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## Liquid Thermal Diffusion: The Prediction of Separations; Experimental Data for $\text{CuSO}_4\text{-CoSO}_4\text{-H}_2\text{O}$ using a Soret Cell of new Design

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To the Graduate Council:

I am submitting herewith a dissertation written by Daniel Hershey entitled "Liquid Thermal Diffusion: The Prediction of Separations; Experimental Data for  $\text{CuSO}_4\text{-CoSO}_4\text{-H}_2\text{O}$  using a Soret Cell of new Design." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemical Engineering.

John W. Prados, Major Professor

We have read this dissertation and recommend its acceptance:

E. E. Stansbury, William H. Fletcher, Herbert L. Lee, F. H. Johnson, D. H. Jerry

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Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

May 27, 1961

To the Graduate Council:

I am submitting herewith a thesis written by Daniel Hershey entitled "Liquid Thermal Diffusion: The Prediction of Separations; Experimental Data for  $\text{CuSO}_4$ - $\text{CoSO}_4$ - $\text{H}_2\text{O}$  Using a Soret Cell of New Design." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemical Engineering.

John W. Grados  
Major Professor

We have read this thesis and  
recommend its acceptance:

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Acting Dean of the Graduate School

LIQUID THERMAL DIFFUSION: THE PREDICTION OF SEPARATIONS;  
EXPERIMENTAL DATA FOR  $\text{CuSO}_4\text{-CoSO}_4\text{-H}_2\text{O}$  USING  
A SORET CELL OF NEW DESIGN

---

A Thesis  
Presented to  
the Graduate Council of  
The University of Tennessee

---

In Partial Fulfillment  
of the Requirements for the Degree  
Doctor of Philosophy

---

by  
Daniel Hershey  
June 1961

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The construction of experimental equipment requires skillful craftsmanship. Mr. B. L. McGill and Mr. T. A. Long translated some of this writer's ideas into useful, workable

equipment. Mr. H. B. Thompson and Mr. E. H. Honeycutt, shop leader, also aided in the construction of the equipment.

## SUMMARY

Investigation of the thermal diffusion phenomenon has transcended the merely academic phase. It is recognized that in some cases thermal diffusion can represent an effective means of separating components, such as isotopes in gases, close boiling components and isotopes in the liquid phase, and electrolytes in aqueous solution. If the separation in a thermal diffusion column could be predicted, it would be possible to scale up, make economic feasibility studies and other pertinent calculations. Thus thermal diffusion would join the mass transfer operations such as distillation, extraction, and the relatively new ion exchange.

Thermal diffusion in gases has been adequately explained. Theories pertaining to liquids have been varied but in general require the determination of postulated quantities, "heats of transport," which have not yet been evaluated. At present there is no unified theory applicable to gases and liquids, since extrapolation of gas concepts to liquids has not been successful.

In this report equations have been derived based on the postulation that irreversible thermal diffusion can be represented as a quasistatic transport process with the Boltzmann equation applicable. By considering gases as being composed of ideal particles, and liquids as condensed gases, a system of equations was derived which allowed, within about

30 per cent, the successful prediction of separations to be expected in helium-argon, neon-argon, non-polar organic liquid pairs and electrolytes in aqueous solution. It was also possible to predict the dependence of the separation upon concentration and temperature.

In the course of the mathematical development unknown quantities such as the partition function of a liquid molecule were introduced. It was necessary to make pragmatic assumptions concerning the form and magnitude of these functions in order to proceed. The justification of these assumptions rests upon analogy, "reasonable" estimates and the apparently successful final result.

Application of the equations to electrolytes in aqueous solution gave agreement within about 30 per cent except for sulfates. The search for the reasons behind the anomalous behavior of the sulfates led to a correction term which takes into account the ion-association and other factors involved in non-ideal behavior of electrolytes. With this correction factor applied to all the electrolytes, sulfates and non-sulfates, the experimental data and calculated predictions were generally within approximately 30 per cent of each other. Based on these results, it would appear that the equations derived will be useful in predicting Soret coefficients, where no data are available. It is suggested that the equations be further tested with the view of extending



the concepts to mixed electrolyte solutions.

The scarcity of reported Soret coefficients prompted a new design for a Soret cell, incorporating two cellophane du Pont PT-600 membranes. The membranes do not permit a macroscopic flow of solution. In addition, they apparently do not affect the distribution of components under conditions of no net transfer and hence do not alter the Soret coefficient. The membranes partitioned the cell so that the "differential" volumes contiguous to the hot and cold zones offered a .050-inch diffusion path with the remainder of the cell offering a .350-inch diffusion path. The entire "differential" volume could be removed as a sample without disturbing the rest of the cell.

With this cell, the  $\text{CuSO}_4\text{-H}_2\text{O}$ ,  $\text{CoSO}_4\text{-H}_2\text{O}$  and  $\text{CuSO}_4\text{-CoSO}_4\text{-H}_2\text{O}$  systems were investigated over a 0.1-0.6 molar range, with temperature gradients of  $159^\circ\text{-}59^\circ\text{F}$ ,  $140^\circ\text{-}40^\circ\text{F}$ , and  $100^\circ\text{-}40^\circ\text{F}$ .

Soret coefficients increased monotonically from  $9.0\text{-}10.3 \times 10^{-3} \text{ }^\circ\text{C}^{-1}$  over a 0.1-0.6 molarity range for  $\text{CuSO}_4$  and  $7.0\text{-}7.4 \times 10^{-3} \text{ }^\circ\text{C}^{-1}$  for  $\text{CoSO}_4$  over the same molarity range. For the mixed salt system, no significant change in Soret coefficient of each component was detected as a result of the mixing. These results are about 10 per cent higher than Bosanquet (2) reported for the same experimental conditions, but with a cell partitioned in two equal halves, separated

by a cellophane membrane. Average values of concentration and temperature for each half were assumed.

At higher temperatures it was found that the Soret coefficient for  $\text{CuSO}_4$  was essentially constant but at the lower temperatures the Soret coefficient decreased with decreasing average temperature. The high temperature behavior is generally in accord with the predicted results, based on the mathematical derivation.

With a membrane life of approximately one month, the cell, once assembled, was operated continuously without dismantling between runs. Such ease of operation is a very attractive feature in conjunction with the effective isolation of the bulk solution by the membranes when removing the samples. It is therefore recommended that further data be obtained, as a function of temperature difference, mean temperature and concentration so that a satisfactory statistical analysis may be undertaken. It is further suggested that a more durable membrane be found and integrated into the design of the cell used in this investigation. A thorough investigation should also be launched to study the effect of this membrane on Soret coefficients.

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## PART I

### INTRODUCTION

Thermal diffusion is a transport process, as are heat transfer and ordinary diffusion. It is more complex than heat transfer and ordinary diffusion because the temperature gradient imposed upon the system usually causes a migration of molecules with a concomitant concentration gradient. The concentration gradient then gives rise to an ordinary diffusive flux in the opposite direction. A steady state is attained when both fluxes are equal. Phenomenologically, this is represented as follows:

$$J_i = \rho \left[ D_i' \xi_i (1 - \xi_i) \text{ grad } T - D_i \text{ grad } \xi_i \right] \cdot \vec{n} \quad (1)$$

where

$J_i$  = the net flux of the  $i^{\text{th}}$  component, moles  
per unit area per unit time

$\rho$  = the molar density of the system, moles per  
unit volume

$D_i'$  = the coefficient of thermal diffusion, area  
per unit time per degree, referred to the  
 $i^{\text{th}}$  component

$D_i$  = the coefficient of ordinary diffusion, area  
per unit time, of the  $i^{\text{th}}$  component

$\xi_i$  = the mole fraction of the  $i^{\text{th}}$  component

$T$  = temperature, degrees absolute

$\vec{n}$  = unit normal vector

The initial recorded observation of a concentration gradient across a system resulting from a temperature gradient is attributed to Ludwig (22), who noted the phenomenon in an aqueous solution of sodium sulfate. Subsequently, Soret (29) investigated this effect more extensively with the result that thermal diffusion is sometimes referred to as the Ludwig-Soret or Soret effect. It is usually found that the heavier component migrates down the temperature gradient. This is generally true for electrolytes in aqueous solution.

Attempts to present a unified, rigorous theory for thermal diffusion in gases and liquids have been unsuccessful due to a lack of knowledge concerning the liquid state. Though the rigorous mathematical treatment of this non-equilibrium phenomenon in non-uniform gases is complex, it has been treated extensively by Chapman and Cowling (6), Chapman (5), Enskog (12), Clark Jones (8) and others with good results. The approach is from the kinetic theory point of view utilizing assumptions concerning the intermolecular interactions, such as:

- a) the molecules behave as rigid elastic spheres;
- b) the molecules exert a repulsive force,  $F$ , which varies inversely as the  $\nu$ th power of the distance  $r$ , that is,  $F = Kr^{-\nu}$ ;

c) the molecules exert an inverse power attraction superimposed on an inverse power repulsion, so that the resultant force is

$$F = K r^{-U} - K' r^{-U'}$$

where  $K$  and  $U$  refer to the repulsive force,  $K'$  and  $U'$  to the attractive force. The Lennard-Jones model of interaction is of this category. A comprehensive survey of thermal diffusion in gases is to be found in the text by Grew and Ibbs (14).

Liquid thermal diffusion theories have been far less satisfactory since they are encumbered by the anomalous and abstruse behavior of liquids. A theoretical explanation of the effect was suggested by van't Hoff (18) in 1887, based on the supposition that the direction of the concentration gradient was in conformity with the principle of equality of osmotic pressure. Experimental results did not confirm the predicted effects and more complex concepts were introduced. Liquid thermal diffusion theories may be partitioned according to two approaches: kinetic and thermodynamic. The kinetic theory approach of Nernst (24), Wirtz (36), and Denbigh (10) conceived of liquid thermal diffusion as the transport of activated solute molecules from one equilibrium site to another in discrete jumps, requiring an "energy of activation." This energy served to break the cohesive bond of solute and solvent, and, in addition, this activation energy

was also assumed to provide the "energy of hole formation." This is the energy required to produce a hole in the solvent.

The thermodynamic approach in non-isothermal systems originated with Eastman (11) and Wagner (34). They imputed to this essentially irreversible phenomenon reversible characteristics by neglecting the irreversible heat conduction. They then proceeded to treat it by the usual means of thermodynamics, introducing a "heat of transfer," defined as the quantity of heat absorbed by a diffusing substance in moving from one region to another. To these quasi-thermodynamic methods was added the theory based on the thermodynamics of irreversible processes utilizing the Onsager reciprocal relations. In developing an irreversible thermodynamic theory, de Groot (15) introduced a "heat of transport," similar to the terms described previously. Macroscopic theories, avoiding the direct utilization of probability theory, vector analysis, statistical analysis and molecular energy terms, were proposed by Porter (25), Wereide (35), Chapman (4), de Groot (15), and others.

Considerable interest is focused at The University of Tennessee on liquid thermal diffusion of electrolytes--single salt and mixed salt solutions. A horizontal continuous, countercurrent thermal diffusion column was designed and operated by Von Halle (16) with organic solutions and a phenomenological theory for the separation behavior was presented.

Further investigation of the operating characteristics of the Von Halle column and other column designs (with aqueous electrolyte solutions) has been conducted (13). In addition, Soret cells have been designed and have proven successful, giving consistent and reproducible results. A Soret or "equilibrium" cell consists essentially of a hot surface, the

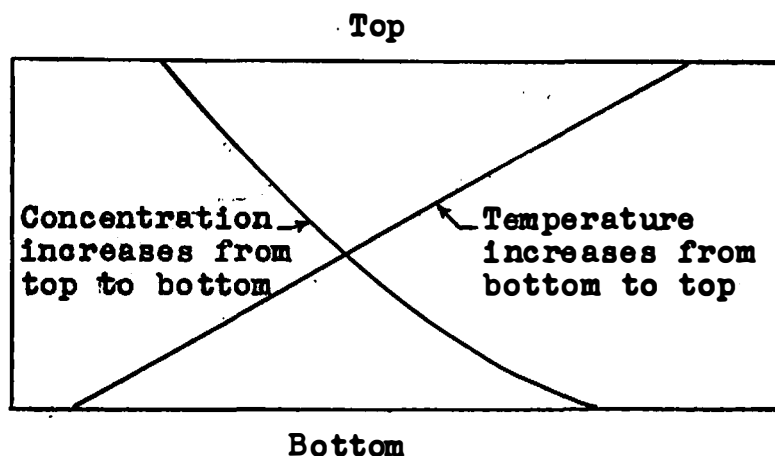


Figure 1. Schematic Representation of a Soret Cell

interstitial liquid and a cold surface, arranged contiguously. The hot surface is on top to avoid convective currents. There is no flow of material into or out of the cell, only a migration of molecules within the system. Long (21) and Bosanquet (2) designed Soret cells and obtained Soret coefficient data for the  $\text{CuSO}_4\text{-CoSO}_4\text{-H}_2\text{O}$  system at a steady state

or "equilibrium." Soret coefficients are generally calculated from the relation

$$\sigma = \frac{1}{\Delta T} \ln \frac{X_2}{X_1} \quad (2)$$

where

$\sigma$  = Soret coefficient

$\Delta T$  = temperature difference across the cell

$X_2, X_1$  = mole fraction of component of interest, at  
the cold and hot side, respectively

Equation 2 can be obtained from Equation 1 at steady state when the net flux,  $J_1$ , is set equal to zero. It is also implicitly assumed that  $D'/D$  is independent of temperature and concentration, and that  $(1-X_1)/(1-X_2)$  is approximately equal to unity.

