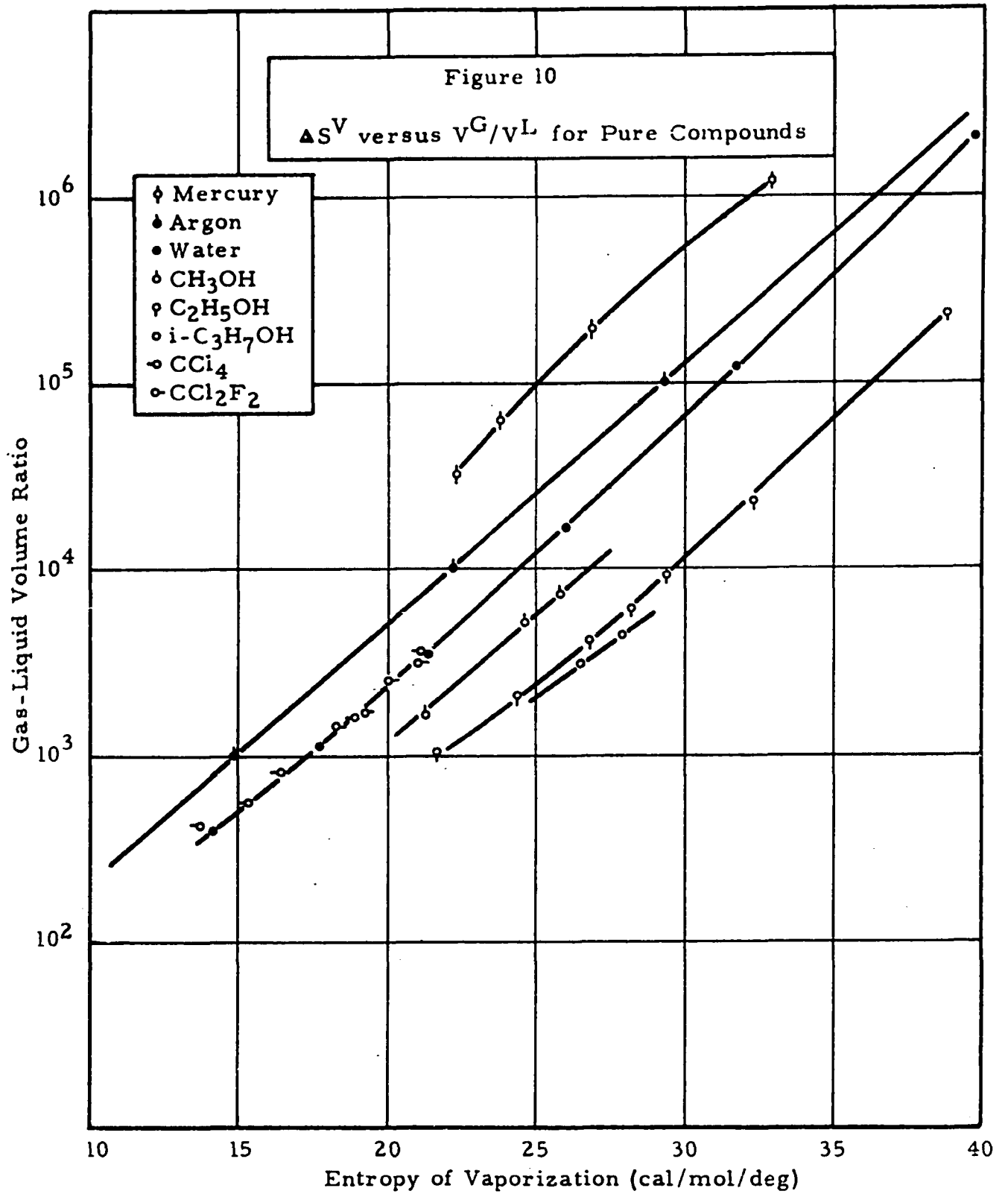
^bFrom the Handbook of Chemistry and Physics.

^cFrom N. E. Dorsey (96).

some discussion. Pitzer (88) believes that metals cannot be considered in this treatment except as a separate class. The entropy attributable to electronic motion will be removed through evaporation and should reduce the entropy of vaporization. The total magnitude of this effect should be 1 cal/mol-degree (90) or less, and is alone insufficient to explain the observed results. However, there is no reason to believe that a single

potential function (from which Pitzer's treatment is derived) will be satisfactory for metallic bonding. In particular, if the function for metals were more symmetrical near the minimum, the behavior exhibited here would be explained as well as other anomalous metallic behavior such as the low coefficients of expansion and liquid heat capacities observed. In short, metals would seem to have to be treated as an almost separate problem.

It is seen from Figure 10 in which S^V is plotted against V_G/V_L for several substances that the sequence water, methanol, ethanol, n-propanol shows a steady increase of rotational hindrance, a result not achieved using Hildebrand's rule (83). The compounds, water, carbon tetrachloride, benzene, and dichlorodifluoromethane have entropies of vaporization that fall on almost the same curve. The restriction of rotation in water should be due mostly to association in the liquid, while restriction in the other compounds must be due to steric hindrance. It is interesting that the two effects should be of almost the same magnitude. The fact that water and the alcohols have a maximum $S_{\text{rotational}}^V$ which diminishes at sufficiently high or low temperature, (e.g. S_{rot}^V practically vanishes for water at 0°C) must indicate a high degree of association in the vapor at low temperatures, and a low degree of association in the liquid at high temperature.



Restriction of Rotation in Alcohols

For several pure alcohols the approximate moment of inertia was calculated for rotation about the O-H bond, which was regarded as fixed. The formulas derived from statistical mechanics were then used to calculate the rotational contribution to the entropy of the vapor (due to rotation about this bond). From these formulas $S_{\text{rot}}^{\text{O}}$ vapor, the rotational contribution to the entropy of the vapor (assuming the molecule to be a rigid rotator) was calculated. ΔS^{V} , the entropy change on vaporization, was determined from literature values for the latent heat of vaporization. The translational contribution to ΔS^{V} was obtained from correlation of this function with the gas-liquid volume ratio. The rotational entropy of the liquid was then obtained from the formula.

$$\Delta S_{\text{rot}}^{\text{V}} = S_{\text{rot}}^{\text{O vapor}} - S_{\text{rot}}^{\text{O liquid}} .$$

An attempt was made to account for this rotational entropy in the liquid. From vapor density measurements it has been shown that methanol vapor consists mostly of hydrogen bonded ring tetramers (91). Assuming this to be true for ethanol, isopropanol, and propanol as well, approximate moments of inertia were calculated for the corresponding tetramers and the rotational entropies of these entities were estimated. The rotational entropy of the liquid still unaccounted for was assumed to be due to the nine new vibrational degrees of freedom acquired in the formation of the tetramer. Approximate wave numbers were determined for these vibrations. A tabular summary of these calculations is given in Table 3.

TABLE 3

CALCULATED ROTATIONAL CONTRIBUTIONS TO THE
ENTROPY OF ALCOHOLS

Alcohol	ΔS^{vap}	$\Delta S_{\text{trans}}^{\text{vap}}$ Pitzer	$\Delta S_{\text{rot}}^{\text{vap}}$	$\Delta S_{\text{rot}}^{\text{vapor}}$	$\Delta S_{\text{rot}}^{\text{tetramer}}$
methanol	27.72	23.25	4.47	19.18	6.398
ethanol	31.49	24.54	6.95	21.04	7.072
isopropanol	32.22	24.18	8.04	24.42	7.580
n-propanol	36.27	29.08	7.19	26.68	7.207

Alcohol	entropy due to nine new vibrations *	entropy con- tribution per vibration	$h\nu/kT$	cm^{-1}
methanol	8.315	0.924	1.950	431
ethanol	7.025	0.781	2.715	480
isopropanol	8.800	0.978	1.905	421
n-propanol	8.283	0.921	1.980	438

*By difference.

Potential Energy Restricting Rotation of CCl_4

Carbon tetrachloride was chosen for an estimation of the potential energy restricting free rotation in the liquid. The partition function for external rigid rotation of a nonlinear molecule is given by Janz (92) as $(8\pi^2 kT/h^2)^{3/2} I_A I_B I_C^{1/2} (\sigma)^{-1}$, where h and k are the Plank and Boltzmann constants respectively. The value of the partition function is thus dependent on two parameters: $I_A I_B I_C$, the product of the principal moments of inertia, and σ , the symmetry number. The external symmetry number for a molecule is defined as the number of indistinguishable positions into which the molecule can be turned by simple rotations. The cube root of this function would give the partition function for one rotational degree of freedom, since partition functions are multiplicative. The difference in entropy due to restricted rotation was calculated and the value of the restricting potential was estimated from Pitzer's tables (93) to be about 2200 cal/mol, as compared with 930 cal/mol for internal rotation of methanol (94) and 3150 cal/mol for internal rotation of ethane (95).

Free Volume and Free Angle Ratio of Pure Compounds

The composite free volume δV^f was calculated for several compounds from equation (4a) using pressures and heats of vaporization obtained from the literature. The free volume V^f from equation (9) was also obtained for these compounds, using both Pitzer's and Hildebrand's

rule for the determination of the translational contribution to the entropy of vaporization. The results are present in Table 4.

It is interesting to note first of all that the compounds which are highly associated, i. e. the alcohols, have δV^f 's that are very much smaller than those of less hindered compounds such as CCl_4 . Also it is to be noted that a given compound has a greater δV^f at a higher temperature (e. g. for acetonitrile, δV^f is 3.46 cc/mol at 45° and 0.0178 at 20°). Both of these results are intuitively expected. In the first place, it is easy to see physically that associated compounds would have a great amount of restricted rotation in the liquid and hence a small free angle ratio. (New vibrational modes would also be expected to appear upon condensation to liquid.) In the second place, as the temperature increases, the interpenetration of the molecules increases due to the enhanced thermal energy; hence the "free volume" increases.

The Use of Hildebrand's Rule for the

Determination of V^f

When ΔS^V for mercury is plotted against $\log(10^3 p/T)$, a straight line with the equation,

$$\Delta S^V = 40.2 - 6.066 \log (10^3 p/T),$$

is obtained, where p is given in millimeters of mercury. It was assumed that all vapors are ideal so that if the pressure of a system is put into this

TABLE 4

CALCULATED FREE VOLUMES FOR PURE COMPOUNDS

Compound	T°C	δV^f	Free Volume V^f (cc/mol)	
			Pitzer	Hildebrand
CH ₃ OH	35	0.0474	0.394	0.783
	45	0.0582	0.587	0.940
	55	0.0732	0.622	1.059
C ₂ H ₅ OH	35	0.0120	0.315	0.638
	45	0.0142	0.476	0.747
	55	0.0176	0.892	0.867
i - C ₃ H ₇ OH	45	0.00229	0.697	0.682
n - C ₃ H ₇ OH	35		0.350	
	55		0.630	
CH ₃ CN	45	3.509	0.576	0.794
Acetone	45	0.321	1.664	0.068
CH ₃ NO ₂	45	2.967	0.371	0.610
C ₆ H ₆	35	0.299	1.409	0.718
	45	0.369	1.665	0.813
	55	0.475	1.758	0.912
CCl ₄	35	0.391	1.344	0.759
	45	0.486	1.695	0.853
	55	0.650	2.134	0.958
CHCl ₃	35	0.244	1.391	0.907
	45	0.310	1.739	1.015
	55	0.389	2.159	1.129

equation, following Hildebrand's rule, the translational contribution to the entropy of vaporization will be obtained (85). The assumption of ideal vapors, of course, fails radically for some systems. When the translational contribution is subtracted from the total entropy of vaporization, the rotational contribution is obtained, from which δ may be calculated. This was done for all of the above compounds and V^f was computed from equation (9). The results are given in Table 4. The compounds acetone, carbontetrachloride, nitromethane, and acetonitrile have free volumes that are less than the product of δV^f , which would correspond to negative values of $\Delta S_{\text{rotational}}^V$. This result is expected for compounds which form gas phase dimers. The magnitude of the free volumes calculated falls within a rather narrow range, viz. 0.35 to 1.08 cc/mol, with most of the calculated values falling in the region 0.8 to 1.08 cc/mol.

Free Volumes of Binary Mixtures

Free volumes for binary mixtures of non-electrolytes have not previously been calculated except by Frank (97) who limited his consideration to vanishingly small concentrations of gases dissolved in normal liquids. In the present research it was desired to study a broader class of solutions and to make observations which would be applicable over the entire mole fraction range.

Calculation of free volume in binary mixtures is complicated by the fact that the liquid and gas phases in equilibrium with one another are not in general of the same composition. When such is the case, equations (4) and (9) are not valid. If, however, a binary mixture forms an azeotrope, three points on the V^f versus mole fraction curve can be obtained: one for the azeotrope and one for each of the pure components.

