The Separation of Ions with Permselective Membranes

A. T. DIBENEDETTO and E. N. LIGHTFOOT
University of Wisconsin, Madison, Wisconsin

This study forms part of a project aimed at obtaining a better understanding of the behavior of nonideal permselective membranes. The object here was to determine the applicability of the Nernst-Planck equations for studying the behavior of ions in aqueous solutions surrounding such a membrane during electrodialysis.

Attention was confined to stagnant and laminar flow systems. The processes studied were transfer of hydrogen ions, silver ions, and mixtures of the two through the cation exchanging membrane Nepton CR-61. The bulk solution concentrations on either side of the membrane varied from 0.01 to 0.20 N, and in all cases the only anions present were nitrate ions. Limiting currents for solutions of silver nitrate were predictable within 15%, with much of the uncertainty resulting from the difficulty in defining the limiting current. For mixtures of silver nitrate and nitric acid the limiting currents were predictable within the range of experimental accuracy but were found to be quite sensitive to small changes in the operating conditions. This sensitivity results from the very high relative mobility of the hydrogen ions. The relative transport of the two cations was primarily a function of relative concentration, relative diffusivities, current density, and ion exchange equilibria and was predictable with an accuracy limited only by the uncertainty of the ionic diffusivities and the ion exchange equilibria.

The diffusivities of the cations in the membrane relative to the diffusivity of nitrate ion were estimated to be about ten times lower than in solution. This was explained by assuming that the cations tended to concentrate about the anionic fixed charges of the membrane thereby partially screening their effectiveness and reducing the mobility of the cations. In mixtures, the membrane diffusivity of the silver ions relative to the hydrogen ions was lower (by a factor of 1.4 to 3.6) than the relative diffusivity in solution. This indicated that silver ions were more easily concentrated about the fixed charges and thereby screened them from both the anions and hydrogen ions.

SINGLE-ELECTROLYTE SOLUTIONS SURROUNDING AN ION EXCHANGE MEMBRANE

Theoretical

A salt solution in steady laminar flow between two parallel cation-exchanging membranes is considered (Figure 1). A direct current is flowing through the solution in a direction perpendicular to the membranes. An expression for the theoretical limiting current density in this system, that is for the average current density when the salt concentration is zero at the cathodic membrane, will be developed. The following assumptions are made: steady state, constant temperature and pressure, dilute solutions, electroneutrality $\sum_i n_i c_i = 0$. A pseudo binary diffusion coefficient $D_i = \dfrac{u_i RT}{|n_i| F}$ can be used to describe the motion of each ion. This point was verified by studies on stagnant solutions in contact with the membrane (*4*).

The equation of continuity may be written for each ion in solution as

$$-D_+ \operatorname{div} (\operatorname{grad} n_+ c_+) - \frac{D_+ n_+ F}{RT} \operatorname{div} (n_+ c_+ \operatorname{grad} E) + \operatorname{div} (n_+ c_+ \underline{v}) = 0 \tag{1}$$

$$-D_- \operatorname{div} \operatorname{grad} (n_- c_-) - \frac{D_- n_- F}{RT} \operatorname{div} (n_- c_- \operatorname{grad} E) + \operatorname{div} (n_- c_- \underline{v}) = 0 \tag{2}$$

Solving simultaneously by making use of the electroneutrality requirements one obtains

$$-D_\pm \operatorname{div} \operatorname{grad} (n_+ c_+) + \operatorname{div} (n_+ c_+ \underline{v}) = 0 \tag{3}$$

$$D_\pm = \frac{D_+ D_- (n_+ - n_-)}{D_+ n_+ - D_- n_-} \tag{4}$$

The current density is obtained by integrating Equations (1) and (2):

$$-D_+ \operatorname{grad} n_+ c_+ - \frac{D_+ n_+ F}{RT} n_+ c_+ \operatorname{grad} E + n_+ c_+ \underline{v} = \frac{I t_+}{F} \tag{5}$$

$$-D_- \operatorname{grad} n_- c_- - \frac{D_- n_- F}{RT} n_- c_- \operatorname{grad} E + n_- c_- \underline{v} = \frac{I t_-}{F} \tag{6}$$

If one neglects convection perpendicular to the membrane surface, $\underline{v}$ equals zero at the membrane surface. The current density at position z can then be given in terms of the concentration gradients at $s = h$. Combining Equations (5) and (6) one obtains

$$\left(\frac{I}{F}\right)_z = \left(\frac{n_+ - n_-}{n_+ n_-}\right) \frac{1}{\left[\dfrac{t_+}{D_+ n_+} + \dfrac{t_-}{D_- n_-}\right]} (\operatorname{grad} n_+ c_+)_{(s=h)z} \tag{7}$$

The average current density to the entire membrane of length L is then

$$\overline{\left(\frac{I}{F}\right)} = \left(\frac{n_+ - n_-}{n_+ n_-}\right) \frac{1}{\left[\dfrac{t_+}{D_+ n_+} + \dfrac{t_-}{D_- n_-}\right]} \left(\frac{1}{L}\right) \int_{z=0}^{z=L} (\operatorname{grad} n_+ c_+)_{s=h} dz \tag{8}$$

It is assumed that the transport numbers and diffusion coefficients are constants (or integrated averages). The limiting current may then be evaluated from Equations (3) and (8) once the velocity $\underline{v}$ and the boundary conditions are specified. These factors depend on the cell geometry, the type of operation, and the hydrodynamics of the fluid.

The authors assume as a model for their system the tangential laminar flow of a large body of fluid past a semi-infinite thin flat plate. This model should give a good description of their system because the path length in the direction of flow is small and because concentration changes are confined to very thin regions near each membrane. The localization of concentration gradients is a result of the high Schmidt number of the diffusing species. In addition the authors shall assume the concentration of salt in the aqueous solution at the cathodic membrane surface to be constant at zero. Salt concentration at the anodic membrane will not affect limiting current under the conditions of operation in this experiment. The authors may then write for the mass transfer coefficient at the cathodic membrane surface (*1*)

$$\left(\frac{k_c}{D_\pm}\right) = 0.332 \left(\frac{\nu}{D_\pm}\right)^{1/3} \left(\frac{U}{z\nu}\right)^{1/2} = \frac{-(\operatorname{grad} n_+ c_+)_{s=h}}{n_+ c^0_+} \tag{9}$$