It was apparent that extensive separation (Soret coefficient) data would be required if equations describing the performance of the horizontal column and other columns were to have any utility. Soret coefficients vary, depending on the component, its concentration, and temperature. Reports of Soret coefficients in the literature are sparse and subject to disagreement and hence an investigation was begun, with the aim of predicting Soret coefficients in liquids, specifically in aqueous solutions of electrolytes.

Equations, based on a combination of theory and

reasonable conjecture, have been derived and are the subject of Part II of this report. These equations enable the calculation of separations without resort to experiment. In addition, another Soret cell has been designed and considerable Soret coefficient data have been obtained for single salt and mixed salt aqueous solutions of  $\text{CuSO}_4$ ,  $\text{CoSO}_4$ , and  $\text{CuSO}_4\text{-CoSO}_4$ . With these data, it was possible to determine the variation of Soret coefficient with varied concentration over the range 0.1 molar to 0.6 molar and with temperature over the range  $100^\circ\text{-}40^\circ\text{F}$  to  $140^\circ\text{-}40^\circ\text{F}$ . The experimental study is treated in Part III.



## PART II

### CHAPTER I

#### DERIVATION OF EQUATIONS FOR PREDICTING THERMAL DIFFUSION SEPARATIONS

In this chapter equations will be derived based on the postulation that irreversible thermal diffusion can be represented as a quasistatic transport process with the Boltzmann equation applicable. By considering gases as being composed of ideal particles, and liquids as condensed gases, a system of equations will be derived from which the separations to be expected can be calculated without resort to experiment. In the course of the mathematical development, unknown quantities such as the partition function of a liquid molecule will be introduced. It was necessary to make pragmatic assumptions concerning the form and magnitude of these functions in order to proceed. It is realized full well that such assumptions as well as the starting postulate itself cannot be justified on any firm theoretical basis, but they must be regarded rather as "educated conjecture." In defense of this approach, however, it should be pointed out that the liquid medium is yet to be satisfactorily elucidated as far as force fields, molecular distribution functions, interactions, etc., are concerned. Many times engineers, when faced with a lack of information relating to their work are forced to make

"educated guesses" in order to proceed, and this was done here. The justification of these assumptions rests upon analogy, "reasonable" estimates and the apparently successful final results.

## I. PERFECT GASES

Initially, thermal diffusion in a monatomic perfect gas system will be considered since it will involve fewer assumptions. The entire derivation for this system will be presented and, thereafter, a parallel derivation for liquids will be given. In the following chapter experimental data will be compared with the predictions from the developed equations.

Because of the slowness of the thermal diffusion process, it will be advantageous to consider this process not as an irreversible transport phenomenon but rather as a quasistatic process. The system will be envisioned as being initially in equilibrium, at a uniform temperature. With the imposition of the temperature gradient, thermal diffusion proceeds quasistatically, during which the system is at all times infinitesimally near a state of equilibrium, so that the Boltzmann distribution function is applicable.

Consider a thermal diffusion apparatus composed of a hot surface, cold surface and interposed perfect monatomic gas. Establishment of the temperature gradient causes a

migration of the atoms, resulting usually in a measurable composition change at the hot and cold surfaces. Assuming a quasistatic transport process, the Boltzmann equilibrium distribution will be introduced.

For atoms in equilibrium, the ratio of the number of atoms in energy states  $r$  and  $s$  is given by the Boltzmann distribution equation,

$$\frac{N_r}{N_s} = e^{-(E_r - E_s)/kT} \quad (3)$$

where

$k$  = the Boltzmann constant

The following nomenclature will be used:

$\eta_{ij}$  = the number of atoms of component,  $i$ , in energy state,  $j$ , per unit volume

( $i = 1, 2, \dots, m$ ;  $j = 0, 1, 2, \dots, n$ )

$T_H, T_C$  = the temperature of the hot and cold wall, respectively, degrees absolute

$N_i$  = the total number of atoms of component  $i$

$V$  = the volume of the cell

$S$  = the cross sectional area of the cell (assumed constant)

$x$  = the linear dimension along the temperature gradient

$L$  = the length of the cell along the temperature gradient

$E_{ij}$  = the energy of an atom of component,  $i$ , in energy state,  $j$

state,  $j$

$E$  = the total energy of the system

$k$  = the Boltzmann constant

Consider the system initially at a uniform temperature,  $T_0$ , with  $N_1/V = \eta_1$ . If at a time,  $t_s$ , one surface is brought to  $T_H$  and the other to  $T_C$ , the temperature gradient will be rapidly established. It will be assumed that at  $t_s$  migration has not yet occurred but is imminent and Equation 3 is applicable. Therefore, from the ideal gas equation, if the pressure of the system is assumed constant, it can be shown that

$$\eta_1 = \frac{T_0}{T} \frac{N_1}{V} \quad (4)$$

or

$$\sum_{i=1}^m \eta_i = \frac{T_0}{T} \sum_{i=1}^m \frac{N_i}{V} \quad (4A)$$

The system possesses an energy per unit volume

$$\left(\frac{E}{V}\right)_{t_s} = \left( \sum_{i=1}^m \sum_{j=0}^n E_{ij} \eta_{ij} \right)_{t_s} \quad (5)$$

It will be helpful to introduce another form of Equation 3,

$$\sum_{j=0}^n \eta_{ij} = \eta_{in} \sum_{j=0}^n \frac{\eta_{ij}}{\eta_{in}}$$

or

$$\sum_{j=0}^n \eta_{ij} = \eta_{in} \sum_{j=0}^n \frac{e^{-E_{ij}/kT}}{e^{-E_{in}/kT}}$$

and finally

$$\sum_{j=0}^n \eta_{ij} = \frac{\eta_{in} \sum_{j=0}^n e^{-E_{ij}/kT}}{e^{-E_{in}/kT}} \quad (6)$$

Let  $P_i$  be defined as the partition function for component  $i$ , then

$$P_i = \sum_{j=0}^n e^{-E_{ij}/kT} \quad (7)$$

If Equations 6 and 7 are combined, with some rearrangement, the result is

$$\eta_{in} = \frac{e^{-E_{in}/kT} \sum_{j=0}^n \eta_{ij}}{P_i} \quad (8)$$

Define  $\sum_{j=0}^n \eta_{ij} = \eta_i$  and change the notation of Equation 8

so that

$$\eta_{ij} = \frac{e^{-E_{ij}/kT} (\eta_i)}{P_i} \quad (8A)$$

and combine this with Equation 5. The result is Equation 9,

$$\left(\frac{E}{V}\right)_{t_s} = \sum_{i=1}^m \sum_{j=0}^n \frac{E_{ij} \eta_i e^{-E_{ij}/kT}}{P_i} \quad (9)$$

Recalling that at time,  $t_s$ , no migration has occurred, Equation 4 is applicable. Substitution of Equation 4 into Equation 9 yields

$$\left(\frac{E}{V}\right)_{t_s} = \sum_{i=1}^m \sum_{j=0}^n \frac{E_{ij} \frac{T_0}{T} \frac{N_i}{V} e^{-E_{ij}/kT}}{P_i} \quad (10)$$

At some time after  $t_s$ , thermal diffusion will commence, proceeding until  $t_f$ , at which time the system has attained a steady state and no further concentration changes can be detected. It is assumed that the thermal diffusion phenomenon, occurring in a system closed to mass transfer, with a fixed temperature gradient, proceeds in a manner such that each incremental volume maintains a constant total energy from time  $t_s$  to time  $t_f$ :  $\left(\frac{E}{V}\right)_{x,t_s} = \left(\frac{E}{V}\right)_{x,t_f}$

To justify this assumption, an appeal will be made to the fact that the number of atoms per unit volume that have migrated from their positions during the  $t_s - t_f$  time period is small compared to the number that have not. Hence the net energy change resulting from the difference between the energy of those atoms that have migrated, and the ones that have replaced them will be small compared to the total energy

of the unit volume.

As a consequence of the above assumption,

$$\left( \frac{E}{V} \right)_{x, t_s} \approx \left( \frac{E}{V} \right)_{x, t_f}$$

and it follows that

$$\left( \sum_{i=1}^m \sum_{j=0}^n \frac{\eta_i E_{ij} e^{-E_{ij}/kT}}{P_i} \right)_{x, t_f} = \left( \sum_{i=1}^m \sum_{j=0}^n \frac{\frac{N_i}{V} \frac{T_o}{T} E_{ij} e^{-E_{ij}/kT}}{P_i} \right)_{x, t_s} \quad (11)$$

Let

$$Q_i = \sum_{j=0}^n E_{ij} e^{-E_{ij}/kT} \quad (12)$$

and substitute  $Q_i$  into Equation 11. The result is Equation 13,

$$\left( \sum_{i=1}^m \eta_i \frac{Q_i}{P_i} \right)_{x, t_f} = \left( \sum_{i=1}^m \frac{N_i}{V} \frac{T_o}{T} \frac{Q_i}{P_i} \right)_{x, t_s} \quad (13)$$

For clarity, Equation 13 will be expressed in concrete form for a binary system, that is, let  $i=1,2$ . Also drop the subscripts  $t_f$  and  $t_s$ . Equation 13 now becomes

$$\left( \eta_1 \frac{Q_1}{P_1} + \eta_2 \frac{Q_2}{P_2} \right) = \frac{T_o}{T} \left[ \left( \frac{N_1}{V} \right) \frac{Q_1}{P_1} + \left( \frac{N_2}{V} \right) \frac{Q_2}{P_2} \right]$$

or

$$\eta_1 = \frac{T_o}{T} \left[ \left( \frac{N_1}{V} \right) + \left( \frac{N_2}{V} \right) \left( \frac{P_1}{P_2} \frac{Q_2}{Q_1} \right) \right] - \eta_2 \left( \frac{P_1}{P_2} \frac{Q_2}{Q_1} \right) \quad (14)$$

Let  $\alpha = \frac{P_1}{P_2} \frac{Q_2}{Q_1}$ . The evaluation of  $\alpha$  will be shown later in this chapter. Equation 14 now is of the form

$$\eta_1 = \frac{T_o}{T} \left[ \left( \frac{N_1}{V} \right) + \alpha \left( \frac{N_2}{V} \right) \right] - \eta_2 \alpha \quad (15)$$

The needed relationship between  $\eta_1$  and  $\eta_2$  can be obtained from the kinetic theory (10, 24) and thermodynamic approaches to thermal diffusion (11, 34). Both of these approaches yield

$$\sigma \propto \frac{Q^*}{T^2} \quad (16)$$

That is, the Soret coefficient,  $\sigma$ , is proportional to  $Q^*$  (an energy of transport term) and inversely proportional to  $T^2$ , where  $T$  is the absolute temperature. For an experiment with a finite temperature gradient,  $T$  is the arithmetic average temperature,  $T_{avg}$ . If  $T_H$  and  $T_C$  are the hot and cold side temperatures, respectively, then

$$T_H T_C = \left( T_{avg} + \frac{\Delta T}{2} \right) \left( T_{avg} - \frac{\Delta T}{2} \right) = T_{avg}^2 - \left( \frac{\Delta T}{2} \right)^2$$

or



$$T_H T_C \approx T_{avg}^2 \quad (17)$$

For the systems considered, the error introduced in neglecting  $(\Delta T)^2/4$  amounts to, at most, 1 per cent. Equation 16 is now of the form

$$\sigma \propto \frac{Q^*}{T_H T_C} \quad (18)$$

or

$$\sigma = \frac{H^*}{T_H T_C} \quad (19)$$

Equations 19 and 2 are combined,

$$\sigma = \frac{1}{\Delta T} \ln \frac{x_2}{x_1} = \frac{H^*}{T_H T_C}$$

yielding

$$\frac{x_2}{x_1} = e^{\frac{H^* \Delta T}{T_H T_C}}$$

or

$$\frac{x_{cold}}{x_{hot}} = \frac{\left( \frac{\eta_2}{\eta_1 + \eta_2} \right)_{cold}}{\left( \frac{\eta_2}{\eta_1 + \eta_2} \right)_{hot}} = e^{\frac{H^*}{T_C} - \frac{H^*}{T_H}}$$

so that in general

$$\frac{\eta_2}{\eta_1 + \eta_2} = r' e^{\frac{H^*}{T}}$$

or

$$\frac{\eta_2/\eta_1}{(1 + \eta_2/\eta_1)} = r' e^{\frac{H^*}{T}} \quad (20)$$

Implicit in the above development is the imputation that  $H^* = H^*_{avg}$ , and that the actual variation in  $H^*$  over the temperature range  $T_H, T_C$  introduces no appreciable error. This was verified for the extremes of experimental conditions employed, and in Appendix Part II-F the verification is shown.