Equation (9) was used for the calculation of V^f for several azeotrope-forming mixtures, using Pitzer's rule for the determination of the translational contribution to the entropy of vaporization. For purposes of comparison, δV^f and V^f from Hildebrand's rule were calculated for some systems. The results are given in Table 5 and are presented graphically in Figures 12 to 29. The straight lines connecting end points in these figures is intended only to show how much the free volume of the azeotrope deviates from the linear relation $V^f = x_1 V_1^f + x_2 V_2^f$.

Consideration of Figures 11 through 22 shows that Pitzer's rule is consistent with linearity of free volume with respect to mole fraction in all of the systems studied. The small deviations from linearity in the calculated results may be attributable to the lack of data for the vapor and liquid densities of the azeotropes at the temperatures in question. In all cases it was assumed, for purposes of calculation, that there is no change in volume on mixing the liquids and vapors; i. e., the molar volume of the liquid azeotrope was obtained similarly.

TABLE 5

FREE VOLUMES OF BINARY MIXTURES
FORMING AZEOTROPES

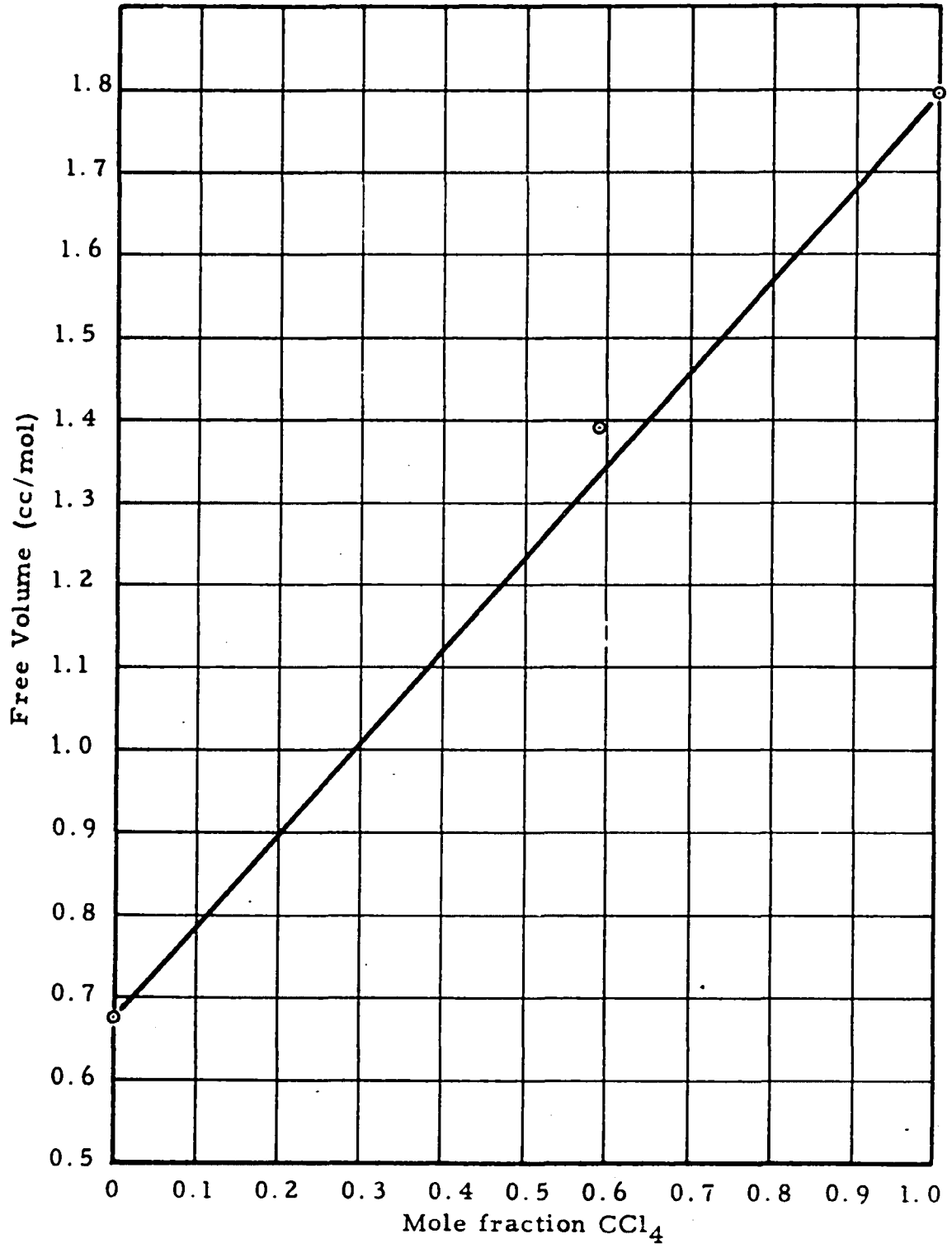
Binary Mixture	Reference	T°C	Mole Fraction	Free Volume (cc/mol)		
				V ^f	Pitzer	Hildebrand
CH ₃ CN-CCl ₄	98	45	0	0.486	1.69	
			.410	0.996	1.29	
			1	3.509	0.58	
CH ₃ CN-C ₆ H ₆	99	45	0	0.369	1.67	0.718
			.457	0.966	1.17	0.763
			1	3.509	0.58	0.794
C ₂ H ₅ OH-C ₆ H ₆	100	45	0	0.369	1.67	0.718
			.375	0.0800	1.24	0.833
			1	0.0142	0.48	0.747
CH ₃ NO ₂ -C ₆ H ₆	101	45	0	0.369	1.67	0.718
			.227	0.456	1.37	0.906
			1	2.967	0.37	0.610
i-C ₃ H ₇ OH-C ₆ H ₆	99	45	0	0.369	1.67	0.718
			.290	0.108	1.36	0.864
			1	0.0023	0.68	0.682
CH ₃ NO ₂ -CCl ₄	101	45	0	0.486	1.73	
			.227	0.499	1.44	
			1	2.967	0.37	
C ₂ H ₅ OH-CCl ₄	102	45	0		1.69	0.853
			.324		1.37	0.936
			1		0.48	0.747
C ₂ H ₅ OH-CHCl ₃	103	35	0		0.319	
			.106		1.25	
			1		1.39	

TABLE 5-- Continued

Binary Mixture	Reference	T°C	Mole Fraction	V ^f	Free Volume (cc/mol)	
					Pitzer	Hildebrand
	103	45	0		0.478	
			.138		1.602	
			1		1.74	
	103	55	0		0.896	
			.152		1.90	
			1		2.16	
CH ₃ OH-C ₆ H ₆	104	35	0		1.409	0.718
			.565		0.846	0.800
			1		0.394	0.783
	104	55	0		1.758	0.958
			.392		1.318	1.18
			1		0.622	1.059
CH ₃ OH-CCl ₄	104	35	0		1.34	0.759
			.511		0.856	0.931
			1		0.394	0.783
CH ₃ OH-CCl ₄	104	55	0		2.13	0.958
			.549		1.26	1.18
			1		0.622	1.059

The free volume-free angle ratio product δV^f and the free volumes calculated using Hildebrand's rule are, on the other hand, seen not to be linear functions of mole fraction.

Figure 11

Free Volume by Pitzer's Rule $\text{CH}_3\text{CN} - \text{CCl}_4$ (45°C)

Free Volume for $\text{CH}_3\text{CN} - \text{C}_6\text{H}_6$

(45°C)

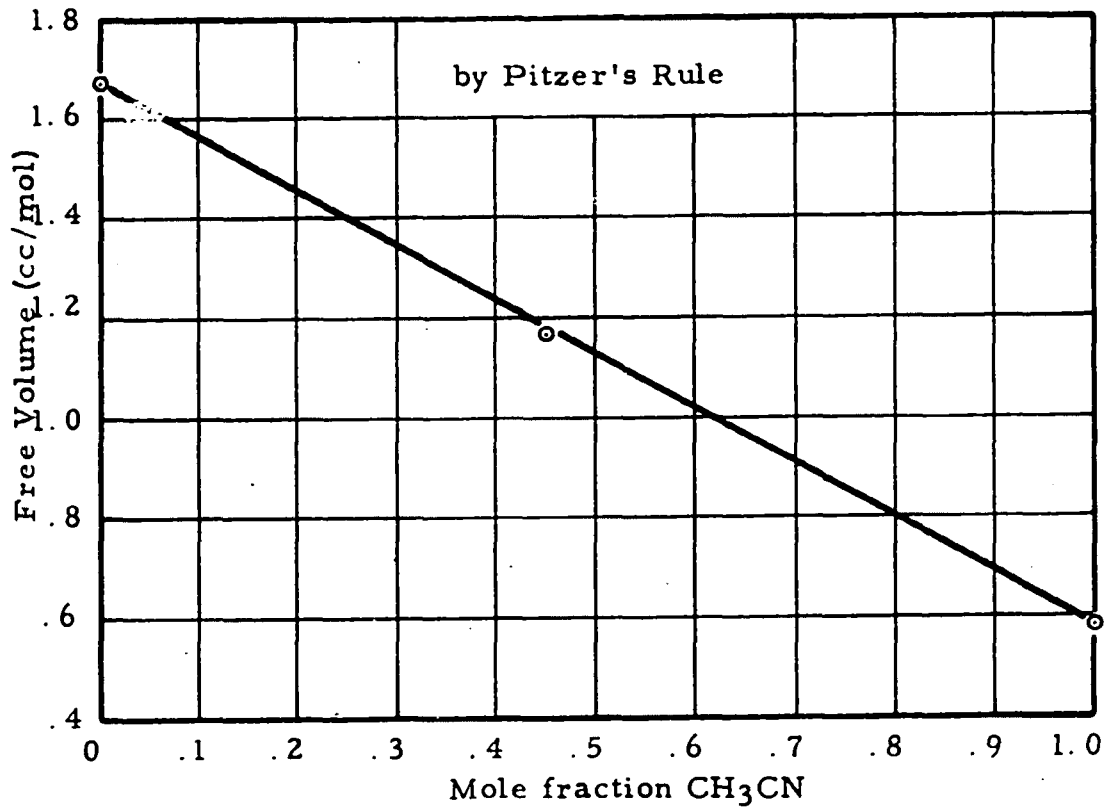
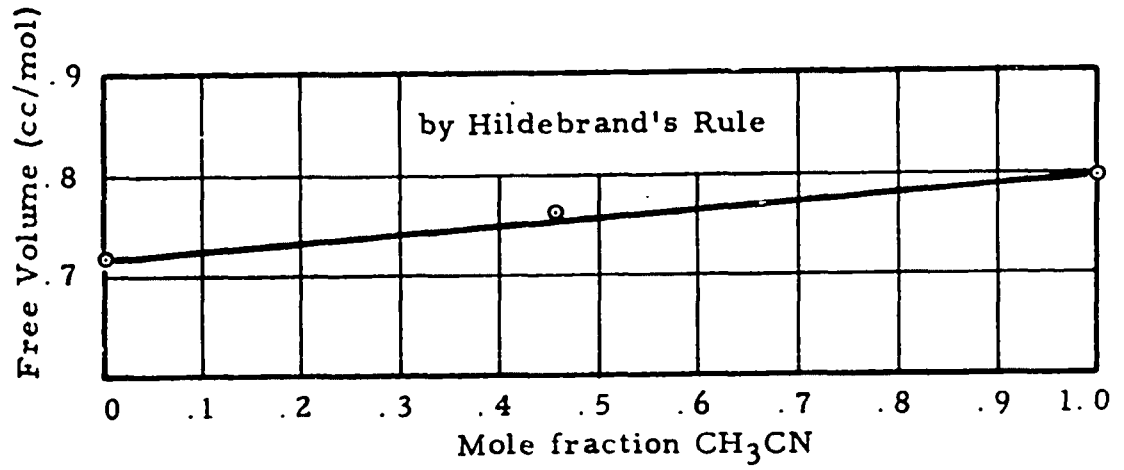


Figure 13

Free Volume for $C_6H_6 - C_2H_5OH$

(45°C)

