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FINAL REPORT

SEA WATER MASS DIFFUSION
COEFFICIENT STUDIES

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AERONUTRONIC DIVISION

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Applied Research Laboratories

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FINAL REPORT

SEA WATER MASS DIFFUSION COEFFICIENT STUDIES

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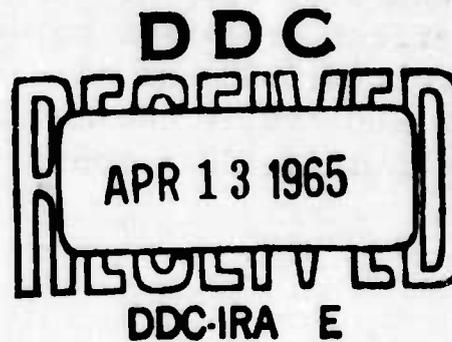
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ABSTRACT

The ordinary diffusion coefficient and the Soret (thermal diffusion) coefficient were measured for a solution of 3.5 weight percent sodium chloride in water; this system was selected as a reasonable binary simulant to the multicomponent sea water system. Ordinary diffusion coefficients were measured, at 25°C, for pressures over the range 1 to 1000 bars; the Soret coefficient was determined at 27°C and approximately 1000 bars pressure, and compared to measured values at 1 bar pressure. The experimental high pressure cells and techniques developed for measuring these properties for binary salt solutions can be modified and adapted for possible analogous measurements with multicomponent solutions.

The influence of pressure on the ordinary diffusion coefficient in 3.5 weight percent NaCl-H₂O at 25°C was found to be negligible over the pressure range 1 to 1000 bars. In view of the widely differing diffusional behavior of the various binary salt constituents, however, a significant pressure effect could exist for a multicomponent mixture such as sea water. Based upon the data from low pressure experiments and a single high pressure experiment in the Soret diffusion apparatus, the Soret coefficient at room temperature likewise appears to be virtually independent of pressure up to 1000 bars. The extrapolated reversal of direction for thermal diffusion in the NaCl-H₂O system at temperatures lower than about 7°C should, however, be investigated at high pressures for possible significance regarding the sea water system itself.

An extensive review and analysis was made of the available literature pertaining to the viscosity and thermal conductivity of multicomponent salt solutions, including sea water. This analysis has shown that these properties are not too different from those of pure water, and can be predicted satisfactorily for engineering purposes by simple additivity relationships based upon the most important salt ions present. Neither the viscosity nor the thermal conductivity appears to exhibit any unusual effect (relative to water) with changes in temperature, pressure, or concentration, and no direct relationships apparently exist between either viscosity or thermal conductivity and the mass diffusional properties of the individual ions.

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SECTION 1

INTRODUCTION

1.1 PRELIMINARY CONSIDERATIONS

There are a number of situations of interest to physical and chemical oceanography where the molecular diffusion of ions in an aqueous solution can be important. These situations include, for example, the molecular transport phenomena that occur in the vicinity of the interface between sea water and sea ice, between undersea instruments or vessels and sea water^{*}, and between the ocean bottom and sediment regions and the surrounding sea water. Important technological problems such as the rate of corrosion of metals by sea water and the performance of undersea batteries are also significantly affected by molecular ionic diffusion processes.

The two most common causes for ion diffusion in these situations are concentration gradients and temperature gradients. The ion flux is directly related to these two driving forces by molecular diffusion coefficients known as the ordinary^{**} diffusion coefficient and the

* In the laminar boundary layer, or in the viscous sublayer of a turbulent boundary layer where molecular processes are of significance.

** Often called isothermal

Soret* coefficient. These coefficients, in general, depend upon concentration, temperature, and pressure. Their definition for binary liquid systems (for example, salt + water), whether concentrated or dilute, has been well established (see Section 1.3). The theoretical prediction of these coefficients is only possible for some dilute binary systems using previously determined property parameters which are usually measured at temperatures near 25°C and at a pressure of one atmosphere. Generally, predictions for concentrated binary solutions and for multicomponent solutions are not now possible. Therefore, it is necessary to measure these coefficients under well defined conditions.

The molecular diffusion properties of sea water, a somewhat concentrated multicomponent salt solution, are not known. The binary aqueous solution diffusion properties of its major salt constituent, sodium chloride, are known only for temperatures near 25°C and for a pressure of 1 atmosphere. Even less is known about these properties for the other salt constituents of sea water.

Since temperatures in the oceans can vary from -2°C to 30°C, and since pressure can vary with depth from 1 atmosphere to approximately 1000 atmospheres, the diffusion properties should be known within these limits of temperature and pressure.

It is known that the diffusion properties of multicomponent salt solutions can be much different than those of binary salt solutions. Both the direction of diffusion and the diffusion rates can be altered depending upon the relative concentrations of the various types of ions in the multicomponent system. Clearly, a detailed understanding of molecular diffusion phenomena in such complex systems can only be obtained after a reasonably good description of diffusion in the various component binary systems has been developed.

* Named after an early investigator of thermal diffusion phenomena in aqueous salt solutions.

The following sections first briefly outline the objectives of the research investigation reported herein and give the equations which exactly define the diffusion properties of interest in this study.

1.2 OBJECTIVES OF THIS INVESTIGATION

In view of the discussion of the preceding section, it is appropriate to consider the diffusion properties of binary systems first, and in particular those of the sodium chloride—water system, before attempting to study the more complex case of sea water itself. Because sodium and chloride ions are the most predominate ions in sea water, a 3.5 percent by weight solution of NaCl-H₂O is a convenient first approximation to typical sea water (7)*.

On this basis, the following objectives were selected for this investigation:

- (i) to measure the binary Soret coefficient and the ordinary diffusion coefficient of the synthetic sea water, 3.5 percent by weight sodium chloride in water, and to correlate the results with known theoretical considerations;
- (ii) to investigate the ordinary and thermal diffusion properties of binary aqueous salt solutions other than the NaCl-H₂O system;
- (iii) to develop an experimental apparatus for measuring the high pressure thermal diffusion properties of multicomponent salt solutions;
- (iv) to determine how the experimental apparatus used to measure the binary ordinary diffusion coefficient can be modified in order to measure the ordinary diffusion properties of multicomponent aqueous electrolyte solutions;
- (v) to relate analytical predictions to experimental results;

* Numbers in parentheses which occur in the text refer to the references listed at the end of this report.

- (vi) to review and analyze the available literature pertaining to the viscosity and thermal conductivity of multicomponent aqueous salt solutions, including sea water, and to relate, where applicable, this property information to the mass diffusion property data.

The scope of the investigation defined by these objectives does not include measurements of the diffusion properties of multicomponent systems. An important aspect of the study will be to determine how pressure affects the ordinary diffusion coefficient and Soret coefficient of the sodium chloride—water system.

1.3 PHENOMENOLOGICAL DESCRIPTION

The diffusion coefficients are defined by general flux-driving force equations of the following form (for binary systems—gaseous, two organic liquids, or one salt in an electrically neutral solvent, $\nabla P = 0$, and no differing body forces acting except for the interionic electrical forces) (49; Eqs. 3.26 and 3.27) (50):

$$\vec{J}_2^N = -CD_{12} \left\{ \nabla x_2 + \sigma_{12} x_1 x_2 \nabla T \right\} \quad (1)$$

or,

$$\vec{J}_2^m = -\rho D_{12} \left\{ \nabla y_2 + \sigma_{12} y_1 y_2 \nabla T \right\} \quad (2)$$

where D_{12} denotes the binary ordinary diffusion coefficient and σ_{12} denotes the binary Soret coefficient (symbols are defined in the nomenclature section). The fluxes are related to species velocities by the equations:

$$\vec{J}_2^N = C_2 \left[\vec{v}_2 - \vec{v}^N \right] \quad (3)$$

$$\vec{v}^N \equiv \frac{1}{C} \sum_{i=1}^n C_i \vec{v}_i \quad (4)$$

$$\vec{J}_2^m = \rho_2 [\vec{v}_2 - \vec{v}^m] \quad (5)$$

$$\vec{v}^m \equiv \frac{1}{\rho} \sum_{i=1}^n \rho_i \vec{v}_i \quad (6)$$

Equations 1 and 2 define the same diffusion coefficients and can be shown to be identical.

The so-called Fick diffusion coefficient is defined by Fick's first law (isothermal conditions)

$$\vec{N}_2 = - D_{\text{Fick}} \nabla C_2 \quad (7)$$

where,

$$\vec{N}_2 = C_2 \vec{v}_2 \quad (8)$$

The inadequacy of an ordinary diffusion coefficient defined in this manner and its nonequivalence with D_{12} have been thoroughly discussed in the literature (51).

A primary objective of this investigation is to learn more about the pressure and temperature dependence of D_{12} and σ_{12} for the 3.5 weight percent sodium chloride—water system.

The basic defining relationships take on somewhat different forms for multicomponent ionic systems. These will be discussed in the sections that follow.

SECTION 2

ORDINARY DIFFUSION COEFFICIENT STUDY

2.1 ANALYTICAL CONSIDERATIONS

The most elementary description of ordinary diffusion in liquids, is given by the Stokes-Einstein relation (50, pp. 513-515),

$$D_{12} = \frac{RT}{6\pi \mu_1 R_2 N_0} \quad (9)$$

for the diffusion of spherical particles of such a size that the solvent (species 1) appears to the diffusing species as a continuum. This relation predicts a temperature dependence of

$$D_{12} \sim (T/\mu_1) \quad (10)$$

which is borne out by experimental results for certain systems, such as the dilute NaCl-H₂O system.

For very dilute ($x_2 \rightarrow 0$), binary electrolyte solutions, the Nernst expression, which neglects interionic forces, has some utility. This simple relation relates D_{12}^0 (D_{12} for $x_2 \rightarrow 0$) to the limiting equivalent conductivities by the equation (49),

$$D_{12}^{\circ} = \frac{|z_{+}| + |z_{-}|}{|z_{+}| |z_{-}|} \frac{RT}{F^2} \frac{\lambda_{+}^{\circ} \lambda_{-}^{\circ}}{(\lambda_{+}^{\circ} + \lambda_{-}^{\circ})} \quad (11)$$

A more elaborate theory has been developed by Onsager and Fuoss (52, pp.105-122, 243-255) and is more generally useful for moderately dilute systems. This theory is inadequate for concentrated systems, as will be seen below.

Gordon (53) has proposed a semi-empirical expression in order to extrapolate D_{12} in the very dilute range to high concentrations. Very little use has been made of Gordon's relation even though quite satisfactory agreement between values calculated from it for high concentrations and experimentally measured values has been obtained. Van Rysselberghe (54) has proposed a similar expression.

The temperature dependence of D_{12} for the NaCl-H₂O system at infinite dilution is shown in Figure 2.1. The D_{12}° values were calculated from Eq. 11 using the limiting equivalent conductivities, λ_i° , in (56, p. 465). The viscosities used for the abscissa are values reported for pure water (56, p.457). The temperature dependence predicted by Eq. 10 is followed nearly exactly. It is apparent that the temperature dependence of D_{12} is significant. For the case given in Figure 2.1, there is a three-fold increase in D_{12} in going from 5°C to 55°C.

All published, reliable, ordinary diffusion coefficient data for the NaCl-H₂O, MgCl₂-H₂O, and CaCl₂-H₂O systems as a function of composition and temperature at 1 atm is presented in Figures 2.2, 2.3 and 2.4.* A smooth

* The sources for the data are as follows:

$D_{H_2O-NaCl}$: Harned & Hildreth (57), Vitagliano & Lyons (58), Dunlop & Gosting (59), Stokes (60), O'Donnell & Gosting (61), Gordon (53), Clack (62)

$D_{H_2O-MgCl_2}$: Harned & Polestra (63), Ohlholm (64)

$D_{H_2O-CaCl_2}$: Harned & Levy (65); Hall, Wishaw, & Stokes (66); Lyons & Riley (67)

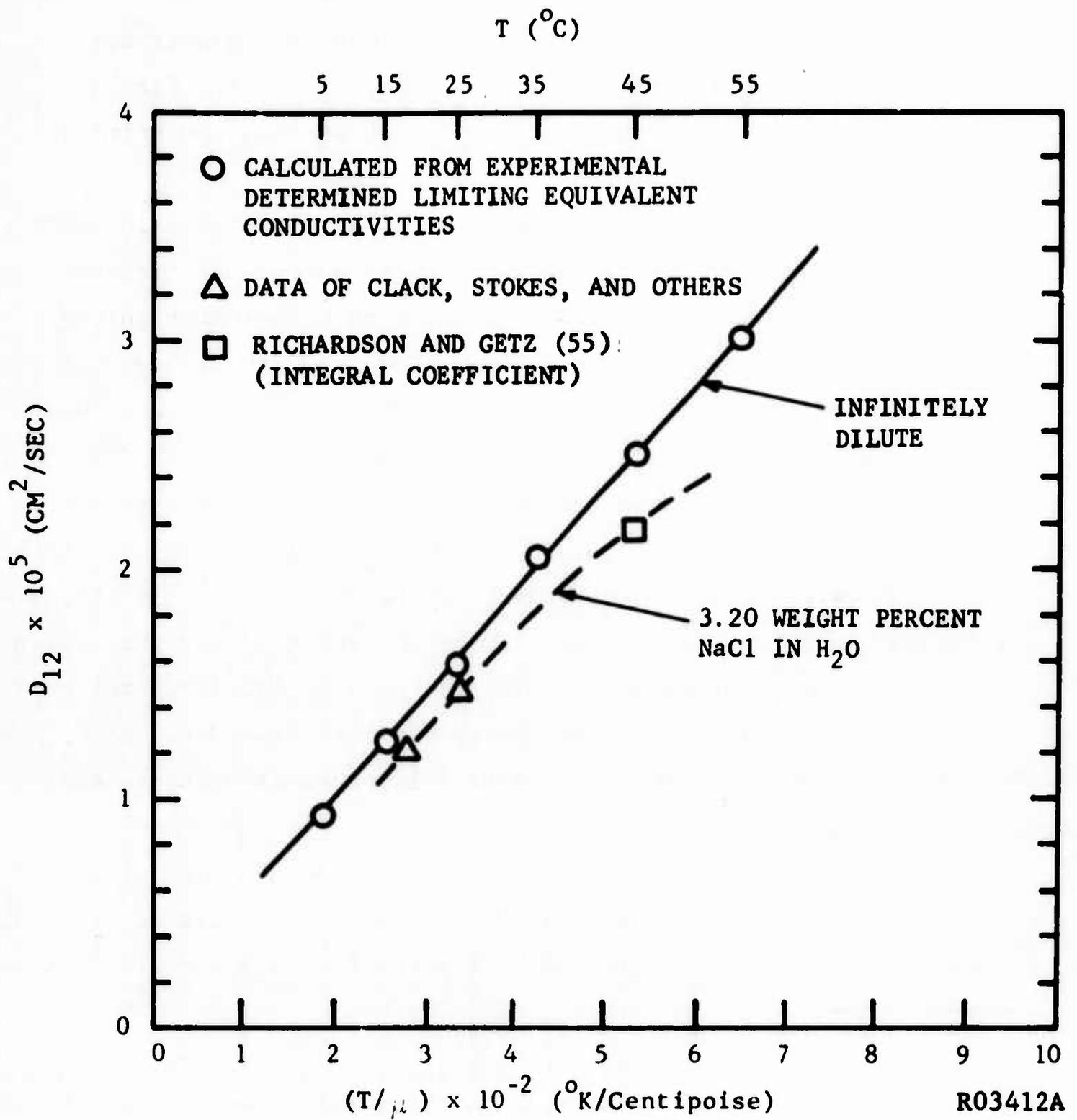
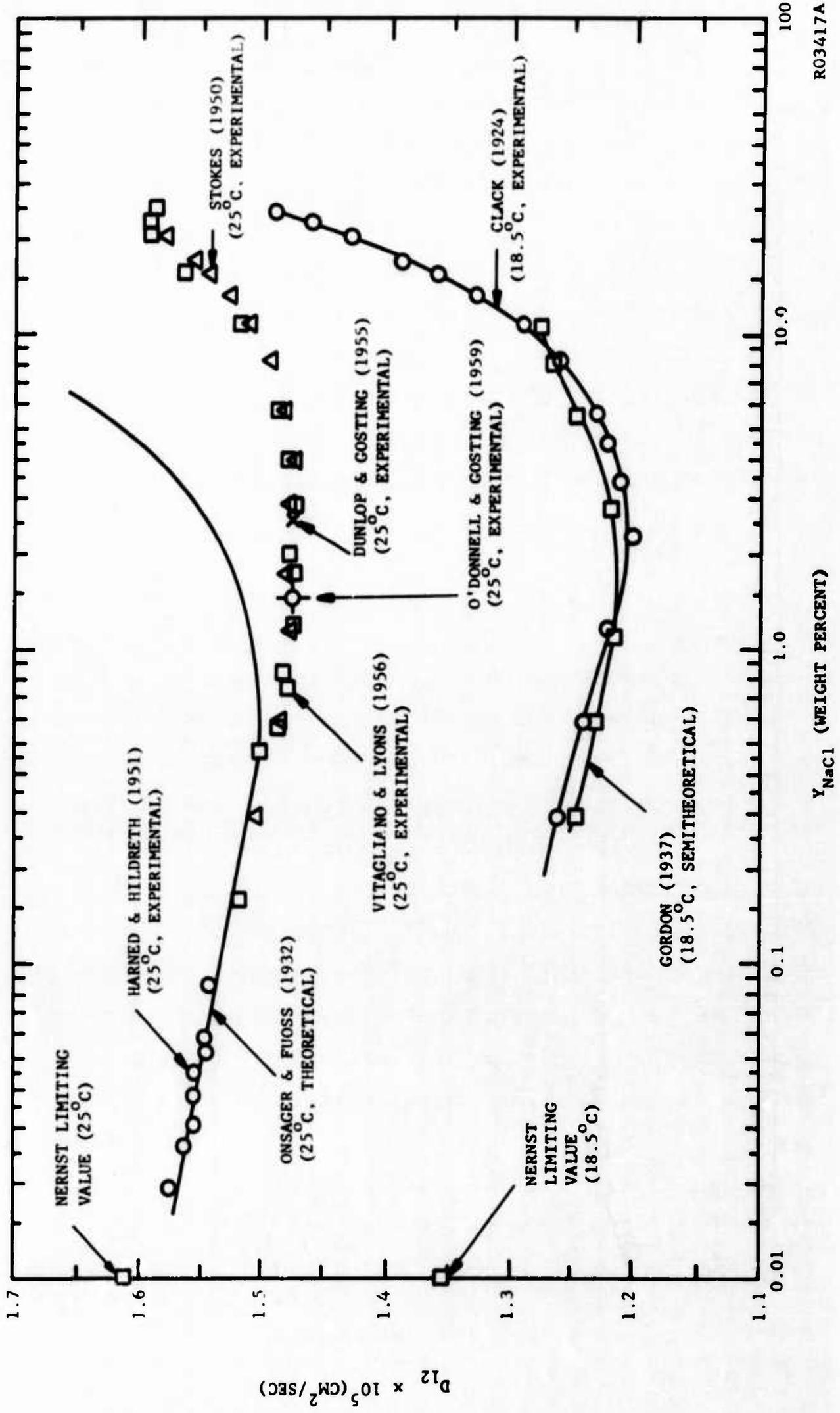
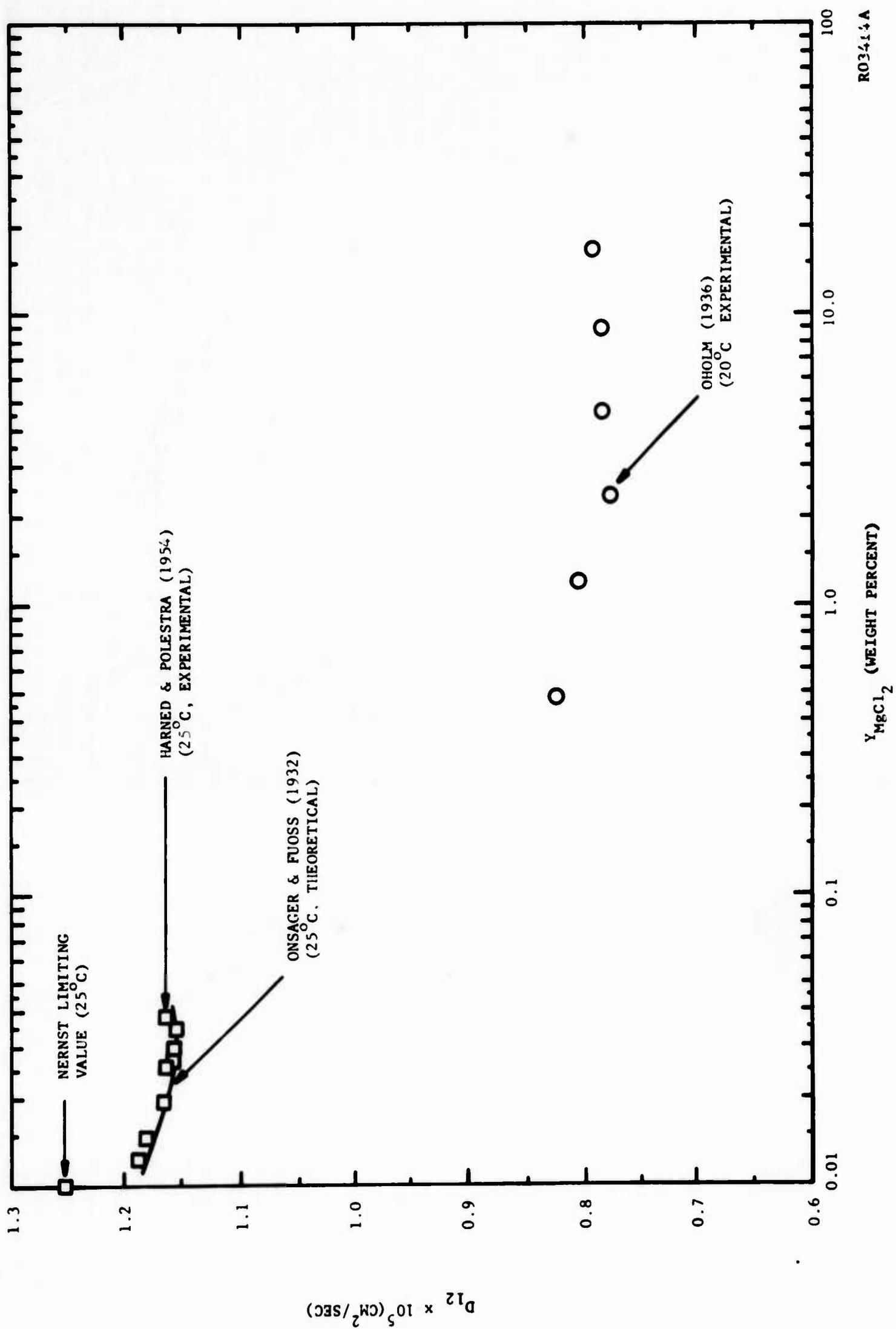


FIGURE 2.1. TEMPERATURE DEPENDENCE OF THE ORDINARY DIFFUSION COEFFICIENT FOR THE NaCl-H₂O SYSTEM AT INFINITE DILUTION (CALCULATED FROM EXPERIMENTALLY DETERMINED LIMITING EQUIVALENT CONDUCTIVITIES) (1 ATM)



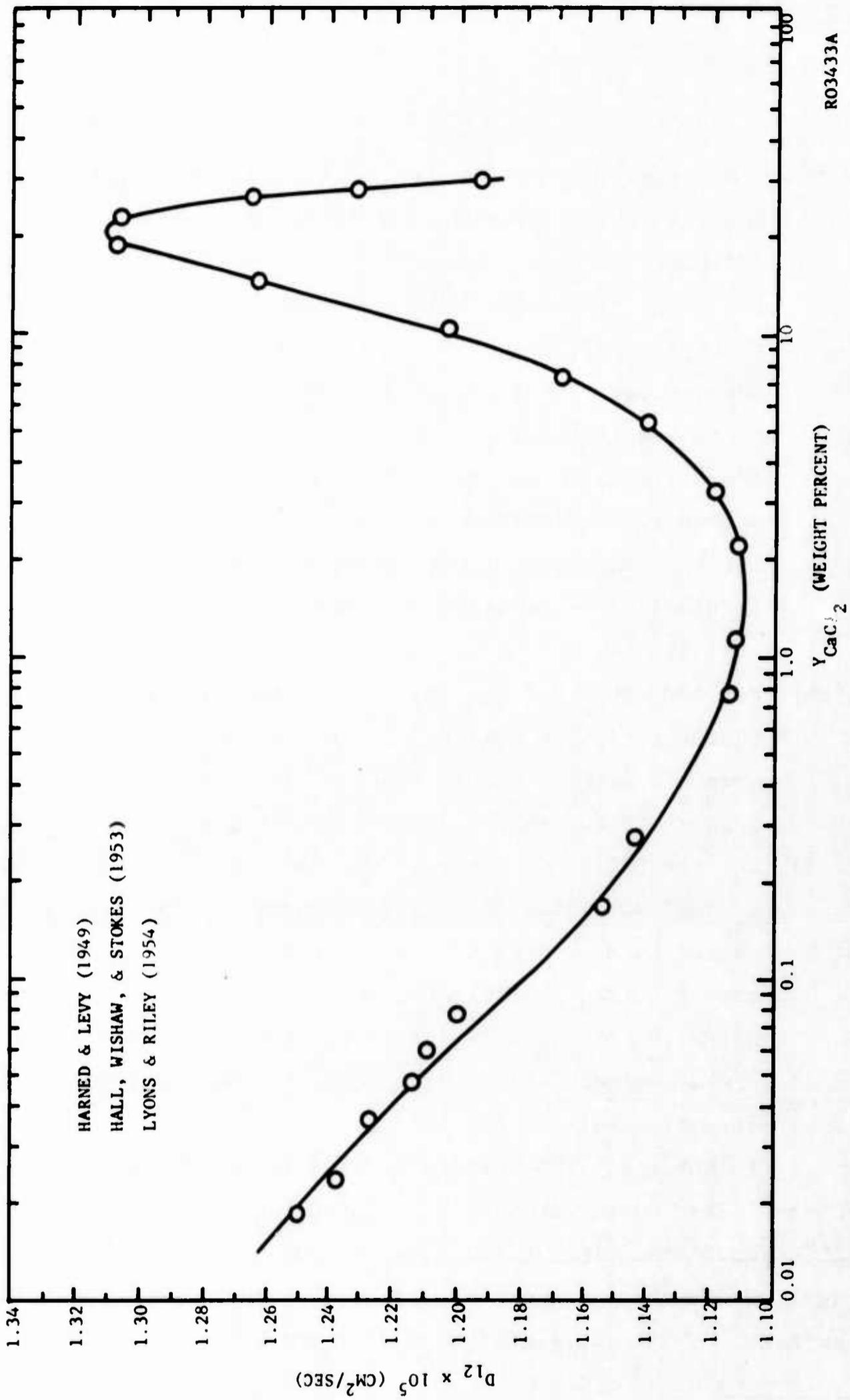
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FIGURE 2.2. ORDINARY DIFFUSION COEFFICIENT FOR THE NaCl-H₂O



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FIGURE 2.3. ORDINARY DIFFUSION COEFFICIENT FOR THE $\text{MgCl}_2\text{-H}_2\text{O}$ SYSTEM (1 ATM)



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FIGURE 2.4. ORDINARY DIFFUSION COEFFICIENT OF THE $\text{CaCl}_2\text{-H}_2\text{O}$ SYSTEM AT 25°C (1 ATM)

curve has been drawn through the $\text{CaCl}_2\text{-H}_2\text{O}$ data. The following is apparent:

- (i) For the $\text{NaCl-H}_2\text{O}$ system, sufficient data is available at all concentrations only for 25°C ; the data extrapolates to the Nernst limiting value; the Onsager-Fuoss (52, pp. 105-122, 243-255) theory is only useful for the dilute region; and Gordon's semi-theoretical method for predicting binary ordinary diffusion coefficients in concentrated salt solutions yields results which are quite close to those obtained experimentally. Gordon's method requires system viscosity and partial molal volume data for the temperatures and concentrations of interest. Because such information is generally not available, this method is of limited utility.
- (ii) For the $\text{MgCl}_2\text{-H}_2\text{O}$ system, very little data at any temperature or concentration is available;* no effort has been made to apply Gordon's method to this system; and the Onsager-Fuoss method appears useful in the very dilute region.
- (iii) For the $\text{CaCl}_2\text{-H}_2\text{O}$ system, only data at 25°C is available; the unusual variation of D_{12} with concentration at this temperature cannot be accounted for by the Onsager-Fuoss theory; if a viscosity correction is made, and if a correction is made for the hydration of the dissolved salt, then the shape of the curve at higher concentrations (including the maximum) can be predicted in an approximate manner (66).

In Table 2.1 the various major salt constituents of a typical sea water are listed along with the associated measured values of D_{12} and σ_{12} for 25°C and 1 atm. This table gives an indication of the relative orders of magnitude of these properties, as well as the lack of essential binary system data. Very little diffusion data has appeared in the literature

* The data given by Ohlm may not be reliable.

TABLE 2.1

RELATIVE MAGNITUDES OF BINARY SORET COEFFICIENTS AND ORDINARY
DIFFUSION COEFFICIENTS FOR THE MAJOR SALT CONSTITUENTS OF
SEA WATER (25° C, 1 atm)

Salt	Approximate wt.% in sea water (7) (calculated as 35gm salt/kilogram of system)	$\sigma_{12} \times 10^3$ ($^{\circ}\text{K}^{-1}$)	$D_{12} \times 10^5$ (cm^2/sec)	Aqueous Concentration (molality)	Wt.% salt	Reference for σ_{12}
NaCl	77.8	2.05	1.54	0.01	0.06	Snowdon & Turner (68)
MgCl ₂	10.9	2.39	1.12	0.01	0.10	Payton & Turner (69)
MgSO ₄	4.7	8.66	0.65	0.01	0.12	Payton & Turner (69)
CaSO ₄	3.6	--	--	--	--	--
K ₂ SO ₄	2.5	5.63	1.32	0.01	--	Snowdon & Turner (68)
CaCO ₃	0.3	--	--	--	--	--
MgBr ₂	0.2	--	--	--	--	--
CaCl ₂	--	3.17	1.21	0.005	--	Payton & Turner (69)

for the $\text{MgSO}_4\text{-H}_2\text{O}$ system, while none has been published for the $\text{CaSO}_4\text{-H}_2\text{O}$ system at any temperature. Table 2.1 also shows the relative concentrations of the various salt constituents of ordinary sea water. Most of the binary D_{12} and σ_{12} are reported only for one concentration, that is 0.01 molal (gm moles salt/1000 gm water). It is apparent that NaCl is by far the major salt constituent, and that of the binary diffusion properties which are known for the various salts in sea water, the D_{12} (and σ_{12}) of $\text{MgSO}_4\text{-H}_2\text{O}$ and the D_{12} of $\text{K}_2\text{SO}_4\text{-H}_2\text{O}$ are much different than the D_{12} for the other salt systems (at 0.01 molal). No data indicating the effect of pressure on D_{12} for any of the binary salt solutions listed in Table 2.1 has been reported.

2.2 EXPERIMENTAL PROGRAM

2.2a Experimental Approach

The diaphragm cell method was selected for measuring the ordinary diffusion coefficients because of its simplicity and accuracy (approximately $\pm 5\%$, or better) (56, pp. 253-261) (49, pp. 75-79).

This technique was developed originally by Northrop and Anson (91). Improvements in the technique have been made by Gordon (92), Stokes (93) (60)(94)(95) and Robinson (100). Measurements at temperatures other than 25°C have been made by Firth and Tyrrell (96). Certain modifications of design have been proposed, notably those of Lewis (97) (use of electrodes to measure differential diffusion coefficients directly), and Smith and Storrow (98) (use of a Selsyn-transmitter for stirring). Direct sampling during the diffusion experiment is usually not employed, though such methods have been used (99).

Methods for reducing the data obtained from such an experiment have been given by Barnes (101), Gordon (92), Stokes (60)(94)(95), Firth and Tyrrell (96), Dullien and Shemilt (102)(103), Olander and coworkers (51)(104)(105), and Robinson (100).