The limiting current for a single 1-1 electrolyte flowing over a cation exchange membrane is then (*1, 5, 6*)

$$\left(\frac{1}{L}\right) \int_0^L \left(\frac{I_L}{n_+ c^0}\right)_z dz = \frac{2 D_+ F}{\left[1 - \left(1 + \dfrac{D_+}{D_-}\right) t_-\right]} \left(\frac{1}{L}\right) \int_{z=0}^{L} 0.332 \left(\frac{\nu}{D_\pm}\right)^{1/3} \left(\frac{U}{\nu z}\right)^{1/2} dz \tag{10}$$

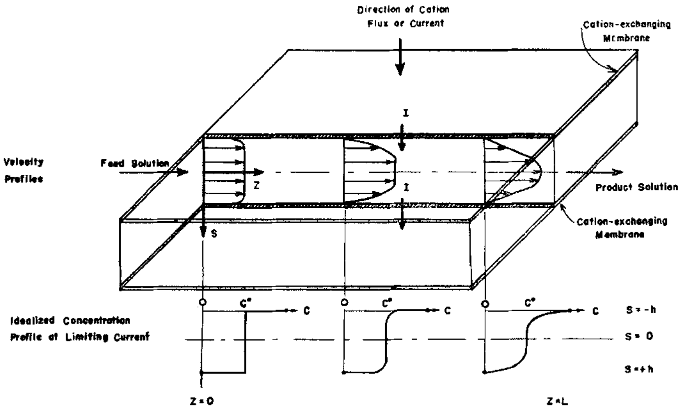

Fig 1. Single chamber of the type of ion fractionator considered in this paper.

One may then integrate Equation (10) and express the average limiting current density as a function of the Reynolds number:

$$\left(\frac{\overline{I_L}}{c^o}\right) = \frac{1.33\, D_+ F}{\left[1 - \left(1 + \frac{D_+}{D_-}\right) t_-\right]} \frac{(\nu/D_\pm)^{1/3}}{(d_e L)^{1/2}} (N_{Re})^{1/2} \qquad (11)$$

Equation (11) is the defining equation for $\overline{I_L}$. It will be of practical interest only if the model upon which it is based reasonably describes the actual system and if the limiting current so defined is useful for design calculations.

Applicability of the model requires that three important conditions are met: correct geometry, boundary conditions, and fluid properties.

The authors' cell geometry does not conform exactly to the boundary-layer model used, but because of the high Schmidt numbers involved, on the order of 1,000, errors resulting from improper geometry are not likely to be important. The requirement of zero concentration at the cathodic membrane cannot be met exactly either; an infinite potential drop across the test chamber is needed for this. However this condition can be reasonably well-approximated at obtainable potential drops because the current is approximately proportional to the differences in boundary concentrations across the cell while the potential drop is more nearly dependent upon their ratio. The critical fluid property is that of an inert solvent. Water does dissociate, but the resulting hydrogen and hydroxyl ions do not play a significant role until the concentration of added electrolyte approaches their order of magnitude, say about 10^{-6} normal. This is a very small fraction of bulk electrolyte concentration in the work reported here.

It remains to be shown that the limiting current predicted by Equation (11) is useful. Clearly the current so predicted is not the maximum current that can be passed through the cell; because of the rapid dissociation of water there is no such limiting current in the practical range of operation. However as cathodic boundary concentrations of added electrolyte approach about 10^{-6} normal, a large fraction of the total current is carried by the hydrogen ions formed by dissociation of water. At about this point the current efficiency for removing the added electrolyte decreases rather abruptly. If the bulk concentration of added electrolyte is very much greater than say 10^{-6} normal, then these conditions will set in near the limiting current predicted by Equation (11). In the remainder of this paper the current at which this unfavorable behavior becomes noticeable will be referred to as the *limiting current.* This definition is both limited in concept and arbitrary. Nevertheless Equation (11) gives a good quantitative indication of the onset of these unfavorable operation conditions; that is it is a useful definition of limiting current.

Experimental

Transport numbers and limiting currents were measured as functions of concentrations and flow rates.

A Lucite six-compartment electrolytic cell with two silver electrodes was used. Figure 2 shows the dimensions of the chambers. The partitions are Nepton CR-61 cation and Nepton AR-111A anion selective membranes. The arrangement of the chambers is shown in Figure 3. All chambers, except for the feed chamber 3, were baffled to insure mixing near the membrane surfaces. The concentration of electrolyte in compartment 3 was several times lower than in the other compartments to permit the study of polarization effects in the feed without having appreciable polarization in the other compartments.

TABLE 1. TRANSPORT NUMBERS FOR SILVER ION JUST BELOW THE LIMITING CURRENT IN NEPTON CR-61 MEMBRANES

t_{Ag}	c^o_{Ag}, meq./ml.	N_{Re}
0.71	0.158	0
0.73	0.137	34
0.74	0.145	221
0.71	0.0167	0
0.67	0.0157	41
0.71	0.0167	216

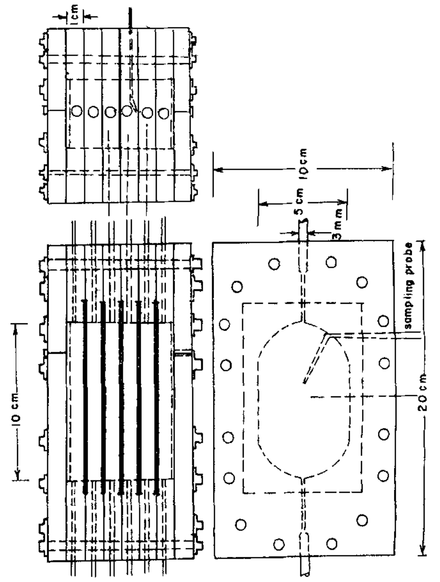

Fig. 2. A six-compartment cell with silver electrodes.

Solutions were prepared with reagent grade silver nitrate, nitric acid, and sodium nitrate in distilled water. The distilled water was degassed to pH 7 to eliminate all carbon dioxide. The solutions were not however protected from further absorption of carbon dioxide from the atmosphere, and it is possible that such absorption could result in a suppression of absorption could result in a suppression of the pH changes measured later. This point was not fully appreciated during the course of experimentation, and it is not possible to estimate the extent of carbon dioxide contamination accurately. It is however felt by the authors that this effect was small, and it seems very unlikely that it would have any substantial effect on the conclusions drawn from the data.

Voltmeter leads were soldered to the electrodes. An ammeter was put in series with the cell. For very low currents the potential across a resistor in series with the cell was used for more accurate measurement. The electrolyte was circulated by gravity flow through the six chambers and recycled to constant-head tanks by a sigma displacement pump. The electrode compartments were connected to maintain a constant concentration and to neutralize electrode reaction products. The membranes were arranged so that a steady flux of silver or hydrogen ions occurred in compartment 3. Data were taken after the system had attained a steady state.