Since the primary concern is with dilute solutions, where  $(1 + \eta_2/\eta_1) \cong 1$ , define

$$\frac{\eta_2}{\eta_1} = r e^{\frac{H^*}{T}} \quad (21)$$

where the quantities  $r$  and  $H^*$  are to be determined. Note the analogy between Equations 21 and 3. From Equations 15 and 21,

$$\eta_1 = \frac{T_o}{T} \left[ \frac{N_1 + \alpha N_2}{V} \right] / (1 + \alpha r e^{\frac{H^*}{T}}) \quad (22)$$

In the determination of  $H^*$  and  $r$ , it will be necessary to invoke limiting conditions such as

$$N_1 = S \int_0^L \eta_1 dx$$

and

$$N_2 = S \int_0^L \eta_2 \, dx$$

with

$$\frac{\eta_2}{\eta_1} = re^{\frac{H^*}{T}}$$

From these equations and Equation 22,

$$N_1 = S \int_0^L \left[ \frac{T_0}{T} \left( \frac{N_1 + \alpha N_2}{V} \right) / (1 + \alpha re^{H^*/T}) \right] dx \quad (23)$$

and

$$N_2 = S \int_0^L \left[ re^{H^*/T} \left( \frac{T_0}{T} \right) \left( \frac{N_1 + \alpha N_2}{V} \right) / (1 + \alpha re^{H^*/T}) \right] dx \quad (24)$$

Based on the assumption of a linear temperature gradient, let

$$T = T_H - \left( \frac{T_H - T_C}{L} \right) x$$

$$dT = - \left( \frac{T_H - T_C}{L} \right) dx$$

Now set  $T = 1/z$ ;  $dT = -dz/z^2$ ; and with an appropriate change of integration limits, Equations 23 and 24 are transformed as follows:

$$N_1 = \left( \frac{SL}{T_H - T_C} \right) \left( \frac{N_1 + \alpha N_2}{V} \right) T_0 \int_{1/T_H}^{1/T_C} \frac{dz}{z(1 + \alpha \operatorname{re}^{H^* z})}$$

$$N_2 = \left( \frac{SL}{T_H - T_C} \right) \left( \frac{N_1 + \alpha N_2}{V} \right) T_0 \int_{1/T_H}^{1/T_C} \frac{\operatorname{re}^{H^* z}}{z(1 + \alpha \operatorname{re}^{H^* z})} dz$$

and noting  $SL=V$ ,

$$N_1 = (N_1 + \alpha N_2) \left( \frac{T_0}{T_H - T_C} \right) \int_{1/T_H}^{1/T_C} \frac{dz}{z(1 + \alpha \operatorname{re}^{H^* z})} \quad (25)$$

$$N_2 = (N_1 + \alpha N_2) \left( \frac{T_0}{T_H - T_C} \right) \int_{1/T_H}^{1/T_C} \frac{\operatorname{re}^{H^* z}}{z(1 + \alpha \operatorname{re}^{H^* z})} dz \quad (26)$$

Equation 26 can be altered by the method of partial fractions:

$$\frac{\operatorname{re}^{H^* z}}{z(1 + \alpha \operatorname{re}^{H^* z})} = \frac{\Psi}{z} + \frac{\Omega}{(1 + \alpha \operatorname{re}^{H^* z})}$$

or

$$\Psi(1 + \alpha \operatorname{re}^{H^* z}) + \Omega z = \operatorname{re}^{H^* z}$$

From this:  $\Psi = \frac{1}{\alpha} ; \quad \Omega = -\frac{1}{\alpha z}$

If this result is combined with Equation 26, some rearrangement yields

$$\left( \frac{\alpha N_2}{N_1 + \alpha N_2} \right) \left( \frac{T_H - T_C}{T_0} \right) = \int_{1/T_H}^{1/T_C} \frac{dz}{z} - \int_{1/T_H}^{1/T_C} \frac{dz}{z(1 + \alpha r e^{H^* z})} \quad (27)$$

If Equations 27 and 25 are added, much simplification is effected and

$$\frac{T_H - T_C}{T_0} = \ln \frac{T_H}{T_C} \quad (28)$$

With elimination of  $T_0$  between Equations 28 and 25, the result is

$$\left( \frac{N_1}{N_1 + \alpha N_2} \right) \ln \frac{T_H}{T_C} = \int_{1/T_H}^{1/T_C} \frac{dz}{z(1 + \alpha r e^{H^* z})} \quad (29)$$

Unfortunately, no method has been found for integrating Equation 29 in a closed form. It has been necessary to resort to an expansion of the integrand in a Taylor series, make appropriate assumptions pertaining to uniform convergence of this series, and then integrate term by term. The mathematical operations are shown in the Appendix, Part II-B. The final result is given below:

$$H^* = \frac{C}{B} \left[ -A \alpha r + (1 - 2A) + \frac{(1 - A)}{\alpha r} \right] \quad (30)$$

where

$$A = \frac{N_1}{N_1 + \alpha N_2} \quad (30a)$$

$$B = \frac{T_H - T_C}{T_H T_C} \quad (30b)$$

$$C = \ln \frac{T_H}{T_C} \quad (30c)$$

It is apparent that Equation 30 is insufficient to determine  $H^*$  and  $r$ . It is necessary, therefore, to consider the following representation of the concentration gradient:

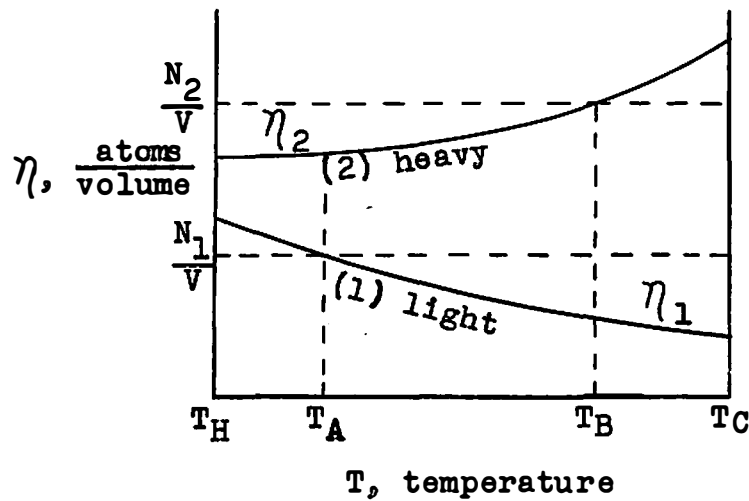


Figure 2. Concentration versus Temperature at Steady State

The curves drawn conform to  $\eta_1 = C_1 e^{d_1/T}$  since it was postulated that  $\eta_2 / \eta_1 = e^{H^*/T}$ . The curves have been drawn to indicate the heavier component migrating down the temperature gradient, which is generally true. This need not be the case since the analytical approach is general and hence it is in-

consequential how a particular system behaves.

At  $T_A$ ,

$$\eta_1 = \frac{N_1}{V} = \frac{T_0}{T_A} \left[ \frac{N_1 + \alpha N_2}{V} \right] / (1 + \alpha \text{re}^{H^*/T_A}) \quad (31)$$

from Equation 22;  $T_0$  is given by Equation 28.

At  $T_B$ ,

$$\frac{\eta_2}{\eta_1} = \text{re}^{H^*/T_B} = \frac{\frac{N_2}{V}}{(\eta_1)_{T_B}} = \frac{\frac{N_2}{V}}{\frac{T_0}{T_B} \left[ \frac{N_1 + \alpha N_2}{V} \right] / (1 + \alpha \text{re}^{H^*/T_B})} \quad (32)$$

again utilizing Equations 22 and 28.

From Figure 2,

$$(\eta_1)_{T_B} + (T_A - T_B) \left( \frac{d\eta_1}{dT} \right)_{T_B} \approx \frac{N_1}{V} \quad (33)$$

if it is assumed that  $d\eta_1/dT$  is approximately constant in the  $T_A - T_B$  range. This seems to be a reasonable assumption since the separations encountered in thermal diffusion cells are usually small.

In summary, there are four non-linear algebraic equations with four unknowns. To add to the difficulty of obtaining a solution, these unknowns are implicitly bound in the equations. The equations (Equations 30, 31, 32, and 33), after some simplification, are presented below. The algebraic manipulation of Equation 33 is shown in detail in the Appendix,

## Part II-C.

$$H^* = \frac{C}{B} \left[ -A\alpha r + (1-2A) + \frac{(1-A)}{\alpha r} \right] \quad (30)$$

where A, B, and C are defined by Equations 30a, 30b, and 30c.

$$1 = \frac{T_o}{T_A} (1 + \alpha \frac{N_2}{N_1}) / (1 + \alpha r e^{H^*/T_A}) \quad (31)$$

$$1 = \frac{\frac{T_o}{T_B} (\frac{N_1}{N_2} + \alpha) (r e^{H^*/T_B})}{(1 + \alpha r e^{H^*/T_B})} \quad (32)$$

$$1 = \frac{T_o (1 + \alpha \frac{N_2}{N_1}) \left[ \alpha r e^{H^*/T_B} \left[ 2 T_B^2 + H^* (T_A - T_B) - T_A T_B \right] + \left[ 2 T_B^2 - T_A T_B \right] \right]}{T_B^3 (1 + \alpha r e^{H^*/T_B})^2} \quad (33A)$$

$$T_o = \frac{T_H - T_C}{\ln T_H / T_C} \quad (28)$$

Equations 28, 30-33A, in conjunction with a knowledge of  $\alpha$ ,  $T_H$  and  $T_C$  enable the calculation of the separation to be expected for two perfect gases. Though the calculation procedure requires a sizable amount of tedium, there are "short cuts" which will be explained in the Appendix, Part II-A. A parallel derivation for liquids is presented below.



## II. LIQUIDS

All that has been written and assumed for gases before Equation 4 will be considered to hold for liquids. This includes the postulation of a quasistatic process and the validity of the Boltzmann distribution. However, because of the relatively small coefficient of expansion of liquids, no temperature dependence will be indicated for  $\eta_1$  at  $t_s$ , that is,

$$\eta_1 \approx \frac{N_1}{V} \quad (4L)$$

or

$$\sum_{i=1}^m \eta_i \approx \sum_{i=1}^m \frac{N_i}{V} \quad (4L-A)$$

The subsequent derivation for the gas system is applicable through Equation 9. Because of the change introduced by Equation 4L, the liquid counterpart to Equation 10 is now

$$\left( \frac{E}{V} \right)_{t_s} = \sum_{i=1}^m \sum_{j=0}^n \frac{E_{ij} \frac{N_i}{V} e^{-E_{ij}/kT}}{P_i} \quad (10L)$$

Again all arguments proceed as before, with the absence of the  $T_0/T$  term. The definitions,  $\alpha = \frac{P_1}{P_2} \frac{Q_2}{Q_1}$  and  $\frac{\eta_2}{\eta_1} = re^{H^*/T}$

are similarly introduced with the following result:

$$\eta_1 = \frac{N_1 + \alpha N_2}{V} / (1 + \alpha r e^{H^*/T}) \quad (22L)$$

and

$$\left( \frac{N_1}{N_1 + \alpha N_2} \right) (T_H - T_C) = \int_{1/T_H}^{1/T_C} \frac{dz}{z^2 (1 + \alpha r e^{H^* z})} \quad (29L)$$

The expansion of the integrand of Equation 29L is shown in the Appendix, Part II-B. The final result is given below:

$$H^* = \frac{C}{B} \left[ -A\alpha r + (1-2A) + \frac{(1-A)}{\alpha r} \right] \quad (30L)$$

where

$$A = \frac{N_1}{N_1 + \alpha N_2} \quad (30L-a)$$

$$B = \ln \frac{T_H}{T_C} \quad (30L-b)$$

$$C = T_H - T_C \quad (30L-c)$$

The rest of the liquid development parallels that for gases in principle but differs in one important aspect. Whereas in Figure 2 it is noted that  $T_A$  and  $T_B$  represent the temperatures where  $\eta_1 = \frac{N_1}{V}$  and  $\eta_2 = \frac{N_2}{V}$ , respectively, this is not the case for liquids. It will be noted from

Equation 15 that for liquids,  $(\eta_1 + \alpha \eta_2) = (\frac{N_1}{V} + \alpha \frac{N_2}{V})$ , so that if  $\eta_1 = N_1/V$  at  $T_A$ , then  $\eta_2 = N_2/V$  also at  $T_A$ . Figure 3 below illustrates this situation.

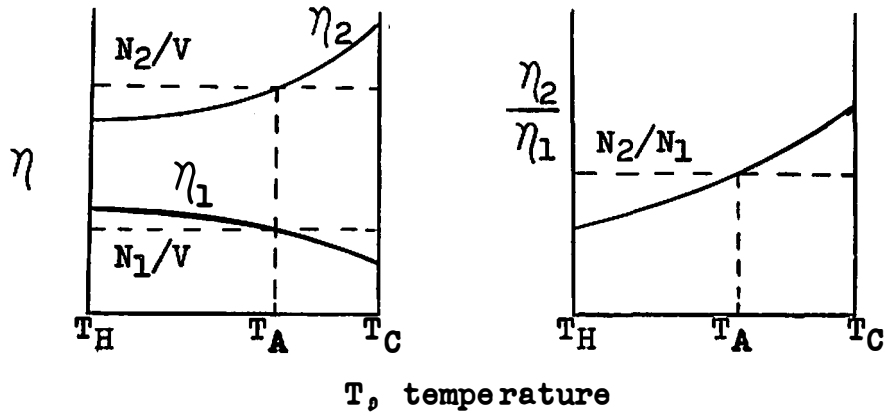


Figure 3. Concentration,  $\eta$  and Concentration Ratio,  $\eta_2/\eta_1$ , versus Temperature at Steady State

Therefore, from Equation 30L it is possible to calculate a set of  $(r, H^*)$  values and there remains the task of culling the correct  $(r, H^*)$  pair from the equations given below.