The general feature of this method is that the solute-solvent system is, at the start of the experiment, separated by a porous glass diaphragm from pure solvent in the upper portion of a vertical, two-compartment cell. Stirrers are situated on both surfaces of the diaphragm so that all the solution in both the top and bottom chambers is kept at uniform concentrations, C_T , C_B . Thus, molecular diffusion takes place only in the pores of the diaphragm. Because it is impossible to predict the diffusion path length and cross-sectional area for such a system, it is necessary to calibrate the cell with a solution whose ordinary diffusion coefficient is known at the temperature of interest and preferably in a concentration range similar to that under investigation. Reliable results have been obtained at concentrations greater than 0.05 molal (>0.3 weight percent NaCl in H_2O , for example). The ordinary diffusion coefficients for the KCl- H_2O system at several temperatures and concentrations have been accurately determined, and KCl concentrations have been accurately determined by absolute methods (electrolytic conductance and optical). For these reasons, this particular system is useful for calibrating the cell (determining the cell constant) (94).

2.2b Equipment and Procedures

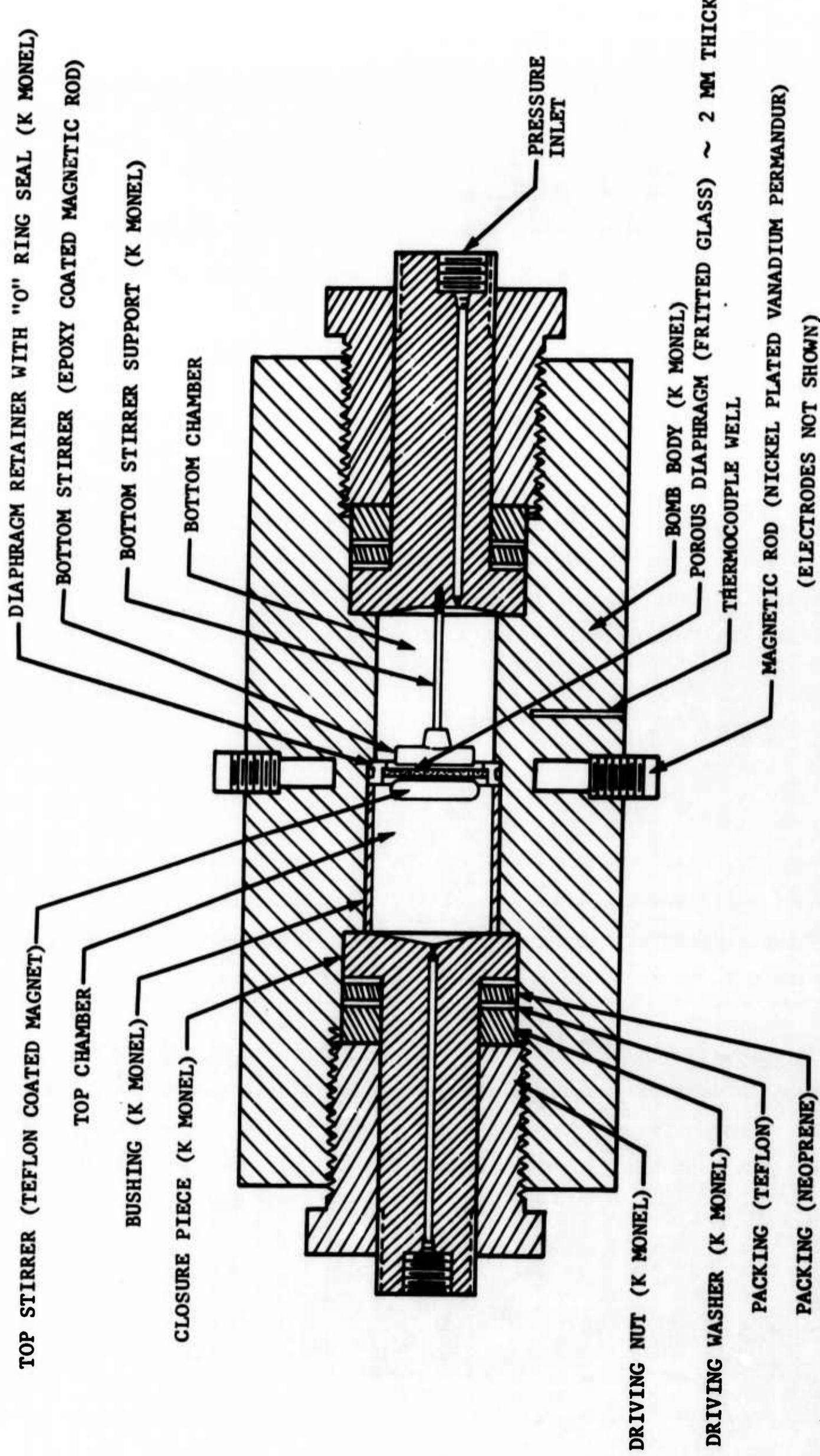
The cell used to measure ordinary diffusion coefficients was a modification of the diaphragm cell originally developed and described by Northrop and Anson (91) and improved by Stokes (93). This cell provides data free from errors due to mixing at the interface, streaming of the heavier liquid through the diaphragm, and due to stagnant layers at the surface of the diaphragm. In addition, our modifications of the cell permit measurement of temperature and concentration within the cell at any time during the experiment.

In order to make ordinary diffusion coefficient measurements at pressures up to 1000 bars (~14,700 psi) without using radioisotope tracer

techniques,* a new cell and magnetic stirring system had to be designed which would have operating characteristics similar to the usual glass atmospheric pressure diaphragm diffusion cells and yet be able to stand the immense pressures. The solution developed for this study was an ordinary diffusion bomb of the design shown in Figure 2.5. The fabricated bomb is shown partially disassembled in Figure 2.6. K Monel was chosen as the bomb material because of its corrosion resistance to saline solutions (106), its nonmagnetic property, and its high tensile strength. For the pressure range of the experiments, it was decided that unsupported area seals would be best from the viewpoint of safety, dependability, and ease of assembly and disassembly (107). The wall thickness of the bomb was determined by using an average of estimates calculated from three conservative design relations: the Maximum Shear Equation (108), the ASME Code Formula (109), and the Lamé Formula (109).

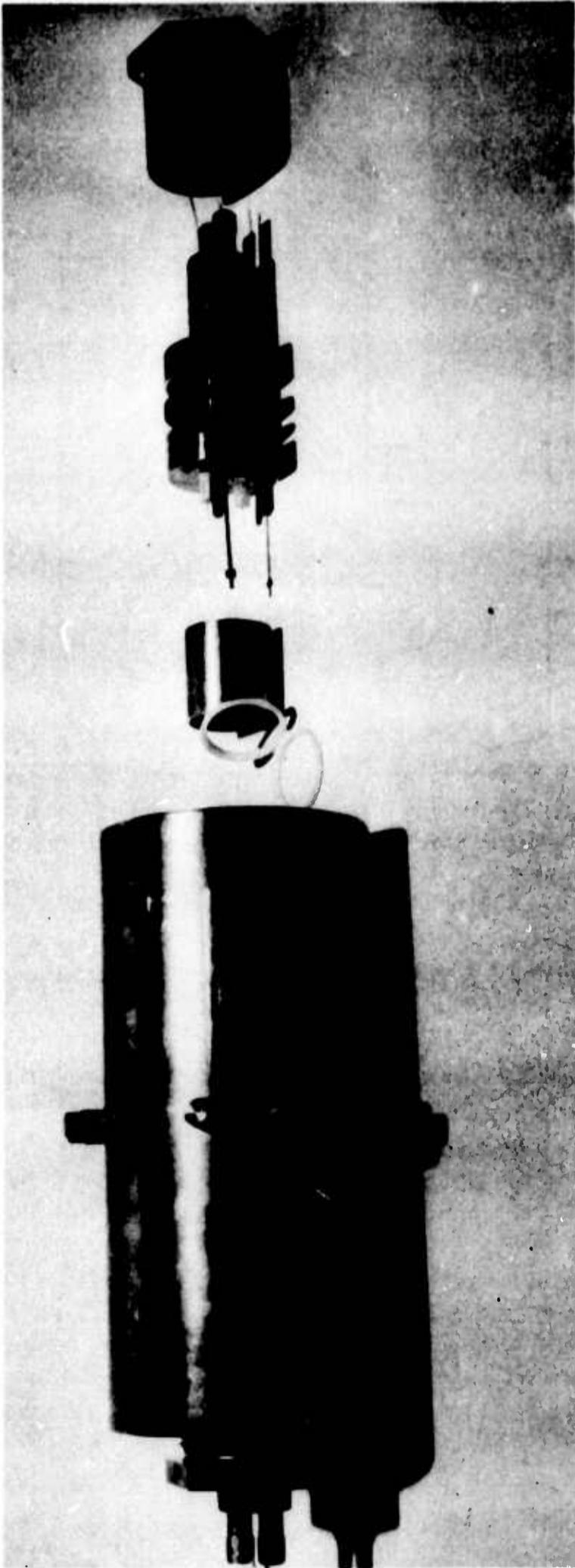
One unique feature of this diffusion bomb design was the inclusion of platinum electrodes attached to each of the end closure pieces (see Figures 2.6 and 2.8) and positioned in the stirred chambers on either side of the porous glass diaphragm. These electrodes, after proper calibration, could be used to follow the concentration changes in each stirred chamber during the course of the diffusion process. It was originally planned that by obtaining such data it would be possible to obtain the true differential diffusion coefficient directly from one experiment without having to make a number of experiments at several different concentrations and then treat the data in a somewhat involved manner in order to derive the differential coefficients from the measured integral coefficients (60)(94)(95). Originally an epoxy-type unsupported area seal was chosen for sealing and insulating the platinum electrodes in the closure pieces because of its apparent simplicity, high electrical

* These techniques were not practical for the salt solutions being investigated.



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FIGURE 2.5. ORDINARY DIFFUSION BOMB



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**FIGURE 2.6. THE ORDINARY DIFFUSION CELL-BOMB PARTIALLY DISASSEMBLED
(ELECTRODES AND STIRRER SUPPORT SHOWN ON END CLOSURE PIECE-
POROUS DIAPHRAGM ASSEMBLY NOT SHOWN)**

resistance, and corrosion resistance (110). Problems in obtaining a good seal between deaerated epoxy cement and the K Monel surface required an alternative sealing method. The one finally selected was a modification of the usual cone - pyrophyllite (a hydrous aluminum silicate - $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$) electrical lead type of seal. A schematic representation of this type of seal is shown in Figure 2.7.

Magnetic stirring of the two cell chambers on either side of the porous glass diaphragm was accomplished by using epoxy and Teflon covered magnets supported and rotated by the magnetic stirring system shown in Figure 2.8. This system was found to be the best of several designs which were tried.

Figure 2.8 also shows the general arrangement of the bomb in the constant temperature bath as it appeared during the course of an experiment. The pressuring system shown in Figure 2.9 was used to transmit, measure, and record the desired pressure in the bomb.

It was found that the most reliable conductance measurements of the salt solutions in the two bomb chambers were made when there was no fluid in the constant temperature bath container. This was because there appeared to be some extraneous and erratic capacitance effects between the insulated leads to the platinum electrodes and the liquid bath medium in contact with them. A Jones bridge (AC resistance bridge; accuracy: 1 part in 10^4 ; sensitivity: 1 part in 10^7) was used to measure the resistance between both pairs of platinized platinum electrodes.

Temperature control in the bath (stirring was achieved by the rotating magnetic arms shown in Figure 2.8) was maintained to within $\pm 0.1^\circ\text{C}$ by circulating fluid maintained at a constant temperature (usually 25.0°C) through the helical coil situated along the inside wall of the bath container.

Salt solution concentrations of the fluid in each of the chambers were measured at the end of the experiment (after depressurizing to 1 atm,

SURFACES EXPOSED
TO THE SALT
SOLUTION

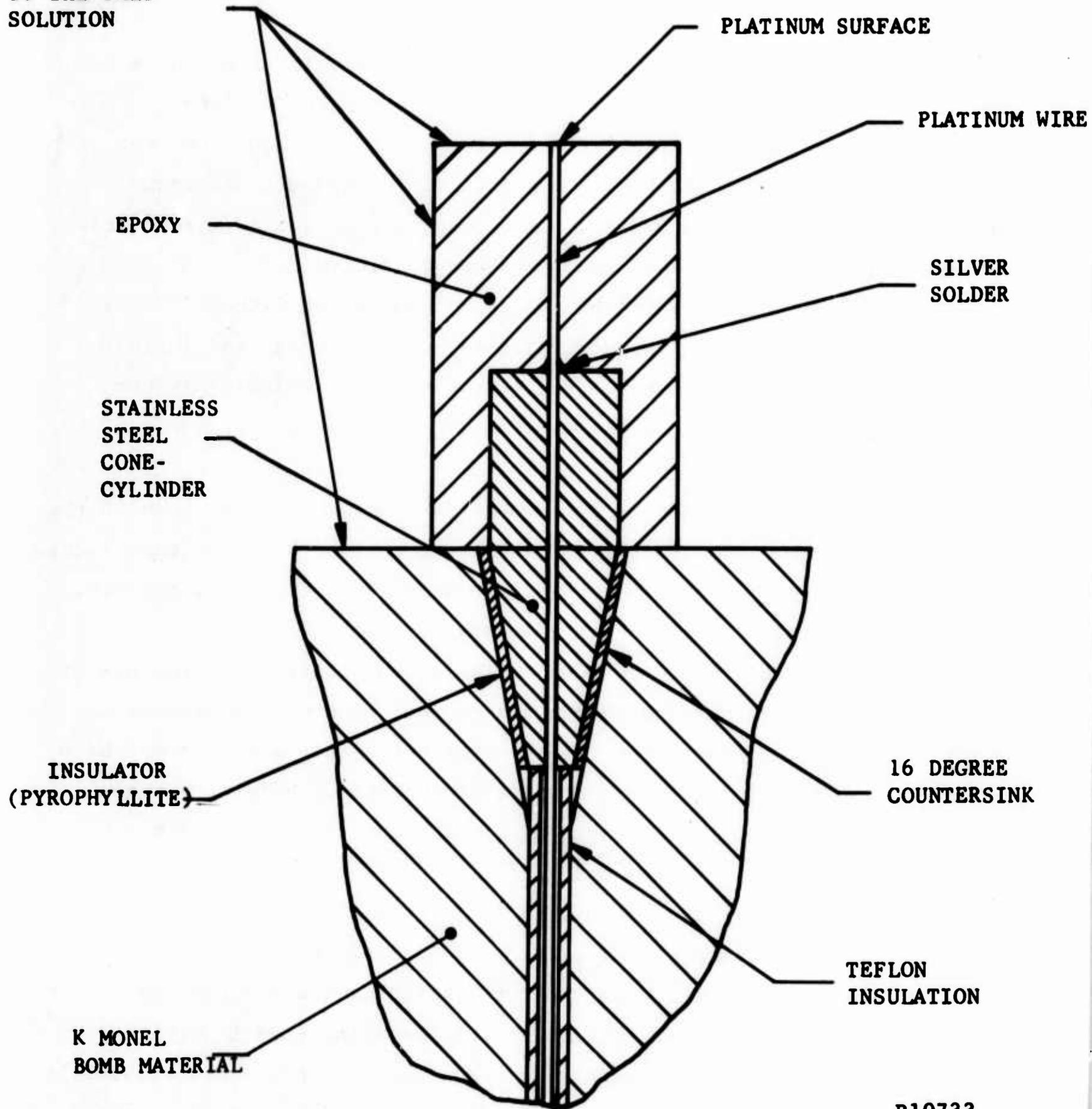
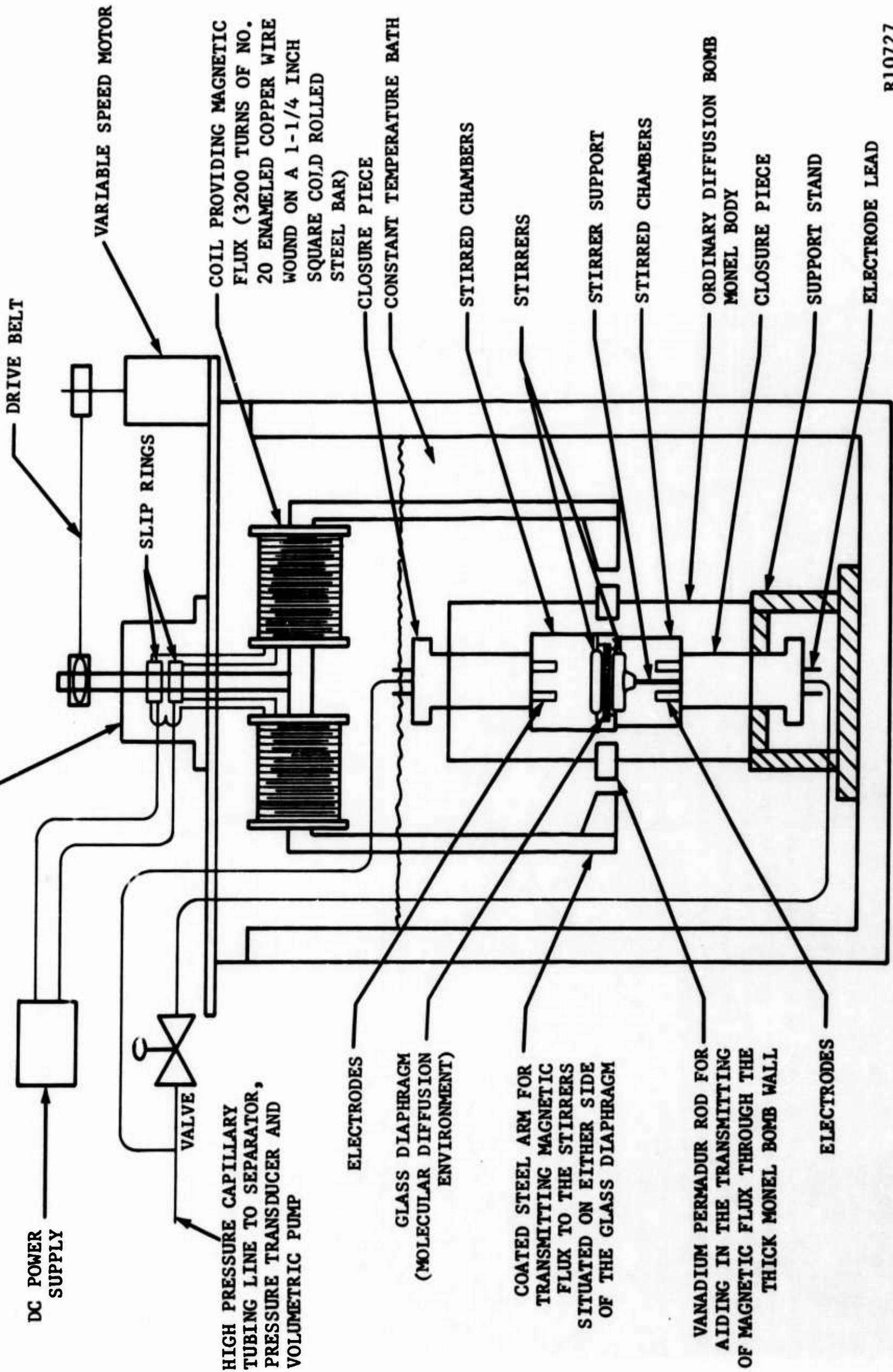
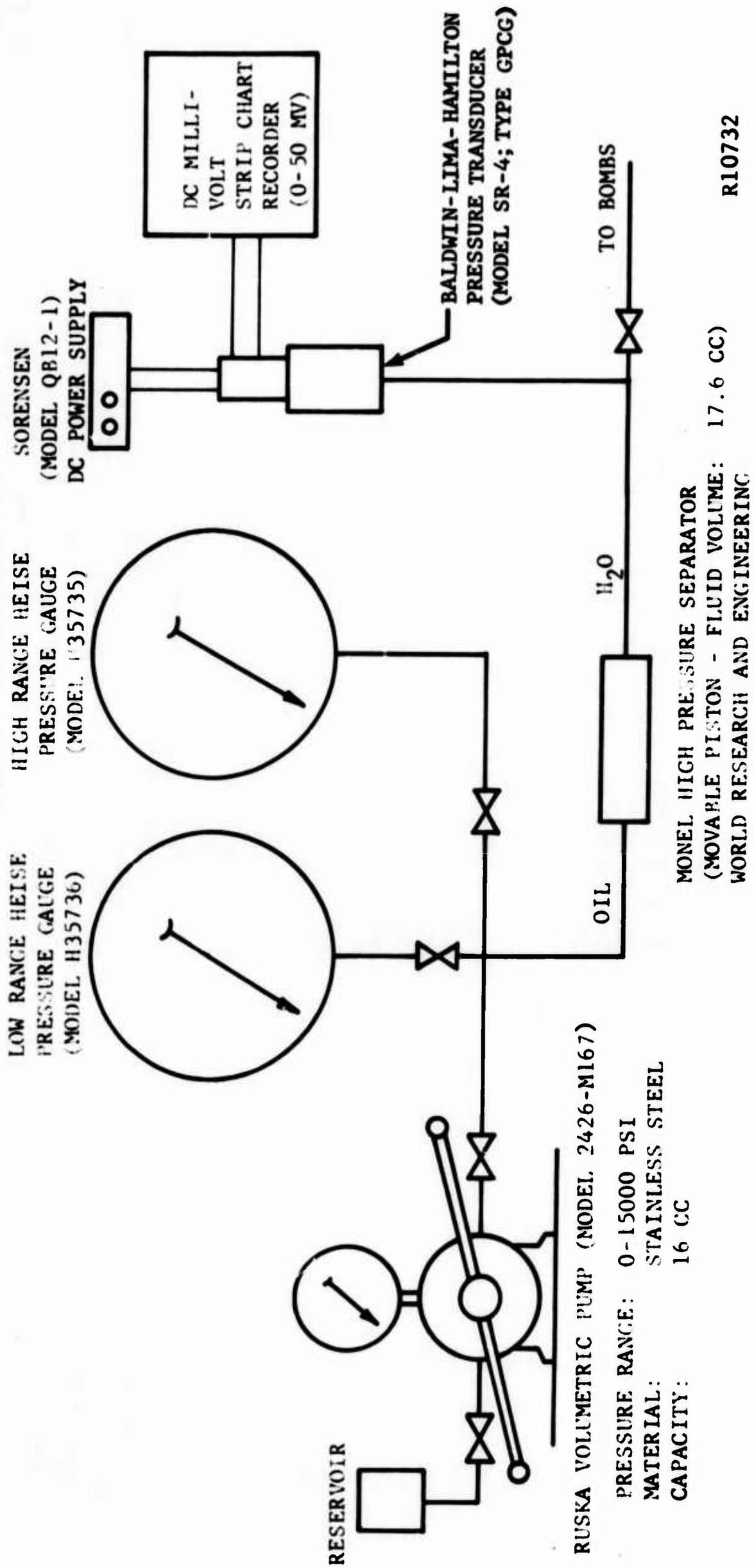


FIGURE 2.7. MODIFIED HIGH PRESSURE ELECTRICAL SEAL FOR
ORDINARY DIFFUSION BOMB



R10727

FIGURE 2.8. ARRANGEMENT OF ORDINARY DIFFUSION BOMB IN CONSTANT TEMPERATURE BATH



R10732

FIGURE 2.9. PRESSURING SYSTEM

and removal of the solution from the bomb) by the use of a small-volume (~2cc) conductance cell (pipette-type cell) used in conjunction with the Jones bridge and another constant temperature bath.

The detailed procedure which was finally developed for use with this bomb is given in Appendix A.1

The volumes of both the top and bottom chambers and the diaphragm pores were measured several times and found to be approximately 38.8 cc, 39.1 cc, and 0.5 cc, respectively.

2.3 RESULTS

The usual measurements made in an ordinary diffusion cell experiment are the molar concentrations of the solutions in each chamber at the end of the experiment, the temperature, the duration of the experiment, and the volumes of the top and bottom chambers as well as the diaphragm pore volume. The integral binary ordinary diffusion coefficient is then calculated from (51)(60)(92)(94-96)(100-105) (assuming no volume change on mixing; $V_T \approx V_B$; $V_{DP}/V_T \approx 0.1$),

$$\bar{D}_{12} = \frac{1}{\beta t} \ln \left[\frac{C_{B_o} - C_{T_o}}{C_{B_f} - C_{T_f}} \right] \quad (12)$$

where the cell constant, β , is defined by

$$\beta \equiv \frac{A}{l} \left\{ V_T^{-1} + V_B^{-1} \right\} \quad (13)$$

and where C_T is usually taken as 0 in experiments with binary aqueous salt solutions since pure water is usually put into the top chamber at the start of the experiment.

The integral coefficient is related to the "true" differential coefficient (such as reported in Figures 2.2, 2.3, and 2.4) by an equation

of a form such that $\bar{D}_{12} \approx D_{12}$ in concentration regions where D_{12} is independent of concentration. This is the case for NaCl-H₂O in the vicinity of 3.5 weight percent salt at 25°C and 1 atm.

The cell constant β is determined by performing a diffusion measurement in the cell with a solution whose D_{12} is well known (such as KCl-H₂O at 25°C).

The actual C_B is not the molar concentration of the salt solution originally put^o into the bottom chamber but, because a preliminary diffusion experiment is always allowed to take place before the actual experiment is started (in order to establish an approximately linear concentration gradient through the diaphragm before the start of the experiment), it must be calculated by a mole balance from,

$$C_{B_o} = C_{B_f} + [C_{T_f} - C_{T_o}] \left[\frac{V_T + \frac{1}{2}V_{DP}}{V_B + \frac{1}{2}V_{DP}} \right] \quad (14)$$

The volume ratio was nearly equal to unity (within 0.4%) for the geometry employed in the ordinary diffusion bomb.

The measurements made with the ordinary diffusion bomb during the first phase of the experiments did not make use of the electrodes.* The salt concentrations were obtained after the bomb had been brought back to 1 atm by removing samples and making use of a small pipette conductivity cell** and the Jones bridge. The concentrations measured in this manner are reported (as C_{T_f} and C_{B_f}) along with other pertinent associated data in Table 2.2. The overall duration of the experiment, t' , and the "back-calculated" initial bottom chamber concentration ($C_{T_o} \equiv 0$),

$$"C_{B_o}'' = C_{B_f} + C_{T_f} \quad (14a)$$

* Initially some problems were encountered with their performance.

** Industrial Instruments, Inc.

ORDINARY DIFFUSION BOMB EXPERIMENTS - FIRST PHASE

EXPERIMENT NUMBER ODB-	SALT SOLUTION	PRESSURE (bars)	STIRRING RATE (rpm)	Y_{Tf} (weight percent)	C_{Tf} (moles/liter)	Y_{Bf} (weight percent)	C_{Bf} (moles/liter)	"C" B_0 (moles/liter)	DURATION OF EXPERIMENT (seconds)	$\bar{D}'_{12} \times 10^5$ (cm^2/sec)
3B	3.5% NaCl	200	40	0.842	0.144	2.569	0.446	0.590	231,300	1.500
5B	3.5% NaCl	400	40	0.558	0.095	2.631	0.457	0.552	158,148	1.382
6B	3.5% NaCl	600	40	0.580	0.099	2.555	0.444	0.543	173,118	1.358
7B	3.5% NaCl	800	40	0.705	0.121	2.581	0.448	0.569	179,322	1.601
8B	3.5% NaCl	1000	40	0.766	0.131	2.214	0.382	0.513	257,880	1.436
9B	3.5% NaCl	1	40	1.436	0.248	2.010	0.347	0.595	252,240	
10B	3.5% NaCl	1	40	0.342	0.058	3.333	0.581	0.439	79,470	1.306
11B	3.5% NaCl	1000	40	0.371	0.063	2.857	0.497	0.560	91,412	1.445
12B	3.5% NaCl	1	40	0.387	0.066	3.084	0.536	0.602	88,530	1.449
13B	3.5% NaCl	1	40	0.164	0.027	3.309	0.576	0.603	83,622	0.582
14B	3.5% NaCl	1	40	0.386	0.066	3.088	0.537	0.603	88,920	1.440
15B	3.5% NaCl	1	40	0.414	0.070	3.096	0.538	0.608	98,100	1.382
16B	3.5% NaCl	1000	40	0.596	0.102	2.705	0.470	0.572	95,760	2.386
17B	3.5% NaCl	1	40	0.841	0.144	2.666	0.463	0.607	231,636	1.439
18B	3.5% NaCl	1000	40	0.485	0.082	2.910	0.506	0.588	87,840	1.929
19B	3.5% NaCl	500	40	0.387	0.066	2.920	0.507	0.573	86,700	1.565
20B	3.5% NaCl	800	40	0.770	0.132	2.548	0.442	0.574	240,780	1.326
21B	3.5% NaCl	800	40	0.495	0.085	2.940	0.511	0.596	93,120	1.868
22B	3.5% NaCl	600	40	0.584	0.100	2.698	0.468	0.568	157,800	1.425
23B	3.5% NaCl	400	40	0.823	0.141	2.587	0.449	0.590	238,380	1.413
24B	3.5% NaCl	800	40	0.300	0.051	3.008	0.522	0.573	77,220	1.316
25B	3.5% NaCl	1000	40	0.793	0.136	2.555	0.424	0.560	240,600	1.432
26B	3.5% NaCl	200	40	0.360	0.061	3.295	0.574	0.635	74,100	1.491
27B	3.5% NaCl	200	40	0.384	0.065	3.096	0.538	0.603	83,100	1.514
28B	3.5% NaCl	1000	70	0.643	0.110	2.545	0.442	0.552	148,980	1.758
29B	3.5% NaCl	1000	70	0.510	0.087	2.913	0.507	0.594	92,040	1.551
30B	3.5% NaCl	1000	70	0.359	0.061	2.909	0.504	0.565	81,720	1.543
31B	3.5% NaCl	1000	70	0.401	0.068	3.021	0.526	0.594	79,560	1.693
32B	3.5% NaCl	1000	70	0.434	0.074	3.042	0.529	0.603	76,380	1.910
33B	3.5% NaCl	1000	70	0.419	0.071	2.940	0.511	0.582	76,260	1.709
34B	3.5% NaCl	1000	70	0.435	0.074	2.986	0.519	0.593	84,180	1.589
35B	3.5% NaCl	1000	70	0.423	0.072	3.880	0.679	0.751	73,200	1.355
36B	3.5% NaCl	800	70	0.957	0.164	2.593	0.451	0.615	238,800	1.4875
37B	3.5% NaCl	800	70	0.382	0.065	3.088	0.552	0.617	67,920	1.623
38B	3.5% NaCl	1000	70	0.383	0.057	2.980	0.518	0.575	68,280	1.5081
39B	1.0% MgCl ₂	1000	70						68,280	
40B	1.0% MgCl ₂	1	70						239,388	
41B	4.313% KCl	1	70	0.545	0.0745	3.762	0.516	0.5905	73,200	1.844
42B	3.5% NaCl	800	70	0.894	0.153	2.509	0.435	0.588	234,402	1.4607
43B	0.15% CaSO ₄	1	70						65,232	

NOTES:

$\bar{D}' = 0.193 (cm^2)$ Dia. # III (Experiments ODB-3B to ODB-32B)

$\bar{D}' = 0.2146 (cm^2)$ Dia. # IV (Experiments ODB-33B to ODB-43B)

$T = 25^\circ C$; $C_{T_0} = 0$

were used to calculate

$$\bar{D}'_{12} = (\beta t')^{-1} \ln \left[\frac{{}^{\text{"C}}_{B_0}}{C_{B_{f'}} - C_{T_{f'}}} \right] \quad (12a)$$

which are also tabulated in Table 2.2. The β values were determined by making diffusion measurements with KCl-H₂O solutions. The considerable scatter in the \bar{D}'_{12} data obtained for experiments run under seemingly identical conditions (compare the \bar{D}'_{12} data from Experiments ODB-28B to ODB-35B) suggested that some random processes or effects were significantly altering the results from one experiment to the next despite the care which was taken to duplicate experimental conditions and techniques.

Based on these results, a second phase of experiments was performed in which a systematic effort was made to uncover the exact source of the data scatter. The results obtained from this second phase of experiments are reported in Table 2.3 along with the experimental (and data reduction) conditions peculiar to each experiment.

A differential error analysis of the effect of pressure on the diaphragm cell constant, β , revealed that,

$$\frac{\Delta\beta}{\beta} = \frac{\Delta A}{A} - \frac{\Delta l}{l} + \frac{\Delta V}{V} \quad (15)$$

For the porous glass disc used (Kimax borosilicate porous discs), $\Delta l/l$ was estimated to be less than 0.01% in going from 1 atm to 1000 atm (l taken to be a constant fraction of the diaphragm thickness), while $\frac{\Delta A}{A}$ was estimated to be less than 0.2% under the same conditions. The quantity $\Delta V/V$ is best estimated by direct experimental measurement (112) but would be expected to be at least less than 5% for these conditions. Thus changes in β with pressure cannot account for the data scatter.