The transport numbers were determined by measuring the amount of silver or hydrogen ions in product compartments 4 and 5. Then

$$t_{Ag} = \frac{(\text{no. of equivs of } Ag^+)\ F}{(I A)\ (\text{time})} \qquad (12)$$

$$t_{NO_3} = 1 - t_{Ag} \qquad (12a)$$

Silver ion concentration was measured potentiometrically with a modified version of the method of Kolthoff and Lingane (5). The over-all accuracy was ± 0.2%. Hydrogen ion concentration was measured potentiometrically with a saturated quinhydrone electrode. The over-all accuracy was ± 0.8%.

Two arbitrary experimental definitions of limiting current were used:

> The current density at which the pH in chamber 4 changed from 7 to 5 within 10 min. of steady state operation, a pH meter was used; and the current density at which a maximum rate of change of potential with current across the whole cell $\Delta E/\Delta I$ was observed.

These are simply measures of the onset of the unfavorable operating conditions discussed above; they have no precise theoretical justification. Other definitions could have been used, for example the current at which the rate of change of ampere efficiency was greatest, but these were chosen for simplicity and reliability with the authors' experimental setup. The first of these two definitions is quite sensitive to operating conditions and details of equipment design. It is not recommended as generally applicable, but it was useful here as a sensitive measure of hydrogen transfer. The second definition is susceptible to precise measurement and can be used even for acidic or basic solutions. It should be generally useful, particularly for truly one-dimensional systems such as the nonflow systems studied here. For an inert solvent dE/dI should become infinite at limiting current. For real systems it will always give too high a limiting current because solvent dissociation will occur thereby suppressing the change in slope. However a sharp change in slope was always observed in these experiments. Figure 4 is a typical result.

Results

Transport Numbers. Figure 5 is representative of the experimental silver ion transport numbers.

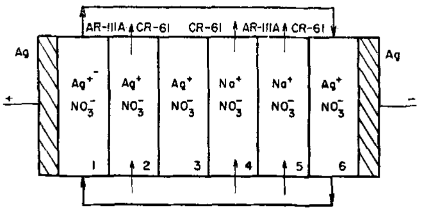

Fig. 3. Schematic diagram of cell for the single-electrolyte system.

At current densities below 1.0 ma./sq. cm. the silver ion transport numbers increased with decreasing current density and an appreciable amount of silver ions showed up in compartment 5. These effects are probably due to a Fickian diffusion of sodium ions from compartment 4 to 3 and silver ions from compartment 6 to 5. The magnitude of this diffusion can be roughly approximated by using Fick's first law:

$$I_j = -D_{jm} F \frac{dc_j}{dx}$$

Assuming a membrane diffusion coefficient of about 10^{-7} sq. cm./sec., a membrane normality of 2.0 equivalents/liter, a membrane thickness of 0.8 mm., and a linear concentration gradient, one calculates a flux of approximately 0.25 ma./sq. cm. No such anomalous transfer was noted at higher current density, and it is probable that it was not an important factor above 2.0 ma./sq. cm. Nevertheless the data in Figure 5 must be considered as tentative since nitrate transport numbers were not measured. This matter is being actively investigated.

Above about 1.0 ma./sq. cm. there is only a relatively small decrease in the transport number of the silver ions (that is membrane efficiency) with increasing current density. When the limiting current is reached, there is then a sharp drop because of hydrogen ion transport. The transport numbers that are of particular interest for Equation (11) are those found on just approaching the limiting current. These values are shown in Table 1.

The over-all precision of the transport numbers, considering analysis, dilution from water transport and sampling technique, is probably ±3%. Within this precision the transport number at the limiting current does not seem to be affected very much by total current, bulk concentration, or flow conditions. A single average value of $t_{Ag} = 0.71 \pm 0.03$ was thus used to correlate limiting current data.

The sharp changes in pH that occurred when silver ions were migrating were not observable with nitric acid. It was thus easier to locate the limiting current by changes in the over-all resistance of the cell. Over the same range of variables the transport number of the hydrogen ions at limiting current was $t_{H^+} = 0.91 \pm 0.03$.

These transport numbers were used to approximate the diffusivity of the cations relative to the nitrate ions in the membrane. If one assumes ideal solutions, a resin normality of 2.0, and a solution normality of 0.3, the concentration of nitrate ion in the membrane is, very roughly

$$(c_{NO_3})_m \, (c_{NO_3} + 2.0)_m = (c_{Ag})_s \, (c_{NO_3})_s = (0.3)^2 \quad (13)$$

$$(c_{NO_3})_m \approx 0.05 \quad (13a)$$

The relative diffusivity is then approximately

$$\frac{t_{Ag}}{t_{NO_3}} = \frac{0.71}{0.29} \approx \frac{D_{Agm}}{D_{NO_3m}} \left(\frac{c_{Ag}}{c_{NO_3}}\right)_m \quad (14)$$

$$\left(\frac{D_{Agm}}{D_{NO_3m}}\right) \approx 0.07 \quad (14a)$$

Similarly

$$\left(\frac{D_{Hm}}{D_{NO_3m}}\right) \approx 0.3 \quad (14b)$$

These compare with the values $(D_{Ag})/(D_{NO_3}) = 0.87$ and $(D_H)/(D_{NO_3}) = 4.9$ in solution. An interpretation of

TABLE 2. EXPERIMENTAL LIMITING CURRENTS

$AgNO_3$—Nepton CR-61 membranes
HNO_3—Nepton CR-61 membranes

$N_{Re} = \frac{d_e U_{avg}}{\nu}$, dimensionless	$\frac{\overline{I_L}}{c^o}$ from pH, $\frac{\text{ma./sq. cm.}}{\text{meq./cc.}}$	$\frac{\text{experimental}}{\text{theoretical}}$ from pH measure	$\frac{\overline{I_L}}{c^o}$ max. resistance, $\frac{\text{ma./sq. cm.}}{\text{meq./cc.}}$	$\frac{\text{experimental}}{\text{theoretical}}$ from max. resist.	c_{Ag}, meq./cc.	c^o_H, meq./cc.
0	16.4	1.19 ± 0.12	22.0	1.60 ± 0.18	0.158	
0	15.8	1.14 ± 0.12	19.6	1.42 ± 0.16	0.145	
0	15.8	1.14 ± 0.12	19.6	1.42 ± 0.16	0.137	
0	16.2	1.17 ± 0.12	18.6	1.35 ± 0.15	0.0167	
34	47.6	0.89 ± 0.13	61.2	1.14 ± 0.16	0.137	
63	65.6	0.90 ± 0.14	77.4	1.06 ± 0.16	0.0196	
95	75.2	0.84 ± 0.14	90.4	1.01 ± 0.16	0.0167	
216	117.0	0.87 ± 0.16	132.0	0.98 ± 0.18	0.0167	
221	117.0	0.86 ± 0.16	132.0	0.97 ± 0.18	0.145	
126	—	—	150.0	0.32 ± 0.12	—	0.07
220	—	—	176.0	0.29 ± 0.12	—	0.07