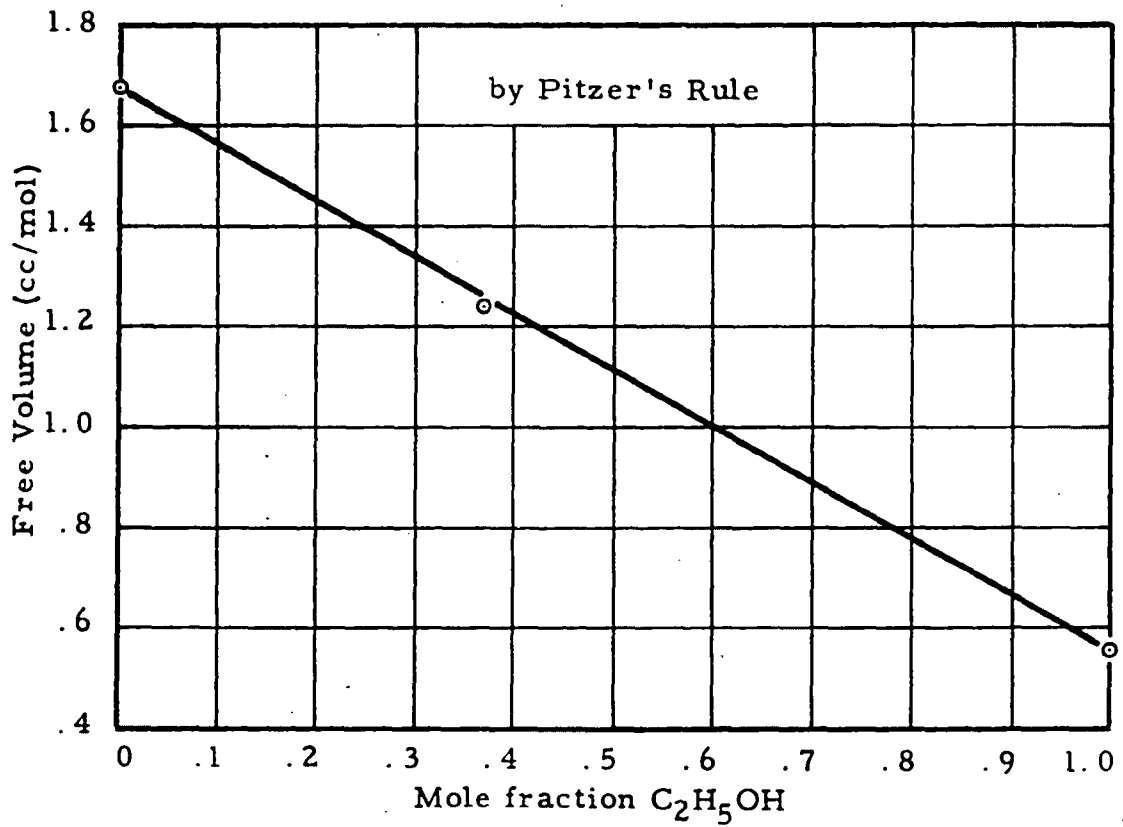
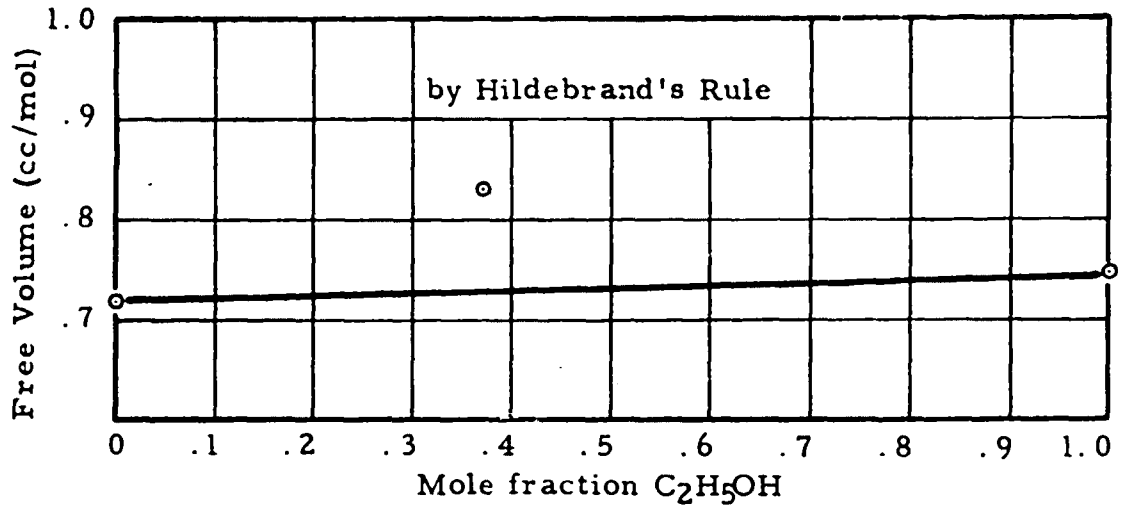


Figure 14

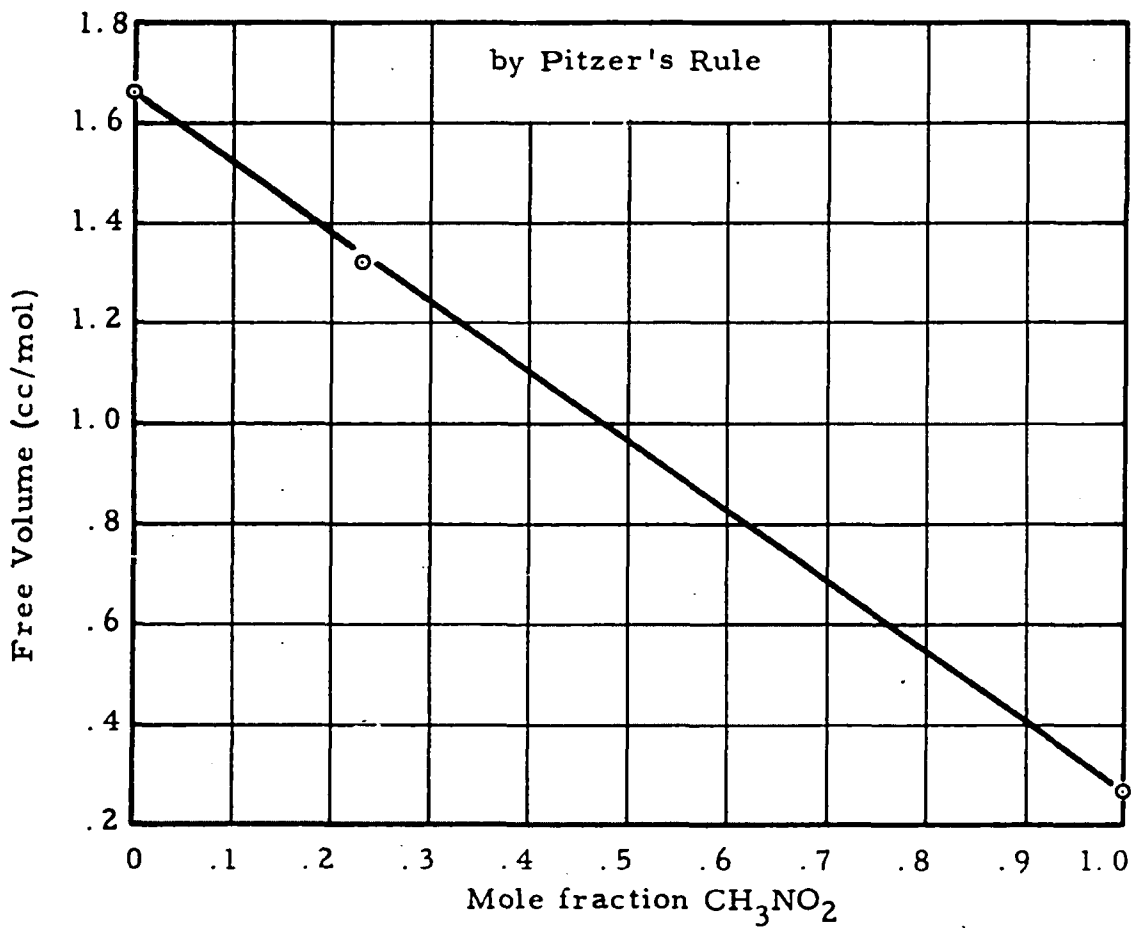
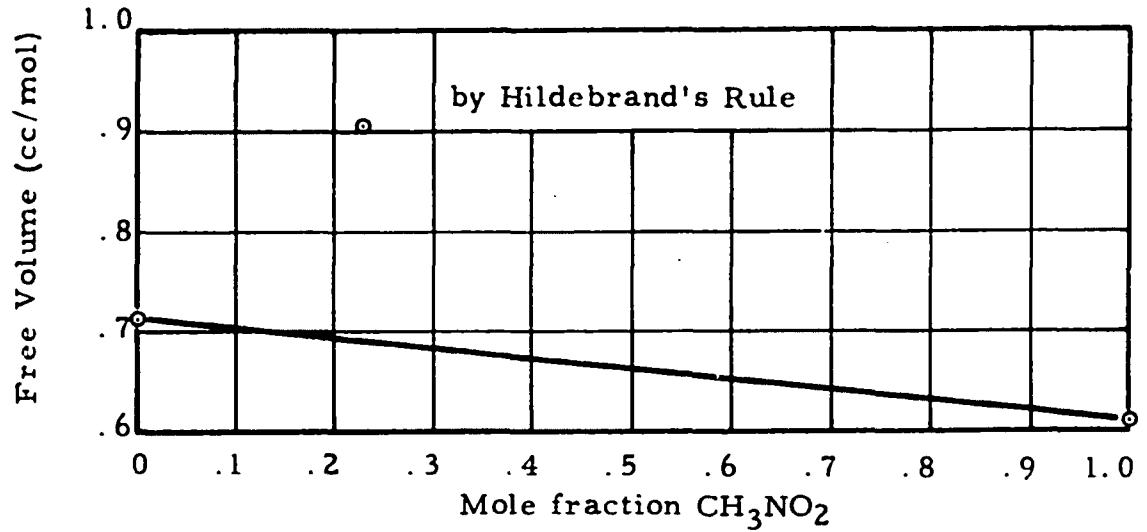
Free Volume for $C_6H_6 - CH_3NO_2$ ($45^\circ C$)

Figure 15

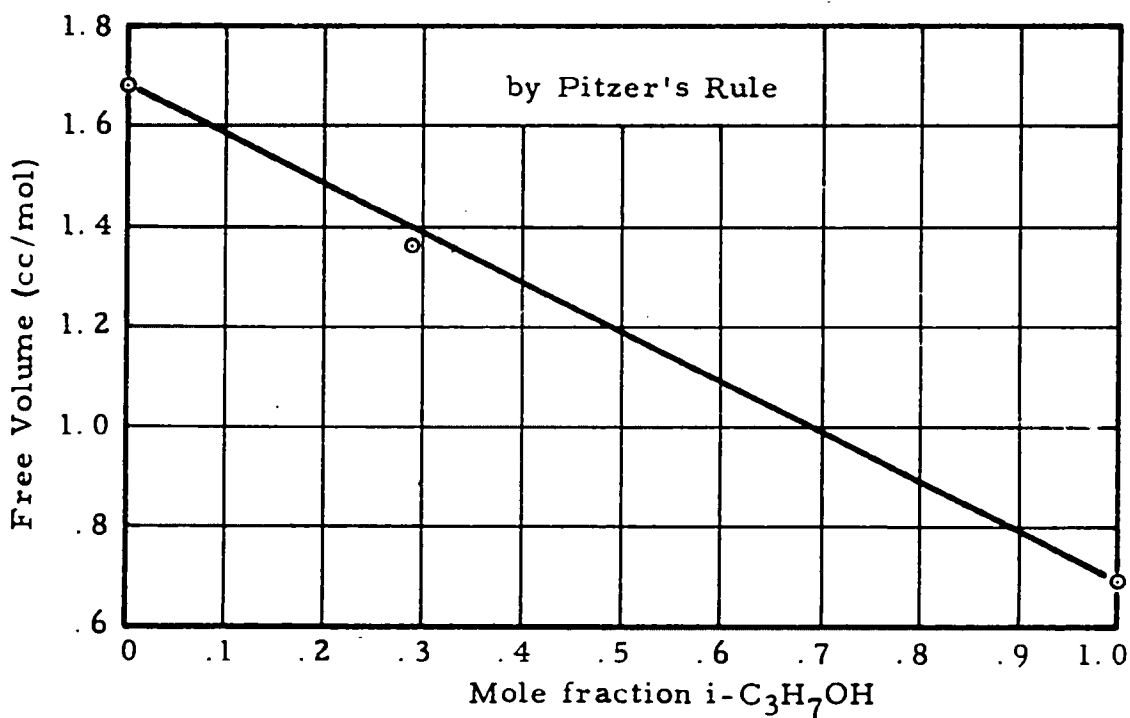
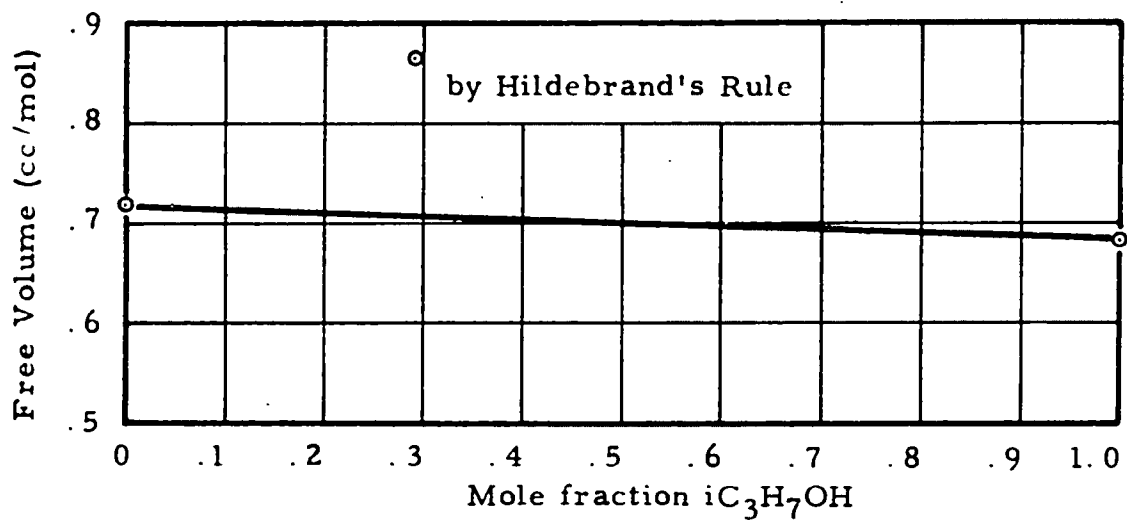
Free Volume for C_6H_6 - iC_3H_7OH ($45^\circ C$)