At  $T_A$ ,

$$\frac{\eta_2}{\eta_1} = \frac{N_2}{N_1} \text{ re } T_A^{H^*} \quad (34)$$

which allows the calculation of a  $T_A$  corresponding to  $(r, H^*)$ . The correct  $(r, H^*, T_A)$  values can be determined by substitution into Equation 35:

$$\left(\frac{\eta_2}{\eta_1}\right)_{T_H} = \text{re}^{\frac{H^*}{T_H}} = \frac{(\eta_2)_H}{(\eta_1)_H} = \frac{(\eta_2)_{T_A} + \left(\frac{d\eta_2}{dT}\right)_{T_A} (T_H - T_A)}{(\eta_1)_{T_A} + \left(\frac{d\eta_1}{dT}\right)_{T_A} (T_H - T_A)} \quad (35)$$

Equation 35 assumes  $(d\eta_2/dT)$  and  $(d\eta_1/dT)$  are constant over the  $T_H, T_A$  interval. This would appear to be justified in view of the small separation obtained in thermal diffusion experiments. This assertion and its justification will be considered in more detail in the Appendix, Part II-G. If the expressions for  $\eta_1$ ,  $\eta_2$ ,  $(d\eta_2/dT)$ , and  $(d\eta_1/dT)$  are substituted into Equation 35, and some rearrangements are made, the result is Equation 36:

$$1 = \frac{e^{H^*/T_A} \left[ T_A^2 (1 + \alpha \text{re}^{H^*/T_A}) - H^* (T_H - T_A) \right]}{e^{H^*/T_A} \left[ T_A^2 (1 + \alpha \text{re}^{H^*/T_A}) + H^* \alpha \text{re}^{H^*/T_A} (T_H - T_A) \right]} \quad (36)$$

The mathematical manipulations are shown in the Appendix, Part II-D.

In summary, Equations 30-I, 34, and 36 permit the evaluation of the correct  $r, H^*$  pair. A calculation "short cut" obviated the need for burdensome trial and error calculations. This will be explained in the Appendix, Part II-A.

### III. THE EVALUATION OF $\alpha$

$$\alpha = \frac{P_1}{P_2} \frac{Q_1}{Q_2}$$

#### 1. Perfect Monatomic Gases

Let  $E_S$  denote the total energy per atom. Therefore,

$$E_S = E_{TR} + E_{ROT} + E_{VIB} + E_{ELECT} + E_{MISC} \quad (37)$$

where

$E_{TR}$  = translational energy

$E_{ROT}$  = rotational energy

$E_{VIB}$  = vibrational energy

$E_{ELECT}$  = electronic energy

$E_{MISC}$  = miscellaneous energy terms

For a perfect monatomic gas,  $E_{ROT}$  and  $E_{VIB}$  are equal to zero. At the temperatures considered, it is assumed that a negligible number of atoms are in excited electronic states, that is, all the atoms are in their ground state, indicated by  $E_{ELECT} \approx E^0$ .

From the principle of equipartition of energy and the definition of a partition function,

$$P = P_{TR} P_{ELECT} P_{ROT} P_{VIB} P_{MISC} \quad (38)$$

Classical statistical mechanics and quantum theory predict

$$P_{TR} = (2\pi mkT)^{3/2} \frac{V}{h^3} = cm^a \beta^{-b} = f(m, \beta) \quad (39)$$

where  $a$ ,  $b$ , and  $c$  are constants and  $\beta = \frac{1}{kT}$ . Assume

$P_{\text{MISC}}$  can be expressed similarly,

$$P_{\text{MISC}} = c' m^{a'} \beta^{-b'} = g(m, \beta) \quad (40)$$

and note for an ideal monatomic gas

$$P_{\text{ROT}} = P_{\text{VIB}} = 1 \quad (41)$$

Then Equation 38 becomes

$$P = (cm^a \beta^{-b}) (c' m^{a'} \beta^{-b'}) e^{-E^0 \beta} \quad (42)$$

From the definition of  $Q$ , it can be shown that

$$Q = - \frac{\partial}{\partial \beta} P \quad (43)$$

and, therefore,

$$Q = - \frac{\partial}{\partial \beta} \left[ (cc') (m^{a+a'}) \beta^{-(b+b')} e^{-E^0 \beta} \right]$$

or

$$Q = -(cc') (m^{a+a'}) \left[ e^{-E^0 \beta} \beta^{-(b+b')} \left[ -E^0 - (b+b') \beta^{-1} \right] \right]$$

(b and b'  $\sim$  2)

Since  $E^0$  generally ranges from several thousand electron volts to higher values, and  $\beta^{-1} = .026$  electron volts, it seems reasonable to assume  $(b+b') \beta^{-1} \ll E^0$ . Then

$$Q = (cc') m^{a+a'} e^{-E^0 \beta} \beta^{-(b+b')} E^0 \quad (44)$$

and

$$\alpha = \frac{P_1}{P_2} \frac{Q_2}{Q_1} = \frac{E_2^{O*}}{E_1^O} \quad (45)$$

The calculation of  $E_2^O/E_1^O$ , the ratio of the ground state electronic energies of components 1 and 2, is obtained by summing the energy of every electron of the atom. The electronic energy is the energy necessary to remove an electron in its ground state from its orbit to infinity, that is, the ionization potential. The data are available in Atomic Energy Levels (23) and other texts. In Figure 4,  $\log Z$  versus  $\log \text{I.P.}$  are plotted, where  $Z$  is the atomic number and  $\text{I.P.}$  is the ionization potential. These data are plotted for  $1s^2 S_{\frac{1}{2}}$ ,  $1s^2 1S_0$ ,  $1s^2 2s^2 S_{\frac{1}{2}}$ , ..., etc., and a curve is drawn relating  $Z$  to  $\text{I.P.}$  for each orbit. In Figure 5 a log-log plot of  $E^O$  versus  $Z^2$  is linear, where  $E^O$  is the sum of the electronic energies of each electron in the atom in its ground state orbit. The orbit energies were obtained from Figure 4.

## 2. The Evaluation of $\alpha$ For More Complicated Molecules in Gases and Liquids

Even for complex molecules it will be assumed that equations similar to Equations 37, 38, and 42 can be written.

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\*The significance of  $\alpha$  is discussed in the Appendix, Part II-H.

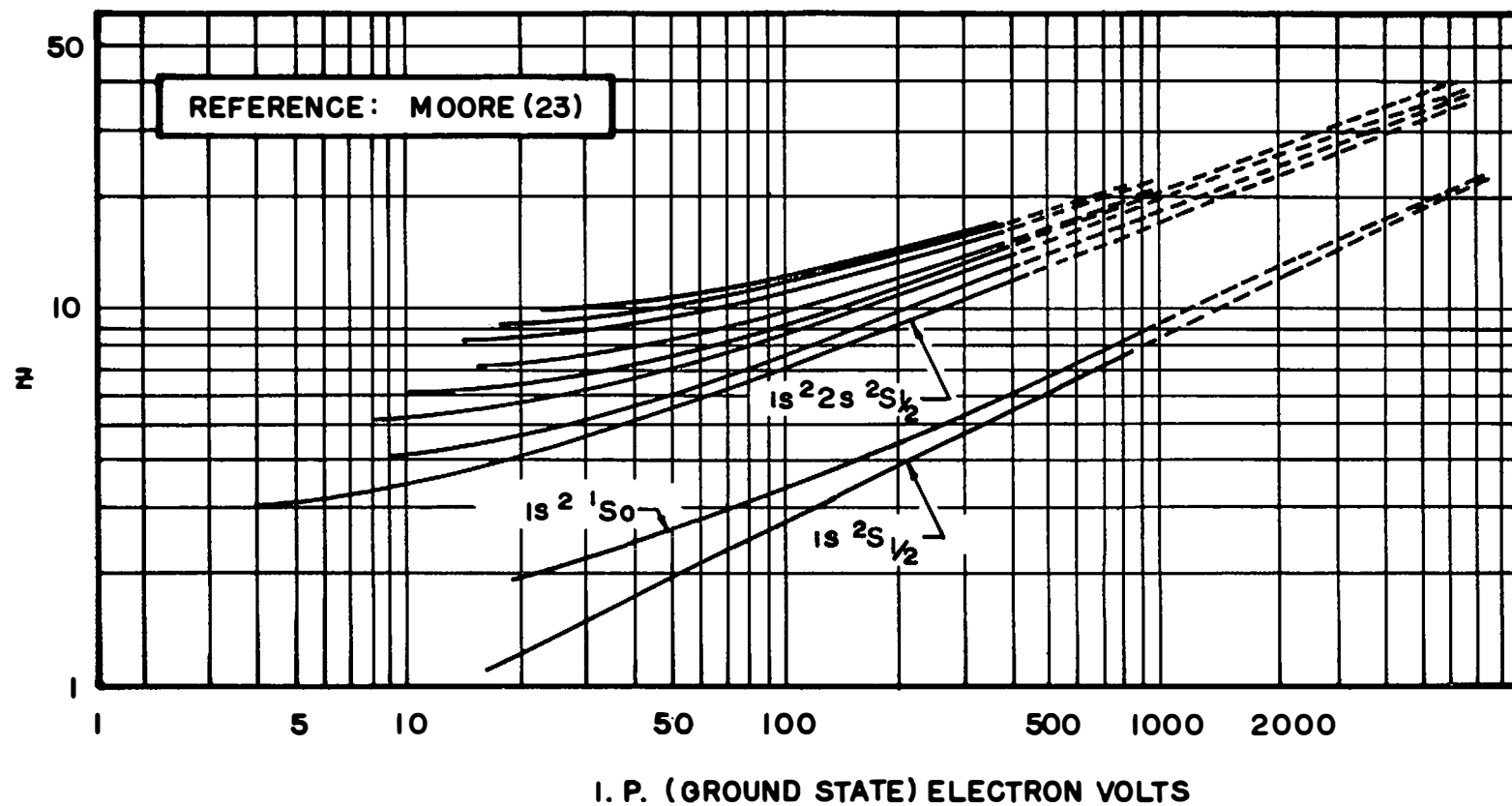


Figure 4. Atomic Number versus Ionization Potential



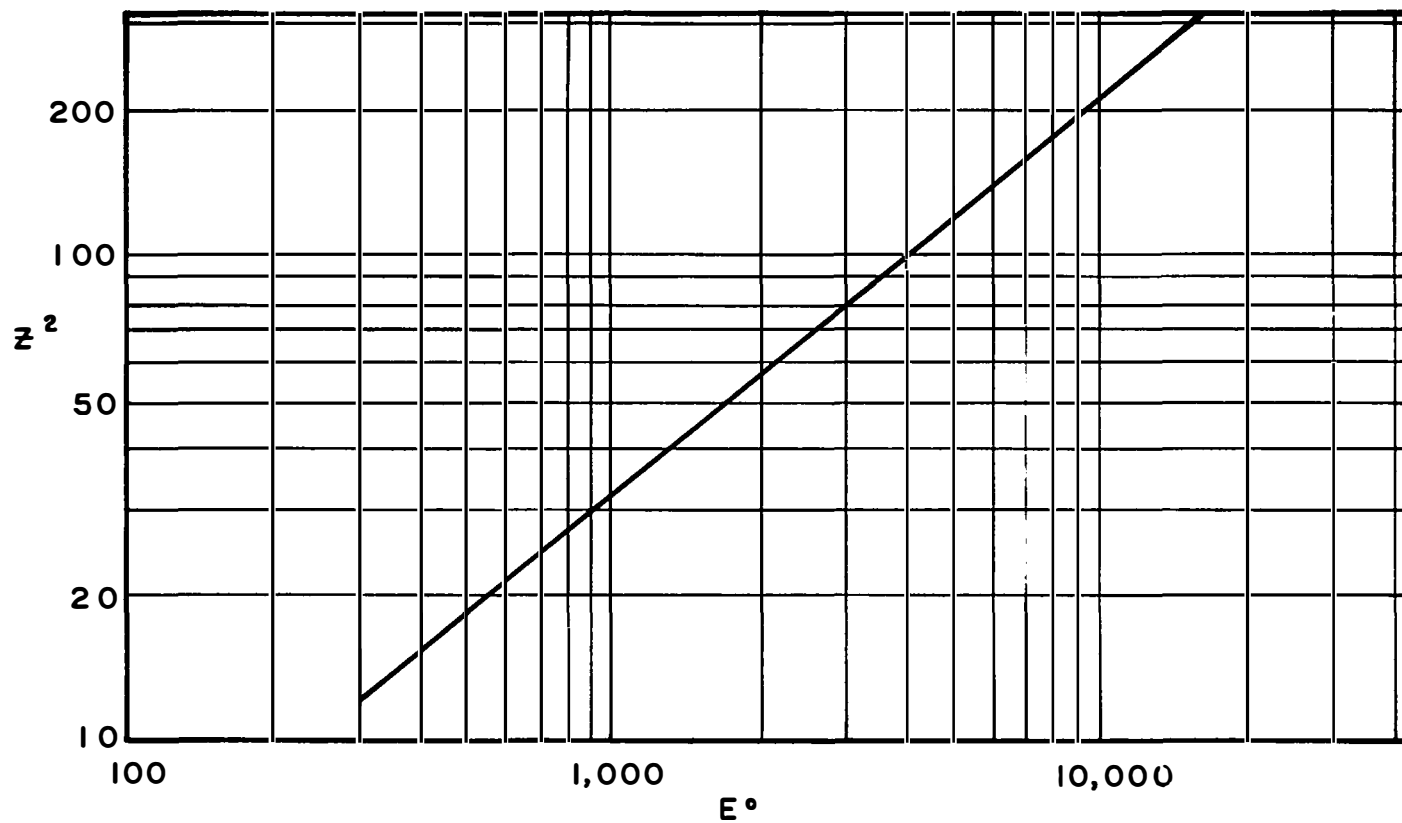


Figure 5. The Square of Atomic Number  
versus Electronic Energy

Included in the miscellaneous energy term could be such quantities as interaction energy or heats of solution. A major difficulty arises because the rotational and vibrational energies are no longer zero. To circumvent this difficulty, the following will be assumed true:

$$P_{TR} = h(m, \beta) = r m^s \beta^{-t} \quad (46)$$

$$P_{ROT} = k(m, \beta) = r' m^{s'} \beta^{-t'} \quad (47)$$

and

$$P_{VIB} = n(m, \beta) = r'' m^{s''} \beta^{-t''} \quad (48)$$

$$P_{MISC} = l(m, \beta) = r''' m^{s'''} \beta^{-t'''} \quad (49)$$

The complex molecule equivalent of Equation 42 is therefore

$$P = (r m^s \beta^{-t})(r' m^{s'} \beta^{-t'})(r'' m^{s''} \beta^{-t''})(r''' m^{s'''} \beta^{-t'''}) e^{-E^0 \beta} \quad (50)$$