TABLE 3. CELL DIMENSIONS AND WORKING EQUATIONS

Volume = 46.2 cc.
Length = 10.16 cm.
$$\text{Equivalent diameter} = d_e = \frac{4 \times \text{cross section}}{\text{wetted perimeter}} = 1.64 \text{ cm.}$$
$$N_{Re} = \frac{d_e U_{avg}}{2} = 173.2\, U_{avg}$$
$$D_{Ag} = 1.65 \times 10^{-5} \frac{\text{sq. cm.}}{\text{sec.}}$$
$$D_{NO_3} = 1.9 \times 10^{-5} \frac{\text{sq. cm.}}{\text{sec.}}$$
$$D_{\pm AgNO_3} = 1.76 \times 10^{-5} \frac{\text{sq. cm.}}{\text{sec.}}$$
$$D_H = 9.3 \times 10^{-5}$$
$$D_{\pm HNO_3} = 3.16 \times 10^{-5} \frac{\text{sq. cm.}}{\text{sec.}}$$
$h = 0.5$ cm.
$t_{Ag} = 0.29 \pm 0.03$
$t_H = 0.91 \pm 0.03$

this difference is that the cations are not uniformly distributed in the membrane phase but rather they are concentrated around the anionic fixed charges. This results in a decrease in the diffusivity of the cations relative to the nitrate ions because of electrostatic attraction to the fixed charges.

This interpretation must be tentative and can be checked by measuring the concentration and diffusivities of all ions in the membrane. This is being done by one of the authors.

Limiting Currents. Table 2 is a summary of the experimental values of $(\bar{I}_L)/(c^o_+)$. The resistance measurements give high values of the limiting current, since the conductivity of the solution is maintained when dissociation of the water becomes important. The pH measurements, on the other hand, should be sensitive indicators, since hydrogen ion leakage (from dissociation of water) is likely to be detectable when the silver concentration at the solution-membrane interface is still appreciable. The situation is aggravated by the very high mobility of hydrogen ion. Secondly, the assumption of constant wall concentration is not completely certain. It is probable that the downstream current densities are higher than predicted. As a result, hydrogen ion leakage probably occurs before the upstream portions of the cell are completely polarized.

The experimental limiting currents now compared with those predicted from Equation (8) for stagnant films and Equation (11) for laminar flow. The dimensions of the cell and other pertinent data are listed in Table 3.

The limiting currents through stagnant films of silver nitrate solutions are predictable from Equation (8):

$$\text{grad}\, n_+ c_+ = \frac{c^o_+}{h} \qquad (15a)$$

$$\left(\frac{\bar{I}_L}{c^o_+}\right)_{\text{theoretical}} = \frac{2}{\left[\dfrac{t_+}{D_+} - \dfrac{t_-}{D_-}\right] h} = 13.8 \pm 1.4 \frac{\text{ma./sq. cm.}}{\text{g.-moles/liter}} \qquad (15b)$$

The comparison between experiment and theory is indicated in Table 2.

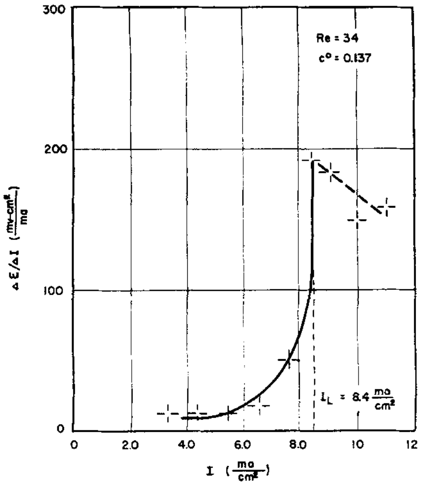

Fig. 4. The limiting current from a maximum rate of change of potential.

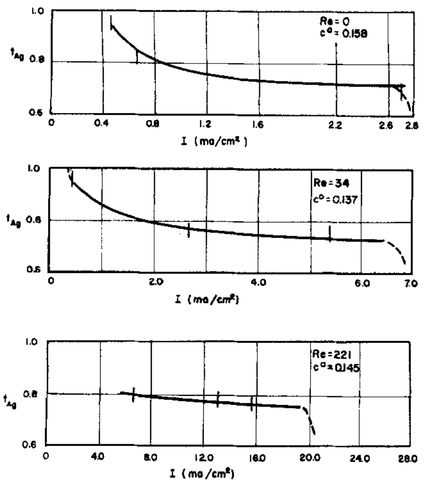

Fig. 5. Transport numbers of silver in a Nepton CR-61 membrane.

Agreement is good with pH measurements but poor with resistance measurements. The limiting currents with silver nitrate solutions in laminar flow are predictable from Equation (11):

$$\left(\frac{\bar{I}_L}{c^o_+}\right)_{\text{theoretical}} = 9.2\, (N_{Re})^{1/2} \frac{\text{ma./sq. cm.}}{\text{g.-mole/liter}} \qquad (16)$$

The comparison between experiment and theory is indicated in Table 2. A plot of the experimental data gives the following results:

$$\left(\frac{\bar{I}_L}{c^o_+}\right)_{\text{experimental}} = 8.8\, (N_{Re})^{0.48} \text{ from pH measurements} \qquad (17)$$

$$\left(\frac{\bar{I}_L}{c^o_+}\right)_{\text{experimental}} = 13.4\, (N_{Re})^{0.43} \text{ from resistance measurements} \qquad (18)$$

Both sets of data agreed well with theory, but the pH measurements showed a Reynolds-number dependence in better agreement with theory. The predicted limiting currents with nitric acid solutions in laminar flow are

$$\left(\frac{\bar{I}_L}{c^o_+}\right)_{\text{theoretical}} = 42\, (N_{Re})^{1/2} \frac{\text{ma./sq. cm.}}{\text{g.-mole/liter}} \qquad (19)$$

Two limiting currents obtained by resistance measurements were low by more than 100%. The resistance measurements appear to be unreliable in this case, but the reasons for this very poor agreement are not known.