TABLE 2.3
ORDINARY DIFFUSION BOMB EXPERIMENTS -- SECOND PHASE

EXPERIMENT NUMBER ODBRS-	SALT IN AQUEOUS SOLUTION	DURATION OF EXPERIMENT ($t_0 - t_f$) (seconds)	Y_{T_f} [weight percent]	C_{T_f} [moles/liter]	Y_{B_f} [weight percent]	C_{B_f} [moles/liter]	"Y" _{B₀} [weight percent]	"C" _{B₀} [moles/liter]	DIAPHRAGM NUMBER	β (cm ⁻²)	$\bar{D}_{12} \times 10^5$ (cm ² /sec)	COMMENTS
1	NaCl	7,200	0.184	0.031	3.340	0.581	3.524	0.612	VII	--	--	Pressurisation error determination; 15 minutes to pressurize to 1000 bars, 14 hours at 1000 bars, 15 minutes to depressurize
2	NaCl	7,200	0.112	0.018	3.275	0.570	3.387	0.588	VII	--	--	Pressurisation error determination; 1 hour to pressurize to 1000 bars, 1 hour to depressurize
3	NaCl	7,200	0.033	0.005	3.515	0.613	3.548	0.618	VII	0.1836	1.230	Determination of the extent of ordinary diffusion at 1 bar for a 2 hour period
4	KCl	84,300	0.438	0.059	3.049	0.416	3.487	0.475	VII	0.1836	--	Calibration of Diaphragm VII for β
5	KCl	71,520	1.286	0.173	3.263	0.446	4.549	0.619	VII	0.6213	--	Calibration of Diaphragm VII for β ; small crack in Diaphragm probably present before experiment
6	NaCl	7,200	0.155	0.025	2.920	0.507	3.075	0.532	VII	--	--	Pressurisation error determination; 15 minutes to pressurize to 1000 bars, 14 hours at 1000 bars, 15 minutes to depressurize
7	KCl	57,744	0.108	0.014	3.825	0.524	3.933	0.538	VII	0.05012	--	Calibration of Diaphragm VII for β
8	NaCl	68,400	0.622	0.1065	3.068	0.533	3.690	0.6395	VII	0.1836	1.256	Ordinary diffusion experiment at 1000 bars; 15 minutes to pressurize, 15 minutes to depressurize
9	NaCl	73,320	0.459	0.078	3.335	0.581	3.794	0.659	VII	0.1836	1.346	Ordinary diffusion experiment at 1000 bars; 15 minutes to pressurize, 15 minutes to depressurize
10	NaCl	73,260	0.518	0.089	3.520	0.614	4.038	0.703	VII	0.1836	1.345	Ordinary diffusion experiment at 1000 bars; 15 minutes to pressurize, 15 minutes to depressurize
11	KCl	242,040	1.800	0.244	2.193	0.297	3.993	0.541	VII	0.5220	--	Calibration of Diaphragm VII for β ; fine crack in diaphragm discovered at end of experiment
12	NaCl	2,400	0.105	0.018	--	--	--	--	VIII	--	--	Use of top electrode pair in bomb to check pressurisation error; bomb in air bath; no stirring for 2 hours initially, then pressurized to 1000 bars in ~15 minutes, held at 1000 bars for ~10 minutes, and then depressurized in ~15 minutes; in situ concentrations measured with top electrodes
13	NaCl	59,794	0.345	0.058	2.540	0.441	2.885	0.499	VIII	0.2525	1.75	Ordinary diffusion experiment at 1000 bars; top electrodes used, concentrations at t_f determined with pipette cell
14	KCl	234,876	1.462	0.1175	2.912	0.397	4.374	0.5945	VIII	0.2525	--	Calibration of Diaphragm VIII for β

EXPERIMENT NUMBER ODBRS-	SALT IN AQUEOUS SOLUTION	DURATION OF EXPERIMENT ($t_0 - t_f$) (seconds)	C_{T_f} [moles/liter]	C_{B_f} [moles/liter]	C_{T_0} [moles/liter]	C_{B_0} [moles/liter]	C_{T_0} [moles/liter]	C_{B_0} [moles/liter]	C_{T_0} [moles/liter]	C_{B_0} [moles/liter]	DIAPHRAGM NUMBER	β (cm ⁻²)	$\bar{D}_{12} \times 10^5$ (cm ² /sec)	COMMENTS
13*	NaCl	57,480	0.058	0.441	0.037	0.464	0.009	0.492	--	--	VIII	0.2525	0.849	Experiment ODBRS-13 with actual time ($t_0 - t_f$) and concentrations used to calculate \bar{D}_{12} - first calibration curve of R_{top} electrodes vs. C used (C_0 used for C); C_B, C_B determined by mole balances
13**	NaCl	57,480	0.058	0.441	0.0665	0.496	0.0185	0.544	--	--	VIII	0.2525	1.39	Experiment ODBRS-13 with actual time ($t_0 - t_f$) and concentrations used to calculate \bar{D}_{12} - second calibration curve of R_{top} electrodes vs. C used (C_0 used for C); C_B, C_B determined by mole balances
15	NaCl	--	0.550	0.550	--	--	--	--	0.594	0.594	--	--	--	Calibration of top electrodes in bomb; concentrations determined by pipette cell; P = 1000 bars
16	NaCl	--	0.061	0.061	--	--	--	--	0.033	0.033	--	--	--	Calibration of top electrodes in bomb; concentrations determined by pipette cell; P = 1000 bars

NOTE: T = 25°C

Since the molar concentrations that were measured at 1 atm pressure in the pipette cell enter into the calculation of \bar{D}_{12} as a ratio (see Eqs. 12 or 12a), the effect of pressure on the C's can be neglected over the pressure range of interest.

An analysis of random errors in the measurement of t and C's and their effect on \bar{D}_{12} shows that (93),

$$\frac{\Delta \bar{D}_{12}}{\bar{D}_{12}} = - \frac{\Delta t}{t_f} + \left\{ \frac{\Delta C_{T_f}}{C_{T_f}} - \frac{\Delta C_{B_f}}{C_{B_f}} \right\} f \quad (16)$$

where f is a function of C_{T_f} and C_{B_f} and increases as t_f increases. This function always had a value of less than 1.5 for the experiments reported here. The experiment duration could be determined to better than 0.1% while the accuracy of the concentration measurements using the extensively calibrated pipette conductivity cell was better than two percent.

These possible sources of error could not, therefore, account for the magnitude of the data scatter reported in Table 2.2.

The first results reported in Table 2.3 reveal that if the ordinary diffusion bomb is brought up to pressure and depressurized very slowly, less nondiffusive bulk transport occurs across the diaphragm. Repeated runs under nearly identical conditions could give nearly the same results (Experiments ODBRS-9 and 10). The porous glass diaphragm was susceptible to cracking as was found after Experiment ODBRS-11.

The evidence thus obtained suggested that a nondiffusive bulk transport of solution occurred during both the pressurizing and depressurizing processes even though pressure was simultaneously transmitted to both the top and bottom chambers of the bomb through high pressure stainless steel capillary tubing of identical lengths (pressure drops equal).

The use of the electrodes attached to the end closure pieces was then initiated. Early problems encountered with these electrodes were at least partially overcome by not using fluid in the constant temperature bath (a crude constant temperature air bath was used instead), by the use of an improved method for attaching the lead wires to the platinum electrode wires, and by improving the operating techniques used to obtain transient resistance values with the Jones bridge.

The calibration of the pair of electrodes in the top chamber (those in the bottom chamber were inoperative due to a broken lead wire) is shown in Figure 2.10 for the pressure limits of interest. The data shown graphically in Figures 2.11 and 2.12 vividly show the presence of the bulk transport effect on pressurizing and depressurizing as well as its magnitude and randomness. In Figure 2.12, the majority of the ordinary diffusion process occurred between t_o and t_f . The pressurizing time, t_o to t_o , and the depressurizing time, t_f to t_f , were kept small. The concentrations at t_f , were obtained using the pipette cell. C_T and C_T were measured in situ with the calibrated electrodes. C_B^f and C_B^o were calculated according to the scheme outlined in Appendix A.2. ODBRS-13* denotes the case when the measured top electrode pair resistances from Experiment ODBRS-13 were reduced to molar concentrations by the first calibration (see Figure 2.10), while ODBRS** denotes the case when the second (more valid) calibration was used.

A summary of essentially all the experimentally measured \bar{D}_{12} and \bar{D}'_{12} data are shown in Figure 2.13 for the various pressures studied. As already noted, the scatter of the \bar{D}'_{12} data is considerable. If the data from ODBRS-13 is treated in the same way as was the data obtained from the other experiments, the \bar{D}'_{12} shown above the mid-scatter line would be obtained. However if the electrode measurements from this same experiment were employed to determine in situ concentration measurements at all times during the experiment, then the interesting result shown in Figure 2.13

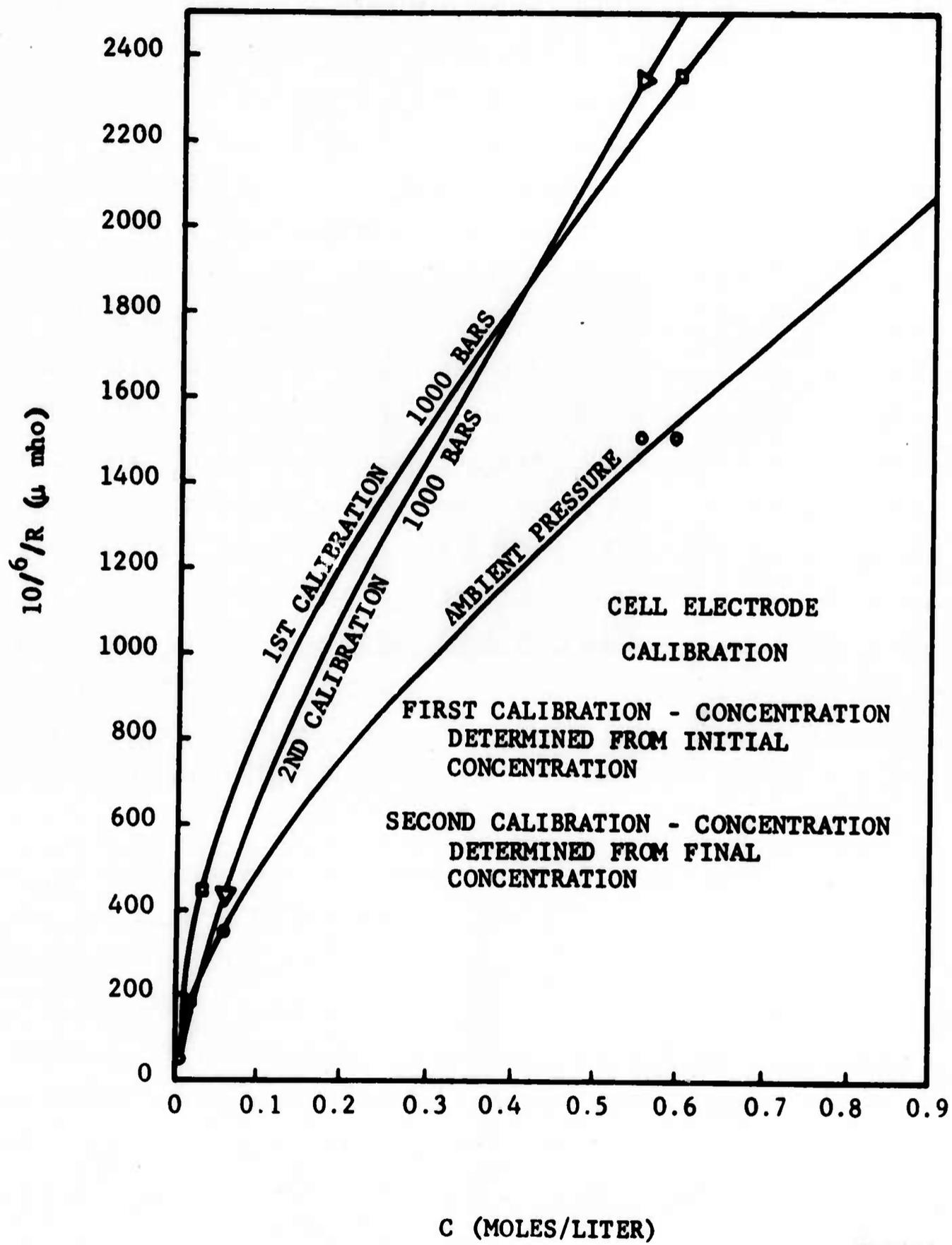
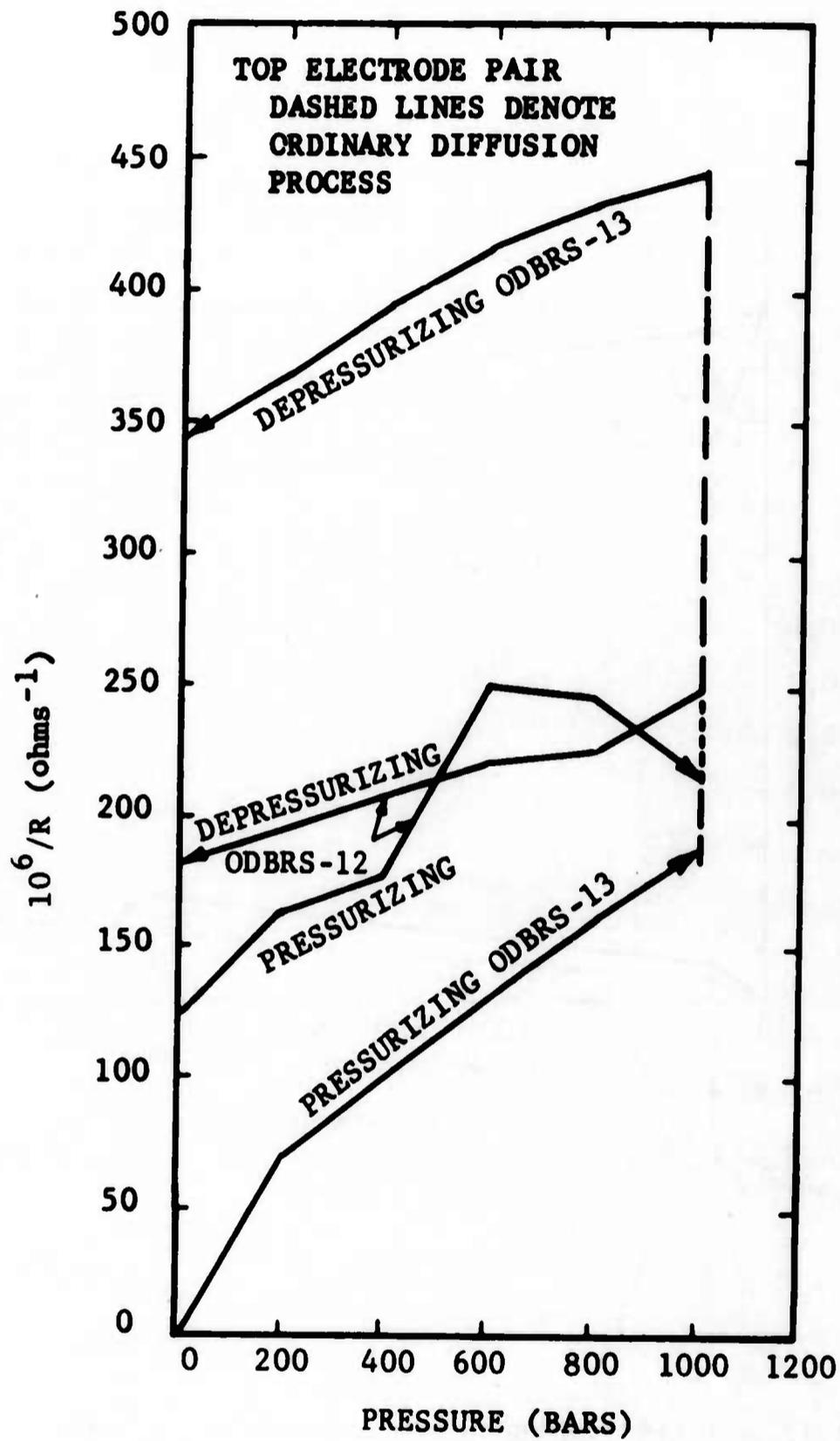


FIGURE 2.10. TOP ELECTRODE PAIR CALIBRATION



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FIGURE 2.11. VARIATION OF CONDUCTANCE WITH PRESSURE IN TOP CHAMBER OF ORDINARY DIFFUSION BOMB

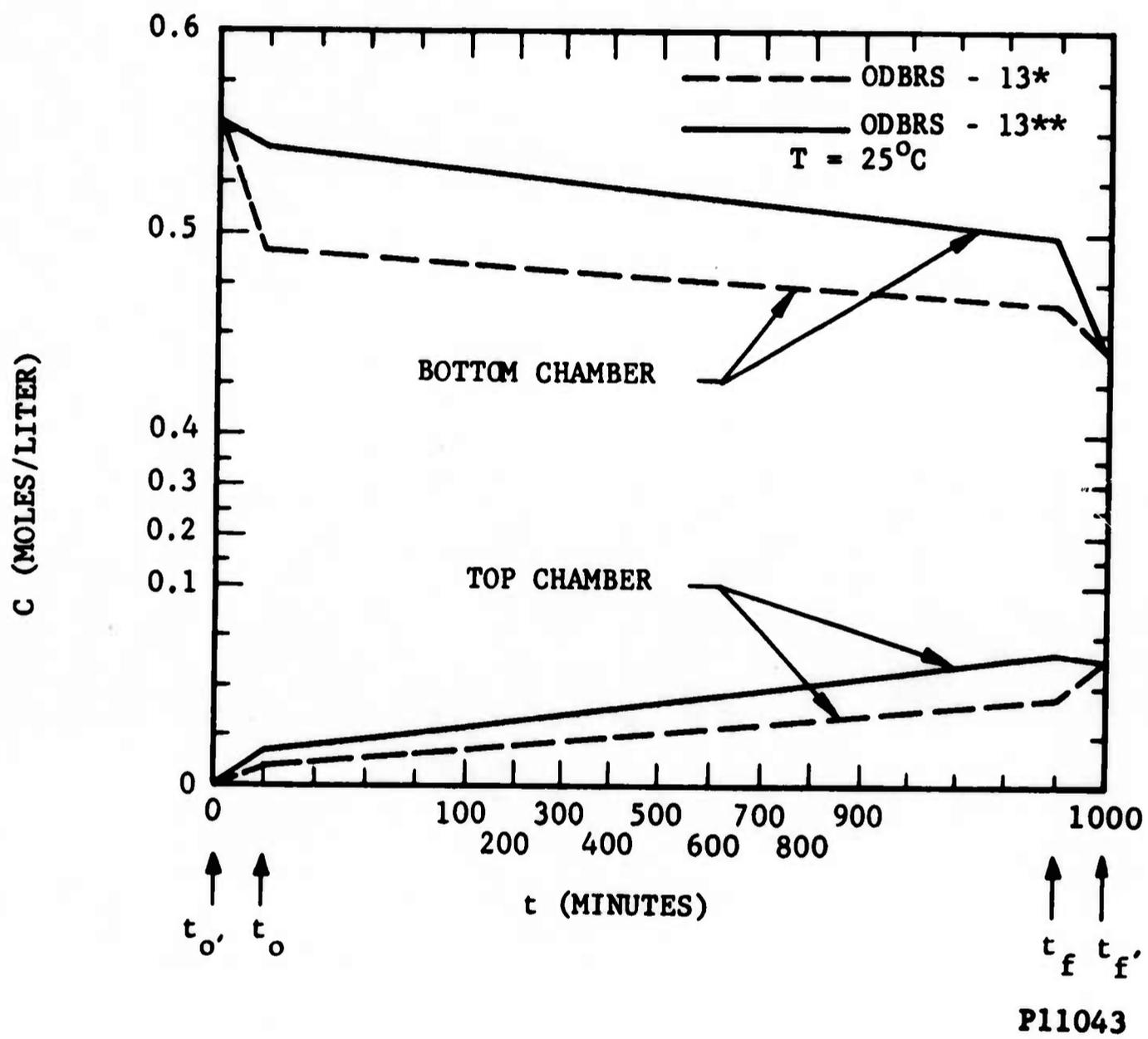


FIGURE 2.12. VARIATION OF MOLAR CONCENTRATION WITH TIME IN THE ORDINARY DIFFUSION BOMB

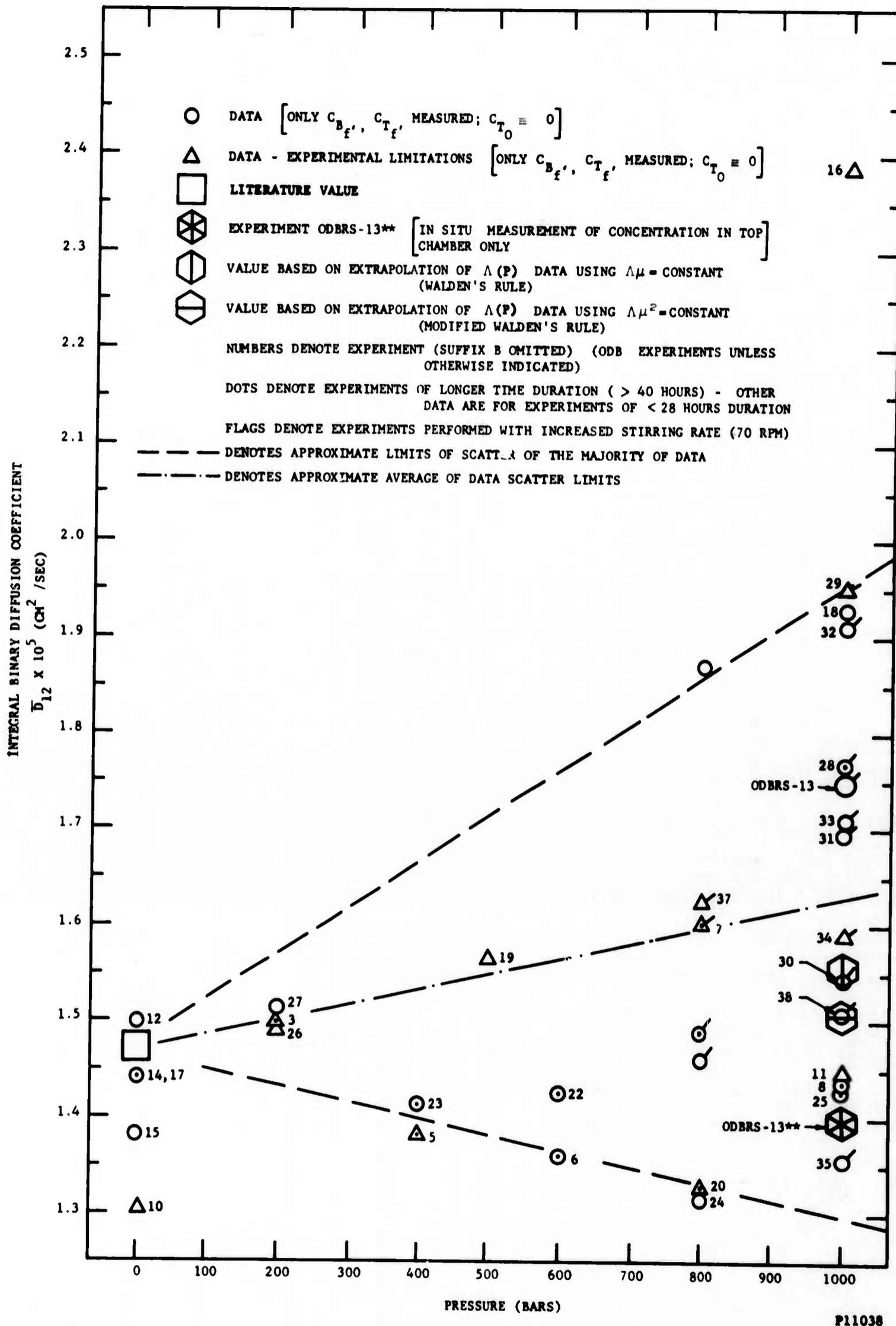


FIGURE 2.13. INTEGRAL BINARY DIFFUSION COEFFICIENT OF 3.5 WEIGHT PERCENT AQUEOUS SODIUM CHLORIDE SOLUTION AT 25°C AS A FUNCTION OF PRESSURE

(large lowest hexagon) is found (second calibration used — see Appendix A.2).

Assuming the validity of the Stokes-Einstein expression (see Eq. 9) as a first approximation, a crude estimate may be made of the effect of pressure on \bar{D}_{12} (or D_{12}) using available conductance data obtained at high pressure (113)(114) and either Walden's rule ($\mu \Lambda = \text{constant}$) or a modified form of Walden's rule which appears to be more valid for salt solutions ($\mu^2 \Lambda = \text{constant}$) (113). The results of estimates of D_{12} at 1000 bars based on both of these extrapolation methods are shown in Figure 2.13.

From these few results it may be now concluded that pressure seems to have little effect on the D_{12} for nominally 3.5 weight percent NaCl in H_2O at $25^\circ C$ over the range 1-1000 bars. Whether the effect is to slightly increase or slightly decrease D_{12} at 1000 bars compared with its value at 1 bar (for $25^\circ C$) remains to be determined by further experimentation.

Future ordinary diffusion bomb experiments (with binary solutions) conducted at pressures greater than 1 bar must use both top and both electrode pairs which have been extensively calibrated. Further, care must be exercised that the pressure transmitting lines to the bomb are flushed clean before each experiment. Under these conditions, \bar{D}_{12} can be calculated with confidence directly from Equation 12.

This new experimental technique (use of the ordinary diffusion bomb) appears to offer a number of advantages over radioisotope techniques (115-118), especially for binary salt systems where in situ concentration measurements are possible without incurring radiation hazards.

2.4 EXTENSION TO MULTICOMPONENT SYSTEMS

The theoretical description of ion diffusion under isothermal conditions in a multicomponent system has been presented in the literature (55) (119-121). A basic result is that, to a good approximation, multicomponent ionic ordinary diffusion coefficients can be measured with the

diaphragm diffusion cell using Eq. 12, but interpreting \bar{D}_{12} as \bar{D}_i^* (a multicomponent ionic ordinary diffusion coefficient dependent, in general, upon temperature, pressure, and the relative concentrations of the ions present) and interpreting the molar concentrations as ionic molar concentrations of the species i .

Since conductance measurements in multicomponent salt solutions do not yield concentration values for the individual ions, some other in situ concentration method must be sought (such as spectrophotometry using high pressure optical windows in the bomb walls) or displacement sampling under pressure. For the types of salts of most abundance in sea water, the high pressure sampling technique would probably be the most practical. Mercury could be used as the displacing fluid. High pressure valves could be attached to the side wall of the ordinary diffusion bomb at points both above and below the diaphragm. The downstream side of these valves could be pressurized to a pressure just slightly greater than the bomb pressure before sampling would be initiated. With the stirrers stopped, the valves could be opened and then the mercury could be injected at the same time that a sample is withdrawn into the tubing attached to the downstream side of the valves with the pressure on this side of the valves being maintained constant (by increasing the volume of the system, i.e., by creating sample volumes in the lines). After having "trapped" samples at high pressure under conditions such that bulk flow across the diaphragm would be minimum, the pressure on the contained and isolated samples could be reduced to 1 bar. Individual ion concentrations could then be measured by flame photometric techniques.

SECTION 3

SORET COEFFICIENT STUDY

3.1 ANALYTICAL CONSIDERATIONS

The phenomenon of thermal diffusion in salt solutions has been recently reviewed by Agar (70) and Tyrrell (49). There has been no attempt to review the binary Soret coefficient data for many of the salts in sea water,* nor to apply considerations of multicomponent effects to synthetic or actual sea water (55).

The Soret coefficient of dilute and concentrated binary salt solutions has been of interest for some time. Early work by Tanner (72) (73)(74)(75) and more recent work by Agar and coworkers (76)(70)(77)(78) (79)(80)(81)(82)(61, pp. 200-223), Turner and coworkers (68)(69), Chanu and coworkers (83)(84)(85)(86), Longworth (87) and Thomaes (88) has consisted primarily of experimental measurements of the binary Soret coefficient, σ_{12} , by optical or conductivity methods.

The only theoretical attempts which have been made in order to predict binary Soret coefficients of salt solutions** have been based

* Von Halle (71) has given a tabular review of all binary Soret coefficient data published before 1957.

** The theory of Bearman (89) is not applicable to salt solutions.

on molar heat of transfer data for the individual ions at the temperatures and concentrations of interest (49). These ionic molar heats of transfer can be related to corresponding quantities for the infinitely dilute state. No theoretical means are available for calculating these latter quantities. Ionic molar heats of transfer are usually determined indirectly by measuring the binary Soret coefficient. Thus, in effect, there are no theoretical tools by which σ_{12} values may be calculated.

The major salt constituents of a typical sea water and their associated Soret coefficients for one concentration (at 25°C) are listed in Table 2.1. From this table of values, it is apparent that significant differences exist between the various values of σ_{12} . No data at any temperature or composition is available for those salts for which σ_{12} values are not listed. Even in the case of those for which σ_{12} values are given, little or no reliable data exists in the literature for the temperatures and concentrations of interest here. No data indicating the effect of pressure in σ_{12} for aqueous salt solutions has been published.

All published, reliable, Soret coefficient data for the NaCl-H₂O and MgCl₂-H₂O systems as a function of composition and temperature are presented in Figures 3.1 and 3.2.* Smooth curves have been drawn through some of the data. The following is apparent:

- (i) For the NaCl-H₂O system, data at temperatures other than 25°C is lacking; data in the 3.5 weight percent region even at 25°C is not available; recent data obtained by Price (79) suggests that σ_{12} does go through a minimum as the concentration is increased; the only data available at a temperature other than 25°C indicates that the temperature dependence of the Soret coefficient is appreciable.

* The sources for the data are as follows: σ_{12} (NaCl-H₂O): Agar (61), pp. 200-223), Agar and Turner (78), Snowdon and Turner (68), Price (79), Chanu (83) (85) and, Chanu and Lenoble (83)

σ_{12} (MgCl₂-H₂O): Payton and Turner (69), Cova (90), and Tanner (75).

σ_{12} (KCl-H₂O): Longworth (106).