(t, t', t'', t''' ~ 2)

With Equations 50 and 43, and proceeding as before, it can be shown again that

$$\alpha = \frac{E_2^0}{E_1^0}$$

if  $(t+t'+t''+t''')\beta^{-1} \ll E^0$ . For atoms that chemically combine to form molecules, it will be assumed that the major interaction affects the outer electrons. The energy of these electrons is much smaller than those closer to the nucleus and hence contribute a very small fraction of the total electronic energy of the atom. Thus any error introduced by

ignoring the interaction effect should be negligible. A similar argument will hold for electrolytes in solution. The ionization will affect the outer electrons and its effect on the total electronic energy will be neglected. For example, the heat of formation of  $\text{CuSO}_4(\text{S})$  is  $-184,700 \text{ cal/g.mol}$  and that of  $\text{C}_2\text{H}_5\text{OH}(\ell)$  is  $-52,230 \text{ cal/g.mol}$ . Since  $1 \frac{\text{electron volt}}{\text{molecule}}$  is equivalent to  $23,050 \text{ cal/mol}$ , the bond energy interactions, as indicated by the heats of formation are approximately 8 electron volts for  $\text{CuSO}_4(\text{S})$  and 2 electron volts for  $\text{C}_2\text{H}_5\text{OH}(\ell)$ . The total electronic energies of  $\text{CuSO}_4$  and  $\text{C}_2\text{H}_5\text{OH}$  are approximately 100,00 EV and 3000 EV, respectively. It seems quite reasonable, therefore, to neglect interaction energies. Similarly, ionization effects in solution are of the magnitude of a few electron volts and can be ignored. Since for electrolytes, electroneutrality is assumed to exist, the salt, in its migration in the cell, will statistically be assumed to be of the (cation-anion) form.

## PART II

### CHAPTER II

#### THE COMPARISON OF PREDICTED AND EXPERIMENTAL RESULTS

The per cent separation was calculated for the helium-argon and neon-argon systems. The temperature gradient was fixed but the concentration was varied, as shown in Figures 6 and 7. A summary of the calculations is given in Table I. The calculated curve is compared with the data of Van Itterbeek (20). Calculated separations based on the Lennard-Jones (6, 12) model, as reported by Hirschfelder, Curtiss and Bird (17), are also shown. For liquids, Soret coefficients were calculated for various values of  $\alpha$ , with a fixed temperature gradient and concentration. The calculated line obtained is shown in Figure 8 for 50 mol per cent concentration in a two-component system with superimposed experimental data. Figure 9 shows a similar calculated curve for a two-component system with the concentration fixed at 1.8 mol per cent of heavier component. In Figure 9, Soret coefficients for various electrolytes are plotted for comparison with the calculated line. Tables II, page 40, and IV, page 46, summarize the calculations of Figures 8 and 9.

A sample of the multiple trial and error calculation procedure is shown in the Appendix, Part II-A.

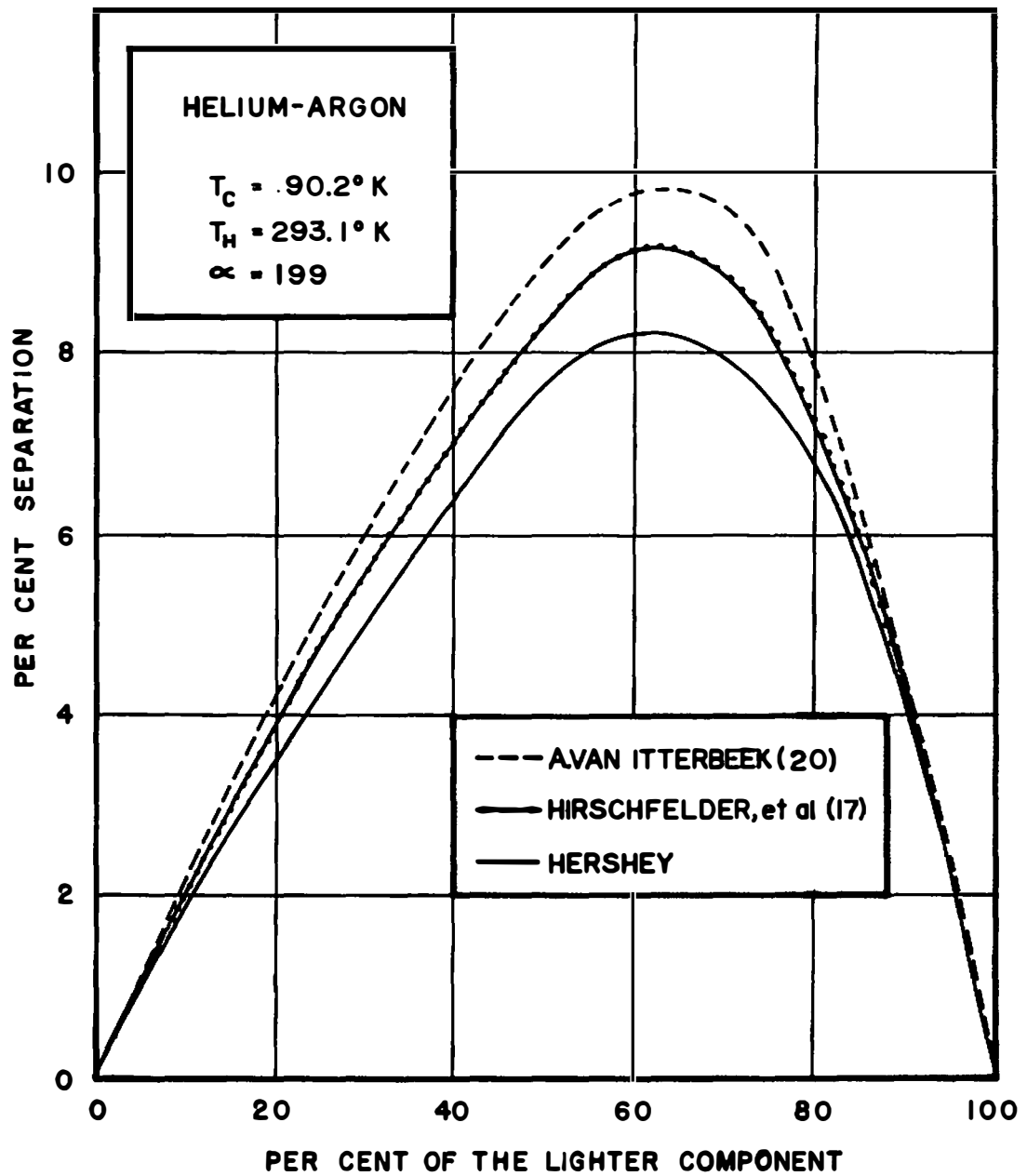


Figure 6. Per Cent Separation versus Concentration for Helium-Argon

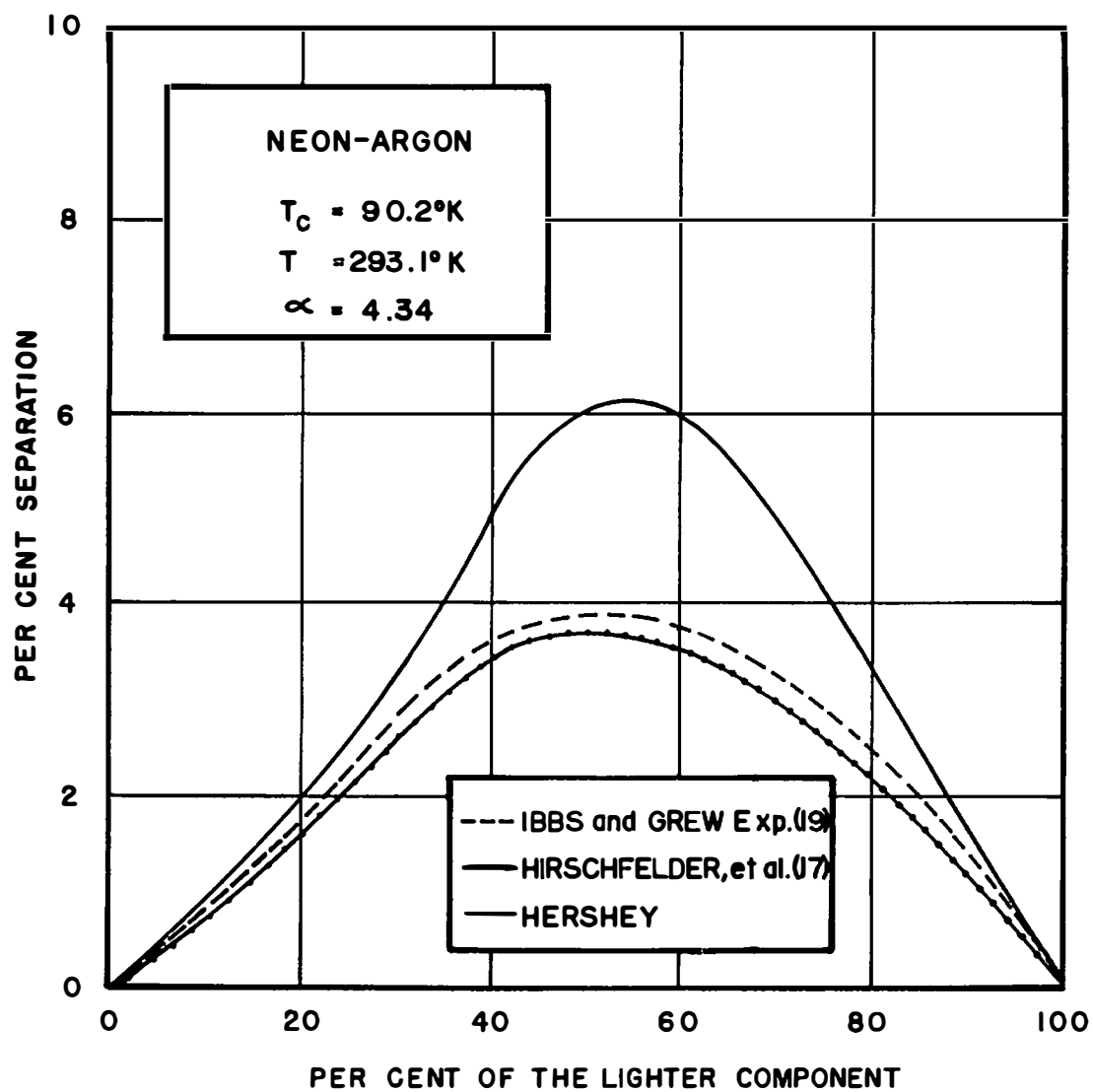


Figure 7. Per Cent Separation versus Concentration for Neon-Argon

TABLE I

SUMMARY OF THE CALCULATIONS OF THE PER CENT SEPARATION FOR GASES

System	$N_2/N_1$	Equation 30 $H^* =$	$(\eta_2/\eta_1)_H$	$(\eta_2/\eta_1)_C$	% Separation
Neon-argon	1	$-125r + 96.3 + \frac{28.8}{r}$	.893	1.144	6.17
( $\alpha = 4.35$ )	$\frac{1}{3}$	$-273r + 28.2 + \frac{20.9}{r}$	.304	.380	4.22
	3	$-47.6r + 132 + \frac{32.8}{r}$	2.88	3.18	1.85
Helium-argon	1	$-153r + 154$	.854	1.142	7.27
( $\alpha = 199$ )	$\frac{1}{3}$	$-452r + 154$	.297	.435	7.42
	3	$-51.0r + 154$	2.78	3.36	3.55
	.176	$-850r + 154$	.166	.254	6.00

Notes:

$$T_H = 293.1^\circ\text{K}, \quad T_C = 90.2^\circ\text{K}.$$

Simplification of Equation 30 is due to the large value of  $\alpha$ .