TWO-ELECTROLYTE SOLUTIONS SURROUNDING AN ION EXCHANGE MEMBRANE

Theoretical

The development is again for a single chamber of a fractionating unit (Figure 1). The same assumptions are also made. The equation of continuity must be written for cations 1 and 2 and anion (−) [Equations (1) and (2)]. Solving the equations of con-

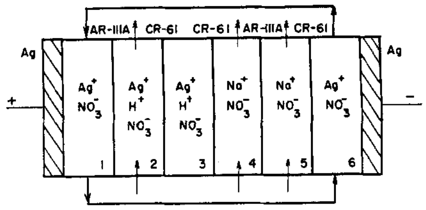

Fig. 6. Schematic diagram of cell for the two-electrolyte system.

tinuity simultaneously by making use of the electroneutrality requirement, one obtains:

$$D_2 n_2[D_{\pm1} \operatorname{div} \operatorname{grad} n_1 c_1 - \operatorname{div} n_1 c_1 \underline{v}] + D_1 n_1 [D_{\pm2} \operatorname{div} \operatorname{grad} \overline{n_2} c_2 - \operatorname{div} n_2 c_2 \underline{v}] = 0 \tag{20}$$

The mean diffusivities $D_\pm$ are defined by Equation (4) with the subscripts referring to the corresponding cation. The two bracketed terms of Equation (20) are mutually dependent, and analytical solution presents some difficulty. If however one assumes independent migration of all ions in the dilute solution, each term can be set equal to zero. This fixes each concentration gradient independently, thus permitting an analytical solution in the same manner as with the single electrolyte. Data presented below, and also the results of a previous investigation (*3, 4*), demonstrate the validity of this assumption.

The current density is obtained by writing the Nernst-Planck equation for each of the three ions and combining with the electroneutrality requirement to obtain [see Equations (5), (6), and (7)]

$$\left(\frac{I}{F}\right)_z \left[\frac{t_1}{D_1 n_1} + \frac{t_2}{D_2 n_2} + \frac{t_-}{D_- n_-}\right] = -\left[\operatorname{grad}\left(1 - \frac{n_1}{n_-}\right) c_1 + \operatorname{grad}\left(1 - \frac{n_2}{n_-}\right) c_2\right]_{s=h,\ z} \tag{21}$$

Since the gradients are fixed independently of one another, one obtains for limiting current

$$(-\operatorname{grad} n_1 c_1)_{s=h} = 0.332 \left(\frac{\nu}{D_{\pm1}}\right)^{1/3} \left(\frac{U}{\nu z}\right)^{1/2} n_1 c_1^{\circ} \tag{22}$$

$$(-\operatorname{grad} n_2 c_2)_{s=h} = 0.332 \left(\frac{\nu}{D_{\pm2}}\right)^{1/3} \left(\frac{U}{\nu z}\right)^{1/2} n_2 c_2^{\circ} \tag{23}$$

The average current density over the entire membrane of length L is then obtained by integration:

$$(\overline{I_L}) = 0.664F \frac{(N_{Re})^{1/2}}{(d_e L)^{1/2}}$$

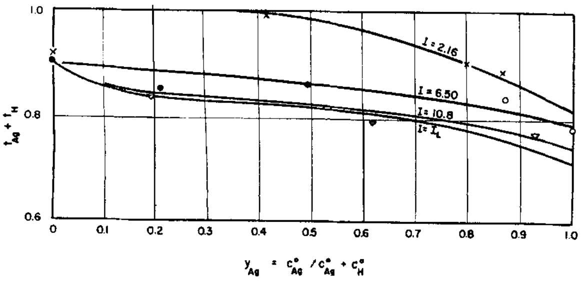

Fig. 7. Efficiency of Nepton CR-61 membrane for system of silver nitrate-nitric acid.

$$\frac{\left[\left(1 - \frac{n_1}{n_-}\right)\left(\frac{\nu}{D_{\pm1}}\right)^{1/3} c_1^{\circ} + \left(1 - \frac{n_2}{n_-}\right)\left(\frac{\nu}{D_{\pm2}}\right)^{1/3} c_2^{\circ}\right]}{\left[\frac{t_1}{D_1 n_1} + \frac{t_2}{D_2 n_2} + \frac{t_-}{D_- n_-}\right]} \tag{24}$$

It can be shown [starting with Equation (28)] that at the limiting current

$$t_1 = \frac{D_1}{D_2} \frac{c_1^{\circ}}{c_2^{\circ}} t_2 = \frac{D_1}{D_2} \frac{c_1^{\circ}}{c_2^{\circ}} (1 - t_1 - t_-) \tag{25}$$

Equation (25) enables one to eliminate two of the transport numbers in Equation (24) and thus make it easier to use. Equation (25) may be rewritten to give

$$\left[\frac{t_1}{D_1 n_1} + \frac{t_2}{D_2 n_2} + \frac{t_-}{D_- n_-}\right] = \frac{(c_1^{\circ} n_2 + c_1^{\circ} n_1) - \left[\left(n_1 - \frac{n_1 n_2 D_2}{n_- D_-}\right) c_2^{\circ} + \left(n_2 - \frac{n_1 n_2 D_1}{n_- D_-}\right) c_1^{\circ}\right] t_-}{n_1 n_2 [D_1 c_1^{\circ} + D_2 c_2^{\circ}]} \tag{26}$$

For the case at hand $n_1 = n_2 = -n_- = 1$.

Combining Equations (24) and (26) one may obtain a working equation for two 1–1 electrolytes sharing the same anion:

$$\frac{(\overline{I_L})}{c_T^{\circ} (N_{Re})^{1/2}} = \frac{4F}{3(d_e L)^{1/2}} \frac{\left[\frac{\nu}{D_{\pm1}}^{1/3} y_1 + \frac{\nu}{D_{\pm2}} y_2\right] [D_1 y_1 + D_2 y_2]}{1 - \left[\left(1 + \frac{D_2}{D_-}\right) y_2 + \left(1 + \frac{D_1}{D_-}\right) y_1\right]} \tag{27}$$

Here

$$c_T^{\circ} = c_1^{\circ} + c_2^{\circ} \tag{27a}$$

The relative transport numbers of the two cations may be found by solving the equation of continuity for each cation. Thus for cation 1:

$$c_1 = \frac{c_1^{\circ}\, 2\, \mu^{\frac{a}{n_1 b}} - \frac{t_1}{D_1(a + n_1 b)} \left\{ \mu^{\circ\, 1 + \frac{a}{n_1 b}} - \mu^{1 + \frac{a}{n_1 b}} \right\}}{\mu^{\frac{a}{n_1 b}}} \tag{28}$$

where:

$$a = \sum_i \frac{t_i}{D_i} \qquad b = \sum_i \frac{t_i}{D_i n_i} \tag{28a}$$

$$\mu = c_1 + c_2 + c_- \tag{28b}$$

By writing the same equation for cation 2 one may obtain the relative transport in terms of the concentrations at the membrane-solution interface. The interfacial concentrations are dependent upon the rate of migration of the ions in the solutions bathing both sides of the membrane, the rate of migration of the ions within the membrane and also upon the equilibrium that exists between phases. A complete description of a three-ion system involves a set of nine flux equations, three electroneutrality conditions, two equilibria, and the appropriate boundary conditions. A complete solution to such a set of equations enables one to obtain interfacial concentrations, membrane efficiency and all transport numbers a priori (*12*).