Figure 16

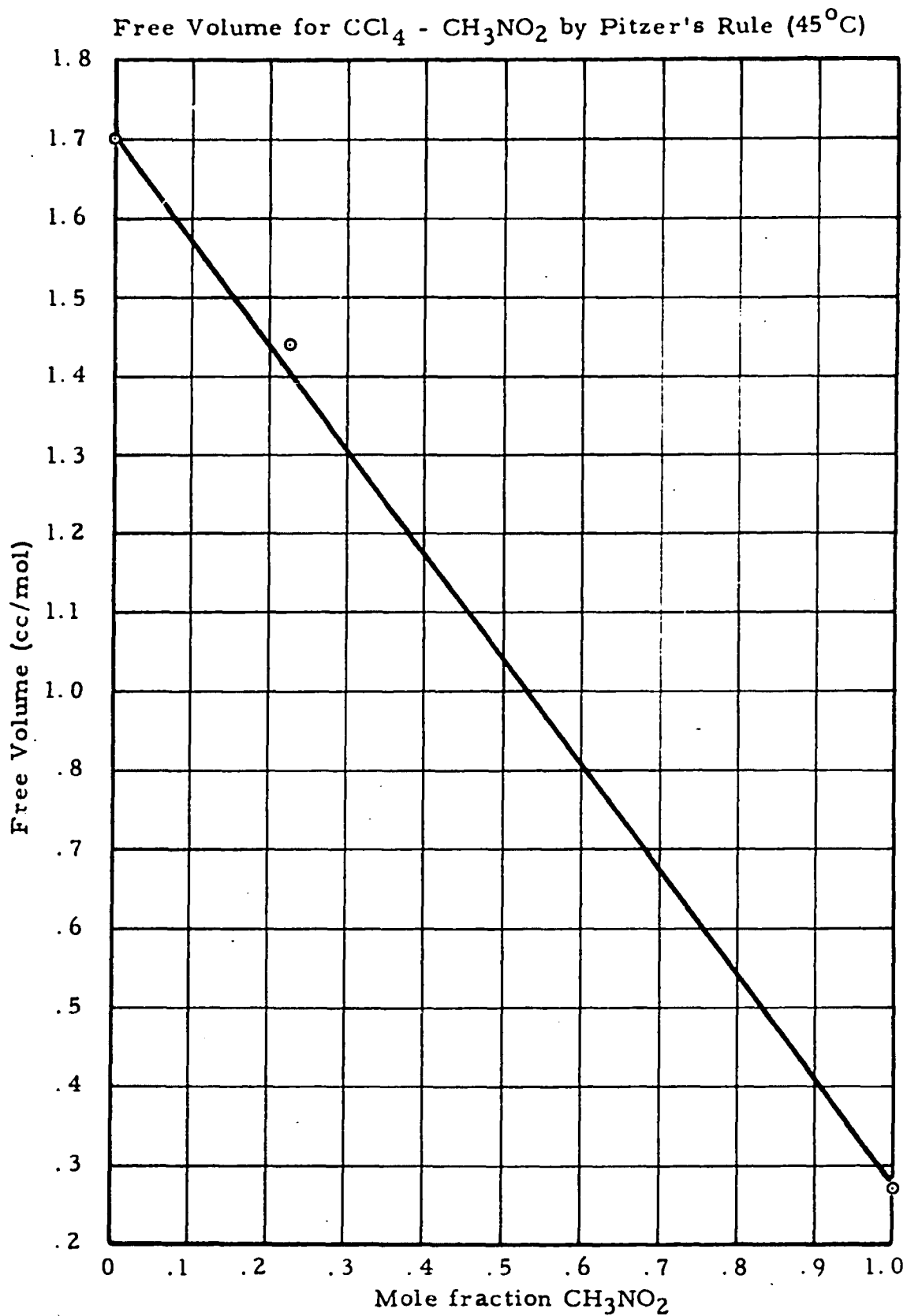


Figure 17

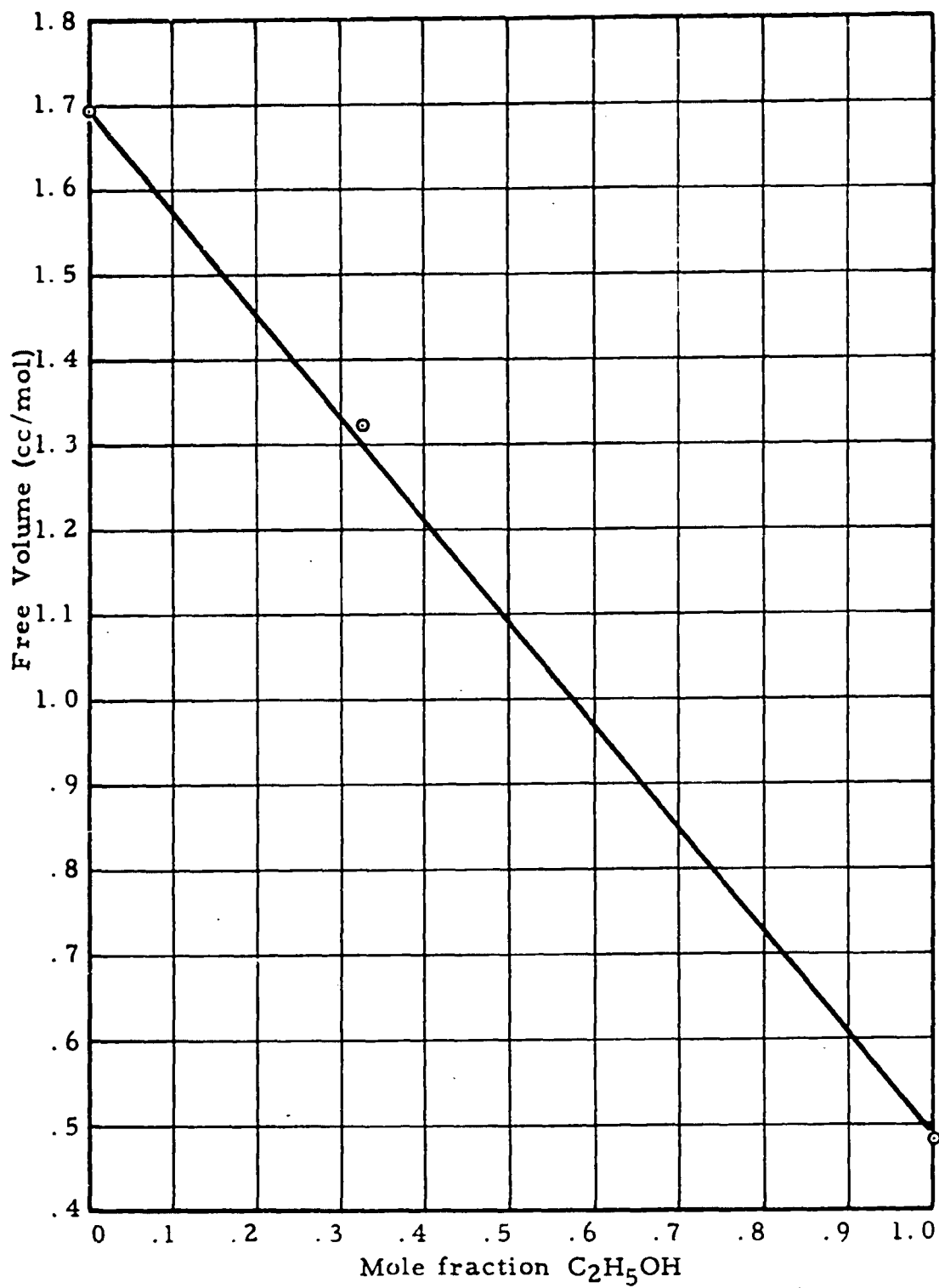
Free Volume for CCl_4 $\text{C}_2\text{H}_5\text{OH}$ by Pitzer's Rule (45°C)