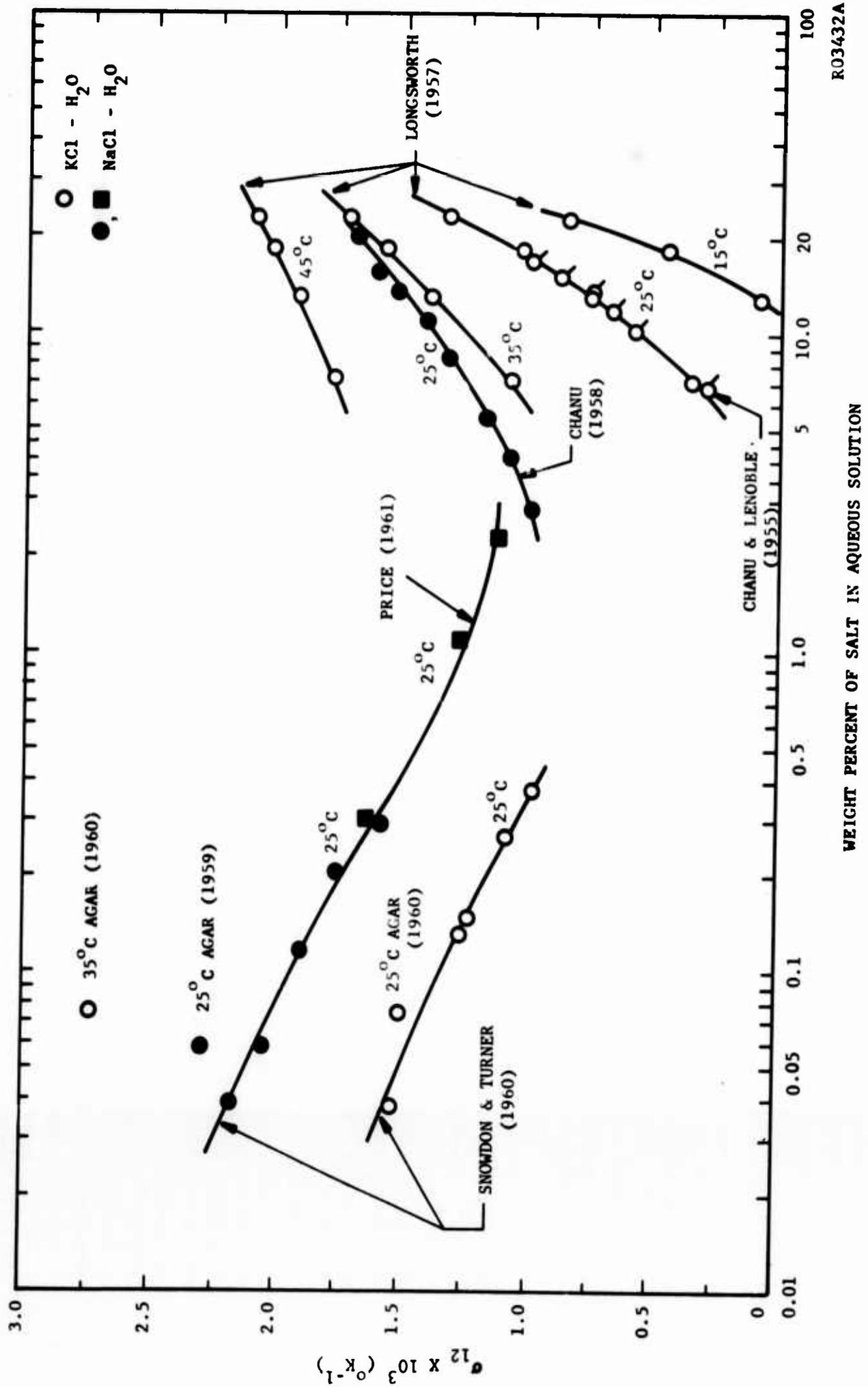
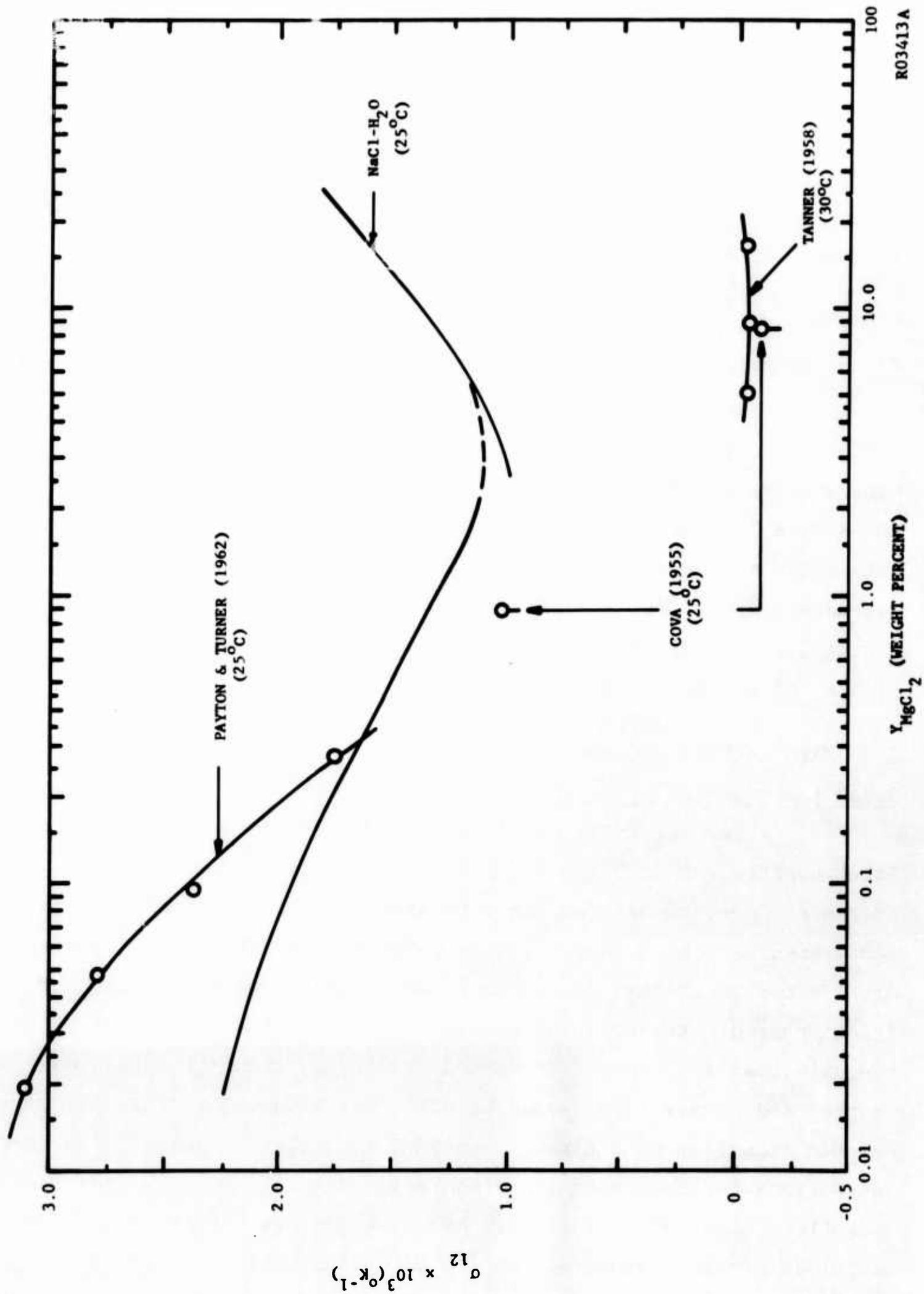


FIGURE 3.1. THE BINARY SORLET COEFFICIENTS OF THE $\text{NaCl}-\text{H}_2\text{O}$ AND $\text{KCl}-\text{H}_2\text{O}$ SYSTEMS AS A FUNCTION OF TEMPERATURE AND COMPOSITION (1 ATM)

R03432A



R03413A

FIGURE 3.2. Soret coefficients for the $\text{MgCl}_2\text{-H}_2\text{O}$ system (1 atm)

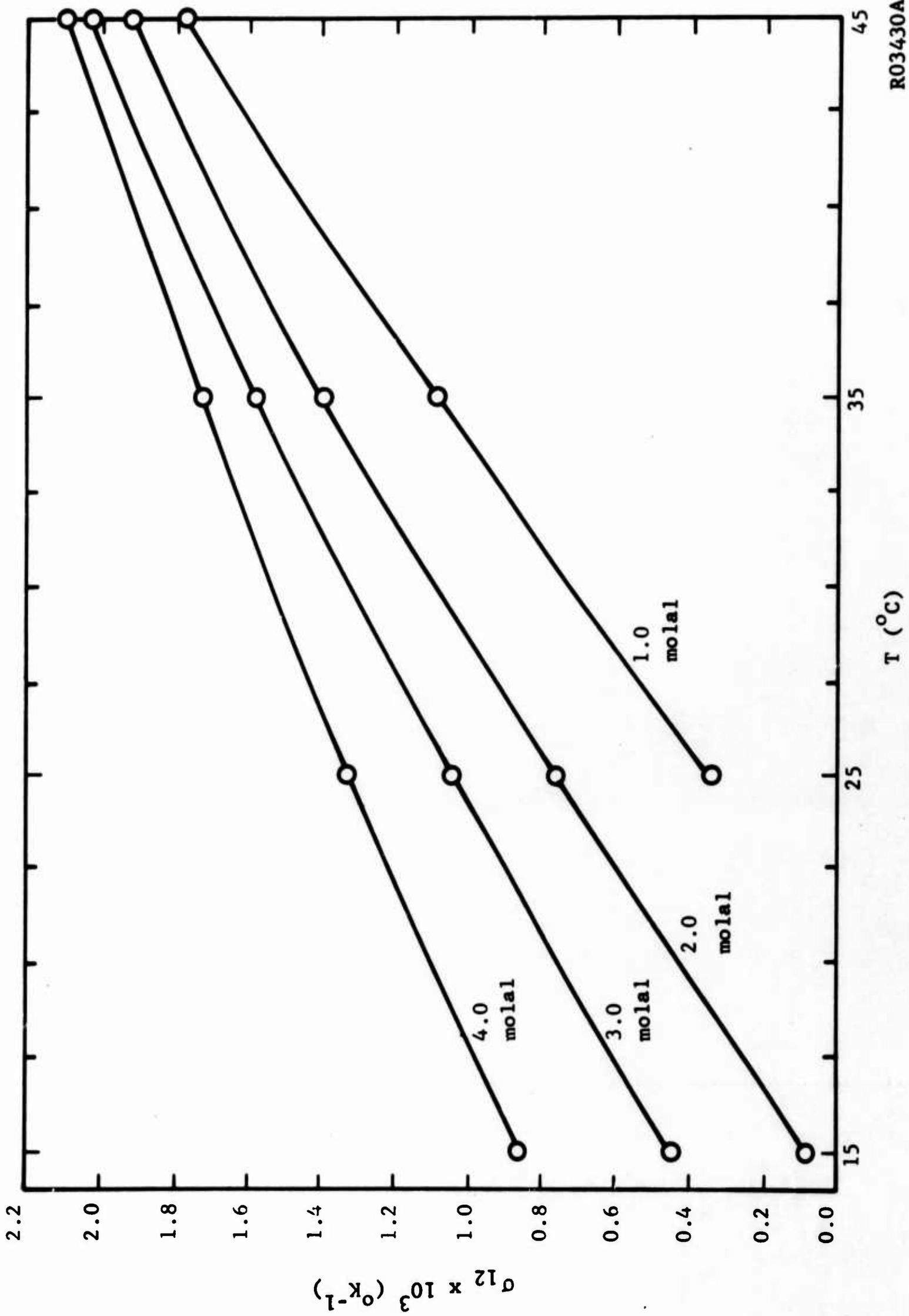
(ii) For the $\text{MgCl-H}_2\text{O}$ system, essentially no data at any temperature is available over a large concentration range; the Soret coefficient is slightly negative at high concentrations (salt migrates to the hot wall); the Soret coefficient, over most of the concentration range, is significantly different than that of the $\text{NaCl-H}_2\text{O}$ system at the same temperature.

It is of interest to consider the temperature dependence of the binary Soret coefficient. This is shown in Figures 3.1, 3.3, and 3.4 for the $\text{NaCl-H}_2\text{O}$ and $\text{KCl-H}_2\text{O}$ systems. Longworth's data are almost the only data which have been reported that consider, systematically, the temperature dependence of σ_{12} for a binary salt solution (in this case, $\text{KCl-H}_2\text{O}$). Figure 3.4 clearly shows the strong temperature dependence of σ_{12} for both dilute and concentrated solutions.

3.2 EXPERIMENTAL PROGRAM

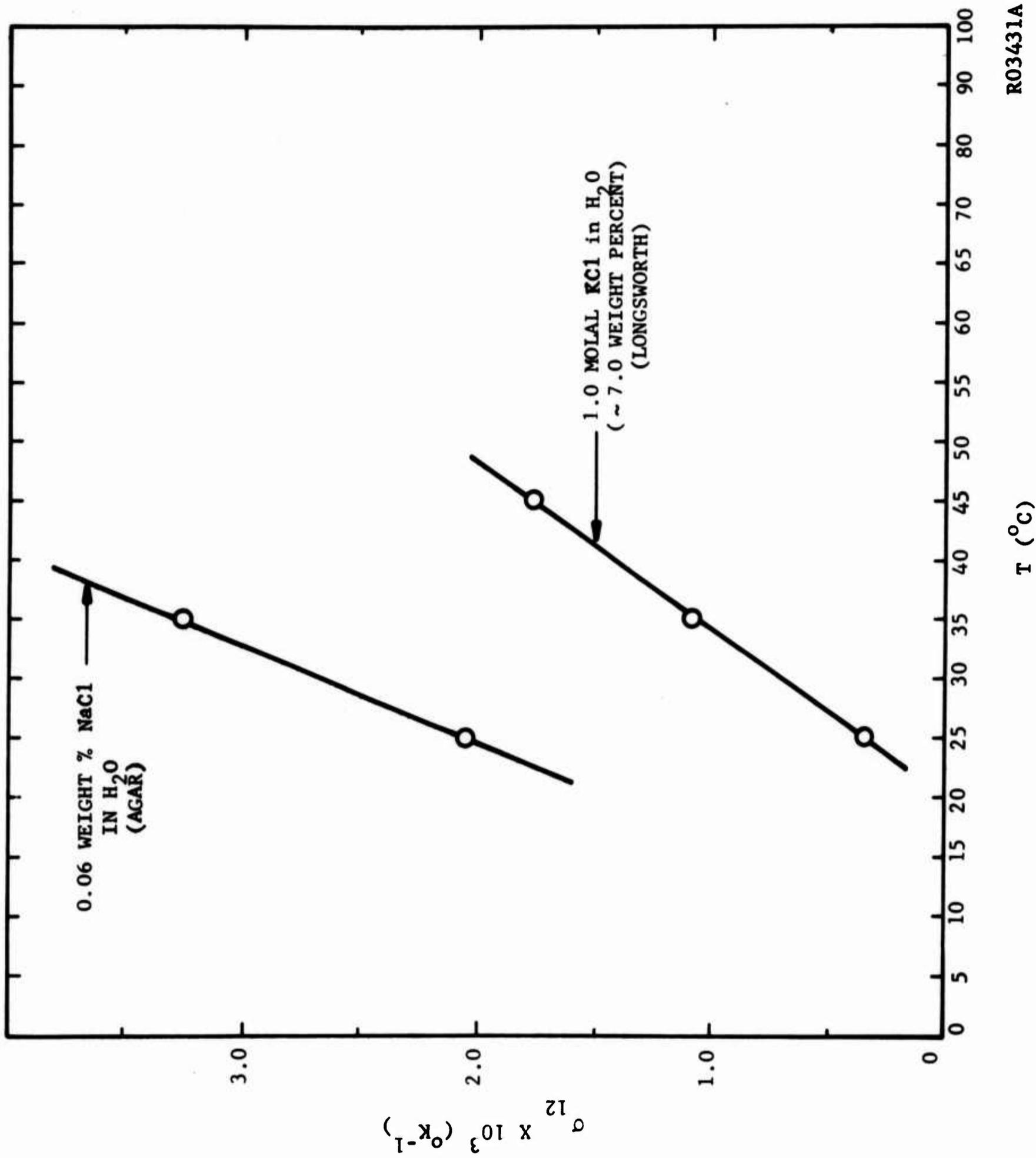
3.2a Experimental Approach

After surveying the various methods available for measuring the Soret coefficient of binary salt solutions, it was apparent that a conductimetric method offered the only single technique capable of making measurements in both dilute and concentrated solutions (optical methods are limited to relatively concentrated solutions in which index of refraction gradients are large enough to be readily measured)(87). Of the two principal conductimetric methods (77)(78), the cell design developed by Agar and Turner (77) seemed to offer the advantages of simplicity, and ease in reduction of the data. In addition, there appeared to be fewer assumptions and uncertainties associated with the theory of the cell operation. Agar and Turner (77) had suggested that this cell would be useful at higher concentrations (>0.05 molal) where convective mixing would be expected to be less of a problem (the hot wall is always situated on top). This technique required the use of an AC electrolytic conductivity bridge sensitive to at least 1 part in 10^4 , and required the temperature at



R03430A

FIGURE 3.3. THE TEMPERATURE DEPENDENCE OF THE BINARY SORLET COEFFICIENT FOR AQUEOUS KCl SOLUTIONS AT SEVERAL CONCENTRATIONS AS A FUNCTION OF TEMPERATURE (1 ATM) (LONGSWORTH DATA)



R03431A

FIGURE 3.4 COMPARISON OF THE TEMPERATURE DEPENDENCE OF THE BINARY SORET COEFFICIENTS OF THE NaCl-H₂O and KCl-H₂O SYSTEMS (1 ATM)

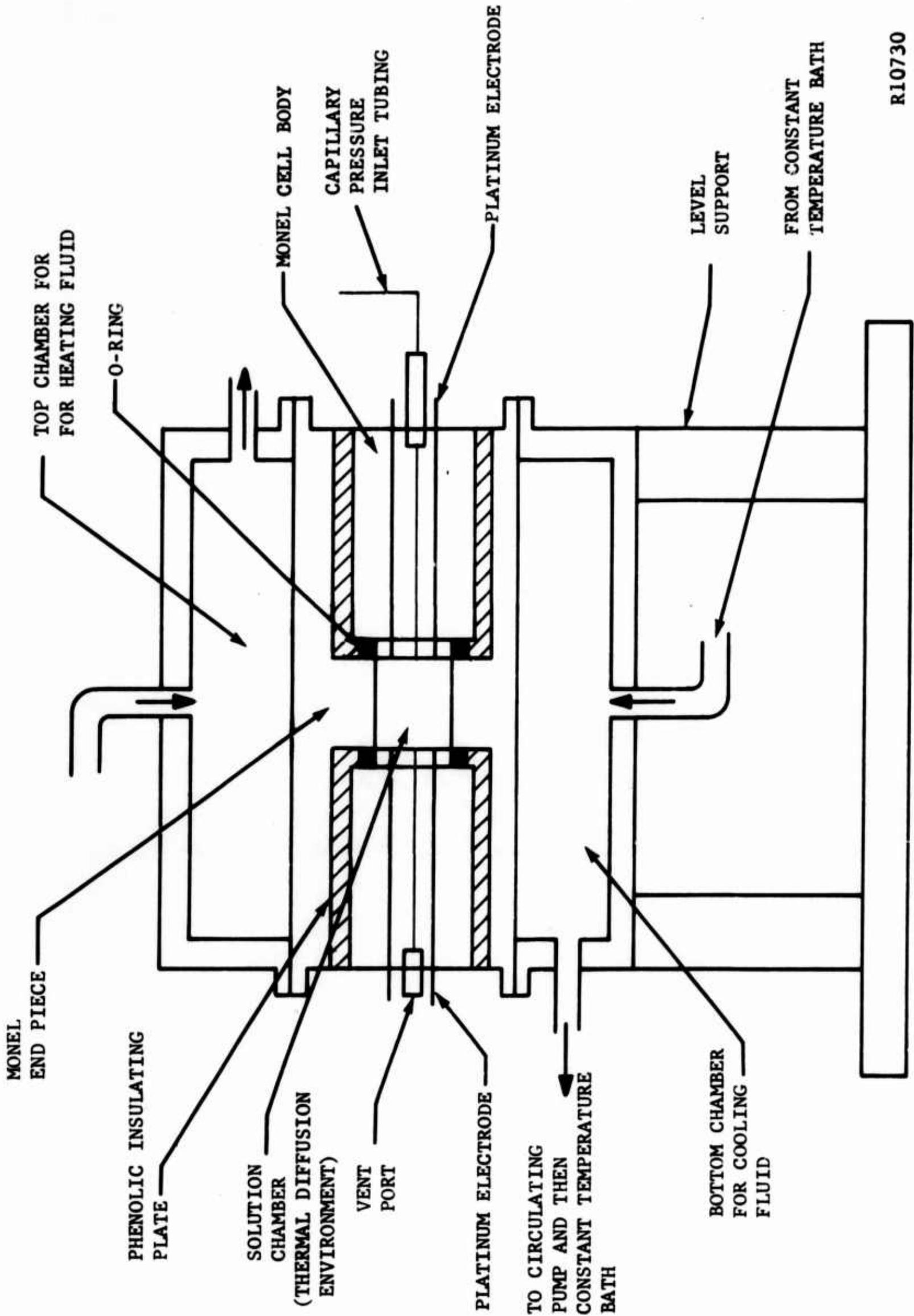
the hot and cold walls of the cell to remain constant within 0.01°C throughout the entire duration of the run (runs lasted 1 to 2 days).

3.2b Equipment and Procedures

The Soret cell used during these tests was a modification of that designed and used by Agar and Turner (77). The cell basically consists of two jackets for heating and cooling with a chamber to contain the solution between them. Provision is made to measure temperatures and concentrations as a function of time.

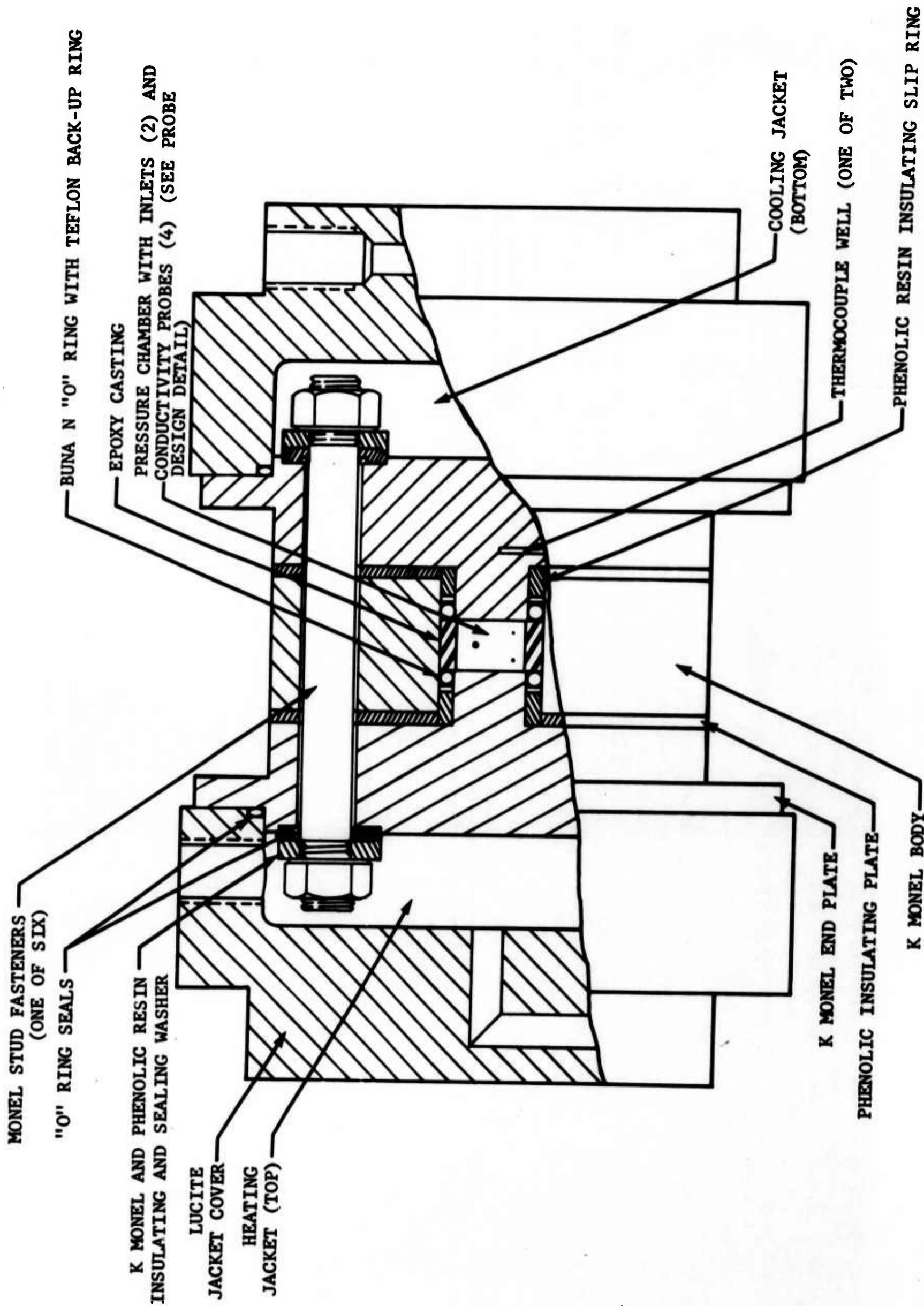
The unique feature of the cell used in this experimental program is the fact that it can be used to make thermal diffusion measurements at pressures up to 1000 bars. A simplified schematic illustration of the cell, called a Soret bomb, is given in Figure 3.5. The detailed design of the bomb and the associated heating and cooling chambers (through which constant temperature fluid is circulated) is shown in Figure 3.6. The size of the central chamber and the mode of installation of the electrode seals are shown in Figure 3.7. As in the case of the ordinary diffusion bomb, the central cell section and the end plates of the Soret bomb were fabricated from K Monel. The wall thicknesses were determined from the usual pressure vessel design equations (108) (109). The bolts which hold the two end plates in position also are insulated from the rest of the bomb in order to minimize nonuniform heat transfer problems in the central cell body itself. The size and number of bolts necessary for the pressures of interest were determined using known techniques of fastener design (111).

Whereas unsupported area seals were used in the ordinary diffusion bomb, in the Soret bomb o-ring seals with back up rings were used. This difference is due to the requirement that the heat flux through the central hole region of the Soret bomb wherein the salt solution is contained should be uniform and one-dimensional. It is therefore undesirable to use bulky gasketing materials having thermal conductivities much different than the surrounding medium. Phenolic resin plates were used in the Soret bomb in order to make the thermal resistances (to heat transfer) nearly equal



R10730

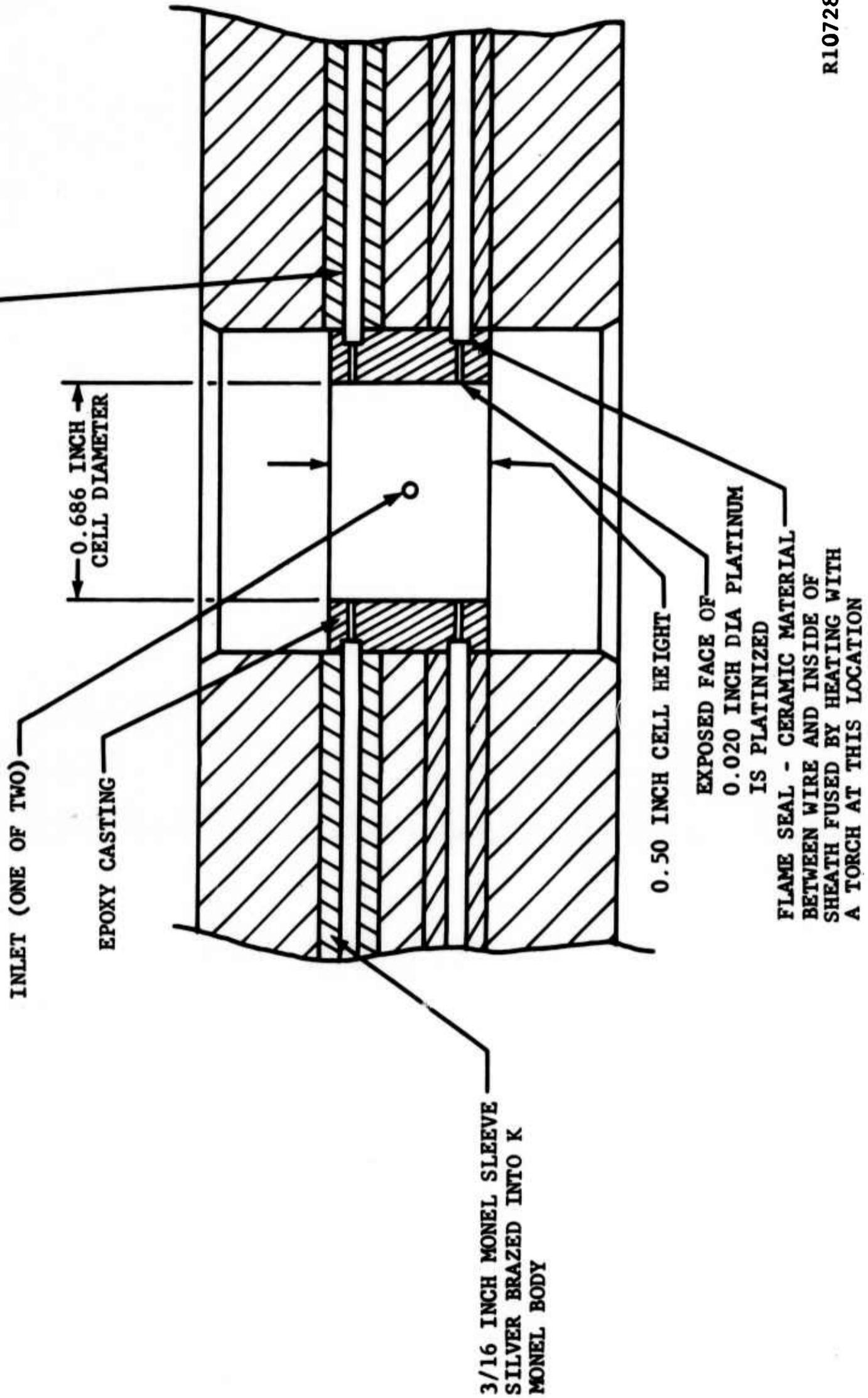
FIGURE 3.5. SORET BOMB ARRANGEMENT (CELL FASTENING BOLTS NOT SHOWN - ENTIRE ASSEMBLY ENCLOSED IN A CONSTANT TEMPERATURE AIR BATH)



R10729

FIGURE 3.6. SORLET BOMB

SHEATHED, INSULATED
 PLATINUM WIRE SEAL:
 0.020 INCH DIA PLATINUM WIRE
 MAGNESIUM OXIDE INSULATING CORE
 COVERED WITH STAINLESS STEEL
 SHEATH WHICH HAS 1/16 INCH O
 SHEATH SILVER BRAZED
 INTO THE MONEL SLEEVE



R10728

FIGURE 3.7. SORET BOMB DETAILS — CONDUCTIVITY PROBES AND PRESSURE CHAMBER

through each section. Referring to Figure 3.8, it is evident that if the thermal resistance along path A-A' is to be the same as along B-B', then

$$\frac{2\Delta X_1}{k_r} + \frac{\Delta X_2 - 2\Delta X_1}{k_m} = \frac{\Delta X_3}{k_w} + \frac{\Delta X_2 - \Delta X_3}{k_m}$$

or

$$\Delta X_1 = \frac{\Delta X_3 (k_m - k_w) k_r}{2 (k_m - k_r) k_w} \quad (17)$$

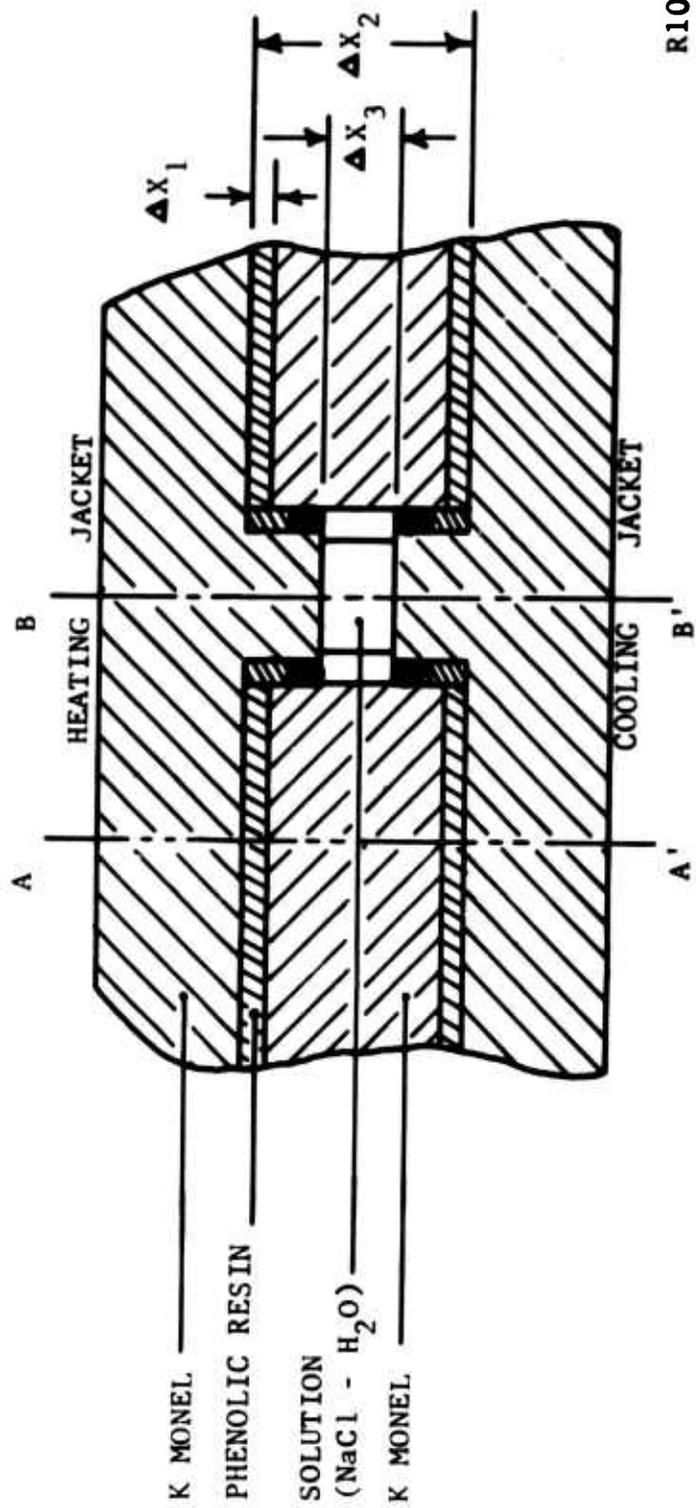
that is, the thickness of the phenolic resin plates could be determined after the cell height had been specified.