This development will utilize an assumption which enables one to obtain relative transport and interfacial concentrations from the properties of the anolyte solution and a measured membrane efficiency. The mathematics is thereby reduced to the solution of three flux equations, one electroneutrality condition, and one equilibrium. The assumption is that the relative transport in the membrane is directly proportional to the relative concentrations in the membrane at the membrane-solution interface:

$$\frac{t_1}{t_2} = \frac{D_{1m}}{D_{2m}} \frac{n_1^2}{n_2^2} \frac{c^I_{1m}}{c^I_{2m}} \tag{29}$$

This assumes that the current within the membrane is primarily due to electromigration because of the following conditions: the amount of Donnan

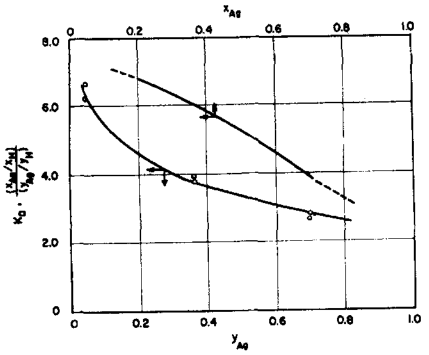

Fig. 8. Equilibrium constant, silver nitrate-nitric acid-Nepton CR-61.

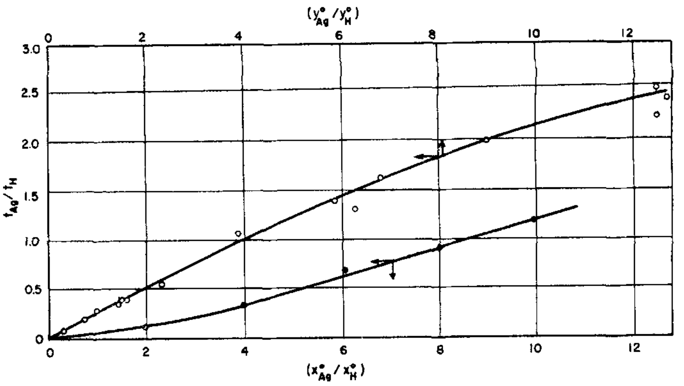

Fig. 9. Relative transport of silver and hydrogen ion in Nepton CR-61 membranes.

sorption is small relative to the fixed charge of the membrane $N_m >> n_- c_-$; the net flux of the restricted ion is small:

$$D_{-m}\, n_- \frac{dc_-}{ds} \approx D_{-m}\, n_-^2 \left[\frac{F}{RT}\right] c_{-m} \frac{dE}{ds}$$

These conditions imply a highly charged, efficient membrane.

Combining Equations (28) and (29) with the expression for the equilibrium at the interface

$$K_D = \frac{c^I_2}{c^I_1} \frac{c^I_{1m}}{c^I_{2m}} \qquad (30)$$

one can get the following equations:

$$\frac{t_1}{t_2} = \alpha \frac{c_1^o}{c_2^o} \qquad (31)$$

$$\alpha = \frac{D_{1m}}{D_{2m}} K_D \left[\frac{u^{o\,\frac{a}{n_1 b}} - \dfrac{t_1}{D_1(a + n_1 b)} \dfrac{\mu^{o\,1 + \frac{a}{n_1 b}} - \mu^{I\,1 + \frac{a}{n_1 b}}}{c_1^o}}{u^{o\,\frac{a}{n_2 b}} - \dfrac{t_2}{D_2(a + n_2 b)} \dfrac{\mu^{o\,1 + \frac{a}{n_2 b}} - \mu^{I\,1 + \frac{a}{n_2 b}}}{c_2^o}} \right] \qquad (32)$$

$$\mu^I = \mu^o - \frac{I}{F} \theta\, b \qquad (33)$$

Experimental

The experimental work was the same as previously described except that mixtures of nitric acid and silver nitrate were used. (Figure 6).

Results

Relative Transport Numbers. Figure 7 shows that the efficiency of the membranes $t_{Ag} + t_H$ may be increased by lowering the current density and/or decreasing the relative amount of silver ion in the solution. The estimated experimental error in $t_{Ag} + t_H$ was about ± 3.5%. The membrane efficiency at limiting current varied from about 71% for silver nitrate to about 91% for nitric acid.

Figure 8 shows the ion exchange equilibrium constant K_D as a function of solution and membrane composition at a solution normality of 0.04 for Nepton CR-61 in contact with nitric acid and silver nitrate. Membranes of this type are highly selective toward the silver ion and also have a lower specific volume in the silver form relative to the hydrogen form (*10*). These facts are indicative of an ion pairing of the silver ions with the fixed charges of the membrane. This investigation shows that the mobility of the silver ions is greatly reduced relative to the hydrogen ions which is also indicative of at least a strong concentrating of silver ions about the fixed charges.

The curve of t_{Ag}/t_H vs. c^o_{Ag}/c^o_H (Figure 9) shows that α (the slope of the secant between the origin and a given point on the curve) decreases from 0.26, initially, to a value of 0.20 at $c^o_{Ag}/c^o_H = 12$. This can be caused by a combination of factors, since α is a complicated function of a number of variables. It is more interesting to plot t_{Ag}/t_H as a function of the relative concentration in the membrane c_{Agm}/c_{Hm}. The slope of the secant from the origin to a point on the curve is equal to the relative membrane diffusivity D_{Agm}/D_{Hm} [Equation (29)]. The relative diffusivity D_{Ag}/D_H in solution is equal to 0.178, whereas in the membrane it varies from about 0.05 for low values of (c_{Ag}/c_H) to about 0.12 for high values of (c_{Ag}/c_H). This difference can be interpreted in terms of ion pairing.