Figure 18

Free Volume for $\text{CHCl}_3 - \text{C}_2\text{H}_5\text{OH}$

by Pitzer's Rule

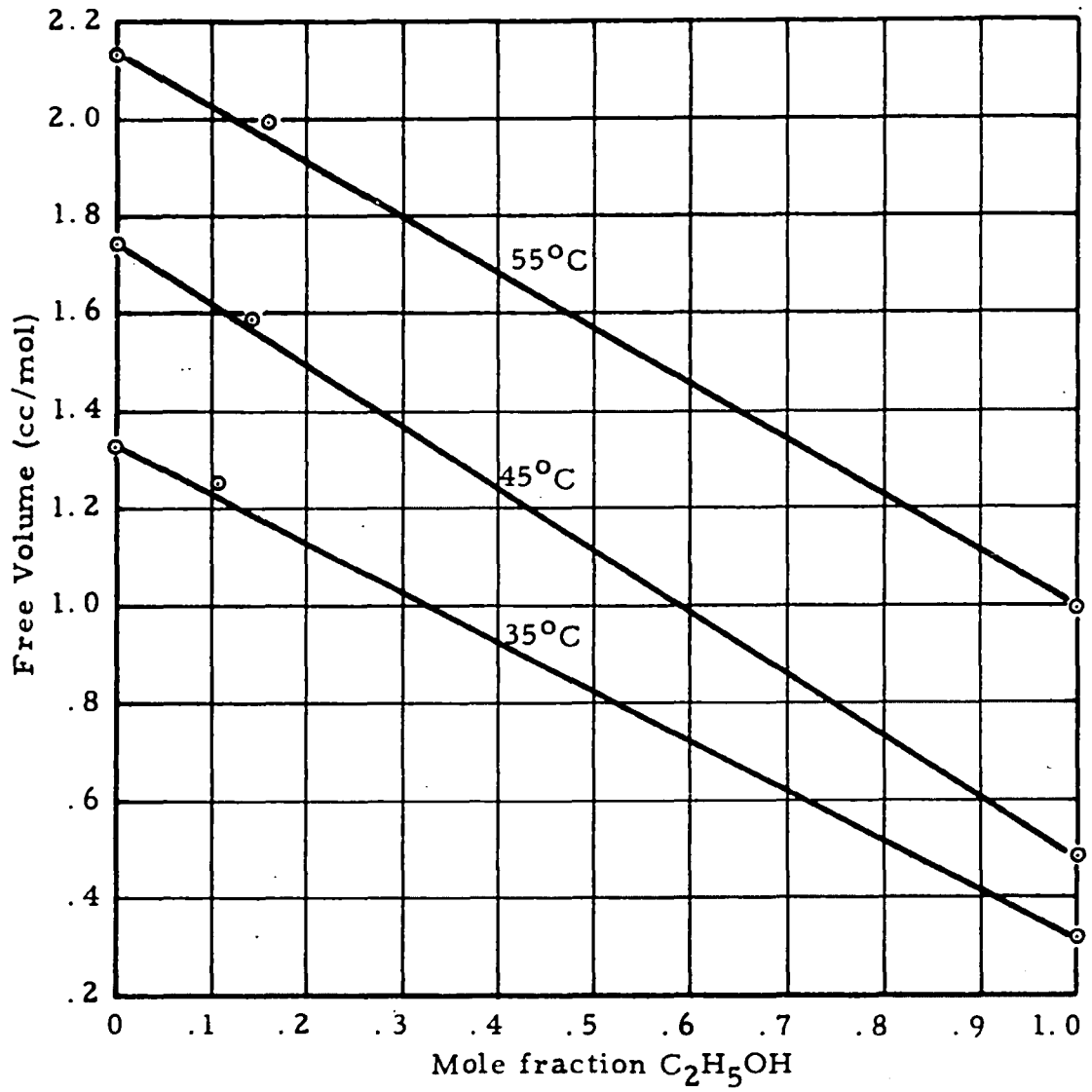


Figure 19

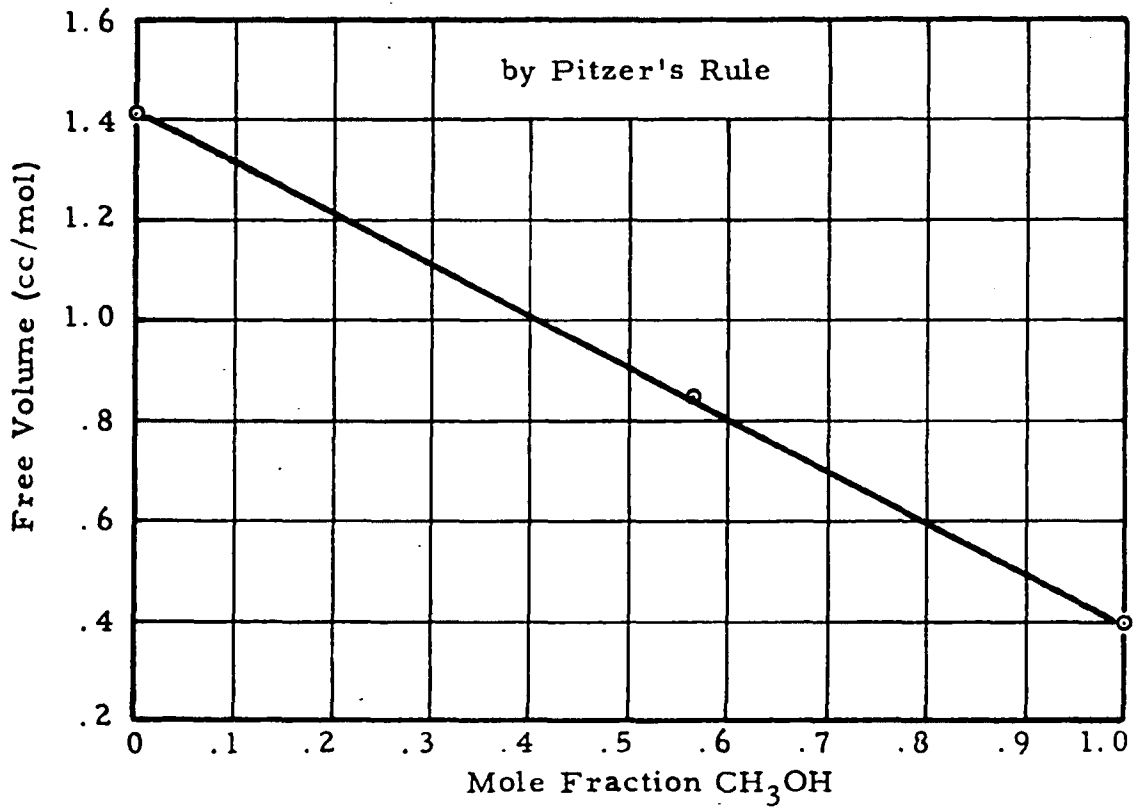
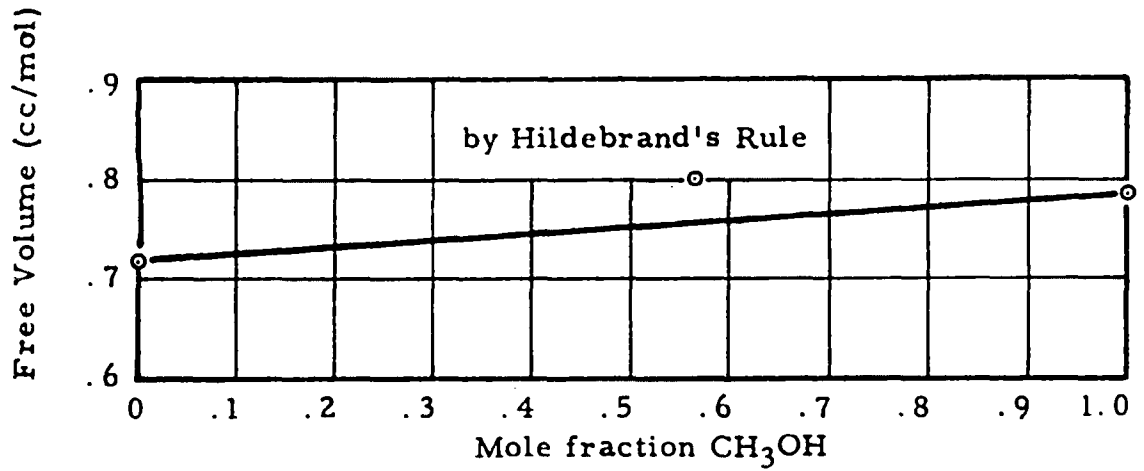
Free Volume for $\text{CH}_3\text{OH}-\text{C}_6\text{H}_6$ (35°C) 

Figure 20

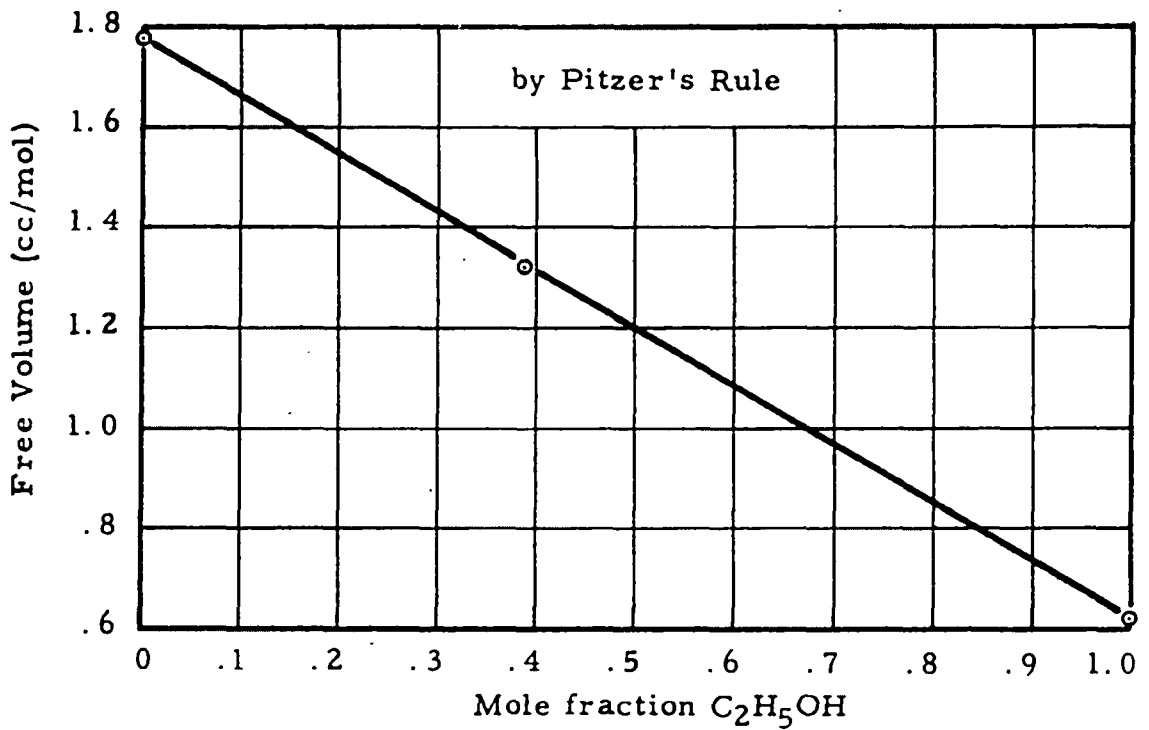
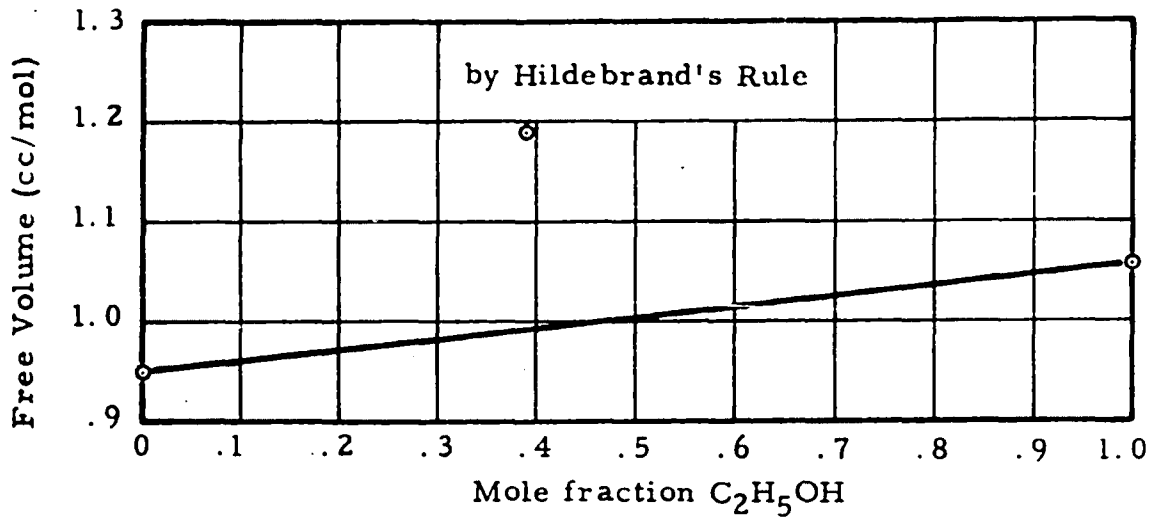
Free Volume for $\text{CH}_3\text{OH} - \text{C}_6\text{H}_6$ (55°C)