The size of the central cavity in the Soret bomb was made similar to that used by Agar and Turner (77).

The operation of the Soret bomb was carried out in a manner exactly similar to that used by Agar and Turner (77), except that the inside of the bomb was pressured up to the desired pressure before the start of an experiment by the transmitting system shown in Figure 2.9. It was found to be especially important to maintain the temperature of the heated and cooling circulating fluids (an oil) constant to within 0.01°C throughout the duration of the experiment. In addition, very careful use of the Jones bridge was required (input bridge voltage ≈ 0.25 volts; voltage frequency ≈ 4000 cycles/sec) in order that the appropriate accuracy in resistance measurements could be obtained. Resistance changes during the course of the experiment were not greater than about 2 ohms.

3.3 RESULTS

By carefully controlling the temperatures of the heated upper plate and the cooled lower plate to within 0.01°C over a twenty four hour period, and by exercising caution in the use of the highly accurate Jones bridge, it is possible to make reliable transient resistance measurements



R10731

FIGURE 3.8. THERMAL RESISTANCE PATHS IN THE SORLET BOMB

(with the electrodes in the Soret bomb) which are indicative of the thermal and ordinary diffusion processes occurring in the center cavity of the Soret bomb. The binary Soret coefficient is then calculated from (for $t > \theta/3$) (111),

$$\sigma_{12} = \frac{R_{\infty} - R_0}{B (\Delta T) R_0 \left[\frac{x}{a} - \frac{1}{2} \right]} \quad (18)$$

where ΔT represents the temperature difference between the inside surfaces of the top and bottom end plates and R_{∞} and R_0 are the stationary state and initial electrode pair resistances determined by appropriate extrapolation of the resistance-time data.

After making a considerable number of improvements in the experimental apparatus (baths, bomb, and bridge connections) it was finally possible to make the first reliable measurement of σ_{12} for the NaCl-H₂O system at a concentration similar to that of sea water and at a pressure of approximately 1000 bars ($T \approx 27^{\circ}\text{C}$) (Experiment SDB-6: top electrodes).

The raw and derived data are tabulated in Table 3.1. Figures 3.9 and 3.10 show how the data was treated in order to obtain the required extrapolated quantities, R_{∞} and R_0 . The consistency and reliability of the data is indicated in these figures (large time data ($t > \theta/3$) is weighted most strongly). The conformity of the data to straight lines, as shown in these figures, is required for consistency with the assumptions implicit in Eq. 18 (111).

Figure 3.11 shows the high pressure result compared with atmospheric pressure data obtained by other investigators. It is apparent that if the pressure does affect σ_{12} for this system at the concentration and temperature considered, the effect must be very slight.

This represents the first application of the Agar-Turner dual electrode type binary Soret cell for measurements at salt concentrations

TABLE 3.1

BINARY THERMAL DIFFUSION EXPERIMENT
AT 1000 BARS PRESSURE
EXPERIMENT SDB-6

Top Electrode Pair:

t (minutes)	(t/θ)	exp-(t/θ)	R (ohms)	(R-R ₀) (ohms)	ln R-R _x
9.1	.0502	0.95103	615.616	3.056	1.1171
15.6	.0861	0.91750	613.031	0.471	-0.7529
25.6	.1413	0.86822	611.687	-0.873	-0.1358
32.9	.1816	0.83393	611.371	-1.189	0.1731
38.7	.2136	0.80767	611.254	-1.306	0.2670
41.1	.2268	0.79708	611.189	-1.371	0.3155
47.9	.2643	0.76774	611.473	-1.087	0.0834
61.5	.3394	0.71219	611.552	-1.008	0.0080
69.2	.3819	0.68256	611.545	-1.015	0.0149
87.0	.4801	0.61872	611.570	-0.990	-0.0100
101.3	.5591	0.57172	611.694	-0.866	-0.1439
115.3	.6363	0.52924	611.770	-0.790	-0.2357
130.2	.7185	0.48748	611.871	-0.689	-0.3725
140.5	.7754	0.46051	611.819	-0.741	-0.2998
155.6	.8587	0.42371	612.000	-0.560	-0.5798
175.3	.9674	0.38006	612.038	-0.522	-0.6501
192.6	1.0629	0.34545	612.118	-0.442	-0.8164
222.6	1.2285	0.29273	612.110	-0.450	-0.7985
1121.4	6.1887	0.00203	615.628	3.068	1.1210
1127.4	6.2219	0.00200	616.140	3.580	1.2754
1138.3	6.2820	0.00190	615.727	3.167	1.1528

Conditions: \bar{T} - 27.253°C : $\Delta T = 9.15^\circ\text{C}$
 Y_{Feed} - 3.5% NaCl : $B = 0.92$ (see reference 78, pp.326-7)
 θ - 181.20 minutes
 (x/a) • 0.81448 (print); 0.85294 (base reversed)

Derived Results: R_x - 612.56 ohms
 R_0 - 610.66 ohms
 σ_{12} - $1.17 \times 10^{-3} \text{ } ^\circ\text{K}^{-1}$; $1.048 \times 10^{-3} \text{ } ^\circ\text{K}^{-1}$

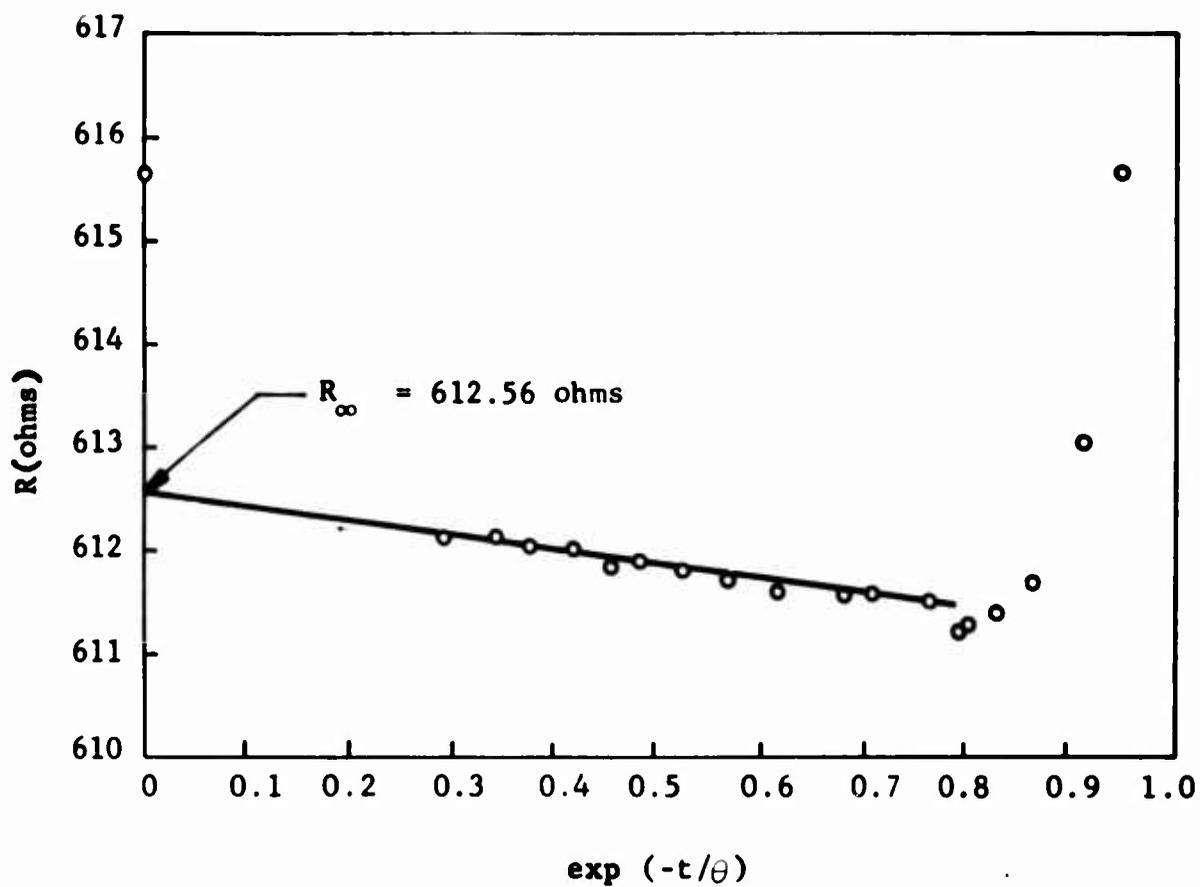


FIGURE 3.9. EXTRAPOLATION OF THE TOP ELECTRODE PAIR RESISTANCE
FOR R_∞ - EXPERIMENT SDB-6

P11040

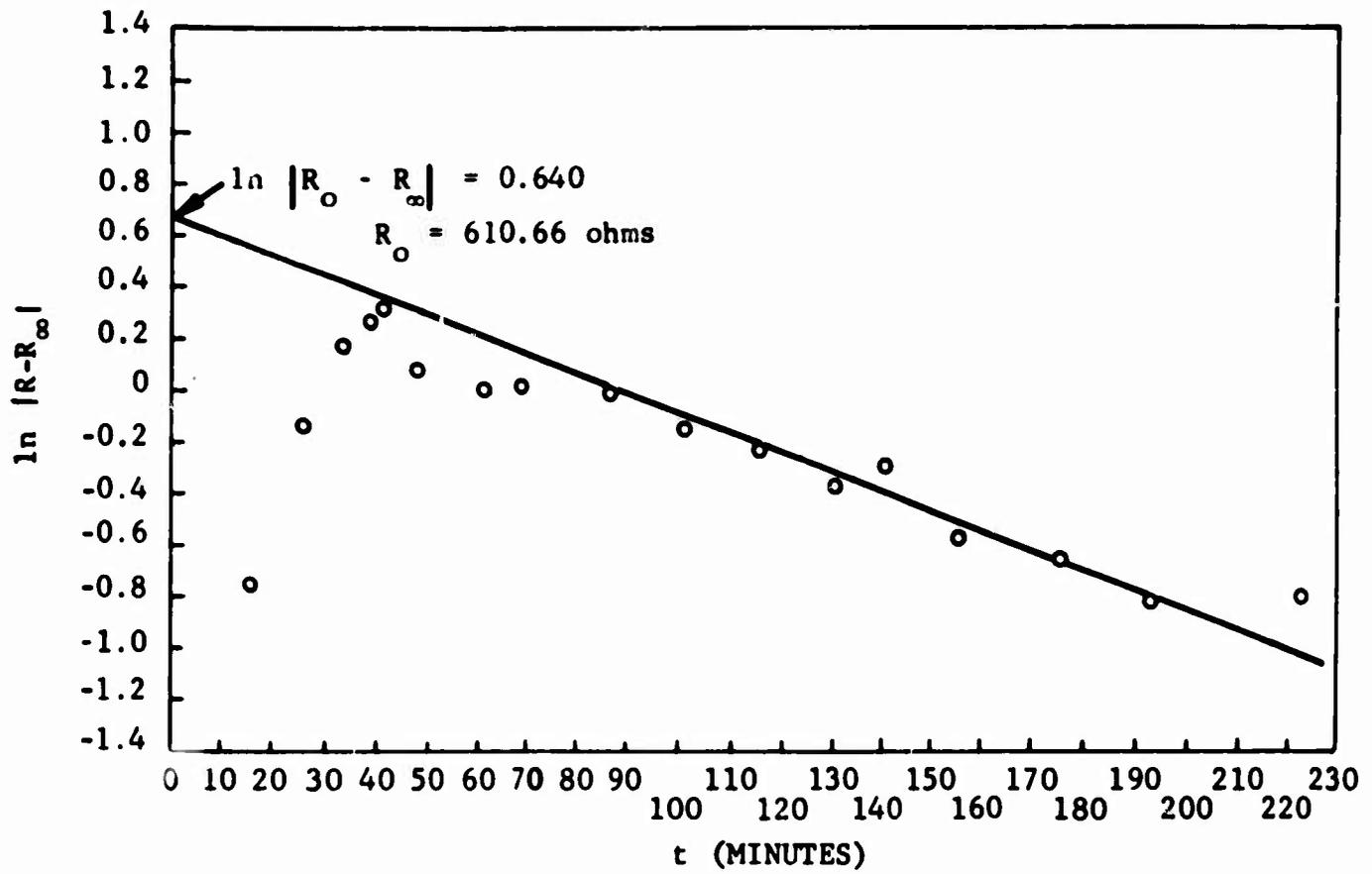
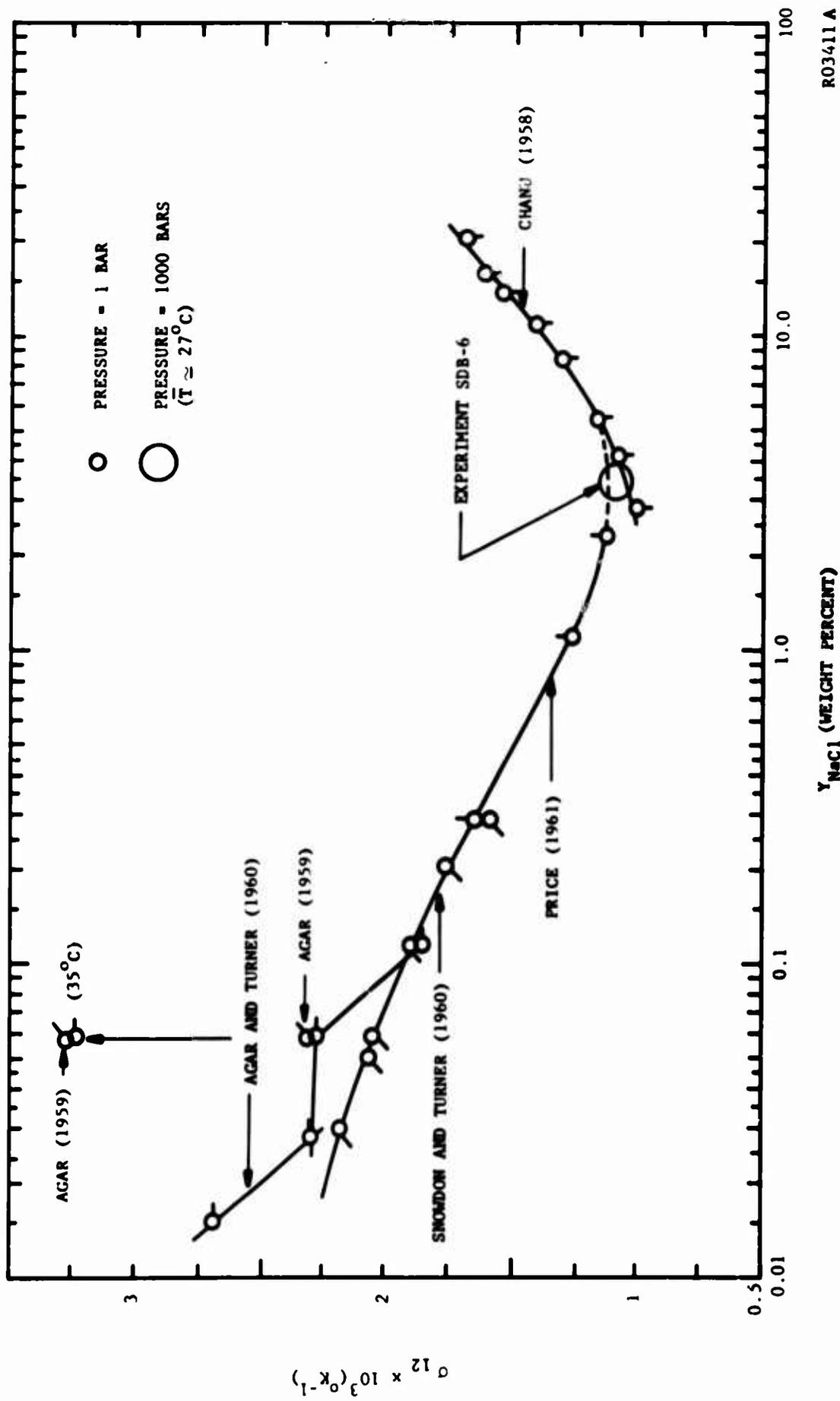


FIGURE 3.10. EXTRAPOLATION OF THE TOP ELECTRODE PAIR RESISTANCE

FOR R_0 - EXPERIMENT SDB-6

P11041



R03411 A

FIGURE 3.11. SORLET COEFFICIENTS FOR THE NaCl-H₂O SYSTEM (25°C)

greater than 0.05 molal and at pressures greater than atmospheric.

Future measurements should be made with better air bath (surrounding the Soret bomb) control, and with a better electrode seal (the bottom electrode pair could not be used because of an imperfect seal between the epoxy and the Monel).

The limitations of the binary Soret cells used by other investigators (90) (125) for high pressure measurements with organic liquids are present in the Soret bomb design employed for this study.

3.4 EXTENSION TO MULTICOMPONENT SYSTEMS

Using the approach of Vinograd and McBain (119), Guthrie, et al. (122) developed a relatively simple expression for the ionic Soret coefficient in a dilute ideal multicomponent ionic system. The ionic Soret coefficient is defined as,

$$\sigma_i \equiv - \left[\frac{\nabla \ln \gamma_i}{\nabla T} \right]_{t \rightarrow \infty} \quad (19)$$

for ion i in the system.

A series of atmospheric pressure experiments were performed using different multicomponent Soret cells suggested by Hershey and Prados (123) and Berkau and Fisher (124) with the NaCl-H₂O system. The data and auxiliary information are reported in Table 3.2.

From these experiments, which were designed to determine the Soret cell design most appropriate for multicomponent aqueous electrolyte solutions such as sea water, it was found that metal cell parts (such as end plates, needles sticking in from the side, etc.) should not contact the multicomponent salt solution.

TABLE 3.2

TEST OF MULTICOMPONENT SOBLET CELL CONFIGURATIONS USING
AQUEOUS SODIUM CHLORIDE SOLUTIONS AT 1 ATMOSPHERE

EXPERIMENT NUMBER	FEED CONCENTRATION Y_T (weight percent)	DURATION OF EXPERIMENT (minutes)	TOP PLATE TEMPERATURE (°C)	BOTTOM PLATE TEMPERATURE (°C)	CHAMBER CONCENTRATIONS AT END OF EXPERIMENT Y_T (weight percent)	CONCENTRATION DIFFERENCE AT END OF EXPERIMENT $(Y_B - Y_T)$ (weight percent)	Cell	Special adaptations to cell	EXPERIMENTAL CONDITIONS Method of concentration analysis	Remarks
MCSC-14	3.71	2800	30.0	20.0	3.59	+0.25	Large cell	none	Weighting to dryness	none
MCSC-16	3.70	5525	31.0	20.5	3.71	-0.065	Large cell	none	Mohr titration	none
MCSC-17	3.67	1342	29.2	21.0	3.59	-0.03	Small cells	Needles in rubber sections	Mohr titration	none
MCSC-18	3.68	1350	31.0	19.6	3.54	+0.04	Small cell	Needles removed from rubber sections	Mohr titration	none
MCSC-19	3.60	5600	27.6	20.2	3.54	+0.02	Small cell	Silicone grease used between brass chambers and the teflon plates	Mohr titration	none
MCSC-20	3.57	1370	31.8	17.5	3.56	-0.02	Small cell	Silver plated copper plates placed between teflon plates & rubber center sections	Mohr titration	none
MCSC-21	3.58	10040	31.9	19.0	3.54	-0.04	Small cell	Silver plated copper plates placed between teflon plates & rubber center sections	Mohr titration	none
MCSC-22	3.61	4200	32.0	17.6	3.63	+0.05	Large cell	Monel screens and cellophane membranes removed	Mohr titration	Air bubbles found in top chamber at end of experiment
MCSC-23	3.67	4130	30.0	19.6	3.61	+0.09	Large cell	Monel screens and cellophane membranes removed	Mohr titration	none

* Small Cells:

- Brass heating and cooling chambers
- Teflon plates between brass and salt solution
- Rubber center sections
- Cellophane diaphragm between rubber center sections
- Hypodermic needles used to fill and empty center sections
- Distilled water circulated through jackets
- Isolation transformers used on baths and circulating pumps

** Large Cells:

- Monel end sections
- Lucite center section
- Monel screen pushed in on top of cellophane membrane
- Distilled water circulated through jackets
- Isolation transformers used on baths and circulating pumps

Micrometer buret used in titration

Since for binary systems (123) (species 2 denotes salt),

$$\sigma_{12} \approx - \frac{1}{T_T - T_B} \ln \left[\frac{y_{2T}}{y_{2B}} \right] \quad (20)$$

for the cell design with sample removal near the heated and cooled plates, and since (124)

$$\sigma_{12} \approx - \frac{2}{T_T - T_B} \ln \left[\frac{y_{2T}}{y_{2B}} \right] \quad (21)$$

for the cell design with a center dividing membrane (or porous barrier to bulk streaming), it is possible to quantitatively check the various design alternatives using the binary Soret coefficient data known at 1 atm. With $\sigma_{12} = 1.2 \times 10^{-3} \text{ (}^\circ\text{K}^{-1}\text{)}$ (see Figure 3.11),

$$Y_{2B} - Y_{2T} \approx + 0.04$$

and,

$$Y_{2B} - Y_{2T} \approx + 0.02$$

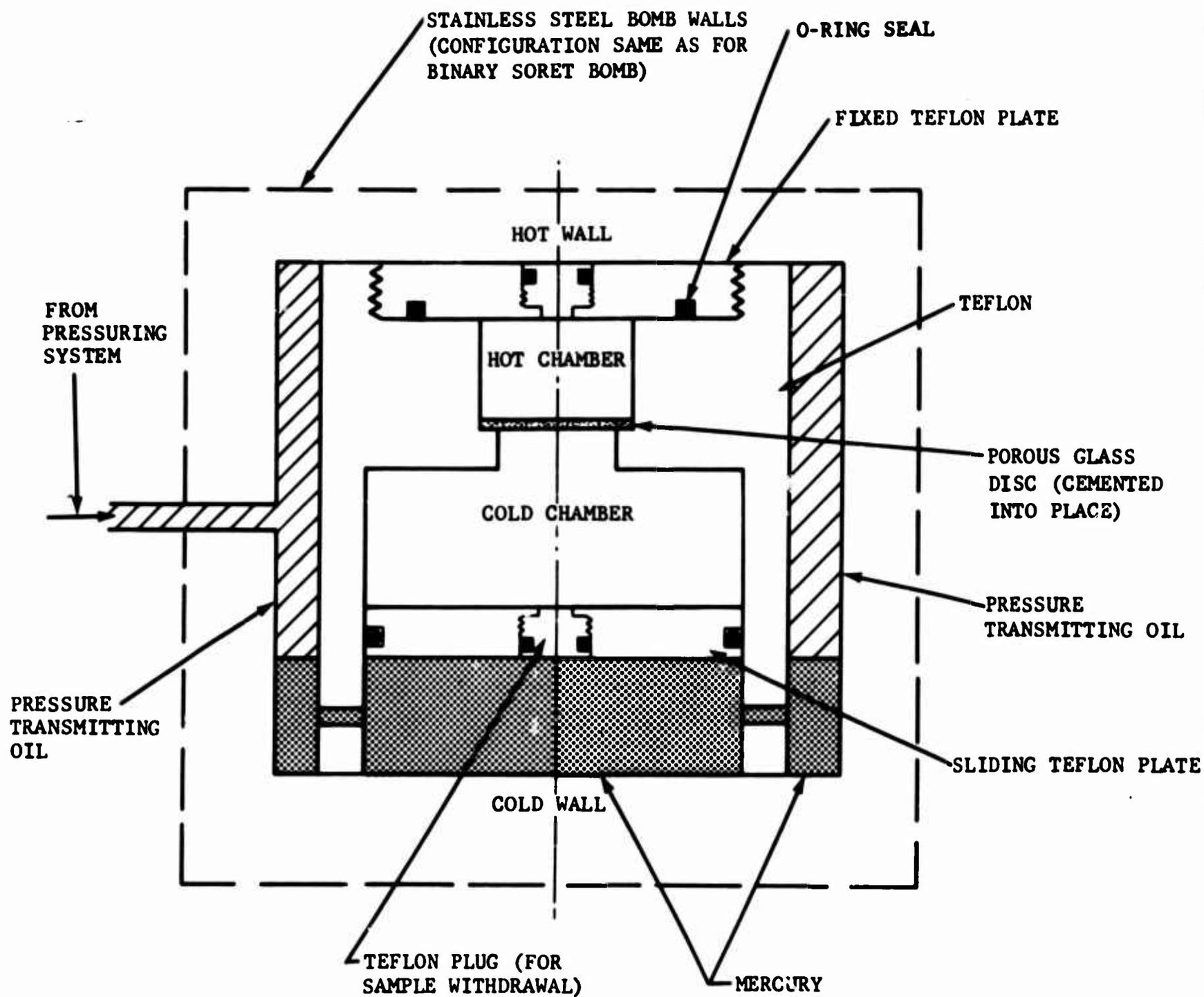
would be the expected concentration differences (in weight percent) for the end sampling and center dividing type multicomponent Soret cells, respectively. Only the Teflon wall, center dividing type cell (without metal parts exposed to the salt solution) yielded measured salt separations comparable to those expected for this type of cell (see Experiments MCSC-18 and MCSC-19).

Since there is always some question as to the effect of a cellophane diaphragm on ion transport rates, a porous glass diaphragm would be a more appropriate choice.

The most desirable multicomponent Soret cell for high pressure

(or atmospheric pressure) measurements is shown in Figure 3.12. It would be contained in a cavity similar in configuration to that used for the binary Soret bomb (see Figure 3.6). Oil and mercury would transmit the pressure to the solution in the Teflon cell via a freely moving o-ring sealed Teflon piston.

The cold chamber would have a much greater capacity than the hot chamber in order to minimize the effect of solution transport through the membrane into the cold chamber during depressurization. No difficulty would be encountered during pressurization since the solution in both chambers would be of uniform concentration.



P11044

FIGURE 3.12. SORET CELL FOR MULTICOMPONENT SALT SOLUTIONS AT HIGH PRESSURE

SECTION 4

VISCOSITY AND THERMAL CONDUCTIVITY OF MULTICOMPONENT SALT SOLUTIONS

4.1 INTRODUCTION

In connection with the program of experimental measurements of the ordinary diffusion coefficient and Soret coefficient in binary and multicomponent salt solutions, a review and analysis of existing literature on the molecular viscosity and thermal conductivity of such electrolytes recently has been carried out. It was desired to relate, where possible, the available information on these other two basic transport properties to the mass diffusional properties. Both experimental viscosity and thermal conductivity data, and methods for correlating and predicting these two properties were included in this study.

As has been pointed out earlier in the literature (34) (47), the available experimental data for sea water itself are meager with regard to viscosity, and absolutely lacking in the case of thermal conductivity. Corresponding data for other multicomponent salt solutions likewise are sparse, and apparently have been obtained only in a few special cases of practical interest or where unusual effects were anticipated. Considerable experimental data on the viscosity of simple binary salt solutions are available, however, covering ranges of concentration and temperature, and, to a lesser extent, of pressure. Thermal conductivity data for binary

electrolytes are somewhat more limited, and are generally reported only for various concentrations.

The primary objective of this review has been the correlation and prediction of the viscosity and thermal conductivity of multicomponent salt solutions as functions of concentrations, temperature, and pressure. Emphasis here has been given to the study of sea water compositions in the temperature range 0°C-30°C and the pressure range 1-1000 atm. A secondary and continuing objective has been, and is, the development of theoretical bases for relating molecular viscosity and thermal conductivity to the mass diffusional transport properties being studied in this investigation.

The discussion to follow will include a preliminary assessment of sea water as a multicomponent salt solution, a review and analysis of the available data and predictions of viscosity and thermal conductivity for those systems which have been studied in detail, and an outline of theoretical relationships between transport properties which might be useful in correlating measurements of the ordinary diffusion coefficient and the Soret coefficient.

4.2 COMPOSITION OF SEA WATER

Inasmuch as the emphasis on multicomponent salt solutions arises solely from the eventual goal of predicting or measuring the transport properties of sea water, a brief consideration of the ionic composition of sea water should be appropriate in the framework of the discussion of simpler salt systems in sections to follow. Defant (7) has given typical compositions of sea water samples having salinities* ranging from 33 gm/kg

* "Salinity" as conventionally defined may be approximately taken to be the weight of dissolved salts (in grams) per kilogram of sea water.

up to 38 gm/kg; an average ionic composition, corrected to a "standard" salinity of 35 gm/kg, is shown in Table 4.1. In this table, the ions H^+ , HCO_3^- , and $H_2BO_3^-$ are listed only as nominal constituents, inasmuch as their true concentrations (excluding undissociated CO_2 and H_3BO_3) will depend on the pH, which is variable from point to point in the oceans.

Another manner of considering the composition of sea water might be in terms of its component salts, or, rather, in terms of the various binary salt solutions which would have to be mixed together in order to synthesize sea water. One possible breakdown along these lines is shown (for a salinity of 35 gm/kg) in Table 4.2, in which priority has been given to the logical "major" binary salt components, and in which the total ion concentration in each individual solution has been fixed at the sea water average of $\sim 1.156M$ for this salinity. It is seen that a few of these component solutions, such as " $CaSO_4$ " and " H_2CO_3 ", are obviously hypothetical at the stated concentrations in view of solubility limitations. Nevertheless, at least the first five salts ($NaCl$, $MgCl_2$, $MgSO_4$, $CaSO_4$, and K_2SO_4) are predominantly formed upon evaporation of sea water to dryness, and have been so identified in the solid crystalline phase.

It is apparent, from either Table 4.1 or 4.2, that sodium chloride is by far the predominating binary salt component of sea water. From Table 4.2, it is seen that the sea water salt system is approximately 83 weight percent $NaCl$ and 11 weight percent $MgCl_2$, so that these two salt components total nearly 94 percent by weight of the entire system. Accordingly, sea water itself is not truly a very good example of a complex multicomponent salt solution, inasmuch as its properties, to a first approximation, might be taken equal to those of a sodium chloride solution of the same concentration, and furthermore, to a second and somewhat better approximation, might be taken equal to those of a mixture containing a major proportion of sodium chloride and a minor proportion of magnesium chloride. The appropriate validity of these approximations will be demonstrated in the discussions to follow.

TABLE 4.1

AVERAGE IONIC COMPOSITION OF SEA WATER

(S = Salinity = 35 gm/kg)

<u>Ions</u>	<u>Molality (~ Molarity, in dilute solution)</u>
Na ⁺	0.4797
K ⁺	0.0103
Mg ⁺⁺	0.0553
Ca ⁺⁺	0.0108
Sr ⁺⁺	0.0002
(H ⁺)	0.0035
Cl ⁻	0.5641
Br ⁻	0.0008
SO ₄ ⁼	0.0291
(HCO ₃ ⁻)	0.0025
(H ₂ BO ₃ ⁻)	0.0004

TABLE 4.2

HYPOTHETICAL COMPOSITION OF SEA WATER
IN TERMS OF COMPONENT SALT SOLUTIONS

(S = Salinity = 35 gm/kg)

<u>Solution</u>	<u>Wt. % of Sea Water</u>
0.578 <u>M</u> NaCl	82.72
0.386 <u>M</u> MgCl ₂	10.97
0.578 <u>M</u> MgSO ₄	2.33
0.578 <u>M</u> "CaSO ₄ "	1.94
0.386 <u>M</u> K ₂ SO ₄	1.38
0.578 <u>M</u> "H ₂ CO ₃ "	0.43
0.578 <u>M</u> HBr	0.14
0.578 <u>M</u> H ₃ BO ₃	0.04
0.386 <u>M</u> "Sr(H ₂ BO ₃) ₂ "	0.03
0.578 <u>M</u> "SrSO ₄ "	0.02

4.3 VISCOSITY OF ELECTROLYTE SOLUTIONS

4.3a Viscosity Data

(1) Sea Water

The available, published data on the viscosity of sea water compositions consist of the original observations of Krümmel (26) and the more recent values of Miyake and Koizumi (33), Darmois and Darmois (6), and Korf and Zakharova (24). The first two of these four cover the concentration range from zero up to ~40 gm/kg salinity and the temperature range 0°C to 30°C; the third consists only of a series of observations on undiluted sea water at 28°C, and the fourth covers a higher concentration range of sea water brines and the temperature range -10°C to 20°C. In Figure 4.1 these data (with the exception of reference 24, which could not be obtained as of the date of this writing) are plotted in the form of "reduced viscosity" μ_r versus weight percent salts in solution ($\frac{\text{salinity}}{10}$), where μ_r is defined as:

$$\mu_r = \frac{\mu}{\mu_w} \quad (4.1)$$

in which μ_r is reduced viscosity,

μ is measured viscosity of solution at given concentration and temperature, and

μ_w is measured viscosity of pure water at the same temperature.