$$\% \text{ separation} = \left( \frac{\eta_2}{\eta_1 + \eta_2} \right)_C - \left( \frac{\eta_2}{\eta_1 + \eta_2} \right)_H$$

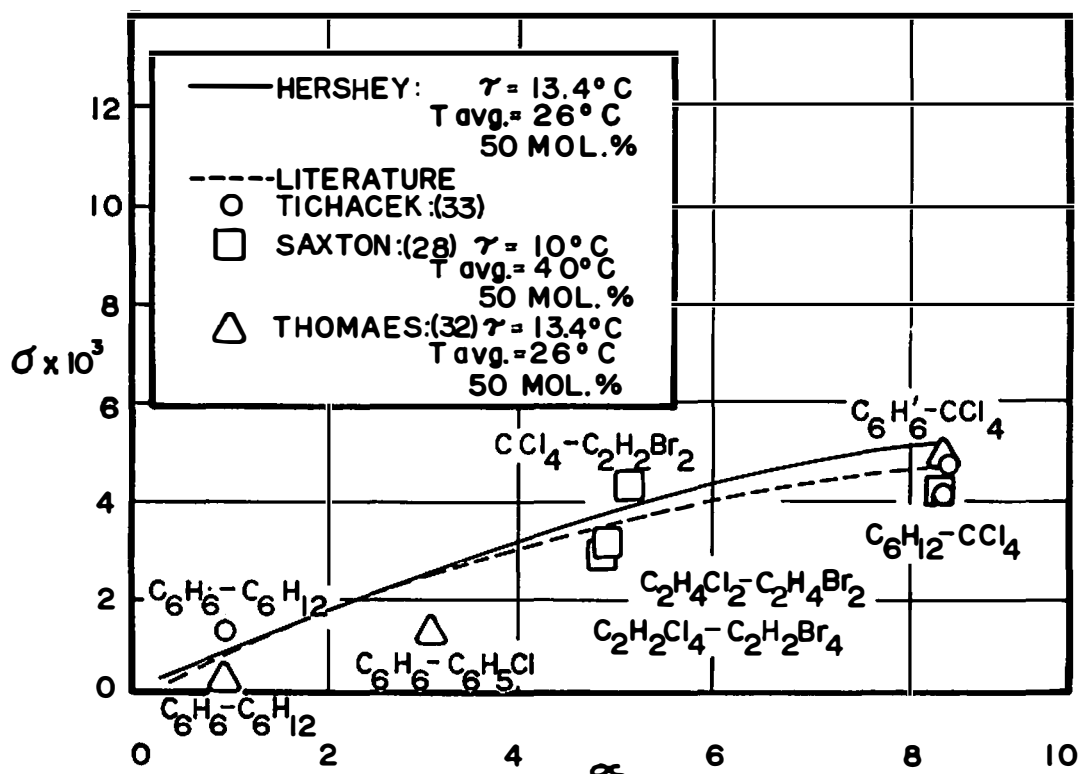


Figure 8. Soret Coefficient versus  $\alpha$  for Organic Liquids

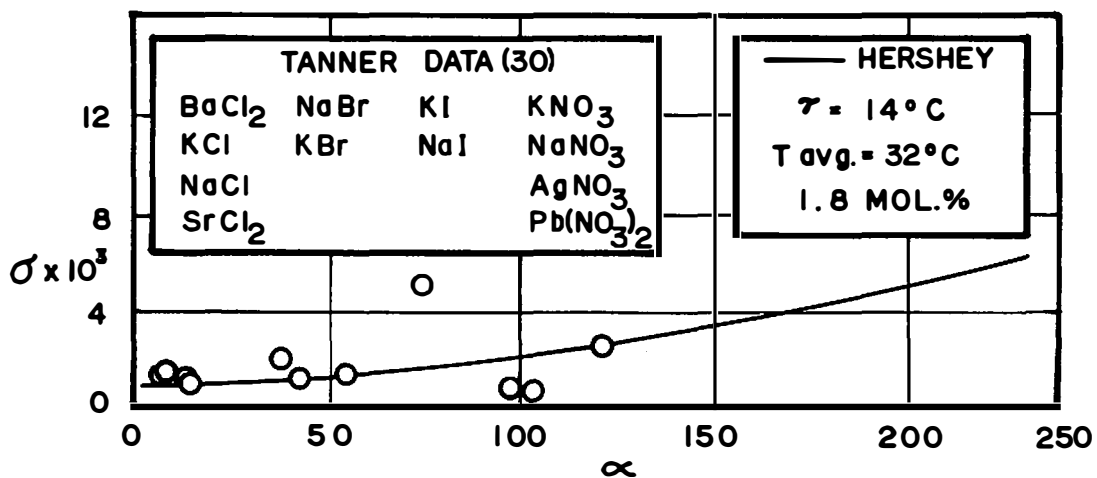


Figure 9. Soret Coefficients versus  $\alpha$  for Various Electrolytes in Aqueous Solutions



TABLE II

SUMMARY OF THE CALCULATIONS OF THE SORÉT COEFFICIENTS  
FOR ORGANIC LIQUIDS, BASED ON EQUATION 30L

$\alpha$	Mol % of Heavy Component	$N_2/N_1$	Equation 30L	$(\eta_2/\eta_1)_H$	$(\eta_2/\eta_1)_C$	$\sigma \times 10^3$ (°C) <sup>-1</sup>
			$H^*/298 =$			
15	50	1	$-.938r + .875 + \frac{.0625}{r}$	.967	1.156	6.50
8.40	50	1	$-.890r + .788 + \frac{.106}{r}$	.921	1.062	5.3
3.08	50	1	$-.755r + .510 + \frac{.245}{r}$	.964	1.038	2.9
1.01	50	1	$-.503r + .004 + \frac{.497}{r}$	.994	1.004	0.4

Note:  $T_H = 32.7^\circ\text{C}$ ;  $T_C = 19.3^\circ\text{C}$

## I. GASES

For the helium-argon and neon-argon systems, it is apparent from Figures 6 and 7 that the calculated results not only predict the proper shape of the curve but also lie within about 30 per cent of the experimental line.

## II. ORGANIC LIQUIDS

Non-polar organic liquid pairs seem to conform as a group to the calculated line in Figure 8. Polar liquid pairs tend to deviate from the line, implying some sort of interaction or molecular association. If the system is limited to "ideal" liquid pairs such as the non-polar groups, it appears as if the calculations are satisfactory within about 25 per cent over the range of  $\alpha$  examined. Closer scrutiny of the deviations of the non-polar systems from the prediction would perhaps reveal the nature of the correction factor required. However, the primary interest at this time concerns aqueous solutions of electrolytes and it is these systems that have received this closer scrutiny.

## III. ELECTROLYTES IN AQUEOUS SOLUTION

Figure 9 shows the calculated line and experimental points for various electrolytes in aqueous solution. The data conform to the calculated line satisfactorily, with the exception of sulfates which are not shown. The sulfate salts,

such as  $\text{CuSO}_4$ ,  $\text{CdSO}_4$ ,  $\text{MgSO}_4$ , and  $\text{Na}_2\text{SO}_4$  deviated markedly from the calculated curve and in all cases gave Soret coefficients that were too high for their corresponding  $\alpha$ . If the sulfate data were to fall on the calculated curve, then the apparent  $\alpha$  must be greater than the calculated  $\alpha$ . This anomalous behavior of the sulfate class of electrolytes has been recognized in studies of conductivity and colligative properties, and has been imputed to ion association, partial dissociation of the salts, complex ion formation or hydration of the ions (26). It appears as if ion association and hydration of the ions are more widely accepted at this time as an explanation of the sulfate class behavior. In an attempt to reconcile the above explanations with the results obtained from the present investigation, one fact stands out prominently: in all cases, if the  $\alpha$  values were greater than the calculated values, these Soret coefficient data would better conform to the calculated curve. Since  $\alpha$  is equal to the ratio of the electronic energy of the salt divided by the electronic energy of water, this implies that the salt behaves as if it were heavier than its molecular weight would indicate. Another way of looking at this is to suppose, for example, that after dissolving 2 moles of a salt in water, the properties observed suggest, statistically, that there are only 1.9 moles present. Some sort of ion association is suggested.

Hydration of the salt in solution is also a valid factor to be considered. Since the development presented in this thesis is concerned only with conditions of no net transfer, the effect of hydration upon the mobility of the ions should be of no consequence. Two possible effects of hydration do seem to be important: (1) the effect upon  $\alpha$  of the associated water of hydration, that is,  $\alpha = \frac{\text{salt} \cdot X \text{H}_2\text{O}}{\text{H}_2\text{O}}$ , and (2) the effect upon the apparent concentration of this "bound" water. In an attempt to correlate all the data with the calculated curves, the presence of hydration effects will be recognized, but discounted in view of what follows.

Suppose all the experimental data were subject to negligible error. What correction factor would need to be applied to  $\alpha$  in order that the experimental Soret coefficient data points would all fall on the calculated line? More specifically, what correction factor should be applied to the atomic number of the salt in order to accomplish this? These correction factors have been determined for all the salts included in Figure 9 and also for the sulfates, at three concentrations. They are tabulated in Table III under the heading, Hershey. The calculated curves are shown in Figure 10, followed by Table IV which summarizes the calculations involved. Table V presents the original Soret coefficient data. Sample calculations are given in the Appendix, Part II-A.

TABLE III  
CORRECTION FACTORS FOR ELECTROLYTES

	2.2 m		1.0 m		0.5 m	
	$\Phi^{-1}$	Hershey	$\Phi^{-1}$	Hershey	$\Phi^{-1}$	Hershey
KCl	1.1	1.1	1.1	1.6	1.1	1.6*
NaCl	1.0	1.6	1.1	2.3	1.1	#
KBr	1.1	0.8	1.1	1.1	1.1	1.3*
NaBr	1.0	0.9	1.0	1.4	1.1	1.7*
KI	1.0	0.5	1.1	0.5	1.1	0.5*
NaI	0.9	0.5	1.0	0.6	1.1	0.7
NaNO <sub>3</sub>	#	2.4	#	2.6	#	1.6*
KNO <sub>3</sub>	1.5	2.0	1.3	1.9	1.2	1.2*
AgNO <sub>3</sub>	0.8	1.2	1.4	1.5	1.2	0.8
Pb(NO <sub>3</sub> ) <sub>2</sub>	-	-	1.9	1.0	1.6	1.1
BaCl <sub>2</sub>	0.8	0.6	1.1	1.0	1.2	1.3
SrCl <sub>2</sub>	0.7	0.6	1.0	1.1	1.1	1.6
CuSO <sub>4</sub>	-	-	2.2	2.7	2.1	3.0*
CoSO <sub>4</sub>	#	1.2	#	2.3	#	3.0
CdSO <sub>4</sub>	1.7	1.0	2.2	1.5	2.1	1.8*
NaSO <sub>4</sub>	1.5	1.2	2.2	2.3	2.1	2.9*
ZnSO <sub>4</sub>	1.5	1.3	2.1	2.3	2.5	2.1
MgSO <sub>4</sub>	1.4	1.6	1.9	3.1	1.9	3.8*
Na <sub>2</sub> SO <sub>4</sub>	1.6	-	1.6	3.6	-	-
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	1.6	1.6	1.6	2.6	1.5	3.3

Notes:  $\Phi^{-1}$  data from reference (26).  
 - Data too limited for extrapolation.

# No data.  
 \* Uncertain extrapolation.

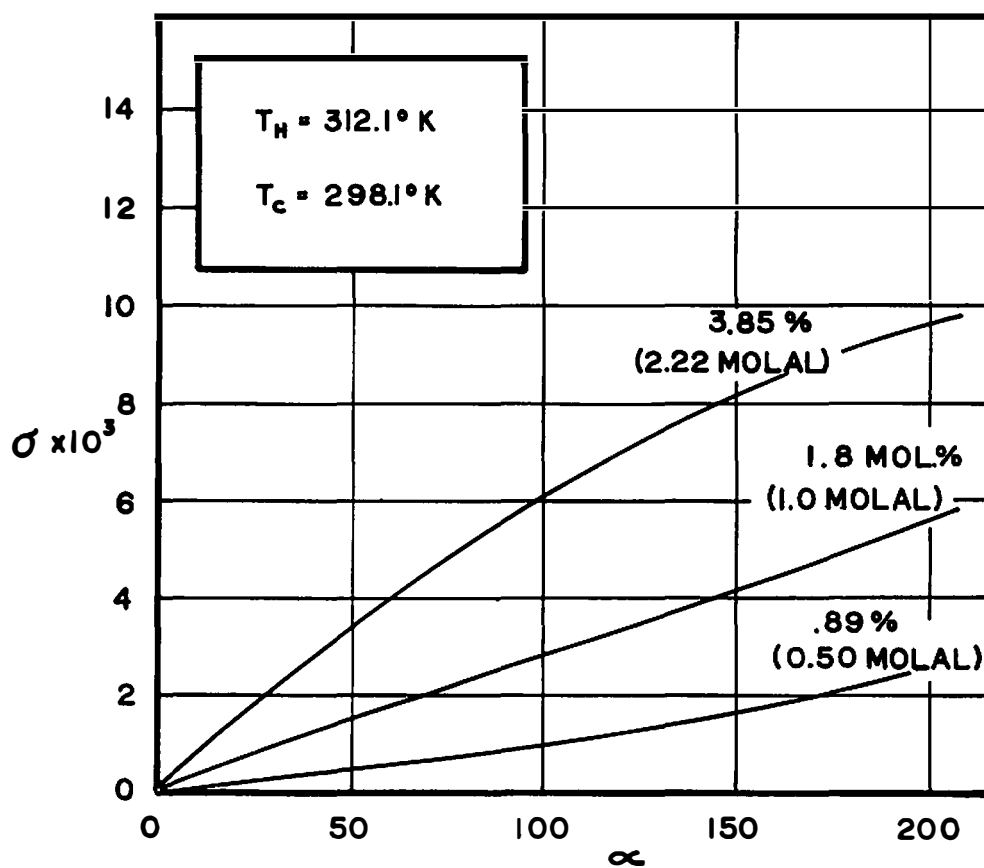


Figure 10. Soret Coefficient versus  $\alpha$  at Various Concentrations Calculated from the Mathematical Development