Figure 21

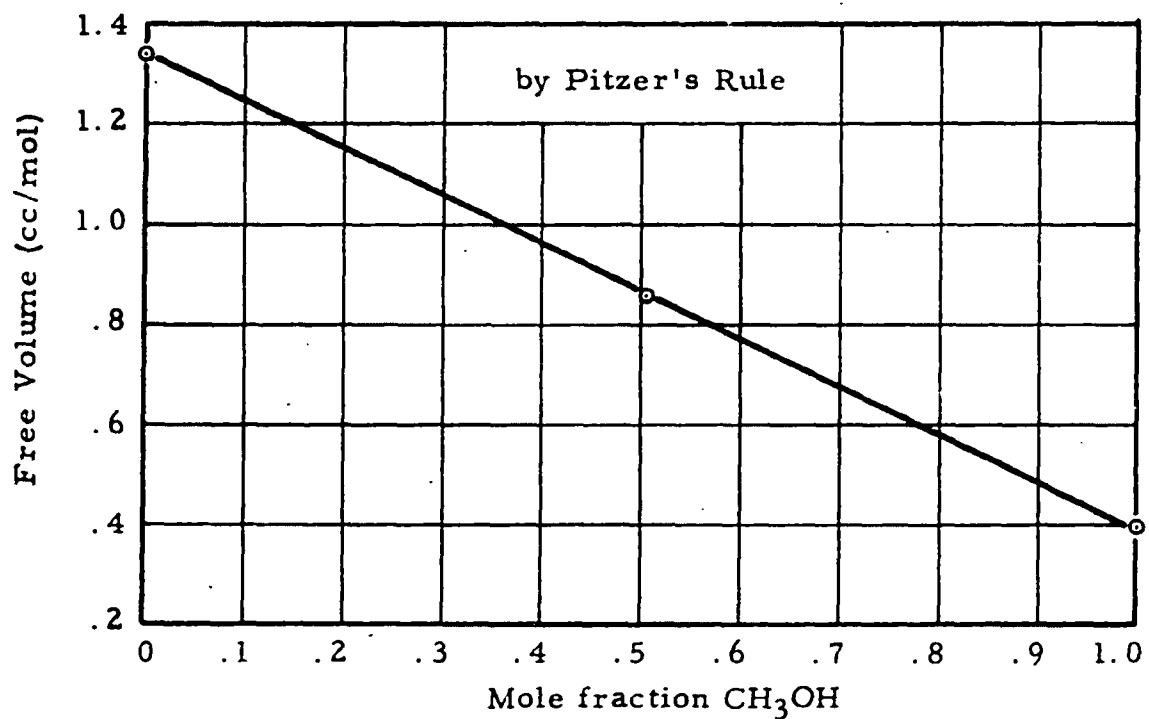
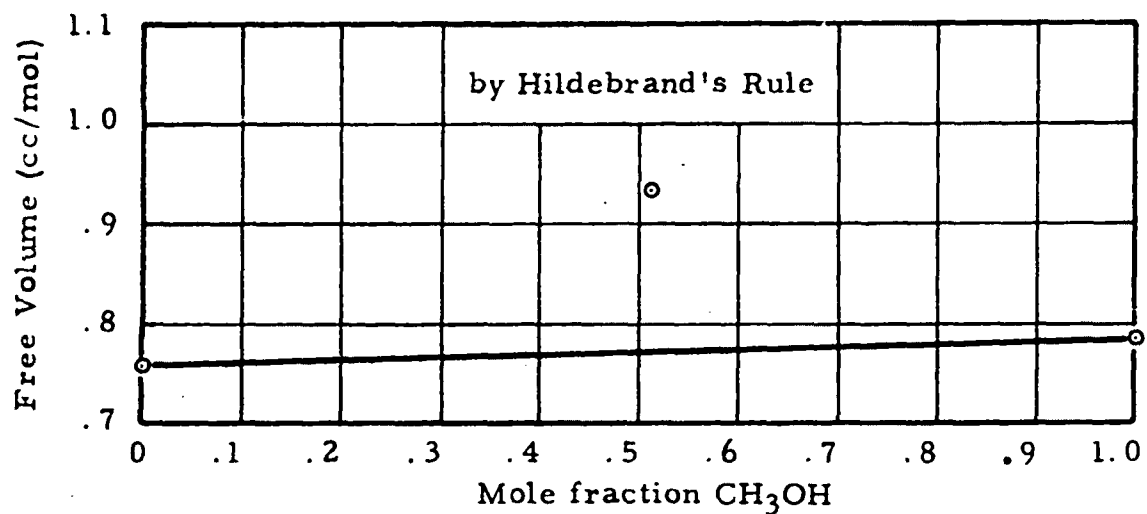
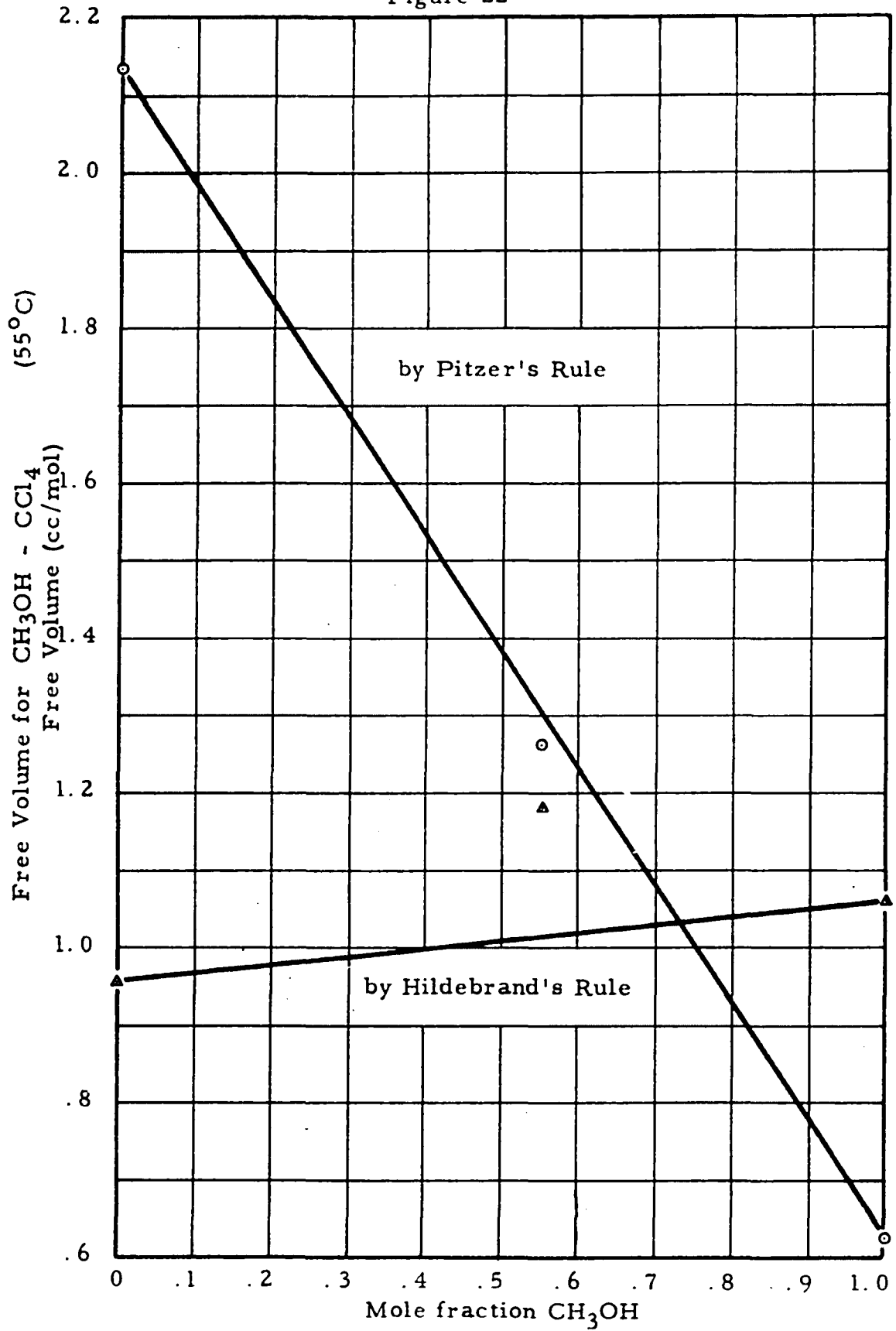
Free Volume for $\text{CH}_3\text{OH} - \text{CCl}_4$ (35°C)

Figure 22



Composite Free Volume δV^f for $\text{CH}_3\text{CN} - \text{CCl}_4$ (45°)

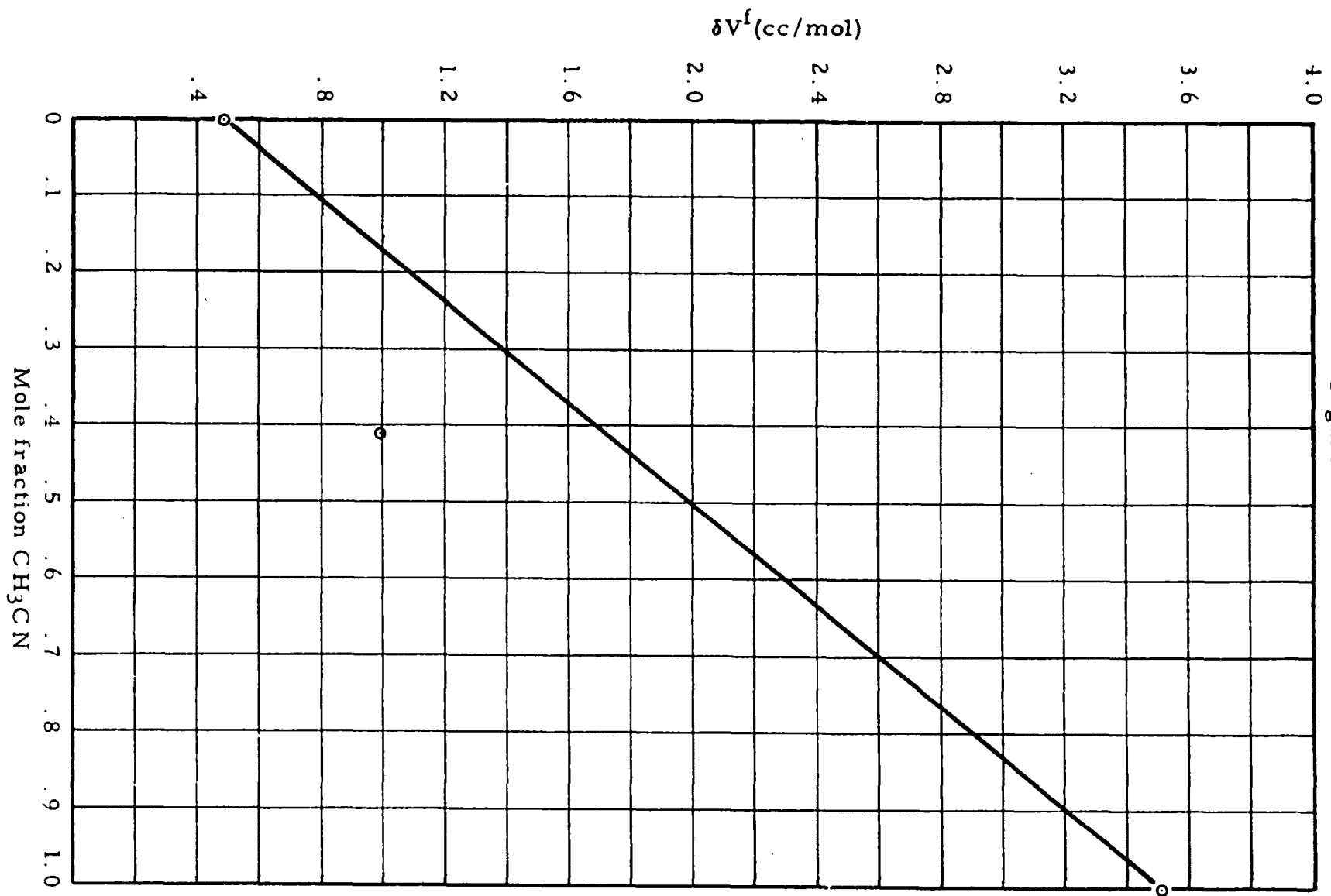


Figure 23

Figure 24

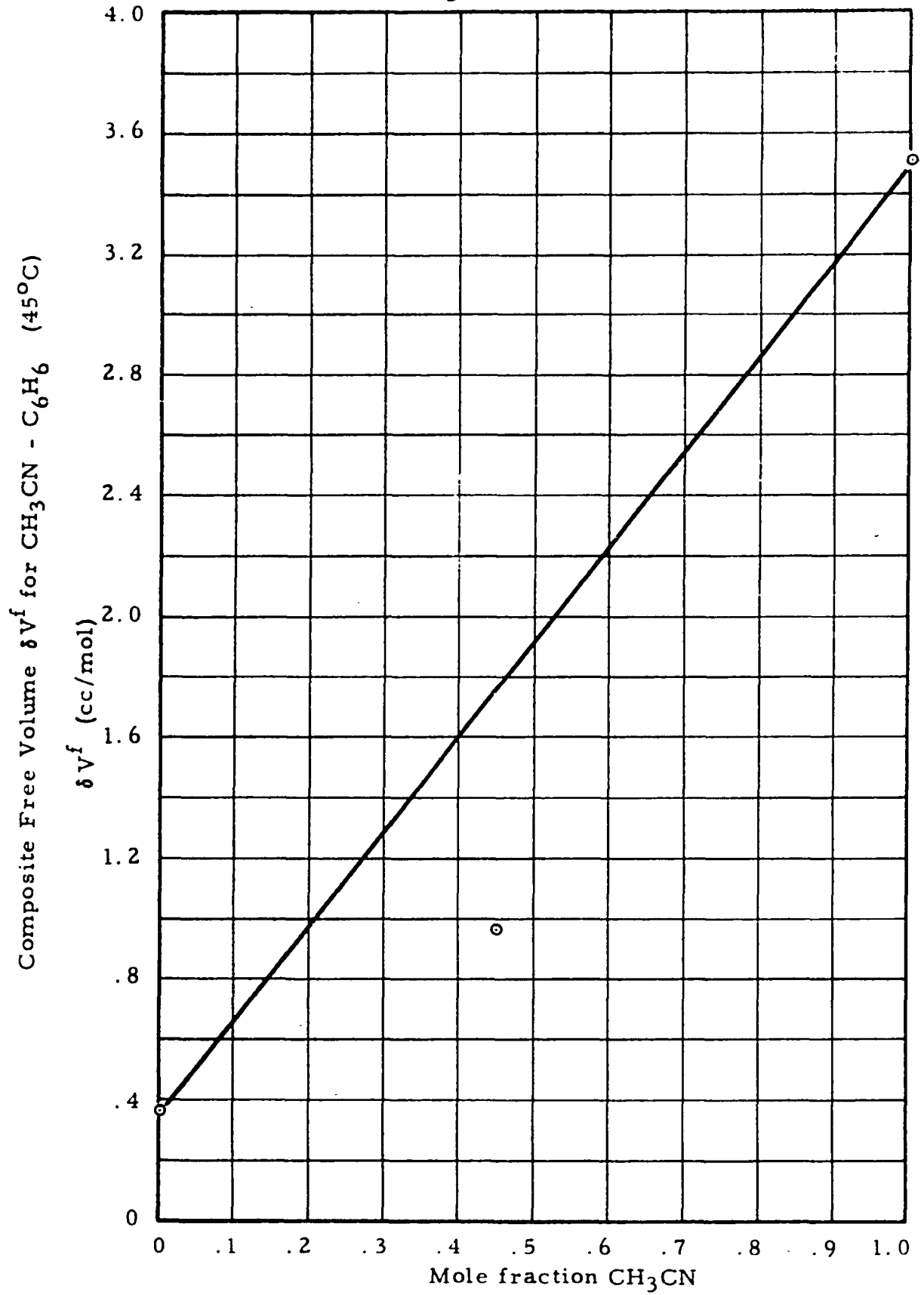


Figure 25

Composite Free Volume $C_3H_7OH - C_6H_6$

(45°C)