Reduced viscosity is a more sensitive and, at the same time, more universal basis for comparing data of several investigators than would be the measured absolute viscosity in centipoises.

The lines shown in Figure 4.1 represent the approximate "best fits" for 5° temperature increments in the range 0°C-30°C. Within the scatter of the data, these lines of reduced viscosity versus concentration were taken to be linear and (with the exception of 25°C and 30°C temperatures) were drawn so as to pass through the origin ($\mu_r = 1$). In subsequent discussion it will be shown that some curvature at low concentrations would be predicted theoretically.

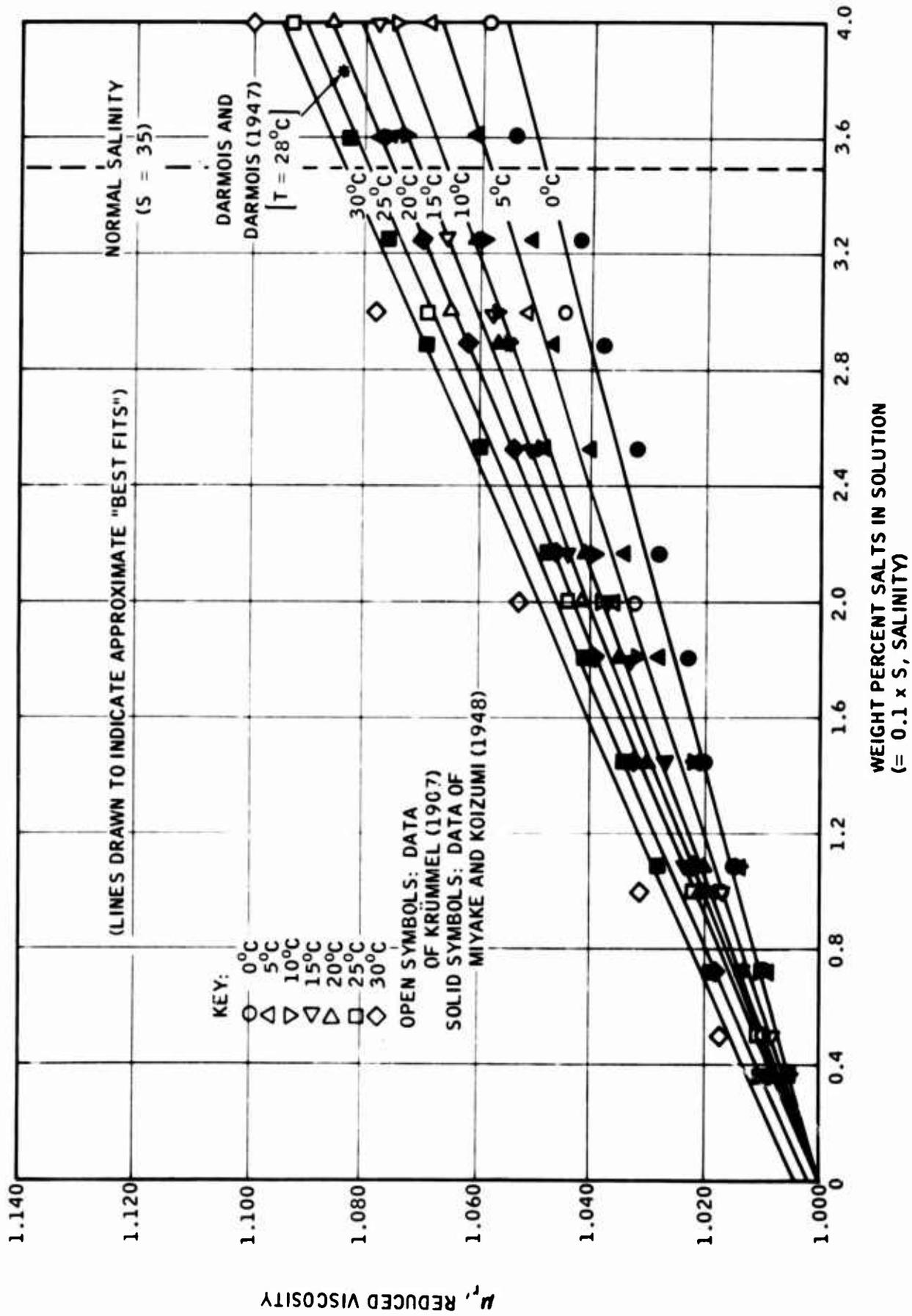


FIGURE 4.1. COMPARISON OF AVAILABLE EXPERIMENTAL MEASUREMENTS OF THE VISCOSITY OF SEA WATER AT ATMOSPHERIC PRESSURE

As far as could be discerned from a survey of the literature, the viscosity of sea water solutions apparently never has been measured as a function of pressure, or for temperatures higher than 30°C.

(2) Other Multicomponent Systems

A limited number of investigations of the viscosities of other multicomponent salt solutions have been reported in the literature. In a recent study of viscosities of the systems $\text{CdCl}_2\text{-MCl-H}_2\text{O}$, where $\text{M} = \text{H}^+, \text{Li}^+, \text{Na}^+, \text{K}^+, \text{and } \text{NH}_4^+$, Galinker, Tyagai, and Fenerli (15) found that in every case the viscosities of mixtures were lower than might have been predicted from simple additivity, owing to the formation of MCd^{+++} complex ions. In an earlier investigation, Tollert (45) had observed a similar interaction in the case of $\text{MgCl}_2\text{-KCl-H}_2\text{O}$, indicating the presence of the complex ion KMg^{+++} . Based upon these findings, some interaction influence in the case of sea water might be expected by virtue of formation of the complex cation NaMg^{+++} , but any such effect would be relatively minor in view of the nearly 10:1 non-stoichiometric, disproportionate excess of Na^+ over Mg^{++} .

(3) Binary Salt Solutions

As might be expected, the great bulk of experimental data on the viscosity of aqueous electrolyte solutions pertain to simple, binary salt solutions. Of primary interest here will be such data on sodium chloride solutions at various concentrations and temperatures. In Figure 4.2 is shown a comparison between the reduced viscosities of sea water solutions and sodium chloride solutions at concentrations from zero to 20 weight percent, and for temperatures in the range 0°C-60°C, where the sodium chloride lines represent the smoothed and averaged data of Sergeevich, Zhuze, and Chestnov (41, 48) and of Suryanarayana and Venkatesan (42). The latter data actually extend up to saturation (~26-27 weight percent NaCl), and will be shown for this range in a subsequent plot; a direct comparison with sea water in the vicinity of "saturation" would not be meaningful, however, inasmuch as sea water, as a multicomponent mixture, does not have a unambiguously-definable "solubility limit".

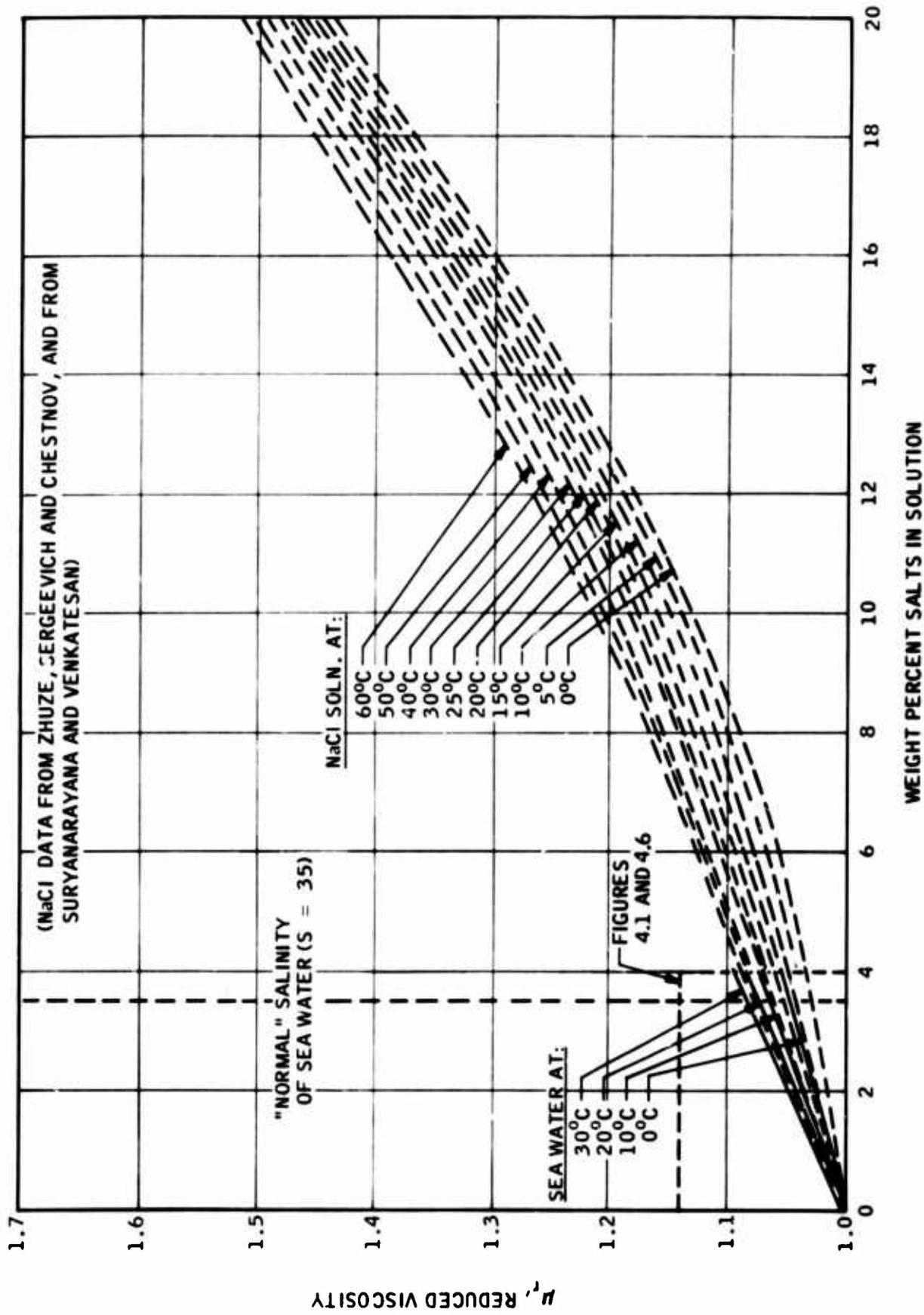


FIGURE 4.2. COMPARISON OF SMOOTHED EXPERIMENTAL VISCOSITY DATA FOR SEA WATER AND AQUEOUS SODIUM CHLORIDE SOLUTIONS AT ATMOSPHERIC PRESSURE

It is seen from Figure 4.2 that sea water solutions at any given weight percent concentration and temperature are more viscous than the corresponding sodium chloride solutions. In the concentration region of normal sea water (~ 35 mg/kg salinity or 3.5 weight percent), the viscosity ratio of sea water to sodium chloride is approximately 1.020 at all temperatures. As will be shown later, this difference is that which would be expected from the contributions of the minor salt ions in sea water.

(4) Pressure Effect

The viscosity data presented up to this point have all represented values at essentially atmospheric pressure. In considering the effect of pressure on viscosity, it is instructive to first consider pure water, for which reasonably extensive data are available. In Figure 4.3 is shown a plot of "relative viscosity" ($\frac{\mu_p}{\mu_0}$) versus pressure for pure water at temperatures in the range 0°C to 75°C , where μ_p is the viscosity at pressure "p" and μ_0 is the viscosity at zero pressure (essentially that at 1 atm). The curves shown represent averages, at least in the lower-pressure range, between the values of Bridgman (4) and the earlier values of Cohen (5). It is seen that viscosity rises with pressure at the higher temperatures, whereas at the lower temperature ($< \sim 30^\circ\text{C}$) there is a small initial decrease in viscosity, followed by a subsequent rise.

For oceanographic purposes only the pressure range 1-1000 atm is of general interest. Figure 4.4 expands this relatively small region of Figure 4.3, for which the relative viscosity of pure water varies only from 0.92 to 1.08 over the entire temperature range 0°C to 75°C . In Figure 4.4 and 4.5 are shown, for comparison with the water data, the relative viscosities of sodium chloride solutions in the concentration range 0-20 weight percent and the temperature range 5°C to 40°C , representing the smoothed data of Sergeevich, Zhuze, and Chestnov (41, 48) for pressures up to 500 atm. (It is understood, in the definition of "relative viscosity" for salt solutions, that " μ_p " and " μ_0 " both refer to solutions of a given concentration, rather than to pure water.) It is seen that the effect of adding

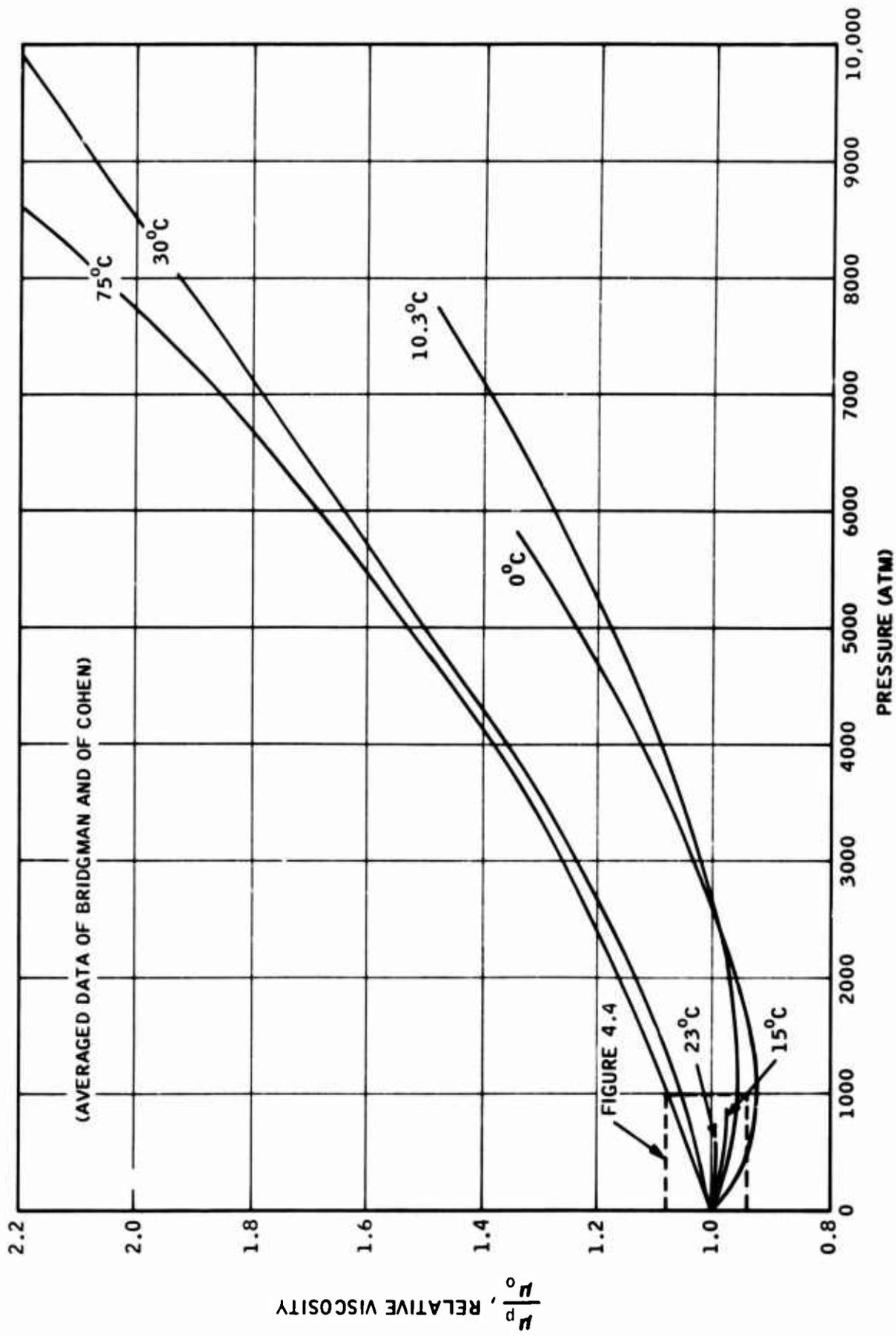


FIGURE 4.3. EFFECT OF PRESSURE ON RELATIVE VISCOSITY OF PURE WATER AT VARIOUS TEMPERATURES

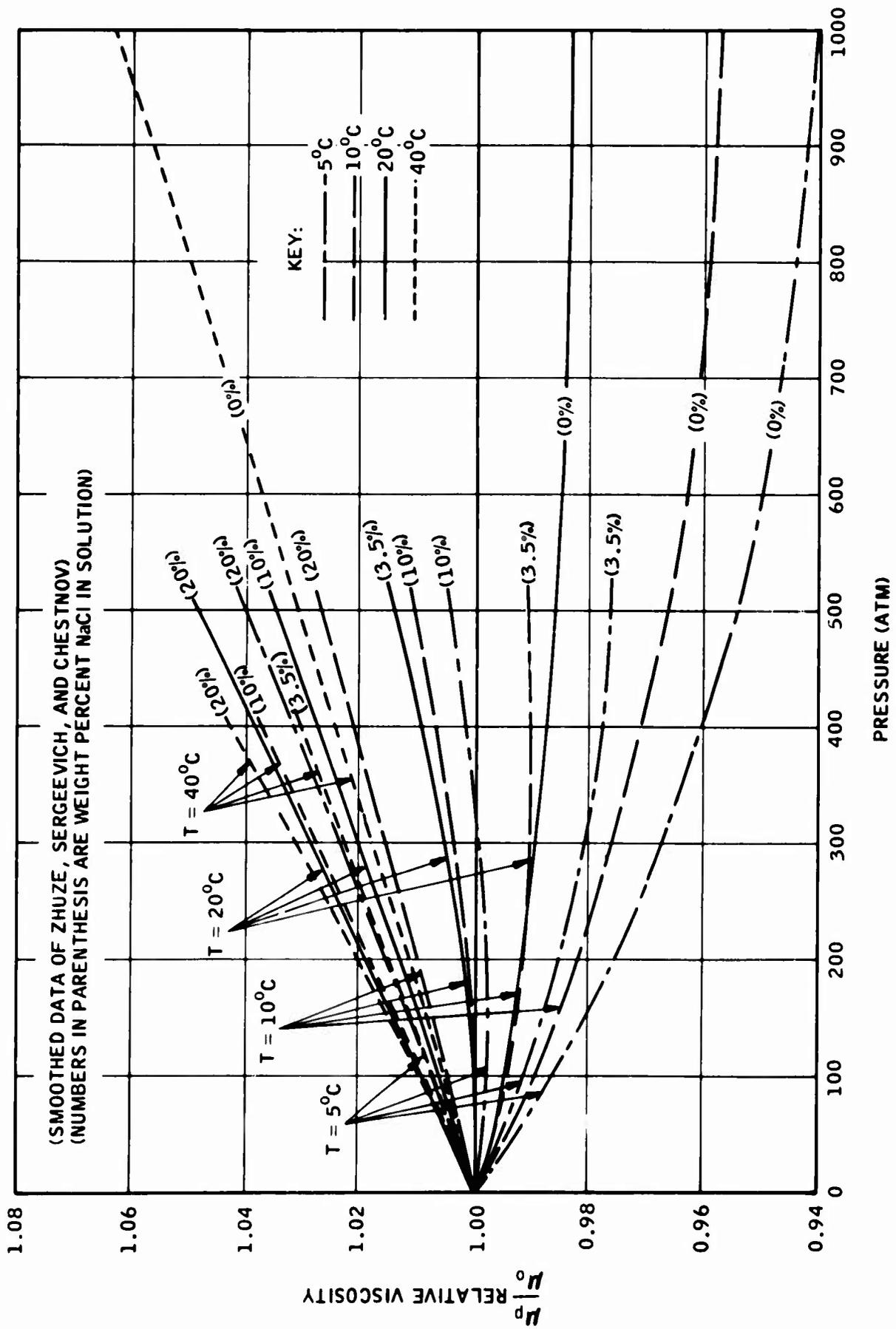


FIGURE 4.4. RELATIVE VISCOSITIES OF AQUEOUS SODIUM CHLORIDE SOLUTIONS IN THE PRESSURE RANGE 0 - 1000 ATM, TEMPERATURE RANGE 5°C - 40°C

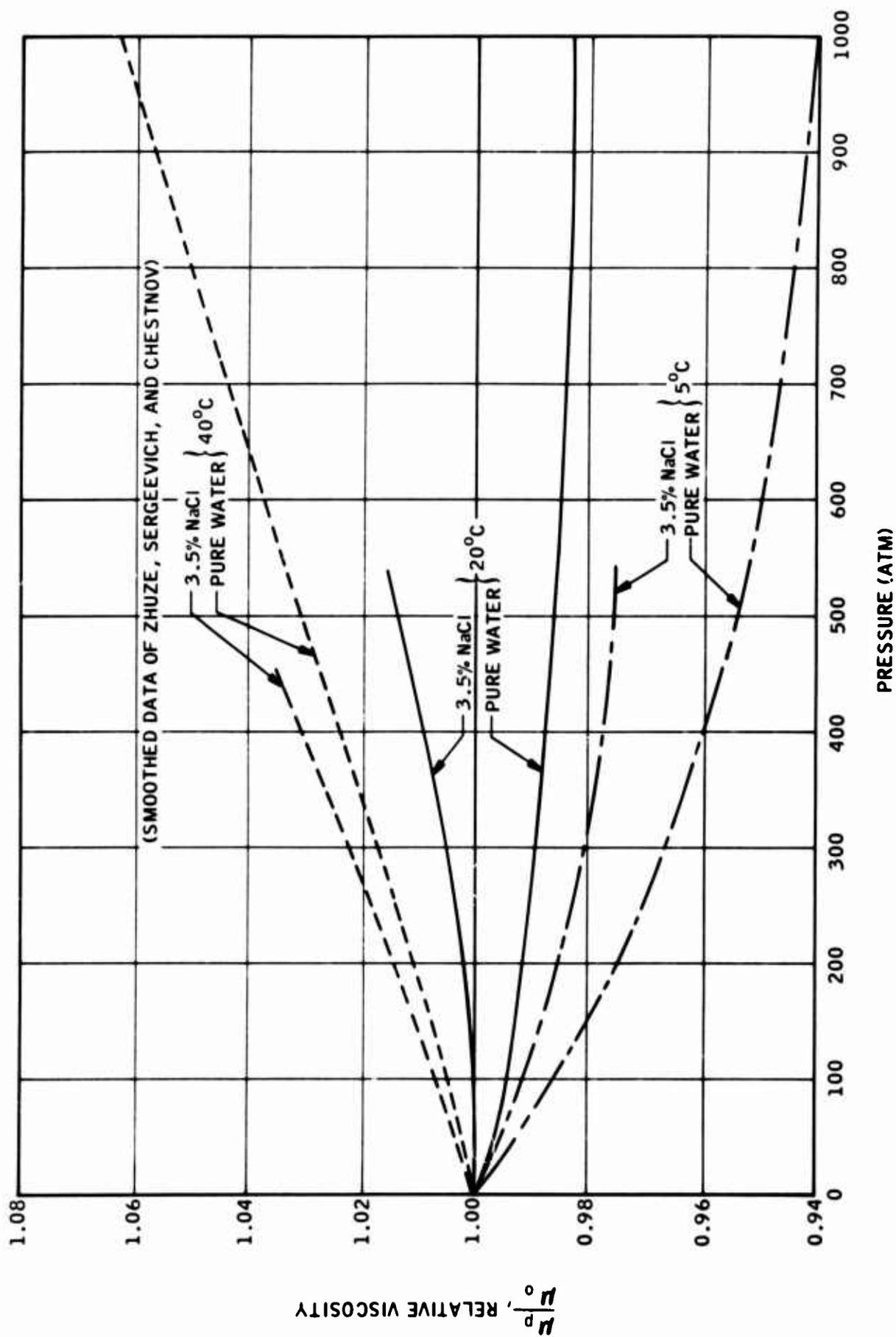


FIGURE 4.5. RELATIVE VISCOSITIES OF AQUEOUS SODIUM CHLORIDE AND PURE WATER IN THE PRESSURE RANGE 0-1000 ATM, TEMPERATURE RANGE 5°C - 40°C

salt to water is to make the pressure effect more positive in every instance. For example, at a temperature of 20°C, the viscosity of pure water at 500 atm pressure is 1.4 percent less than at 1 atm, whereas that of 3.5 weight percent sodium chloride solution at 500 atm pressure is 1.4 percent greater than at 1 atm.

b) Viscosity Correlations

Numerous methods for correlating the viscosities of electrolyte solutions versus concentration, temperature and pressure have been proposed, some having at least partial theoretical justification, and others being no more than strictly empirical. Of these various correlations, the more-accepted ones recently have been reviewed in a survey article by Kozłowska (25). The method consistently receiving the greatest attention, at least in the correlation of viscosity versus concentration, has been that based upon the original equation of Jones and Dole (18), which, in its more generalized form, is now written as follows:

$$\mu_r = 1 + A\sqrt{C} + BC + DC^2 \quad (4.2)$$

in which μ_r is reduced viscosity,

C is concentration, moles/liter,

A, B and D are coefficients, having the units (moles/liter)^{-½}, (moles/liter)⁻¹, and (moles/liter)⁻², respectively.

The "A" coefficient in this equation can be calculated theoretically for simple systems, while any determination of the "B" and "D" coefficients is at least partly empirical, and must be based on experimental values. While other correlations of viscosity versus concentration have been suggested, they generally have been found to be less satisfactory.

The variation of viscosity of electrolyte solutions with temperature normally is correlated by means of an Arrhenius-type relationship, in which viscosity, in effect, is considered as a reciprocal "rate constant" for viscous flow. The Arrhenius activation energy thus obtained for the solution, however, generally has only been related semiempirically to the

electrolyte concentration, as, for example, in terms of the percentage of saturation (27, 44). The relatively meager data available on the viscosities of electrolyte solutions at elevated pressures has been correlated with the changes of conductivity resulting from increases in pressure (35).

Most correlations or predictions of viscosity have been applied to the relatively less-complicated case of simple binary electrolytes. Those few correlations valid for mixtures generally have been based upon some sort of additivity principle, in which experimental knowledge of the contributions of each individual ion or salt component is required as input.

The various methods for correlating or predicting the viscosities of aqueous electrolyte solutions will be discussed in further detail, and inferences will be drawn where appropriate regarding their applicability toward the sea-water system.

(1) The Jones-Dole Correlation

The "complete" Jones-Dole correlation expressed by equation 4.2 can be considered in somewhat simpler form in regions of either very low or very high concentration. The limiting law first proposed by Falkenhagen (10) for the case of extreme dilution is the following:

$$\mu_r = 1 + A\sqrt{C} \quad (4.3)$$

From considerations of Debye-Hückel theory, in which the ions are considered to act as point charges, the coefficient "A" can be predicted theoretically, either for binary electrolytes, or, by suitable definition of the "ionic strength" for mixtures. The positive coefficient "A" generally has a numerical value in the vicinity of $0.006 \text{ (moles/liter)}^{-\frac{1}{2}}$ for monovalent electrolytes, and in the range $0.01\text{-}0.03 \text{ (moles/liter)}^{-\frac{1}{2}}$ for electrolytes containing polyvalent ions (25). Thus, for the concentration region ($<0.01M$) where equation 4.3 by itself truly does represent the sole effect of concentration on viscosity, the maximum measurable increase in viscosity over that of pure water is only a small fraction of one percent.

For electrolyte concentrations in the range $0.01M < C < 1.0M$ the "classical" form of the Jones-Dole equation is a reasonably good approximation:

$$\mu_r = 1 + A\sqrt{C} + BC \quad (4.4)$$

At concentrations much higher than this, however, a small quadratic term is required, as indicated by equation 4.2 for the general case. One misconception which is sometimes taken for granted is that both of the non-linear terms $A\sqrt{C}$ and DC^2 can be completely neglected throughout an intermediate concentration region (i.e., from $0.1M$ to $1.0M$), so that the viscosity equation could be written simply as:

$$\mu_r \approx 1 + BC \quad (4.5)$$

To be sure, viscosity-concentration relationships may be essentially linear in this region, but the lines thus obtained do not extrapolate back to the origin ($\mu_r = 1$). More correctly, the quasi-linear relation at intermediate concentration should be written as:

$$\mu_r \approx (1 + X) + (B + Y)C \quad (4.6)$$

in which "X" and "Y" represent small, but not completely negligible contributions from the non-linear terms. Indeed, if equation 4.6 is made to satisfy exactly both value and derivative at the inflection point of the true equation 4.2:

$$X = \left(\frac{3}{16}\right)(A)^{4/3}(D)^{-1/3} \quad (4.7)$$

$$Y = \left(\frac{3}{2}\right)(A)^{2/3}(D)^{1/3} \quad (4.8)$$

Unlike the coefficients "A" and "D", both of which are always positive, the coefficient "B" in the Jones-Dole equation can, in relatively rare instances, take on a negative value. In general, however, the coefficient "B" is positive, and of sufficient order of magnitude to account for most of the observed increase in the viscosity of electrolytes over that of pure

water. Ion hydration (particularly of cations) has been assumed to account for the major positive contribution to the "B" coefficient, whereas breaking of the structure of the adjacent water (particularly by anions) may lead to what is observed as a "negative viscosity" effect (19, 20). Both of these influences may be classed as "ion-solvent" interaction, in contrast to the "ion-ion" interaction which determines the value of the "A" coefficient.

Several correlations of the Jones and Dole "B" coefficient versus other measurable or calculable properties of electrolyte solutions have been proposed. Bramhall (3), for example, has proposed an empirical correlation between viscosity and density, in which relative increase (or decrease) in viscosity coefficient "B" is found to be proportional to the percentage contraction (or expansion) of the water volume fraction. Fisher and Zaitseva (13), on the other hand, have derived a theoretical procedure, based upon a hydrodynamic theory of ion motion, for estimating the contribution of ion hydration alone to the overall "B" coefficient; their method, however, does not account for the Coulomb ion-ion interaction contribution in the concentration region where the Debye-Hückel formalization begins to break down.

Perhaps the most widely used, albeit strictly empirical, method for estimating values of the "B" coefficient for binary electrolytes has been that based upon the additivity of individual " B_{ion} " contributions. It has been found, for example, that the viscosity of aqueous K_2SO_4 can be estimated reasonably well from the additivity principle and the known viscosity behavior of aqueous KCl, NaCl, and Na_2SO_4 . Inasmuch as no ion in solution can exist by itself, the assignment of individual " B_{ion} " values must be somewhat arbitrary. Kaminsky (19, 20) has proposed such an assignment based upon the starting assumption that $B_{K^+} \equiv B_{Cl^-} \equiv \frac{1}{2}(B_{KCl})$ at all temperatures.

A natural temptation with the " B_{ion} " method would be to assume that the additivity principle (based on ionic molarities) holds true for

multicomponent as well as for binary electrolytes. As will be pointed out later, this assumption is probably an oversimplification; but nonetheless, for a mixture such as sea water (which is dominated by the two major ions Na^+ and Cl^-), it may yield surprisingly accurate predictions. A comparison between reduced viscosity values for sea water solutions (a) predicted from this assumption and (b) representing averaged experimental data accordingly is shown in Figure 4.6 for the concentration range 0 - 4 percent, and the temperature range 0 - 35°C. By comparison of Figure 4.6 with Figure 4.1, it is seen that the predictions generally agree with the experimental data within the limits of uncertainty of the data itself.