TABLE IV  
SUMMARY OF THE CALCULATIONS OF THE SORÉT COEFFICIENTS  
FOR ELECTROLYTES, BASED ON EQUATION 30L

$\alpha$	Mol % of Heavy Component	$N_2/N_1$	Equation 30L	$(\eta_2/\eta_1)_H$	$(\eta_2/\eta_1)_C$	$\sigma \times 10^3$ (°C) <sup>-1</sup>
			$H^*/305 =$			
300	0.89	.009	$-81.0r + .460 + \frac{.00243}{r}$	.00880	.00940	4.6
100	0.89	.009	$-52.6r + .052 + \frac{.00474}{r}$	.00897	.00906	0.71
300	3.85	.04	$-23.1r + .846 + \frac{.00308}{r}$	.0355	.0420	11.8
100	3.85	.04	$-20.0r + .600 + \frac{.0080}{r}$	.0381	.0418	6.15
50	3.85	.04	$-16.6r + .334 + \frac{.0133}{r}$	.0391	.0410	3.25
300	1.77	.018	$-46.8r + .688 + \frac{.00281}{r}$	.0168	.0190	8.60
100	1.77	.018	$-35.7r + .286 + \frac{.00643}{r}$	.0175	.0182	2.74
50	1.77.	.018	$-26.3r - .052 + \frac{.00948}{r}$	.0180	.0183	0.75
5	1.77	.018	$-4.58r - .834 + \frac{.0166}{r}$	.0180	.0180	0

Note:  $T_H = 312.1^\circ\text{K}$ ;  $T_C = 298.1^\circ\text{F}$ .

TABLE V  
SORET COEFFICIENTS OF ELECTROLYTES  
IN AQUEOUS SOLUTION

Investigator - Tanner (30)

Salt	$T_{\text{hot}} - T_{\text{cold}}$ (°C)	Mean Temperature (°C)	Mol % Heavy Component	$\sigma \times 10^3$ (°C) <sup>-1</sup>
KCl	13.9	31	0.89	0.50
	"	"	1.77	0.94
	"	"	3.85	1.40
NaCl	14.0	33	0.89	0.80
	"	"	1.77	1.46
	"	"	3.85	1.80
KBr	13.9	31	0.89	0.8
	"	"	1.70	1.33
	"	"	3.85	1.80
KI	14.1	31	0.85	0.30
	"	"	1.76	0.45
	"	"	3.85	1.10
NaI	14.1	34	0.89	0.40
	"	"	1.77	0.79
	"	"	3.85	1.30
NaBr	14.0	34	0.89	1.60
	"	"	1.77	2.06
	"	"	3.85	2.20
BaCl <sub>2</sub>	14.1	31	0.89	3.20
	"	"	1.78	2.64
	"	"	3.85	2.30
SrCl <sub>2</sub>	14.0	31	0.89	2.06
	"	"	1.77	1.50
	"	"	3.85	1.0
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	14.2	31	0.89	2.81
	"	"	1.80	2.35
	"	"	3.85	2.30



TABLE V (continued)

Salt	$T_{\text{hot}} - T_{\text{cold}}$ (°C)	Mean Temperature (°C)	Mol % Heavy Component	$\sigma \times 10^3$ (°C) <sup>-1</sup>
CdSO <sub>4</sub>	14.0	31	0.89	6.85
	"	"	1.79	5.85
	"	"	3.85	5.40
CoSO <sub>4</sub>	14.2	31	0.89	7.90
	"	"	1.77	6.10
	"	"	3.85	2.90
CuSO <sub>4</sub>	13.0	31	0.89	11.8
	"	"	1.78	10.15
	-	-	-	-
MgSO <sub>4</sub>	14.9	31	0.89	6.17
	"	"	1.79	4.73
	"	"	3.85	2.70
NiSO <sub>4</sub>	14.6	31	0.89	7.6
	"	"	1.92	6.38
	"	"	3.85	3.3
ZnSO <sub>4</sub>	14.2	31	0.89	7.80
	"	"	1.80	6.95
	"	"	3.85	4.00
Na <sub>2</sub> SO <sub>4</sub>	14.4	31	3.85	9.20
	"	"	1.76	8.50
	"	"	3.85	9.2
AgNO <sub>3</sub>	14.2	34	0.89	4.20
	"	"	1.77	5.17
	"	"	3.85	7.60
Pb(NO <sub>3</sub> ) <sub>2</sub>	13.8	34	0.89	6.55
	14.2	"	1.77	8.60
	"	"	3.85	8.90
KNO <sub>3</sub>	14.1	31	0.89	0.20
	"	"	1.77	1.22
	"	"	3.85	3.60
NaNO <sub>3</sub>	13.8	32	0.89	0.4
	"	"	1.77	1.36
	"	"	3.85	3.10

This correction factor represents a deviation of the electrolyte in solution from its "ideal" behavior and should somehow be related to deviations in expected colligative properties. A measure of the deviations in expected colligative properties is given by the van't Hoff Factor,  $i$ , defined as follows:

$$i = \frac{\Delta T_f}{(\Delta T_f)_o} = \frac{\Delta T_b}{(\Delta T_b)_o} = \frac{\Delta P}{(\Delta P)_o} = \frac{\pi}{(\pi)_o}$$

where

$\Delta T_f$  = freezing point lowering

$\Delta T_b$  = boiling point raising

$\Delta P$  = vapor pressure lowering

$\pi$  = osmotic pressure

$(\Delta T_f)_o$  = F.P. lowering of nonelectrolyte

The quantities without the subscript zero refer to the electrolyte and those with subscripts to the nonelectrolyte of the same concentration.

Therefore, a correction factor analogous to the "Hershey" values in Table III should be  $\frac{\nu}{i}$ , where  $\nu$  is the number of ions produced by an electrolyte at infinite dilution. If an electrolyte behaved ideally, the ratio  $\frac{\nu}{i}$  would be unity. van't Hoff Factors are not readily available but osmotic coefficient data are. From Robinson and Stokes (26),  $\nu g \cong i$ , where  $g$  is defined as the "rational"

osmotic coefficient. The molal osmotic coefficient,  $\phi$ , is tabulated extensively, and is equal approximately to  $g$ . Therefore, if the approximations are valid,  $\frac{V}{i} \approx \frac{1}{\phi} = \phi^{-1}$ . Values of  $\phi$  are tabulated in Table VIII in the Appendix, Part II-E.

As noted from Table III, the two correction factors are of the same order of magnitude, and in most cases are in good agreement. Where one factor increases or decreases, the other behaves similarly. Figure 11 shows the values of the Soret coefficient for various electrolytes compared with the values predicted from the mathematical development.

The variation of Soret coefficient with temperature was calculated and plotted as shown in Figure 12. It was noted that there was a slight dependence of Soret coefficient upon temperature and the functional relationship was linear. As a comparison, data found in the literature were also presented in Figure 12 and it was noted that these data could also be displayed linearly with a small temperature dependence.

The concentration dependence of the Soret coefficient was calculated and as indicated in Figure 10, the Soret coefficient should increase with increasing concentration. This is a typical behavior, supported by the data in the literature. The experimental data presented in this report, as shown in Part III, Chapter II, also confirm this calculated

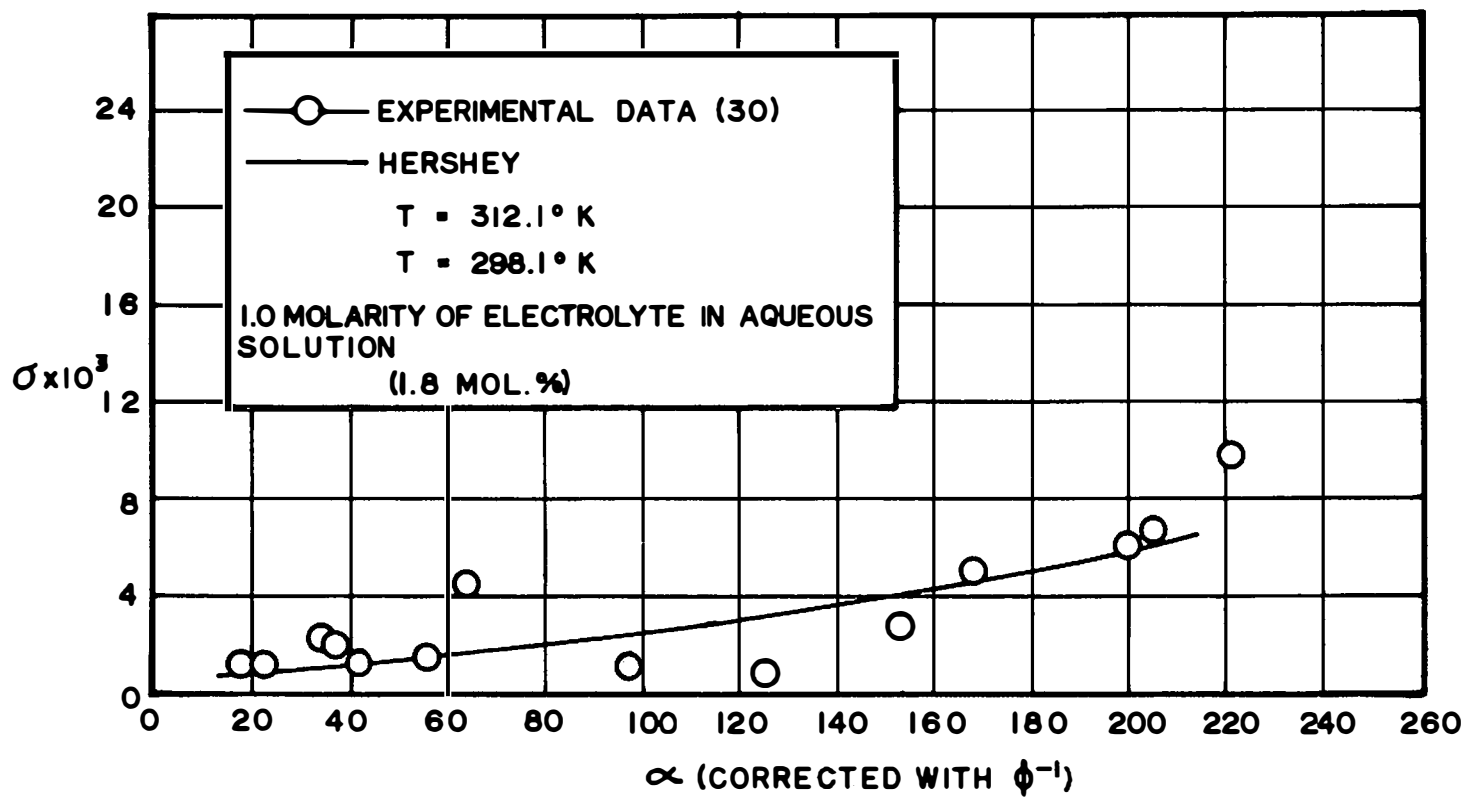


Figure 11. Soret Coefficient versus Corrected  $\alpha$  for Various Electrolytes in Aqueous Solution