Since the silver ions are more easily paired (or concentrated about the fixed charges), they tend to screen both the hydrogen and nitrate ions from the effects of the fixed charges. A fraction of the silver ions can be thought of as being immobilized by the electrostatic attractions with the fixed charges. If it is assumed that all of the decrease in the relative diffusivity is due to silver ion pairing, then the percent association of the silver ions with the resin matrix is calculated to vary between 72% for low values of (c_{Ag}/c_H) to about 33% for high values of (c_{Ag}/c_H).

It was also found that the relative transport was insensitive to changes in Reynolds number of from 63 to 220. This has also been found to be true for solutions of glycine and sodium chloride in contact with an Amberplex anion exchange membrane (*3*). Theoretically this indicates that the individual concentration profiles are linear and independent. Measurements of concentration profiles showed this to be true (*4*).

Another way of examining the distribution factor α is to plot $(t_{Ag})/(t_H)$ $(c^o_H)/(c^o_{Ag})$ vs. current density (Figure 10). The data scatter at any particular current density which is to be expected since α is a complicated function of concentration, flow rate, etc. There is however a tendency for α to decrease with increasing current density. If a single curve is drawn through the data, a limit of about 0.18 is approached at high current density. The theoretical limit of $\alpha = D_{Ag}/D_H = 0.178$ is obtained from Equation (18). Extrapolating the curve to zero current density gives one a value of $\alpha = 0.35$. The theoretical limit at zero current density is obtained from Equation (32) as $\alpha = \left(\frac{D_{Ag}}{D_H}\right)_m K_D$.

Using the calculated values of $(D_{Ag}/D_H)_m$ from Figure 9 and the equilibrium constants from Figure 8 one obtains values for α varying between 0.35 for low values of (c_{Ag}/c_H) and about 0.30 for high values of (c_{Ag}/c_H). The same agreement between experiment and theory has been obtained before by these authors on a glycine-

Table 4. Experimental Limiting Currents
AgNO₃—HNO₃—Nepton CR-61 membrane

Experimental values		Theoretical values			
$\frac{\overline{I_L}}{c^o_T}$, ma./sq. cm. / moles/liter	$\frac{\overline{I_L}}{c^o_T N_{Re}^{1/2}}$, ma./sq. cm / moles/liter	$\frac{\overline{I_L}}{c^o_T}$	$\frac{I_L}{c^o_T N_{Re}^{1/2}}$	y_{Ag}	N_{Re}
214	—	85-2,000	—	0.143	0
105	—	58-175	—	0.445	0
52	—	31-58	—	0.760	0
408	51	400-1,760	50-220	0.18	63.5
568	47	480-720	41-60	0.42	146
328	41	320-440	40-55	0.44	63.5
173	29	190-310	32-52	0.46	36.5
172	22	96-320	12-40	0.76	63.5
456	31	145-470	10-32	0.82	216

sodium chloride-Amberplex anion exchange membrane system (3). In that investigation α varied from 0.027 at zero current to 0.500 at high current. The theoretical values were 0.026 to 0.530.

Limiting Currents. The limiting currents were found by measuring the rate of change of resistance as a function of current density. Figure 4 is a typical result. The experimental limiting currents were compared with those obtained from Equations (27) and (33):

$$\frac{\overline{I_L}}{c_T^o (N_{Re})^{1/2}} = \frac{(2.56\, y_{Ag} + 2.10\, y_H)(1.65\, y_{Ag} + 9.3\, y_H)}{1 - (5.9\, y_H + 1.87\, y_{Ag})\, t_{NO_3}} \quad \text{[see (27)]} \quad (34)$$

$$\frac{\overline{I_L}}{c_T^o} = 36\, \frac{y_H + 0.178\, y_{Ag}}{1 - (5.9\, y_H + 1.87\, y_{Ag})\, t_{NO_3}} \quad \text{[see (33)]} \quad (35)$$

The experimental results are tabulated in Table 4. The range of theoretical values are based on absolute errors of ± 0.03 in the transport numbers for the nitrate ions. In the region $0.05 < y_{Ag} < 0.6$ the uncertainty of the theoretical limiting current due to small positive errors becomes enormous because the denominators of Equations (34) and (35) get very small. The experimental limiting currents generally fell within this range. Since diffusivities were calculated for ions at infinite dilution, and the nitrate ion transport numbers were determined from the differences $(1 - t_H - t_{Ag})$, it is surprising that the experimental values agreed as well as they did with theory. Actually the equations are unreliable under these conditions, since even the heterogeneity of a single sheet of membrane might be enough to cause large differences from one section to the next.

CONCLUSIONS

The Nernst-Planck equations describe the behavior of ions near a membrane. It is possible to assume independent migration of the ions and the pseudo-binary diffusion coefficients can be evaluated from available mobility data.

Limiting currents are predictable within the range of variation in the experiments. Under certain conditions the predicted values are very sensitive to small variations in the physical properties of the system.

The relative transport of two cations is primarily a function of relative concentration, relative diffusivity, current density, and ion exchange equilibria with the hydrodynamics of the solutions being less important. The derived equations can be used to predict the separability.

The diffusivities of the cations in the membrane relative to the diffusivity of nitrate ion are ten times lower than in solution. This is explained by the assumption that the cations tend to concentrate nearer the anionic fixed charges of the membrane. The net results are a decrease in mobility of the cations and a partial screening of the effectiveness of the membrane.

In mixtures the diffusivity of silver ions relative to hydrogen ions in the membrane is smaller (by a factor of 1.4 to 3.6) than the relative diffusivity in solution. This indicates that silver ions are more readily concentrated about the fixed charges and thereby screen the fixed charges from both the migrating anions and the hydrogen ions. Calculated values of between 33 to 72% association of silver ions is consistent with the fact that the equilibrium distribution strongly favors the silver.

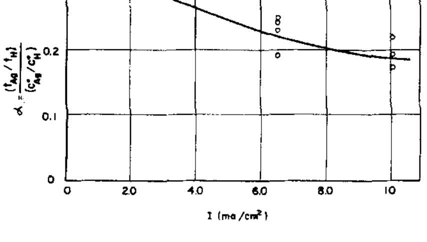

Fig. 10. The distribution coefficient as a function of current density.

ACKNOWLEDGMENT

The financial support of both the Wisconsin Alumni Research Foundation and the University of Wisconsin Experiment Station is appreciated.