(2) Other Viscosity-Concentration Correlations

Several authors (25, 35) concerned with electrolyte viscosity have chosen to apply the classical Jones-Dole equation in its "inverse" form, i.e., in terms of reduced fluidity rather than reduced viscosity:

$$\frac{1}{\mu_r} = \frac{\mu_w}{\mu} \approx 1 - A\sqrt{C} - B'C - D'C^2 \quad (4.9)$$

in which B' and D' are new coefficients having the units (moles/liter)⁻¹ and (moles/liter)⁻², respectively. In the region of extreme dilution where Falkenhagen theory is applicable, the relative changes in viscosity are so small that the coefficient "A" has essentially the same value whether equation 4.2 or equation 4.9 is used. The empirically determined "B'" and "D'" coefficients, on the other hand, are somewhat different numerically than their "B" and "D" counterparts. Indeed, if the missing " $C^{3/2}$ " term and corresponding higher terms are added to create a homologous series, the new coefficients of the "inverse" Jones-Dole equation then can be exactly related mathematically to the coefficients of the "conventional" Jones-Dole equation.

Another type of viscosity-concentration correlation has been the empirical "exponent" method proposed by Andrussov (1,2). In this correlation,

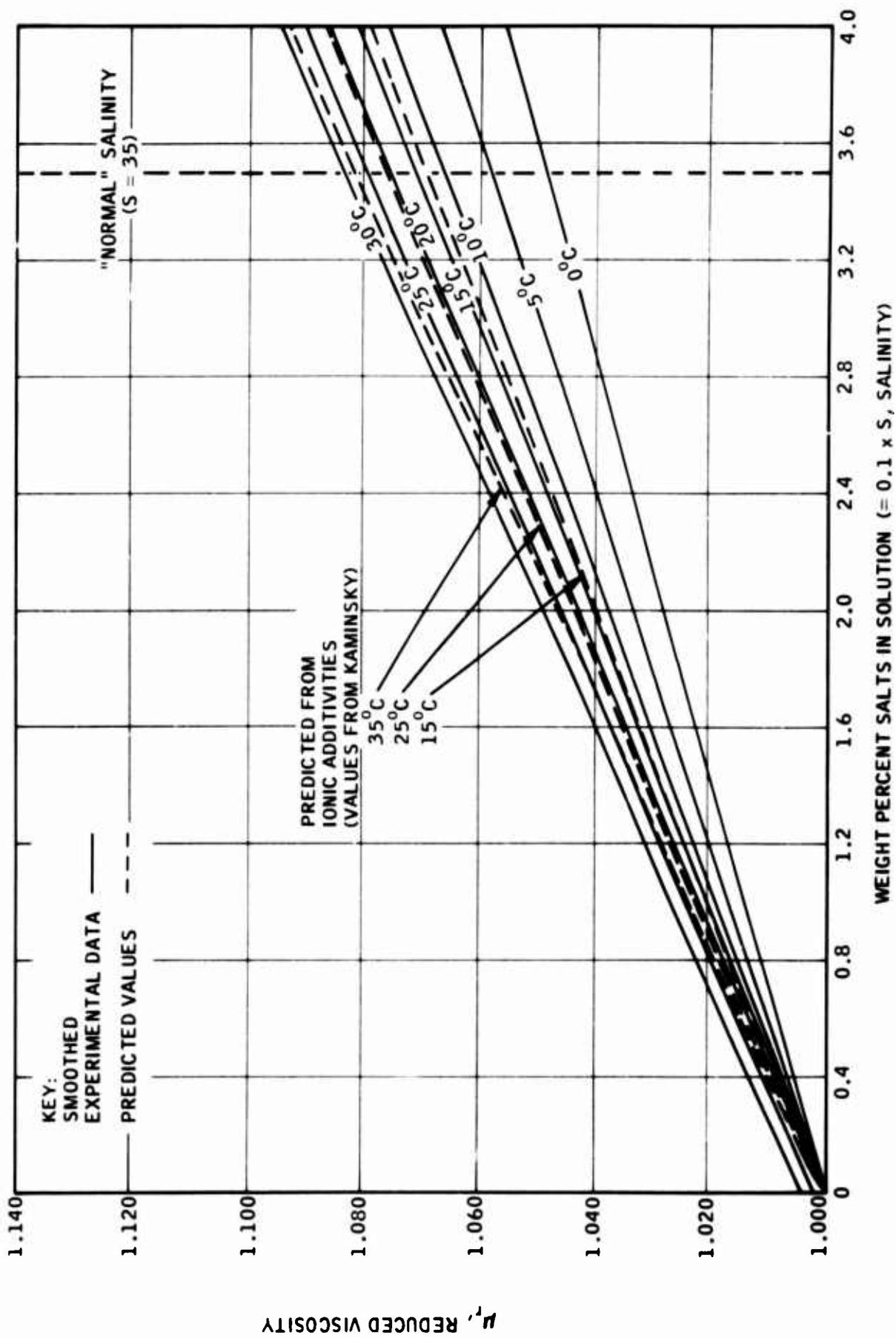


FIGURE 4.6. COMPARISON BETWEEN PREDICTED AND EXPERIMENTAL VALUES OF THE VISCOSITY OF SEA WATER AT ATMOSPHERIC PRESSURE

viscosity and concentration are related exponentially as follows:

$$\frac{\mu_2}{\mu_1} \approx \left[\frac{C_2}{C_1} \right]^\Psi \quad (4.10)$$

in which μ_2 and μ_1 are viscosities at concentrations C_2 and C_1 , respectively, and where the exponent " Ψ " itself is correlated by means of a "Jones-Dole" type expansion:

$$\Psi \approx \Psi_0 + a(C_2 - C_1)^{1/2} + b(C_2 - C_1) + c(C_2 - C_1)^{3/2} + \dots \quad (4.11)$$

(units of a, b, c, etc. are (moles/liter)^{-1/2},
(moles/liter)⁻¹, (moles/liter)^{-3/2}, etc.)

Normally, the "reference" concentration " C_1 " is fixed at some arbitrarily low level ($\sim 0.001M$) in the region where viscosity can be described by the ideal Falkenhagen theory.

The advantage claimed by Andrussow for the "exponent" method was that the empirical coefficients " Ψ_0 ", "a", "b", "c", etc. were much less dependent on temperature than are the coefficients "A", "B", and "D" of the Jones-Dole equation. Offsetting this advantage, however, as later pointed out by Kaminsky (21) is the disadvantage that the coefficients " Ψ_0 ", "a", "b", "c", etc. are truly constant only over a relatively limited range of concentrations, so that several sets of coefficients must be specified to cover the entire concentration range from zero up to saturation. Indeed, if equations 4.3, 4.10 and 4.11 are combined and simplified for the case of very small values of " C_1 ", the result is:

$$\mu_{r2} = \frac{\mu_2}{\mu_w} \approx 1 + \ln \left[\frac{C_2}{C_1} \right] \left[\Psi_0 + a\sqrt{C_2} + bC_2 + cC_2^{3/2} + \dots \right] \quad (4.12)$$

from which it is seen that any direct correspondence with the general form of the Jones-Dole correlation is impossible, owing to the presence of the highly non-linear " $\ln \left[\frac{C_2}{C_1} \right]$ " factor.

One final method of correlating the viscosities of both electrolytes and non-electrolytes as functions of concentration, especially for concentrations in the vicinity of saturation, is that originally proposed by Suryanarayana and Venkatesan (42, 43), as follows:

$$\frac{\mu}{\mu_s} \approx \alpha e^{\beta \left(\frac{C}{C_s} \right)} \quad (4.13)$$

in which μ_s is viscosity of the saturated solution at a given temperature, α and β are constants for any given temperature, and C_s is the saturation solubility at the given temperature.

Kume and Tanaka (27, 44) later attempted to generalize and improve this type of correlation to include temperature effects as well, and did find that for most aqueous electrolytes a plot of " $\ln \left(\frac{\mu}{\mu_s} \right)$ " versus " $\left(\frac{C}{C_s} \right)$ " yielded points on a single smooth (but not-quite-linear) curve, irrespective of either temperature or concentration, rather than on a series of straight lines for different temperatures, as would be predicted from equation 4.13. They were unable, however, to characterize these curves, except empirically for each electrolyte.

(3) Viscosity-Temperature Correlations

Most correlations of electrolyte viscosity versus temperature have been based upon equations of the Arrhenius type, similar to those used to correlate the viscosities of pure liquids:

$$\mu \approx K e^{E_{vis.}/RT} \quad (4.14)$$

in which μ is viscosity, cp.

K is pre-exponential factor, cp.

$E_{vis.}$ is energy of activation for viscous flow, kcal/mole.

T is temperature, $^{\circ}K$.

$R = 0.001987$ Kcal/mole- $^{\circ}K$.

The activation energy for viscous flow " $E_{vis.}$ " can be predicted theoretically. in the case of non-associated liquids, by means of the theory of rate processes originally developed by Eyring (8).

In Figure 4.7, Arrhenius-type viscosity-temperature correlations are compared for pure water, normal sea water ($S = 35$ gm/kg), and aqueous sodium chloride solutions from 3.5 weight percent concentration up to saturation. It is seen that the electrolyte viscosities as functions of temperature generally parallel that of pure water, so that any effect of concentration on the total activation energy for viscous flow must be relatively minor. It is also apparent that the activation energy " $E_{vis.}$ " for water alone varies rather substantially with temperature, ranging from ~ 5.0 Kcal at 0°C down to ~ 3.0 Kcal at 100°C . The variation, however, is continuous throughout the entire temperature regime; there is no unusual effect at or below 0°C (as is the case with electrolytic conductivity).

It is evident from equation 4.14 that if both the viscosity of water and the viscosity of aqueous electrolytes approximately follow the Arrhenius law, reduced viscosity " μ_r " also should follow this law. From Figures 4.1 and 4.2 it can be seen that the reduced viscosities of sea water and of aqueous sodium chloride generally increase slightly with rising temperature, so that the total activation energies " $E_{vis.}$ " for the electrolyte solutions are slightly less than that of pure water. However, attempted Arrhenius correlations of reduced viscosities versus temperature showed that " $\Delta E_{vis.}$ " (the difference in activation energy between the electrolyte and pure water) varied too widely over even small ranges of temperature for this type of correlation to be of much value. Kaminsky (19, 20) encountered similar behavior in attempting to correlate the Jones-Dole individual " B_{ion} " contributions versus temperature. From consideration of equation 4.2 for the generalized Jones-Dole correlation, it is of course apparent that reduced viscosity " μ_r " and Jones-Dole coefficient " B " cannot both follow the Arrhenius relationship simultaneously.

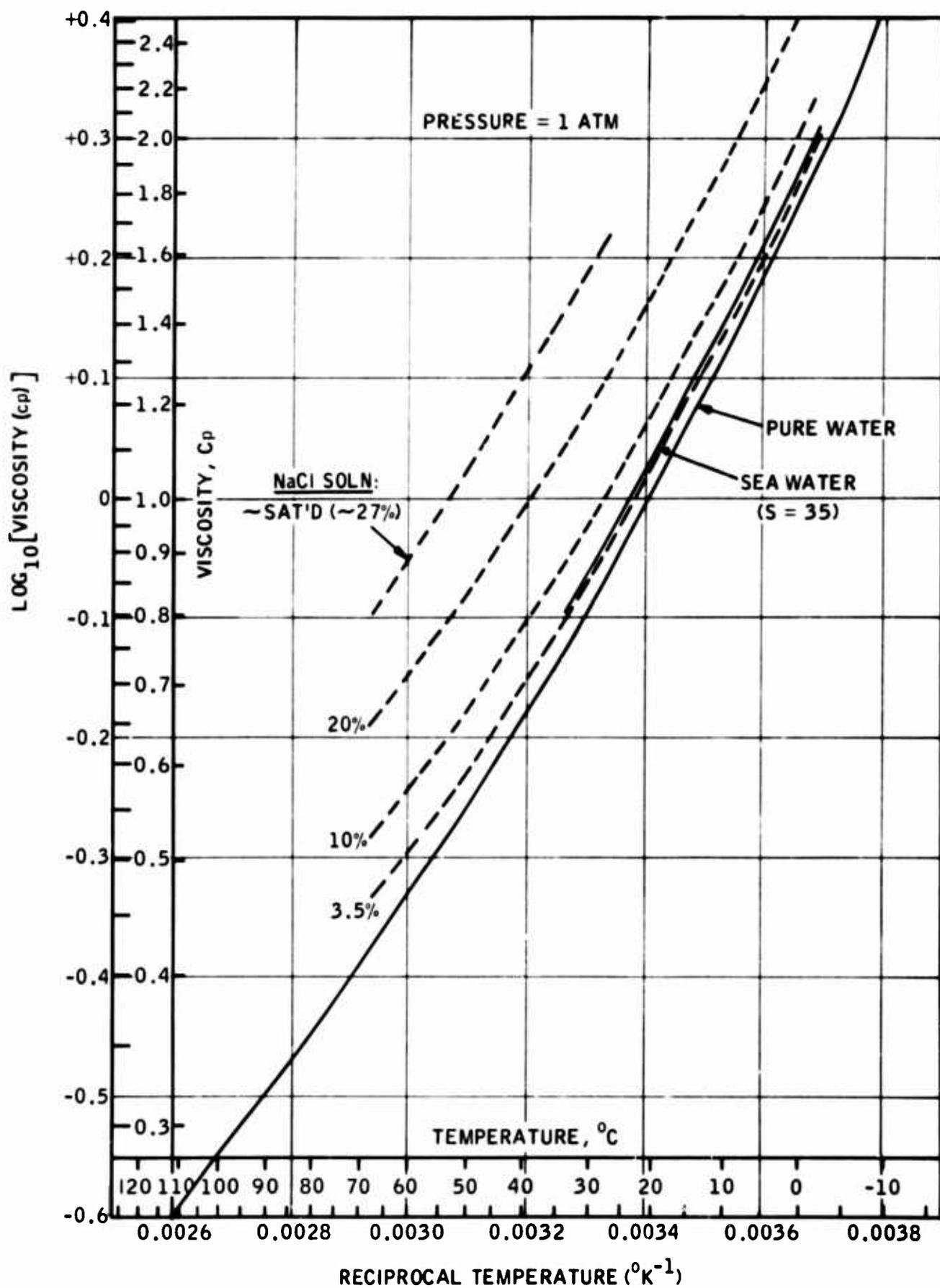


FIGURE 4.7. VISCOSITY-TEMPERATURE VARIATION FOR PURE WATER, SEA WATER, AND AQUEOUS SODIUM CHLORIDE SOLUTIONS

The "degree of saturation" correlations of viscosity versus concentration by Kume and Tanaka (27, 44) have already been mentioned. In correlating certain electrolyte viscosities versus temperature, they found that a better Arrhenius-type fit could be obtained if viscosity at a constant percentage of saturation were correlated, rather than viscosity at a fixed nominal concentration (weight percent or molality). The resulting equation was:

$$\left(\frac{\mu_r}{\mu_s}\right)_{C_s} = S_x = [K_r(S_x)] e^{-\frac{[E_r(S_x)]}{RT}} \quad (4.15)$$

in which S_x is "degree of saturation", and where $K_r(S_x)$ and $E_r(S_x)$ are empirical functions of S_x which are characteristic for any electrolyte.

Rao and Panicker (37) determined the viscosities of certain supersaturated electrolyte solutions, and found that, at a fixed concentration, viscosity followed a decreasing linear relationship with rising temperature for some electrolytes, and the more usual exponential or "Arrhenius" relationship with temperature for others. They apparently did not observe any anomalous behavior of viscosity in the vicinity of the saturation point itself. Fujita (14), on the other hand, found apparent small discontinuities in the activation energies for viscous flow of dilute Na_2CO_3 solutions at the two temperatures where corresponding discontinuities in saturation solubility occur, and cited similar observed abnormalities of electrolytic conductivity for dilute Na_2SO_4 solutions. It is not known whether any such anomalous behavior exists in the case of a complex mixture such as sea water.

(4) Viscosity-Pressure Correlations

Aside from theoretical relationships between viscosity and pressure proposed for pure, nonassociated liquids (4), little attention has been given to correlating viscosity with pressure for aqueous solutions of electrolytes. Podolsky (35) has outlined a method based upon experimental knowledge of the effect of pressure on electrical conductance, but

was able to test it only in the two cases of aqueous KCl and aqueous NaCl. In view of the relatively poor agreement between data and theory apparently obtained in the latter case, this correlation may not be of too much value in predicting the very small second-order effect of electrolyte concentration on relative viscosity at elevated pressure.

(5) Viscosity Correlations for Multicomponent Electrolytes

As pointed out in the previously-cited review article by Kozłowska (25), the viscosities of multicomponent electrolyte solutions have been correlated empirically both on a basis of ionic strength and on a basis of total molarity (or molality). Galinker, Tyagai and Fenerli (15) recently proposed some alternative "additivity" relations (for mixtures of non-polar liquids and the like) which might be valid for aqueous electrolytes as well:

Additivity of viscosities:

$$\mu \approx \mu_1 x_1 + \mu_2 x_2 + \dots \quad (4.16)$$

Additivity of cube roots of viscosities:

$$\mu^{1/3} \approx \mu_1^{1/3} x_1 + \mu_2^{1/3} x_2 + \dots \quad (4.17)$$

Additivity of logarithms of viscosities:

$$\log \mu \approx x_1 \log \mu_1 + x_2 \log \mu_2 + \dots \quad (4.18)$$

Additivity of kinematic fluidities:

$$\frac{\rho}{\mu} \approx x_1 \left(\frac{\rho_1}{\mu_1} \right) + x_2 \left(\frac{\rho_2}{\mu_2} \right) + \dots \quad (4.19)$$

in which μ is viscosity.

x is mole fraction, and

ρ is density;

Subscripts "1", "2", etc. refer to component 1, component 2, etc.

In applying these four relations to multicomponent electrolyte solutions, of course, the "components" would be understood to be the minimum necessary number of binary salt solutions (of roughly equal concentrations) to make up the mixture, rather than merely the individual

solid crystalline salts plus water. Accuracy moreover could be improved by replacing absolute viscosities with reduced viscosity differences, as follows:

Additivity of viscosities:

$$(\mu_r - 1) \cong (\mu_{r_1} - 1)x_1 + (\mu_{r_2} - 1)x_2 + \dots \quad (4.20)$$

Additivity of cube roots of viscosities:

$$(\mu_r^{1/3} - 1) \cong (\mu_{r_1}^{1/3} - 1)x_1 + (\mu_{r_2}^{1/3} - 1)x_2 + \dots \quad (4.21)$$

Additivity of logarithms of viscosities:

$$\log_{10} \mu_r \cong x_1 \log_{10} \mu_{r_1} + x_2 \log_{10} \mu_{r_2} + \dots \quad (4.22)$$

Additivity of kinematic fluidities:

$$\frac{\rho_r}{\mu_r} \cong x_1 \left(\frac{\rho_{r_1}}{\mu_{r_1}} \right) + x_2 \left(\frac{\rho_{r_2}}{\mu_{r_2}} \right) + \dots \quad (4.23)$$

The various "additivity" rules, equations 4.20 through 4.23, were tested for the sea water system, and were found to yield essentially equally good predictions of viscosity. Equation 4.20, of course, will be recognized to be equivalent to the additivity-of-" B_{ion} " method used in calculating the predictions shown in Figure 4.6. Galinker et al.(15), on the other hand, postulated that the latter three relations are better for predicting mixture viscosity in the general case. In view of the relative domination of the sea water system by the two ions Na^+ and Cl^- , linear additivity (equation 4.20) is probably as good an assumption as would ever be required for any practical purpose.

(6) Sample Predictions of Sea Water Viscosity

Inasmuch as the theoretical or empirical methods of prediction just discussed appear to offer little or no advantage over what experimental data is available, the recommended method embodies use only of experimental correlations.

(a) Predict the viscosity of ordinary sea water ($S = 35 \text{ gm/kg}$) at 5°C and 500 atm.

$$\mu \text{ of H}_2\text{O at } 5^\circ\text{C, 1 atm} = 1.519 \text{ cp} \quad [\text{Figure 4.7}]$$

$$\mu_r \text{ of 3.5\% sea water at } 5^\circ\text{C, 1 atm} = 1.059 \quad [\text{Figure 4.1}]$$

$$\frac{\mu_p}{\mu_o} \text{ of 3.5\% NaCl at } 5^\circ\text{C and 500 atm} = 0.976 \quad [\text{Figure 4.4}]$$

$$\begin{aligned} \mu \text{ of 3.5\% sea water at } 5^\circ\text{C and 500 atm} \\ \approx (1.519)(1.059)(0.976) = \underline{1.570 \text{ cp.}} \end{aligned}$$

(b) Predict the viscosity of 10% sea water brine at 60°C and 1 atm.

$$\mu \text{ of H}_2\text{O at } 60^\circ\text{C, 1 atm} = 0.470 \text{ cp.} \quad [\text{Figure 4.7}]$$

$$\frac{(\mu_r)_{\text{sea}}}{(\mu_r)_{\text{NaCl}}} \text{ at any given weight concentration} \approx 1.020 \quad [\text{Figure 4.2}]$$

$$\mu_r \text{ of 10\% NaCl at } 60^\circ\text{C and 1 atm} = 1.212 \quad [\text{Figure 4.2}]$$

$$\begin{aligned} \mu \text{ of 10\% sea brine at } 60^\circ\text{C and 1 atm} \\ \approx (0.470)(1.020)(1.212) = \underline{0.581 \text{ cp.}} \end{aligned}$$

4.4 THERMAL CONDUCTIVITY OF ELECTROLYTE SOLUTIONS

a. Thermal Conductivity Data

(1) Sea Water

No published data apparently are available on the thermal conductivity of sea water. Krümmel (26) once estimated thermal conductivity values at 17.5°C for sea water salinities from zero up to $S = 35 \text{ gm/kg}$ by making the rather questionable assumption that the thermal diffusivity of sea water was everywhere equal to that of pure water. His resulting values are plotted in Figure 4.8 for comparison with presently predicted sea water values and available experimental data for aqueous NaCl.

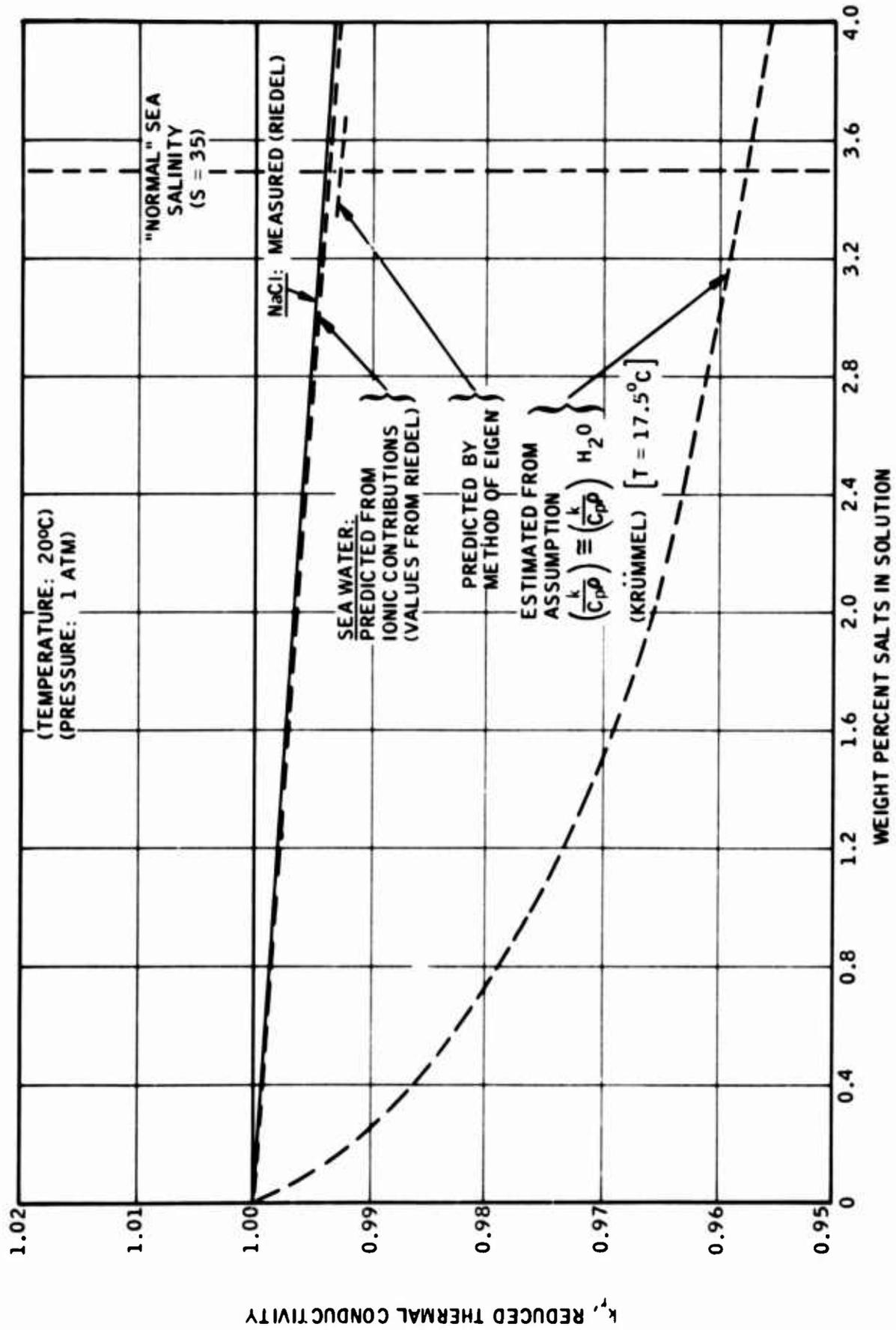


FIGURE 4.8. COMPARISON OF PREDICTED THERMAL CONDUCTIVITY OF SEA WATER AND MEASURED THERMAL CONDUCTIVITY OF SODIUM CHLORIDE SOLUTIONS

(2) Binary Salt Solutions

A fair amount of thermal conductivity data for binary electrolyte solutions is available, although most of it pertains only to room-temperature conditions. In general, with only a few exceptions, thermal conductivity drops with increasing electrolyte concentration, although the relative effect is much smaller than is the case for viscosity. Riedel (39) has tabulated thermal conductivity data for NaCl solutions (along with many other salts, acids, and bases) at concentrations from zero up to saturation and for a temperature, in general, of 20°C. For all practical purposes the change (decrease) in thermal conductivity for most salts appears to be linear with concentration (molarity) throughout the entire range.

In Figure 4.8 the "reduced" thermal conductivity function (k_r) for sodium chloride is plotted versus concentration in the range zero to four percent by weight, and with " k_r " defined, analogously to " μ_r ", as follows:

$$k_r = \frac{k}{k_w} \quad (4.24)$$

in which k_r is reduced thermal conductivity

k is thermal conductivity of electrolyte, cal/cm-sec-°C.

k_w is thermal conductivity of pure water, cal/cm-sec-°C.

It is seen that, at the 3.5 weight percent concentration level, the change in thermal conductivity of aqueous NaCl relative to that of pure water amounts to only 0.6 percent. In subsequent discussion, a comparison will be made between experimental thermal conductivity values for NaCl and predicted thermal conductivities for sea water, as indicated in Figure 4.8.

On the basis of thermal conductivity measurements for relatively concentrated solutions of NaOH and KOH in the temperature range 0°C to 80°C, Riedel (38) concluded that any effect of temperature on reduced thermal conductivity " k_r " for these two systems was negligible, or at least was much smaller than the " k_r "-concentration effect itself.

In line with this finding, Riedel (39) further proposed (in the study previously cited) that the same assumption should hold true for any binary electrolytes considered. Thus, the reduced thermal conductivity correlation for aqueous NaCl solutions shown in Figure 4.8 might be presumed to hold true over a wide range of temperatures, rather than merely at 20°C.

(3) Pressure Effect

No data apparently are available on the thermal conductivities of aqueous electrolytes at superatmospheric pressures. In view of the relatively weak effects of concentration and temperature on reduced thermal conductivity " k_r " (as compared to the corresponding effects on reduced viscosity " μ_r "), it might be reasonable to assume that the presence of a dissolved salt in water leads to no special effect of pressure on thermal conductivity, and that pressure dependence for aqueous electrolytes can be satisfactorily approximated by that for pure water.

The variation in the absolute thermal conductivity of pure water with temperature and pressure, as reported by Bridgman (4), is shown in Figure 4.9. It is seen that the thermal conductivity of water increases only by about 20 percent as temperature is raised from 0°C to 100°C (and, in fact, goes through a maximum in the temperature region above 100°C). It is further seen that thermal conductivity, at various temperatures, increases by about 6 percent with an elevation in pressure to 1000 atm. The pressure effect is roughly comparable to that observed in the case of viscosity, but the influence of temperature, obviously, is much less.

b. Thermal Conductivity Correlations

(1) Relations of the "Jones-Dole" Type

If the temperature and pressure dependence of the thermal conductivity of aqueous electrolytes are taken to be that of pure water, the only remaining correlation of interest is that which relates thermal

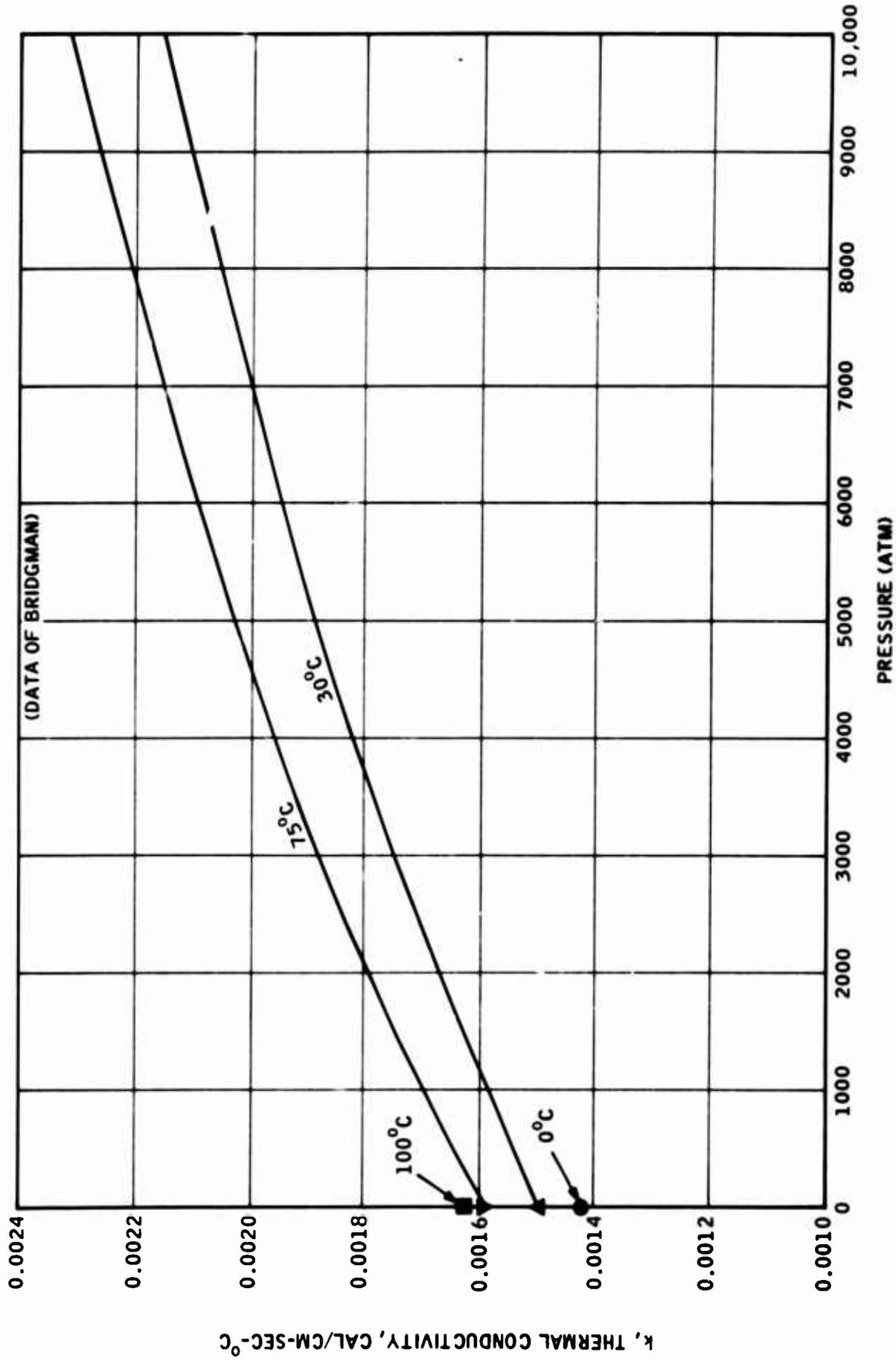


FIGURE 4.9. EFFECT OF TEMPERATURE AND PRESSURE ON THERMAL CONDUCTIVITY OF PURE WATER

conductivity to concentration. Presumably a semi-empirical relation of the "Jones-Dole" type might apply:

$$k_r \approx 1 + a'\sqrt{C} + b'C + d'C^2 \quad (4.25)$$

in which k_r is reduced thermal conductivity,

C is concentration, moles/liter,

a' , b' , and c' are coefficients, having the units

of $(\text{moles/liter})^{-\frac{1}{2}}$, $(\text{moles/liter})^{-1}$, and $(\text{moles/liter})^{-2}$,

respectively.