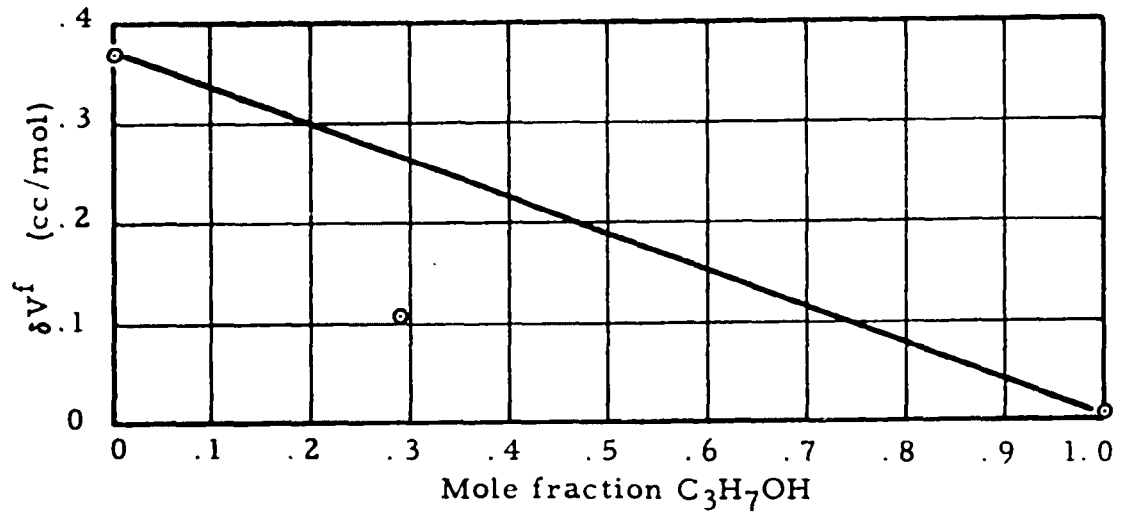


Figure 26

Composite Free Volume $C_2H_5OH - C_6H_6$

(45°C)

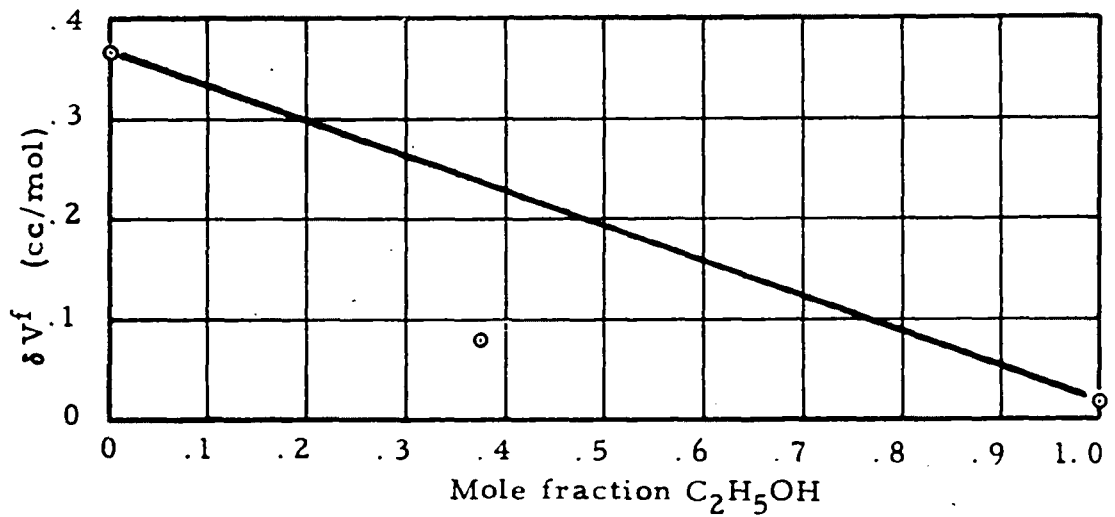


Figure 27

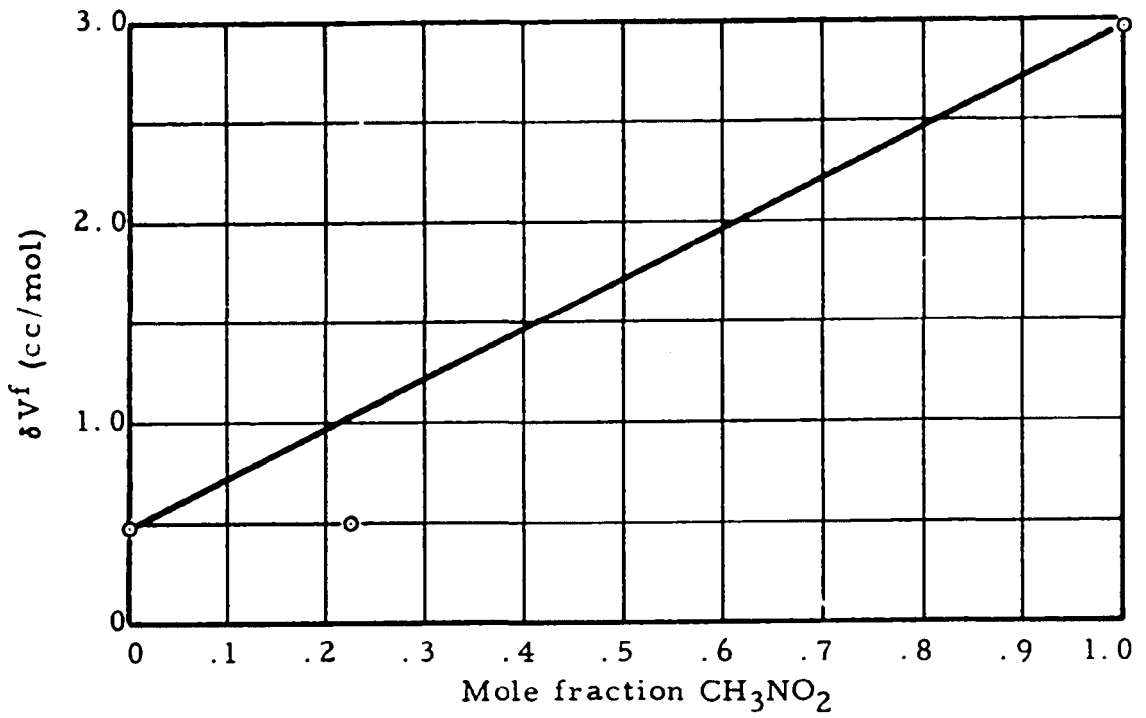
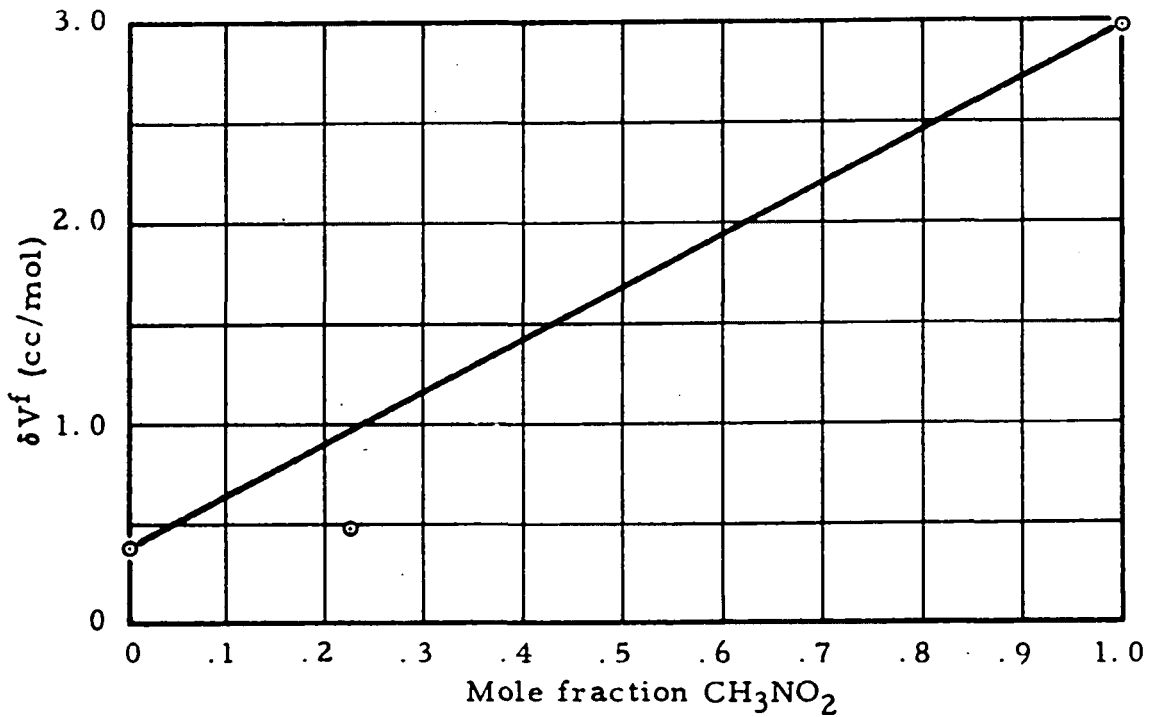
Composite Free Volume $\text{CH}_3\text{NO}_2 - \text{CCl}_4$ (45°C)

Figure 28

Composite Free Volume $\text{CH}_3\text{NO}_2 - \text{C}_6\text{H}_6$ (45°C)

CHAPTER III

SUMMARY OF RESULTS AND CONCLUSIONS

The research reported in Part I was prompted by a desire to extend the applicability of Murphy and Taber's phenomenological treatment of membrane processes. The primary aim was to derive equations which would describe ion flux in osmionic demineralization cells which contained more than two ionic species. Further limitations on the generality of Murphy and Taber's equations were also to be removed in the present research.

The equations derived in Part I fulfill these aims and have been programmed for the IBM 650 computer, for the special case in which only one cation (or anion) is present. The numerical solutions to the equations which were computed agree well with experimental results obtained by the Southern Research Institute.

Since ion selective membrane and ion reversible electrode processes are completely analogous, the equations derived in Part I have great versatility. They may be applied without modification to systems containing any combination of electrodes and membranes.

The present computer program will handle only up to five membranes and / or electrodes; however, if a larger machine than the 650 is available, the program could easily be revised to handle any number of membranes.

Part II examines the applicability of the free volume theory to binary solutions of non-electrolytes. The rotational contributions to the entropy of vaporization was calculated using Pitzer's rule for a number of single non-electrolytes. It was shown for four aliphatic alcohols that the rotational contribution could be accounted for by tetramer formation in the vapor phase.

Free volumes were calculated for several azeotropes using both Hildebrand's and Pitzer's rule for the rotational contribution to the entropy of vaporization. It was seen that Pitzer's rule is consistent with linearity of free volume with respect to mole fraction in all of the systems studied. This result suggests that it would be interesting to obtain sufficient experimental data to calculate the free volumes over the entire mole fraction range for a number of binary mixtures. If the free volume calculated according to Pitzer's rule could be shown in general to be a linear function of mole fraction, this rule would be promoted to very great utility in the prediction of the thermodynamic properties of binary solutions.

APPENDIX

A PROGRAM FOR COMPUTER SOLUTION OF EQUATIONS 39

Function of the Program

Given the data described below, the program will solve equations (39) at values of $x = x_0 + n \cdot \Delta x$ (where n is an integer) by a fourth order Runge-Kutta method (105). As written, the program will solve the differential equations for a double or single effect osmionic demineralization cell containing one anion (or cation) with not more than four ionic species of the opposite polarity.

Instructions for Using the Program

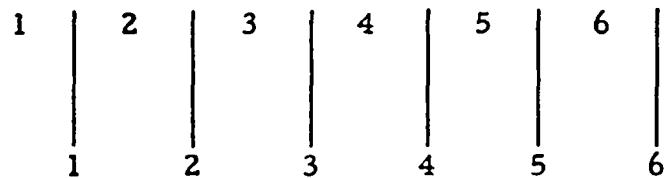
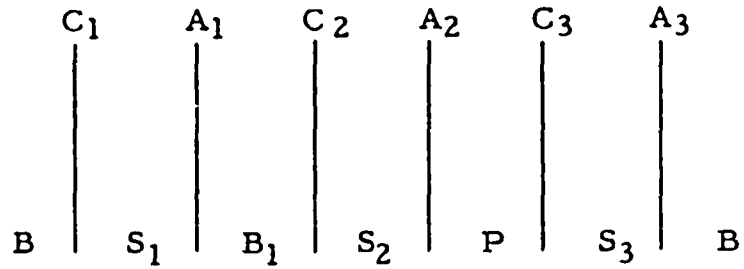
Input Data. The user must supply the following data each time the program is to be used:

I2	The number of membranes in the system: 4 for a single effect and 6 for a double effect cell.
I1	The number of cationic species present.
I0	n : The total number of ion species present.