NOTATION

a = constant equal to $\sum_i \frac{t_i}{D_i}$ sec./sq. cm.
b = constant equal to $\sum_i \frac{t_i}{D_i n_i}$ sec.-moles/sq. cm.-equiv.
c_i = concentration of ion i, moles/liter
d_e = equivalent diameter of a duct, cm.
D_j = diffusion coefficient for ion j, sq. cm./sec.
$\underline{D_\pm}$ = mean diffusion coefficient for an electrolyte, sq. cm./sec.
E = electrical potential, v.
F = Faraday's constant, cal./v. equiv.
h = one half the distance between two parallel membranes, cm.
I = electric current density passing through a cell with respect to stationary coordinates, ma./sq. cm.
k_c = mass transfer coefficient, cm./sec.
K_D = equilibrium constant for an ion exchange reaction
L = path length parallel to the membrane surface (z direction), cm.
$\overline{N_m}$ = average normality of the permselective membrane, equiv./liter
n_i = valence of ion i including the sign (negative for anions and positive for cations)
R = gas constant, cal./mole-°K.
s = distance perpendicular to membrane surface, (cm.)
T = absolute temperature, °K.
t_j = average transport number for ion j
U = average velocity of the fluid parallel to the membrane surface (in the z direction), cm./sec.
u_j = mobility of ion j, sq. cm./sec.-v.
$\underline{v}$ = mass average velocity, cm./sec.
$\underline{w}$ = molar average velocity, cm./sec.

x_j = mole fraction of ion j in the membrane based on the molar concentration c_m^o
y_j = mole fraction of ion j in the solution based on the molar concentration c_S^o
z = distance parallel to the membrane surface, cm.
α = separation factor
θ = thickness of the stagnant diffusion layer, cm.
μ = total ionic concentration, moles/liter
ν = kinematic viscosity of the solution, sq. cm./sec.

Dimensionless Groups

N_{Re} = Reynolds number = $d_e U/\nu$
N_{Sc_i} = Schmidt number for ion i = ν/D_i

Superscripts

o = bulk of the solution
I = interface between the membrane and the solution
$-$ = an anion
$+$ = a cation
$\bar{I}$ = bar over symbol represents an average value

Subscripts

$\pm$ = mean value
A or $-$ = an anion
c or $+$ = a cation
i, j = ion i and ion j respectively
1, 2 = ion 1 and ion 2 respectively
L = limiting condition
m = membrane phase
s = solution phase
T = total

LITERATURE CITED

1. Bird, R. B., W. E. Stewart, and E. N. Lightfoot, "Transport Phenomena," Chap. 21 and p. 410, Wiley, New York (1960).
2. Cowan, D. A., and J. H. Brown, *Ind. Eng. Chem.*, **12**, 1445 (1959).
3. DiBenedetto, A. T., and E. N. Lightfoot, *ibid.*, **50**, 691 (1958).
4. DiBenedetto, A. T., Ph.D. thesis, Univ. Wisconsin, Madison, Wisconsin (1960).
5. Kolthoff, I. M., and J. J. Lingane, *J. Am. Chem. Soc.*, **58**, 1524, 2457 (1936).
6. Levich, B., *Acta Physicochim. U.R.S.S.*, **17**, 259 (1942); **19**, 117 (1944).
7. ———, *Disc. Faraday Soc.*, **1**, 37 (1947).
8. Lin, C. S., E. B. Denton, H. S. Gaskill, and G. L. Putnam, *Ind. Eng. Chem.*, **43**, 2136 (1951).
9. Rosenberg, N. E., and C. E. Tirrell, *ibid.*, **49**, 780 (1957).
10. Springer, E. L., M.S. thesis, Univ. Wisconsin, Madison, Wisconsin (1958).
11. Tobias, C. W., M. Eisenburg, and C. R. Wilkie, *J. Electrochem. Soc.*, **99**, No. 12, p. 359 C (1952).
12. Wills, G. B., and E. N. Lightfoot, *A.I.Ch.E. Journal*, **7**, 273 (June, 1961).

Manuscript received March 10, 1961; revision received June 28, 1961; paper accepted June 30, 1961.

Volumetric Properties of Gas Mixtures Containing One or More Polar Components

R. F. BLANKS and J. M. PRAUSNITZ
University of California, Berkeley, California

A study has been made of the second virial coefficients of binary gas mixtures containing one or two polar components. Methods for calculating these coefficients are presented. The interaction coefficient B_{ij} for a polar-polar interaction cannot be calculated with the Stockmayer potential with pure component parameters only; such calculations tend to underestimate the strong forces of attraction between dissimilar polar molecules. It is shown that the characteristic distance for the reduced dipole moment for two dissimilar polar molecules is less than the arithmetic average of the distance parameter of the similar molecules by an amount which can be related to the enthalpy of complex formation. When this corrected collision diameter is used in the Stockmayer potential, good results can be obtained for interaction coefficient B_{ij}. In the case of a polar-nonpolar mixture the coefficient B_{ij} depends on dispersion and on induction forces. Techniques are proposed for estimating these forces from pure component parameters, and it is shown that for accurate calculation of B_{ij} it is necessary to correct for the displacement of the dipole from the center of the polar molecule. The paper concludes with some illustrations of how these ideas may be applied to typical chemical engineering problems.

The aim of this work is to present techniques for estimating volumetric properties in the moderate density region for gas mixtures containing one or more polar components. Previous studies on the volumetric properties of gas mixtures are almost entirely concerned with nonpolar mixtures, but this work considers the available experimental data and theory for gas mixtures which contain one or more polar components. This study is confined to intermediate densities, for it is only under such conditions that the results of statistical thermodynamics can be conveniently utilized in applying the theory of intermolecular forces to the prediction of macroscopic properties.

For densities up to approximately one-half of the critical, the pressure of either a pure or mixed gas is adequately represented by the virial equation terminated after the second virial coefficient:

$$P = \frac{RT}{v}\left[1 + \frac{B}{v}\right] \qquad (1)$$

For a pure gas, B is a function of temperature only. For a mixture, B is also a function of composition, and it has been shown theoretically (*6, 13*) that the composition dependence for a mixture containing n components is given by

$$B = \sum_i^n \sum_j^n y_i y_j B_{ij} \qquad (2)$$

Prediction of the volumetric properties of gaseous mixtures in the moderate density region therefore reduces to the prediction of the various coefficients B_{ij} which depend on the temperature and on the physical properties of the components i and j. For mixtures containing one or more polar components three types of second virial coefficients are needed. First there is the case where $i = j$, and in this case the virial coefficient B_{ii} (or B_{jj}) refers to interactions between