Inasmuch as thermal conductivity for most aqueous electrolytes decreases with rising concentration, it should be expected that one or more of the coefficients a' , b' , and d' will prove to be negative in value.

A simplified version of equation 4.25 considered by Riedel (39) was based upon the finding that, for most neutral salts, the decrease in thermal conductivity is very nearly linear in molar concentration:

$$k_r \approx 1 + b'C \quad (4.26)$$

where b' is understood to be negative for most electrolytes. Riedel then split the b' coefficient up into b'_{ion} contributions, based upon $b'_{Na^+} = 0$, in a manner analogous to that previously discussed for the B coefficient in the Jones-Dole equation for viscosity. This assumption of the additivity of b'_{ion} contributions, at least for binary electrolytes, was deemed to be valid on the basis of the relatively extensive amount of data available for such systems.

As was done in the case of viscosity, the assumption of additivity of individual b'_{ion} contributions was applied to the sea water system. The resulting prediction is shown in Figure 4.8 for comparison with the experimental NaCl values and the previous estimation of Krümmel (26). For a concentration of 3.5 weight percent salts in solution ($S = 35$ gm/kg), the predicted reduced thermal conductivity of sea water is 0.9937, compared to the observed value of 0.9940 for aqueous sodium chloride at the same concentration. In contrast to this close correspondence, the " k_r " value estimated

for sea water by Krümmel, based upon the assumption of equal thermal diffusivities, was ~ 0.9575 . Apparently this crude an assumption is invalid for this type of comparison.

Litvinenko and Radchenko (29) also tested an equation of the "Jones-Dole" type:

$$k_r \approx 1 + a'\sqrt{C} + b'C \quad (4.27)$$

They found that values of b' were negative for nearly all aqueous electrolytes, whereas values of a' were small, but positive in a few cases. Their results will be further discussed in the section to follow.

(2) Correlations Based Upon Apparent Molal Thermal Conductivity

A second method of relating the change in thermal conductivity of an electrolyte to the proportion of dissolved salt has been that based upon the concept of apparent molal thermal conductivity, defined as follows:

$$\phi_k = \frac{(1000 + mM)k - 1000k_w}{m} \quad (4.28)$$

in which ϕ_k is apparent molal thermal conductivity, cal/cm-sec- $^{\circ}$ C,

m is molality, moles salt/1000 gms water,

M is molecular weight of salt, gm/mole, and

k_w is thermal conductivity of pure water, cal/cm-sec- $^{\circ}$ C.

Kapustinskiy and Ruzavin (22) attempted to show a linear correlation between ϕ_k and \sqrt{m} , in which values of the extrapolated limit, ϕ_k° , were taken to be an additive function of the contributions of the ions present.

Prudnikov (36), on the other hand, demonstrated that this type of correlation, at least for molalities in the vicinity of $1.0m$ and greater, was inconsistent with the experimentally-observed linear variation of total thermal conductivity with concentration.

Litvinenko and Radchenko (29), as cited previously, proposed a semi-empirical relation of the "Jones-Dole" type (equation 4.27) between

electrolyte thermal conductivity and concentration. They also examined the "partial molal thermal conductivity" concept, and found that by far the greater fraction of the limiting value ϕ_k^0 could be ascribed merely to volume changes between pure water and solution, and with thus only a small portion of ϕ_k^0 was actually related to ion-solvent interaction. A correspondence could be shown between this latter portion of ϕ_k^0 and their empirical b' coefficient in equation 4.27.

In view of the difficulty of defining a total mole quantity in a multicomponent mixture such as sea water, the apparent molal thermal conductivity approach appears to be of questionable value for predicting the behavior of such systems.

(3) Correlation Between Thermal Conductivity and Sonic Velocity

An entirely different approach to the correlation of thermal conductivity of aqueous electrolytes has been proposed by Eigen (9), who based his method on a demonstrated correspondence between thermal conductivity and sonic velocity. The thermal conductivity of pure water is considered to be the sum of two terms:

$$k_w = k_1 + k_A \quad (4.29)$$

in which k_w is the measured thermal conductivity of pure water, cal/cm-sec-°C,

k_1 is the (theoretically) calculated thermal conductivity of pure water as a non-associated liquid, cal/cm-sec-°C, and

k_A -- the difference between these two -- is the thermal conductivity anomaly of water arising from association, cal/cm-sec-°C.

In the case of an aqueous electrolyte, both contributions to the thermal conductivity are modified:

$$k = k_1' + k_A' \quad (4.30)$$

in which the primes denote values for the electrolyte solution.

The first term (k_1 or k_1') in equation 4.29 or equation 4.30 can be shown to be essentially proportional only to the sonic velocity:

$$k_1' \approx \left(\frac{U}{U_w} \right) k_1 \quad (4.31)$$

in which U is sonic velocity of electrolyte, m/sec, and

U_w is sonic velocity of pure water, m/sec.

Inasmuch as the sonic velocity in most electrolyte solutions is greater than that in pure water, k_1' may be expected to exceed k_1 for pure water. In contrast, the second term (k_A or k_A') in equation 4.29 or equation 4.30 is decreased in direct proportion to increasing electrolyte concentration:

$$k_A' \approx k_A(1 - \alpha'C) \quad (4.32)$$

in which α' is a constant, (moles/liter)⁻¹, and C is concentration, moles/liter. Values of the constant α' can be calculated for simple binary salt solutions if specific heat data are available for the electrolyte.

As an approximate application of this correlation, the thermal conductivity of ~3.5 percent ($S \approx 35$ gm/kg) sea water at 20°C and atmospheric pressure was predicted from equations 4.29 through 4.32, based upon sonic velocity data for sea water as summarized by Wilson (47), but with the constant α' in equation 4.32 calculated for binary NaCl electrolyte rather than for sea water. The result of this prediction was an estimated reduced thermal conductivity (k_r) value of 0.9928 at these conditions, which may be compared in Figure 4.8 to the value of 0.9937 predicted from ionic additivities. Since the former of these two values was arrived at by taking the difference between the positive " k_1 " correction and a larger and negative " k_A " correction (with approximations in both of these), the latter " k_r " value predicted by the relatively simpler (albeit more empirical) method is considered the better of the two.

(4) Sample Predictions of Sea Water Thermal Conductivity

Inasmuch as completely theoretical methods of predicting thermal conductivity for multicomponent salt solutions appear to offer no advantage over empirical procedures based primarily upon experimental data for binary salt solutions and for pure water, the latter are recommended.

(a) Predict the thermal conductivity of ordinary sea water ($S = 35$ gm/kg) at 5°C and 500 atm.

$$k \text{ of H}_2\text{O at } 5^{\circ}\text{C, 1 atm} = 0.001428 \text{ cal/cm-sec-}^{\circ}\text{C} \quad [\text{Figure 4.9}]$$

$$\frac{k_p}{k_o} \text{ of H}_2\text{O at 500 atm} \approx 1.031 \quad [\text{Figure 4.9}]$$

$$k_r \text{ of 3.5 percent sea water (20}^{\circ}\text{C, 1 atm)} = 0.994 \quad [\text{Figure 4.8}]$$

$$k \text{ of 3.5 percent sea water at } 5^{\circ}\text{C and 500 atm} \\ \approx (0.001428)(1.031)(0.994) = \underline{0.001463 \text{ cal/cm-sec-}^{\circ}\text{C}}$$

(b) Predict the thermal conductivity of 10 percent sea water brine at 60°C and 1 atm.

$$k \text{ of H}_2\text{O at } 60^{\circ}\text{C, 1 atm} = 0.001559 \text{ cal/cm-sec-}^{\circ}\text{C} \quad [\text{Figure 4.9}]$$

$$k_r \text{ of 10 percent sea water (20}^{\circ}\text{C, 1 atm)} \approx 0.982 \quad [\text{Extrapolated from Figure 4.8}]$$

$$k \text{ of 10 percent sea water brine at } 60^{\circ}\text{C and 1 atm} \\ \approx (0.001559)(0.982) = \underline{0.001531 \text{ cal/cm-sec-}^{\circ}\text{C}}$$

4.5 THEORETICAL RELATIONSHIPS BETWEEN TRANSPORT PROPERTIES

Considerable work has been reported in the investigation of theoretical relationships between viscosity, electrical conductivity, and diffusion coefficients in aqueous solutions of electrolytes. Thus far, those relations which have been developed either hold true only in extremely dilute solution, or else contain empirical elements requiring some experimental measurements before predictions can be extrapolated. Thus far no theoretical relations have been suggested between electrolyte thermal conductivity and any of these other three transport properties.

The simplest type of theoretical relationships between viscosity, electrical conductivity, and diffusion coefficient are those based originally

upon Walden's (46) rule, and more recently outlined by Robinson and Stokes (40), Harned and Owen (16), McLaughlin (31) and others:

$$\mu \propto \frac{1}{\Lambda} \quad (4.33)$$

$$D \propto \Lambda \quad (4.34)$$

in which μ is viscosity, cp,

Λ is equivalent conductance, $\frac{\text{mhos-cm}^2}{\text{equivalent}}$

D is diffusion coefficient, cm^2/sec , and

" \propto " indicates proportionality, but by an unspecified factor, and where Λ approximately can be defined as:

$$\Lambda \approx \frac{1000(L-L^0)}{C^*} \quad (4.35)$$

in which L is the specific electrical conductivity of the solution, mhos/cm.,

L^0 is specific electrical conductivity of pure water, mhos/cm., and

C^* is electrolyte concentration in eqivs./liter.

Equations 4.33 and 4.34 can, of course be combined to yield a reciprocal relation between viscosity and diffusion coefficient:

$$\mu \propto \frac{1}{D} \quad (4.36)$$

In using equations 4.33, 4.34, or 4.36, of course, it must be borne in mind that these relations apply only to very dilute ($<0.01M$) solutions of electrolytes, and for a given temperature and pressure.

For electrolytes of higher concentration, both equivalent conductance and diffusion coefficient have been correlated versus concentration by semi-empirical relationships of the "Jones-Dole" type (16):

$$\Lambda \approx \Lambda^0 \left[1 + A_{\Lambda} \sqrt{C} + B_{\Lambda} C \right] \quad (4.37)$$

$$D \approx D^0 \left[1 + A_D \sqrt{C} + B_D C \right] \quad (4.38)^*$$

* The third term was added in order to maintain consistency with Eq. 4.37.

in which Λ° is $\lim_{C \rightarrow 0} \Lambda, \frac{\text{mhos-cm}^2}{\text{equiv.}}$

D° is $\lim_{C \rightarrow 0} D, \text{cm}^2/\text{sec.}$

$A_{\Lambda}, B_{\Lambda}, A_D, B_D$ are coefficients having appropriate units.

In line with the limiting rules discussed previously, " A_{Λ} " and " A_D " are both negative, and both have essentially the same value as " $(-A)$ " in the conventional Jones-Dole expression for viscosity.

The similarity between these semiempirical laws for viscosity behavior and electrical conductance behavior has led to several proposed relationships between the two, valid over wide ranges of concentration and temperature. Falkenhagen and Leist (11,12), for example, have shown that calculable viscosity "corrections" must be applied when predicting electrical conductivity for electrolyte solutions in the region of high concentration. Other relationships between viscosity and electrical conductance have been proposed by Kelbg (23), and by Izmailov (17) (the latter, an empirical correlation of the product of the two versus temperature).

A somewhat different approach has been taken by workers in the field of irreversible thermodynamics, including Laity (28), and more recently, Miller (32) and Lorenz (30). Theoretical relationships have been derived between the Onsager interionic interaction coefficient L_{12} ($= L_{21}$) and both electrical conductance and diffusion coefficient. (The L_{12} coefficient arises when transport equations are written in terms of total ionic "flows" in a solvent-fixed reference frame, taking the place of the more conventional individual equations for mass diffusion and electrical conductance.) Miller (32) has pointed out, however, that no such theoretical relationships can exist between the solution viscosity and either of these other two transport properties, inasmuch as viscous phenomena differ from diffusion and thermal conduction phenomena in tensorial order.

The conclusion is drawn that any existing empirical correlations between viscosity (μ) and either D or Λ for electrolyte solutions of appreciable concentration must be strictly accidental.

Based upon all preceding considerations, it is concluded that no suitable completely theoretical relationships presently exist between either viscosity or thermal conductivity and the mass diffusion properties considered in Sections 2 and 3. If this is true in the relatively simple case of binary electrolytes, it should also be true in the case of multi-component mixtures such as sea water.

4.6 SUMMARY AND CONCLUSIONS

The molecular viscosity and thermal conductivity of binary and multicomponent salt solutions have been investigated by recourse to the pertinent literature. Both experimental data and methods of theoretical or semi-empirical prediction have been included in this study. The primary application of these data and methods has been directed toward estimation or calculation of the transport properties of sea water systems at various concentrations, temperatures, and pressures. A secondary emphasis has been given to methods for relating these two bulk transport properties to the individual molecular ordinary and Soret diffusion coefficients. The literature consulted for this study included more than 100 references covering work mostly reported during the past 20 years.

The following conclusions may be drawn from the studies undertaken to date:

(1) The viscosity behavior of reasonably dilute aqueous electrolyte solutions greatly resembles that of pure water, in that temperature has a much greater effect than either pressure or concentration. Viscosity, in other words, drops by a factor of nearly 10 as temperature is raised from 0°C to 100°C , whereas pressure effects over the range 1-1000 atm generally amount to less than ± 8 percent. The viscosity of a 3.5 weight

percent solution of either sodium chloride or sea water is higher than that of pure water by an amount ranging from 3 percent to 8 percent, depending on the temperature.

(2) The thermal conductivity of aqueous electrolytes generally appears to be less sensitive to either temperature, pressure, or concentration than viscosity. In the case of pure water, thermal conductivity increases by about 20 percent as temperature is raised from 0°C to 100°C, and increases by about 6 percent as pressure is elevated from 1 atm up to 1000 atm. The thermal conductivity of aqueous sodium chloride and most other similar salt solutions is less than that of pure water, but the relative decrease for a 3.5 weight percent concentration is less than 1 percent.

(3) For most practical purposes, sea water can be considered to be essentially a 3.5 weight percent solution of sodium chloride, but with a relatively minor proportion of magnesium chloride. In ordinary engineering calculations the bulk transport properties (that is, viscosity and thermal conductivity) of sea water can be estimated reasonably well from available data on sodium chloride solutions, although some corrections based upon data as yet unmeasured might be necessary in the case of more highly concentrated brines where the solubility limits of certain minor salt constituents of sea water would be exceeded. (An indication of available experimentally measured transport properties of pure water, aqueous sodium chloride, and sea water is shown in Table 4.3).

(4) Theoretical relationships do exist between viscosity, electrical conductance, and diffusivity but are strictly applicable only for the case of very dilute electrolyte solutions in which the ions can be considered to act as point charges which are effectively not hydrated by the solvent. Any relationships between viscosity or thermal conductivity and ordinary or Soret mass diffusion coefficients for salt solutions in a concentration region of practical interest would no doubt have to contain some elements of empiricism.

TABLE 4.3. AVAILABILITY OF TRANSPORT PROPERTY DATA

	VISCOSITY (μ)	THERMAL CONDUCTIVITY (K)
PURE WATER	TEMPERATURE: -10°C TO 374°C PRESSURE: 0 TO 11,000 ATM CONCENTRATION: (0% SALTS)	TEMPERATURE: 0°C TO 300°C PRESSURE: 0 TO 12,000 ATM CONCENTRATION: (0% SALTS)
AQUEOUS SODIUM CHLORIDE	TEMPERATURE: 0°C TO 55°C PRESSURE: 0 TO 600 ATM CONCENTRATION: 0% TO ~ 27%	TEMPERATURE: 20°C PRESSURE: 1 ATM CONCENTRATION: 0% TO ~ 27%
SEA WATER	TEMPERATURE: 0°C TO 30°C PRESSURE: 1 ATM CONCENTRATION: 0% TO 4% (+BRINES)	TEMPERATURE: _____ PRESSURE: _____ CONCENTRATION: _____

It should be noted that the results reported above include the first attempt to apply the semiempirical Galinker method to the prediction of the viscosity of sea water. In addition, several techniques were used to predict the thermal conductivity of sea water and the usual prediction method (equal thermal diffusivities) was shown to be in considerable error.

SECTION 5

GENERAL SUMMARY AND CONCLUSIONS

This investigation has resulted in the development of special high pressure cells capable of measuring the ordinary and thermal diffusion properties of binary salt solutions for pressures in the range of 1 to 1000 bars. The equipment was used to measure these properties for the 3.5 percent by weight sodium chloride—water system. The results were correlated with available approximate prediction techniques. All binary ordinary and thermal diffusion coefficient data available for the most predominate salts of the sea water system were compiled and analyzed.

Studies were made of the apparatus required in order to make meaningful measurements of the ordinary and thermal diffusion properties of multicomponent aqueous salt solutions such as sea water. Appropriate designs and operating techniques were developed based upon the results of these studies.

An extensive review and analysis was made of all available literature pertaining to the viscosity and thermal conductivity of salt solutions, including sea water. Several theoretical prediction methods were applied to the sea water system.

On the basis of the results obtained, the following general conclusions may be made (see Sections 2, 3, and 4 for more detail and supporting data):

- (i) the effect of pressure on both the ordinary diffusion coefficient and the Soret coefficient of the NaCl-H₂O system at 25°C in the pressure range of 1 to 1000 bars is sufficiently small that it can be neglected; the ordinary diffusion results are consistent with estimates based on various extrapolation methods;
- (ii) the binary diffusion properties of the major salt constituents of sea water are sufficiently different that the diffusion behavior of sea water probably can not be predicted on the basis of only the NaCl-H₂O system behavior; thus, a significant pressure effect could still exist for the sea water system even though none was found for the NaCl-H₂O system (at 25°C);
- (iii) the thermal diffusion effect in the NaCl-H₂O system is so temperature dependant that at about 7°C the Soret coefficient would be expected to be zero (no thermal diffusion effect) and at lower temperatures, the Soret coefficient takes on negative values — that is, the thermal diffusion effect is reversed and molecular salt transport can now occur from warm regions in the fluid to the colder regions instead of vice versa.
- (iv) the viscosity and thermal conductivity of dilute aqueous electrolyte solutions, including sea water, are very similar to the corresponding properties of pure water; the thermal conductivity appears to be less sensitive to temperature, pressure, and concentration than the viscosity; engineering estimates of these two bulk transport properties can be made by assuming that sea water is essentially a three and one half weight percent sodium chloride in water solution.

Two major areas will require further investigation. These are the multicomponent diffusion problem (oriented towards the sea water case) and the problem of how temperature affects the diffusion properties at

temperatures where the density of water exhibits a maximum with temperature ($\sim 4^{\circ}\text{C}$). Further binary experiments must be made with the $\text{NaCl-H}_2\text{O}$ system as well as the other binary aqueous salt solutions which constitute sea water in order to confirm the results so far obtained.

APPENDIX A.1

PROCEDURE FOR ORDINARY DIFFUSION COEFFICIENT MEASUREMENT AT HIGH PRESSURE

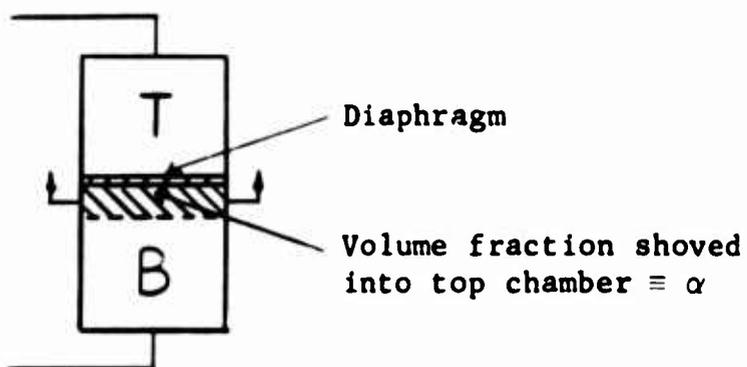
1. Disassemble the pressure cell completely. Wash all parts in hot water. (Use wire brush to remove rust before washing). Rinse in distilled water. Dry parts by acetone rinse and air dry.
2. Wash diffusion diaphragm in Special Vacuum Washing Apparatus, using distilled water. Rinse in acetone, and dry by pulling air through.
3. Boil stock NaCl solution under vacuum, and a supply of distilled water under vacuum.
4. Check condition of diaphragm. Measure bomb temperature. Place diaphragm in beaker of degassed NaCl solution. Put beaker under bell jar, and evacuate. Allow to stand under vacuum for 1 hour - shaking occasionally to dislodge bubbles. Flush diaphragm.
5. Assemble pressure cell in following order:
 - (a) install bottom closure piece, packing washers, etc. first. Place temporary plug in pressure inlet - making sure the capillary section is in place in the pressure inlet hole.
 - (b) Place cell on stand and fill bottom section with NaCl solution above diaphragm seat.
 - (c) Loosen temporary plug on bottom, and allow a few drops of salt solution to run out. Retighten, and note gas bubble evolution in cell. Repeat until no more gas is evolved. Dislodge any air bubbles from the cell side wall.

- (d) Press diaphragm into place, through the NaCl solution, using a piece of plastic pipe.
 - (e) Using a plastic syringe, remove excess NaCl solution from above the diaphragm. Be careful not to touch diaphragm with the syringe. Rinse top cell section 4 times with distilled water, removing each rinse before adding the next. Do not pour rinse directly on the diaphragm.
 - (f) Fill the top half of cell with distilled H₂O to ~½ inch above the sealing step. Dislodge bubbles, insert top sleeve liner, and squirt water between it and cell wall to dislodge bubbles.
 - (g) Start the run timer.
 - (h) Assemble the top closure piece, packing washers, drive nut, and knurled retaining cap. Insert smoothly, and screw down the driving nut. (Remove excess water as it is forced out the pressurizing line.)
 - (i) Insert the capillary section in top pressurizing hole.
6. Move assembled cell to bath, and connect pressurizing lines to top and bottom pressure inlets. Tape lines to cell body for alignment.
 7. Place cell in bath and start stirrer.
 8. Pressurize cell over desired time interval with the displacement pump. No stirring until pressure is reached.
 9. Allow stirring to continue for the desired time measuring the electrode pair resistances at regular time intervals. Depressurize over the desired time period.
 10. Stop stirrer and remove cell from the bath.
 11. Disconnect pressure connection at top of cell, and insert temporary plug. Turn cell over, and remove bottom pressure connection.
 12. Install retainer ring and remove bottom closure piece, washers, etc.
 13. Using a plastic syringe, remove bottom solution and transfer to sample bottle.
 14. Invert the cell and repeat with top section.
 15. Disassemble cell, and wash all parts thoroughly. Rinse with distilled water and acetone. Air dry. Check condition of diaphragm.

APPENDIX A.2

APPROXIMATE ESTIMATE OF THE BULK TRANSPORT OF SOLUTION
IN THE ORDINARY DIFFUSION BOMB ON DEPRESSURING

For Experiment ODBRS-13* (t_f to $t_{f'}$):



Mole Balance for Top Chamber:

$$\alpha V_B C_{B_f} + [V_T - \alpha V_B] C_{T_f} = V_T C_{T_{f'}} \quad (\text{A.1})$$

Mole Balance for Bottom Chamber:

$$(1 - \alpha) V_B C_{B_f} = V_B C_{B_{f'}} \quad (\text{A.2})$$

But $V_T \cong V_B$, therefore,

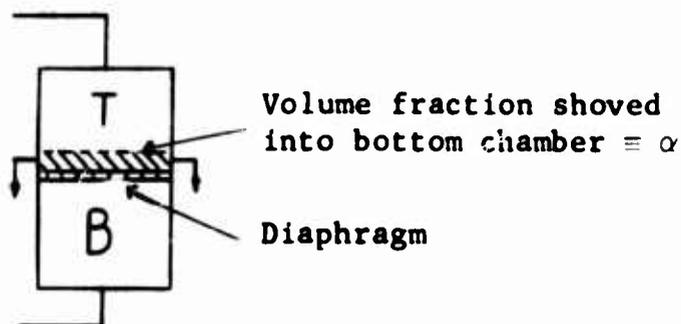
$$\alpha C_{B_f} + (1 - \alpha) C_{T_f} = C_{T_{f'}} \quad (\text{A.3})$$

$$(1 - \alpha) C_{B_f} = C_{B_{f'}} \quad (\text{A.4})$$

These two equations may be solved for the unknowns, α and C_{B_f} . The quantity, C_{B_o} , is then found from (see Eq. 14),

$$C_{B_o} = C_{B_f} + [C_{T_f} - C_{T_o}] \quad (A.5)$$

For Experiment ODBRS-13** (t_f to t_f'):



Mole Balance for Bottom Chamber:

$$\alpha V_T C_{T_f} + [V_B - \alpha V_T] C_{B_f} = V_B C_{B_f}' \quad (A.6)$$

Mole Balance for Top Chamber:

$$(1 - \alpha) V_T C_{T_f} = V_T C_{T_f}' \quad (A.7)$$

But $V_T \approx V_B$, therefore,

$$\alpha C_{T_f} + (1 - \alpha) C_{B_f} = C_{B_f}' \quad (A.8)$$

$$(1 - \alpha) C_{T_f} = C_{T_f}' \quad (A.9)$$

These last two equations may be solved for the unknowns, α and C_{B^f} . C_{B^o} is found from Eq. A.5. \bar{D}_{12} can then be calculated, using the electrode determined values of C_{T^o} and C_{T^f} , from Eq. 12.

It should be noted that C_{T^f} and C_{B^f} are the usual pipette cell measured concentrations measured for the solutions withdrawn from the ordinary diffusion bomb after depressurizing to 1 atm.

NOMENCLATURE

- a = coefficient in Eq. 4.11 (moles/liter)^{-1/2}
- a = height of binary Soret cell (cm)
- a' = coefficient in Eq. 4.25 (moles/liter)^{-1/2}
- A = diaphragm pore cross-sectional area available for diffusion (cm²)
- A = "Jones-Dole" coefficient (moles/liter)⁻¹
- b = coefficient in Eq. 4.11 (moles/liter)⁻¹
- b' = coefficient in Eq. 4.25 (moles/liter)⁻¹
- B = "Jones-Dole" coefficient (moles/liter)⁻¹
- B = property parameter in Eq. 18
- B' = coefficient in Eq. 4.9 (moles/liter)⁻¹
- c = coefficient in Eq. 4.11 (moles/liter)^{-3/2}
- C = molar concentration (moles/liter)
- C* = equivalent concentration (equiv/liter)
- d' = coefficient in Eq. 4.25 (moles/liter)⁻²
- D = "Jones-Dole" coefficient (moles/liter)⁻²
- D' = coefficient in Eq. 4.9 (moles/liter)⁻²
- D_{Fick} = Fick diffusion coefficient (cm²/sec)
- D₁₂ = binary ordinary diffusion coefficient (D₁₂ = D₂₁) (cm²/sec)
- E_r () = function defined in Eq. 4.15 (Kcal/mole)
- E_{vis} = activation energy for viscous flow (Kcal/mole)
- F = Faraday's constant
- f = a function of C_{B_f} and C_{T_f} (see Eq. 16)

- J_2 = flux density of species 2 (mole/cm²sec, or gm/cm² sec)
- k = thermal conductivity (cal/cm sec °C)
- k_A = thermal conductivity anomaly of pure water [Eqs. 4.29
and 4.32] (cal/cm sec °C)
- k_A' = thermal conductivity anomaly of electrolyte [Eqs. 4.30
and 4.32] (cal/cm sec °C)
- k_1 = ideal thermal conductivity of pure water [Eqs. 4.29
and 4.31] (cal/cm sec °C)
- k_1' = ideal thermal conductivity of electrolyte [Eqs. 4.30
and 4.31] (cal/cm sec °C)
- K = constant in Eq. 4.14 (cp)
- K_r () = function defined in Eq. 4.15 (cp)
- l = effective diffusion path length through diaphragm (cm)
- L = specific electrical conductivity (mhos/cm)
- L_{12} = Onsager interaction coefficient (units depend on associated
driving force and flux)
- m = molality (moles/1000 gms H₂O)
- M = molecular weight (gm/gm mole)
- \underline{M} = molarity (moles/liter)
- N_2 = mole flux of species 2 relative to stationary coordinates
(mole/cm²sec)
- N_o = Avogadro's number (6.023 x 10²³ molecules/gm mole)
- P = pressure (atm or bar)
- R = gas constant = 0.001987 (Kcal/mole °K)

- R = electrical resistance between a pair of electrodes (ohm)
- R_2 = radius of diffusing solute particle
- S = salinity (gm/Kg H₂O)
- S_x = degree of saturation $\left[\frac{C}{C_s}\right]$
- t = time (seconds)
- T = temperature (°K)
- v_i = velocity of species i (cm/sec)
- U = sonic velocity (m/sec)
- x = mole fraction
- x = distance measured up from cold wall in binary Soret cell (cm)
- X = constant defined in Eqs. 4.6 and 4.7
- X_i = thickness of section i in Soret bomb
- Y = constant defined in Eqs. 4.6 and 4.8 (moles/liter)⁻¹
- Y = weight percent
- y = mass fraction
- Z_i = ionic valence (including sign) of ion i ($z_i = 0$ for electrically neutral species, such as H₂O) ($|z_i|$ = number of protonic charges per ion = number of gm equivalents of ion i/gm mole of ion i)

Greek Symbols:

- α = constant defined in Eq. 4.13
- α = net volume fraction of solution in ordinary diffusion chamber which is bulk transported across cell diaphragm due to depressuring process (see Appendix A.2)
- α = signifies proportionality in Eqs. 4.33 and 4.34

- α' = constant defined in Eq. 4.32 (moles/liter)⁻¹
 β = cell constant (cm⁻²)
 β = constant defined in Eq. 4.13
 Δ_0 = difference between the value of the argument at pressure P and that at 1 atm
 λ_i = equivalent conductivity of ion i (mho cm²/gm-equivalent of ion i)
 θ = characteristic ordinary diffusion relaxation time (sec) =

$$\frac{a^2}{\pi^2 D_{12}}$$

 Λ = equivalent conductance $\left[\frac{\text{mhos cm}^2}{\text{gm equivalent}} \right]$
 μ = viscosity (cp or gm/cm sec)
 ρ = density (gm/cm³)
 π = 3.1416
 ϕ = partial molal quantity (units vary with application)
 ψ = function defined in Eqs. 4.10 and 4.11
 v_0 = coefficient defined in Eq. 4.11
 σ_i = multicomponent ionic Soret coefficient (°K⁻¹)
 σ_{12} = binary Soret coefficient ($\sigma_{12} = -\sigma_{21}$) (°K⁻¹)

Subscripts:

- B** = bottom chamber
D = denotes coefficient in Eq. 4.38
DP = diaphragm pores
F = feed solution
f = end of ordinary diffusion experiment before pressure has been reduced

- f' = end of ordinary diffusion experiment after pressure has been reduced to 1 atm
- i = species i
- ion = denotes coefficient for individual ion contribution
- k = denotes function with respect to thermal conductivity
- m = Monel
- o = start of ordinary or thermal diffusion experiment when pressure in bomb has been established
- o' = start of ordinary diffusion experiment before pressure has been increased from 1 atm
- P = denotes property at indicated pressure P
- r = denotes "reduced" property (ratio, electrolyte: pure water)
- r = phenolic resin
- s = denotes property at saturation
- T = top chamber
- w = denotes property for pure water
- w = NaCl-H₂O solution
- Λ = denotes coefficient in Eq. 4.37 for equivalent conductance
- 0 = denotes property at zero pressure
- 1,2 = denotes two different concentrations in Eqs. 4.11 and 4.12 — more generally, these subscripts denote species 1 and 2; species 2 is taken to be the solute species
- 1,2,... = denotes number signifying each component in Eqs. 4.16 through 4.23
- ∞ = stationary state (t → ∞)

Superscripts:

- ' = quantity associated with the beginning and end of an ordinary diffusion experiment when the pressure is at 1 atm
- 0 = denotes limiting value for infinite dilution
- m = mass-average reference system
- N = mole-average reference system

Overbars:

- \rightarrow = vector
- $\bar{}$ = mean or average; integral property (integrated with respect to time and concentration)

Mathematical:

- ∇ = "del" or "nabla" operator
- ln = natural or naperian logarithm

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