Z1 to Z5	z_i : The charge on the i^{th} ionic species.
Z6 to Z10	λ_i^0 : $Z(5+i)$ = the equivalent ionic conductivity of the i^{th} ion at infinite dilution.
Z11 to Z15	A_i : $Z(10+i)$ = A_i in equation (43a).
Z16 to Z20	B_i : $Z(15+i)$ = B_i in equation (43a).
Z21 to Z25	F_i^C : $Z(20+i)$ = F_i^C in equation (44).
Z26 to Z30	F_i^A : $Z(25+i)$ = F_i^A in equation (44).
Z31 to Z35	G_i^C : $Z(30+i)$ = G_i^C in equation (44).
Z36 to Z40	G_i^A : $Z(35+i)$ = G_i^A in equation (44).
Z41	D^s : The distance between membranes in solution.
Z42	D^m : The thickness of the membranes.
Z43	DB : The average distance traversed by an ion in the external brine.
DO	Δx : The increment in x between successive approximations.
CO	x_0 : The initial value of x .
C1 to C10	$C_1(s)$: The concentration of the first ionic species in solution s .
C7 to C(6+I0)	The concentration of the second species.
C13 to C(12+I0)	The concentration of the third species.
C19 to C(18+I0)	The concentration of the fourth species.
C25 to C(24+I0)	The concentration of the fifth species.
Y12 to Y16	v_s : $Y(10+s)$ = v_s , the linear velocity of solution s .

Indexing of the solutions and membranes for a double effect

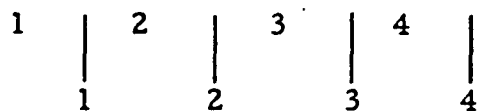
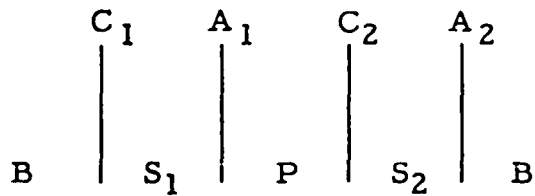
cell is to be according to the following diagram:



Thus the external brine is solution 1, S₁ is solution 2, and so forth.

C₁ is membrane 1, and so forth. For a single effect cell the dia-

gram to be used for indexing of solutions and membranes is as follows:



The indices for ionic species must be such that the single anionic (or cationic) species is listed last.

Data not applicable to the system under consideration need not be furnished.

Preparation of Data Cards. The set of data cards which is intended to be read by the program as input for a single run is called a "read group."

Values of I variables must be punched as integers at the right end of the designated ten-column field. Leading zeros must be punched. Values of C, D, Y, and Z variables must be punched in floating point form. Floating point form for the IBM 650 is described as follows: Let the number under consideration be $.n_1n_2n_3n_4n_5n_6n_7n_8 \times 10^p$, with $n_1 \neq 0$. Then the floating point form of the number, as punched on the data card, will be $n_1n_2n_3n_4n_5n_6n_7n_8yy$, where $yy = 50+p$. If the number is zero, it is usually punched as 0000000000. For example, the integer 2 would be punched as 0000000002, while the floating point number 125 would be punched as 1250000053, since $125 = .12500000 \times 10^3$. Plus signs may be punched as "12" punches or omitted; minus signs must be punched as "11" punches. In either case, the sign is punched in the same column as the right-most digit of the number. Up to five values may be punched on each data card.

The format of numeric data cards is as follows:

Columns 1 -10	Value of 1st variable
Columns 11-20	Value of 2nd variable
Columns 21-30	Value of 3rd variable
Columns 31-40	Value of 4th variable
Columns 41-50	Value of 5th variable
Columns 51-55	Alphanumeric name of 1st variable
Columns 56-60	Alphanumeric name of 2nd variable
Columns 61-65	Alphanumeric name of 3rd variable
Columns 66-70	Alphanumeric name of 4th variable
Columns 71-75	Alphanumeric name of 5th variable

The alphanumeric name of a variable must be punched as a letter (C, D, I, etc.) followed by a numeric subscript. In the last data card of a read group, punch an "*" in column 75.

Running the program. Place the GAT control boards in the 533 and 407. Set the 650 console switches as follows:

Storage entry switches	70 9000 9999
Programmed	STOP
Half Cycle	RUN
Storage selection	Immaterial
Control	RUN
Display	Program Register
Overflow	SENSE
Error	STOP

Place the program deck in the READ hopper of the 533 followed by the data cards. On the 407, set all switches to "N;" End of File to "ON," and Independent Operation to "OFF".

Press "COMPUTER RESET" then "PROGRAM START" on the 650 and the "START" button on the 533. When the computer stops on 70 9000 xxxx, press "END OF FILE" on the 533.

To interrupt or stop the program, press "PROGRAM STOP" on the 650.

An example. Suppose it is desired to calculate the theoretical demineralization to be expected from the experimental conditions given for "Run number 1" by Lacey.¹ Using a double effect cell, he gives the following starting conditions:

Spacing between membranes	0.082 cm
Membrane thickness	0.08 cm
Membrane dimensions	4 in x 30 in
Distance through Brine	50 cm
Salt Used	NaCl
Concentration of P and S feed	0.058 N
Concentration of Brine	4.0 N
Flow Rate of P and S streams	0.46 gph

The input data required for the program is as follows:

¹R. E. Lacey, Office of Saline Water, U. S. Department of Interior, Contract No. 14-01-001-193, Progress Report 2, 4 (1960) [unpublished].

I2	6
I1	1
I0	2
Z1	1
Z2	-1
Z6	50.9
Z7	75.5
Z11	1.34
Z12	1.44
Z16	0.386
Z17	0.407
Z21	0.045
Z22	0.0045
Z26	0.0
Z27	0.0307
Z31	0.05
Z32	0.0106
Z36	0.0085
Z37	0.05
Z41	0.082
Z42	0.08
Z43	50.0

The values of the equivalent ionic conductivities of the sodium and chloride ions are taken from Robinson and Stokes (106).

The values for A, B, F, and G in equations (43a) and (44) are estimated from Lacey's data (68).

DO	1	This is a convenient increment with which to start
CO	0	
C1	4.0	
C2	0.058	
C3	0.058	
C4	"	Chloride ion concentrations need not be given, since they will be computed by the program.
C5	"	
C6	"	
Y12	0.58	
Y13	1000	Any arbitrary large number will do for the velocity of the internal brine.
Y14	0.58	
Y15	0.58	
Y16	0.58	

The data cards may then be punched as follows:

```

00000000200000000010000000061000000051
I0          I1          I2          D0

1000000051100000005150900000527550000052
Z1          Z2          Z6          Z7

1340000051144000005138600000504070000050
Z11         Z12         Z16         Z17

450000004945000000470000000003700000049
Z21         Z22         Z26         Z29

3000000049106000004985000000484500000049000000000
Z31         Z32         Z36         Z37         C0
    
```

40000000515800000049400000005158000000495800000049
 C2 C3 C4 C5 C6

820000004980000000495000000051
 Z41 Z42 Z43

58000000501000000054580000005058000000505800000050
 Y12 Y13 Y14 Y15 Y16 *

The printed output on the 570 will be

1000000051400000005165053436493999994515901816149
 C0 C1 C2 C3 C4

57205019495886885349
 C5 C6

20000000514000000051721776884939999988516002984549
 C0 C1 C2 C3 C4

56417911495973145449
 C5 C6

and so forth.

This output data is to be interpreted as follows: at $x = CO = 1$ cm, the values of the concentrations of sodium ions in the six compartments are:

C^B	C1	4.0	gram-ions per liter
C^{S1}	C2	0.0650	
C^{B1}	C3	3.99	
C^{S2}	C4	0.0590	
C^P	C5	0.0564	
C^{S3}	C6	0.0597	

Similarly, the concentrations at $x = CO = 2.0$ are given in the next set of output data. The program will continue to compute and print concentration values at increments of x until "PROGRAM STOP" is pressed by the operator. The increment in x will be multiplied by two whenever the previous value of C^P differs from the current value by less than 0.0003. This particular run was continued until successive values of C^P were the same. The "steady state" is reached at $x = 137$ cm, where the value of C^P is 0.0110 gram-ions per liter. Lacey's experimental value at 30 cm is 0.013.

The Compiler Program

The GATE (107) program to be compiled and assembled by the IBM 650 is as follows:

```

LOAD AND GO
500 USED IN SUBROUTINES
40 IS HIGHEST STATEMENT NUMBER
DIMENSION C(160, 6, 1)Y(20) X(160, 6, 1) N
Z (50) D (10) I (10) K (2 )
1      5, I4, 1, 1, I2,
2      C(I0, I4)= 0.
3      5, I3, 1, 1, I0-1,
4      Z0=ZI3*C(I3, I4)/ ZI0
5      C(I0, I4)=C(I0, I4) Z0
6      10, I4, 1, 1, I2,
7      D14= 0.
8      10, I3, 1, 1, I1,
9      Z0 =ZI3*C(I3, I4)
10     DI4 = DI4 Z0
11     17, I3, 1, 1, I0,
12     17, I4, 1, 1, I2,
13     X(I3, I4) = C(I3, I4)*(AZI3)*(Z5 I3) - 10. P(Z(10 I3)) N
        *(DI4P(Z(15 I3)))/1000.
14     I5 =20 IF (-1)PI4 Q0. MI5 = 5
15     I6=I4 1 IF I4 S I2 MI6 = 1
16     X(5 I3, I4) = Z(I5, I3) Z(10 I5 I3)*SQRT. (C(I3, I4) N
        *C(I3, I6))
17     X(I0 I3, I4) = Y0*LN. (C(I3, I6)C(I3, I4) )
18     21, I3, 1, 1, I0,
19     21, I4, 1, 1, I2,
20     I7 = 41 IF I4 S 1 M I7 = 43
21     X(I3, I4) = (Z42 ZI7)*X(I3, I4) X(5 I3, I4) / (ZI7 * X(5 N
        I3, I4 X(I3, I4) ) Z0= 0.
        Z0 = 0.
22     26, I4, 1, 1, I2,
23     DI4 = 0.
24     25, I3, 1, 1, I0,
25     DI4 = A(ZI3)*X(I3, I4) DI4
26     Z0 = Z0 1. /DI4
27     Y1 = 0.
28     33, I4, 1, 1, I2,
29     30, I3, 1, 1, I0,
30     Y1 = Y1-ZI3*X(I3, I4)*X(10 I3, 4)/A(ZI3)/DI4/Z0

```



```

31      Y(1 I4) = 0.
32      33, I3, 1, 1, I0-1,
33      Y(1 I4) = Y(1 I4) X(I3, I4)*ZI*X(10 I3, I4) / AZ I3
34      36, I3, 1, 1, I0-1,
35      36, I4, 1, 1, I2,
36      X(5 I3, I4) = -X(I3, I4)*ZI3 * ((DI4*X(10 I3, I4) / ZI3) N
      -Y1-Y(1 I4)) / 96500. / 96500. / Z4 / DI4 / AZI3
37      LINK. (1, 3)
      SEGMENT 2 END
      LOAD AND GO
      500 USED IN SUBROUTINES
      40 IS HIGHEST STATEMENT NUMBER
      DIMENSION C(160, 6, 1) Y(20)
      X(160, 6, 1) Z(50) D(10) I(10)
      K(2)
1      READ
29     K2 = 2
      Y0 = 2479.
2      LINK. (2, 1)
3      5, I3, 1, 1, I0-1,
4      5, I4, 2, 1, I2,
5      C(5 I3, I4) = (X(5 I3, I4-1) -X(I3, I4)) *1000. / Z41 / Y N
      (10 I4)
6      K2 = K2 1
7      15, I3, 1, 1, I0-1,
8      15, I4, 2, 1, I2,
9      C(10 I3, I4) = C(I3, I4) IF K2 1
10     C(20 I3, I4) = C(I3, I4) IF K2 1
11     C(15 I3, I4) = C(5 I3, I4)*D0
12     D10 = 6.
13     D10 = 3. IF K2 U 2
14     D10 = 3. IF K2 U 3
15     C(20 I3, I4) = C(20 I3, I4) C(1 I3, I4) / D10
16     GO TO 22 IF K2 U 4
17     20, I3, 1, 1, I0-1,
18     20, I4, 2, 1, I2,
19     D10 = 0.5 IF K2 S 3 M D10 = 1.
20     C(I3, I4) = C(10 I3, I4) C(15 I3, I4)*D10
21     LINK. (2, 1)
22     24, I3, 1, 1, I0-1,
23     24, I4, 2, 1, I2,
24     C(I3, I4) = C(20 I3, I4)
25     C0 = C0 D0
26     TC0... C(I0-1, I2)
27     K2 = 0
28     LINK. (2, 1)

      PROGRAM 1 END

```

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