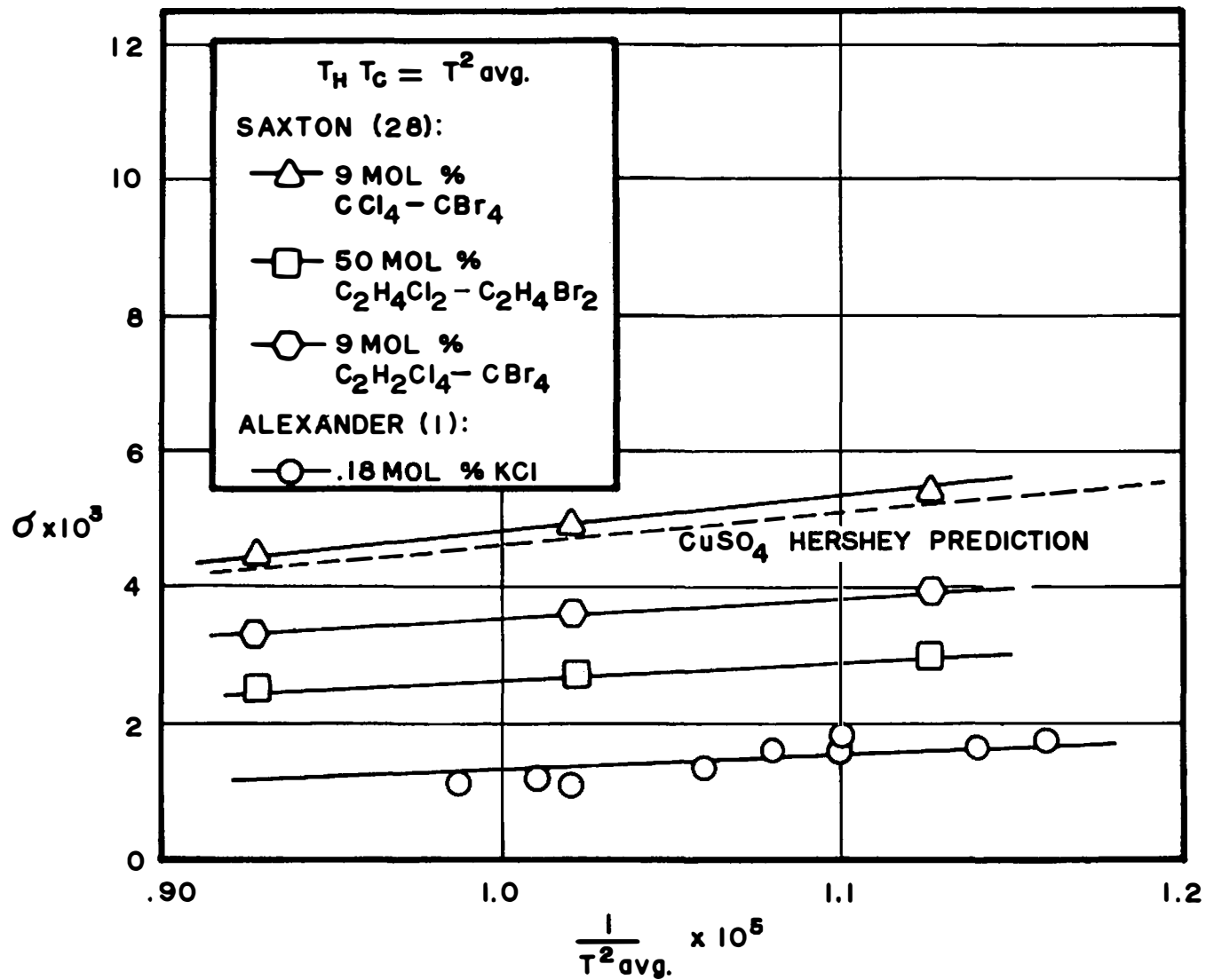


Figure 12. Soret Coefficient versus the Reciprocal of the Square of the Average Temperature

behavior.

On the basis of the results summarized in Figures 6, 7, 8, 11, and 12, and Table III, it is felt that the prediction of Soret coefficients for electrolytes in aqueous solution is now possible.

Part III which follows describes the experimental apparatus, procedure and results. Experimental values of the Soret coefficient were compared with calculated values.

## PART II

### CHAPTER III

#### CONCLUSIONS AND RECOMMENDATIONS

A mathematical development based on a quasistatic approach to irreversible thermal diffusion has been developed. By considering gases as being composed of ideal particles, and liquids as condensed gases, a system of equations was derived which allowed, within about 30 per cent, the successful prediction of separations to be expected in helium-argon, neon-argon, non-polar organic liquid pairs and electrolytes in aqueous solution.

The overall agreement between predicted and experimental results is encouraging, and while it obviously does not provide justification for any specific steps in the development, it does indicate that the results may be used with reasonable confidence for estimating separations where theoretical and experimental results are lacking.

It was also possible to predict the dependence of the separation upon concentration and temperature.

It is suggested that this approach be further tested with the view of extending the concepts to mixed electrolytes.

## PART III

### CHAPTER I

#### A NEW DESIGN FOR A SORET CELL

Two of the major experimental difficulties involved in obtaining separation data from a Soret cell are sampling techniques and the determination of the point of attainment of a steady state condition. Sampling difficulties hinge upon the requirement that there must be no disruptive convection currents caused by the technique. Some designs circumvent both of the above difficulties by not removing a sample from the cell. A cell described by Tanner (30) utilized a transparent glass Soret cell and an optical system which measured the deflection of a beam of light passed through the cell. Chipman (7) had two electrodes in the solution. Both of these schemes could monitor the concentration changes and note simultaneously the arrival at steady state and the concentration at that point. These methods, however, are not easily applied to the two-salt aqueous solutions since the change in the property measured would now also be a function of amount of each salt present. It would be necessary to measure two independent properties of the system simultaneously.

The cell used in this investigation is sketched in Figure 13, with photographs of the entire system shown in



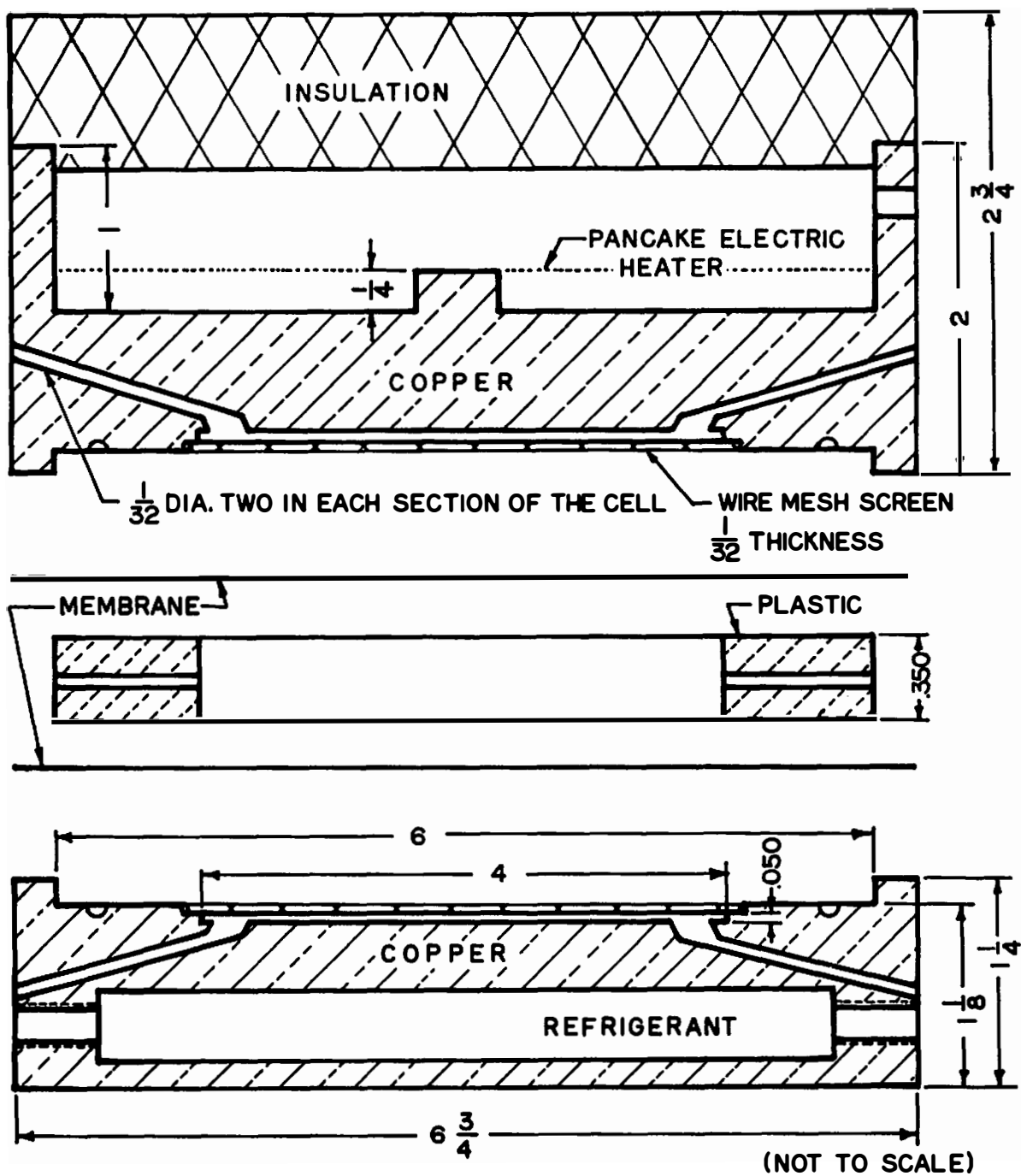


Figure 13. Drawing of the Thermal Diffusion Cell

Figures 14 and 15. The cell design allows the removal of 7-ml samples from the hot and cold ends without disrupting the remainder of the cell. This is accomplished by placing two cellophane membranes close to each end. Long (21) found that these porous membranes, though resistant to rapid macroscopic flow of solution, apparently did not affect the distribution of components under conditions of no net transfer. With a Beckman spectrophotometer available for analysis of samples as small as 1 ml, the cell design incorporated: (1) a minimal diffusion path and (2) solution samples that were representative of end conditions and not averages of each half of the cell. The systems chosen were  $\text{CuSO}_4\text{-H}_2\text{O}$ ,  $\text{CoSO}_4\text{-H}_2\text{O}$ , and  $\text{CuSO}_4\text{-CoSO}_4\text{-H}_2\text{O}$ . The concentration, mean temperature and temperature gradient were varied for the systems. A graphical summary of the results obtained is shown in Figures 16-20 of Chapter II.

## I. CELL DESIGN

The cell consisted essentially of three circular sections, two of copper and a plexiglas spacer between the copper sections. Each of the copper sections had an outside diameter of 6-3/4 inches and an inside diameter of 4 inches, with an .050-inch diffusion path. Cellophane membranes separated the copper sections from the plastic spacer. The plastic spacer provided the bulk of the diffusion path, 0.350

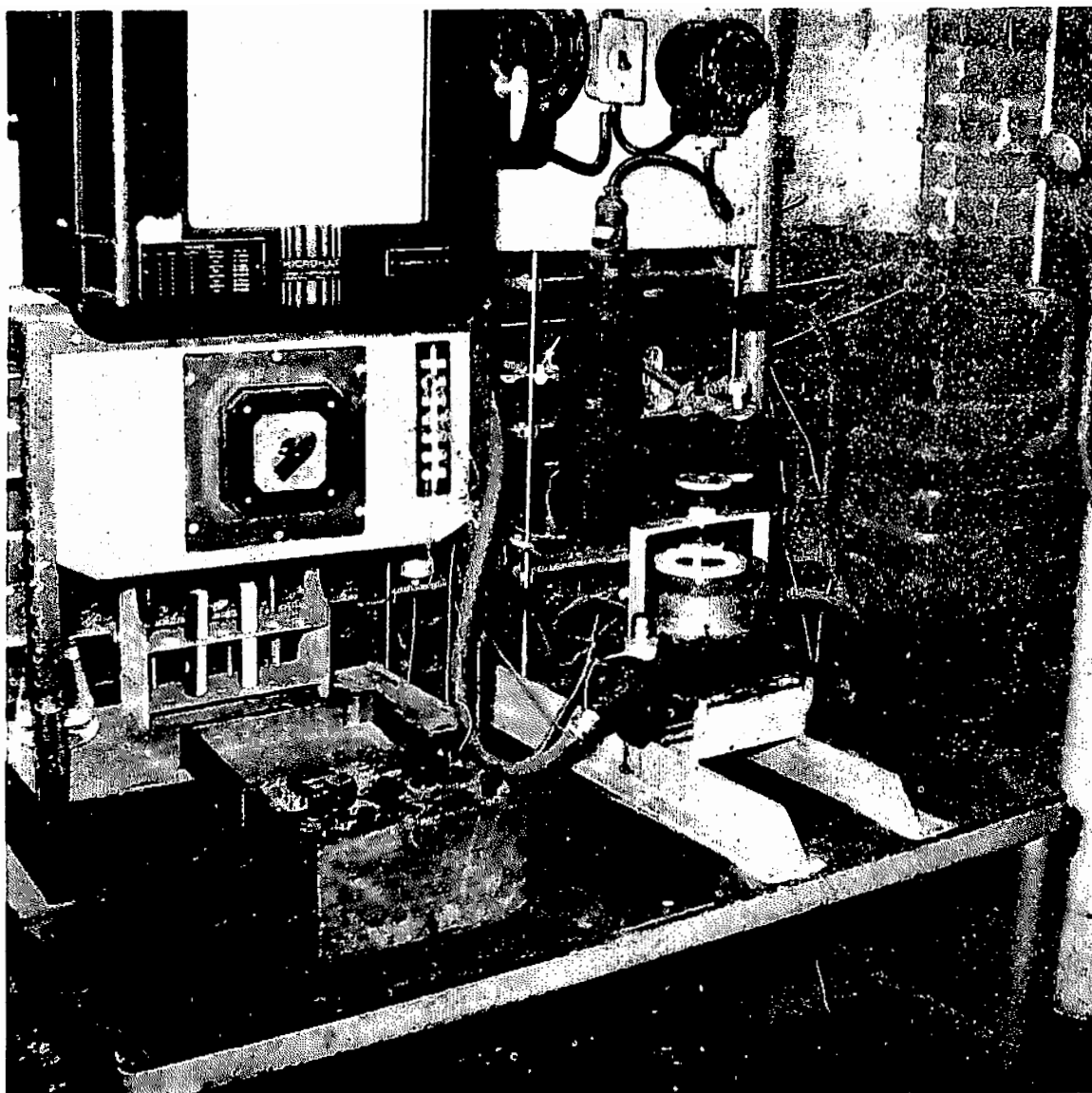


Figure 14. Photograph of the Apparatus with the Cell in an Upright Position.

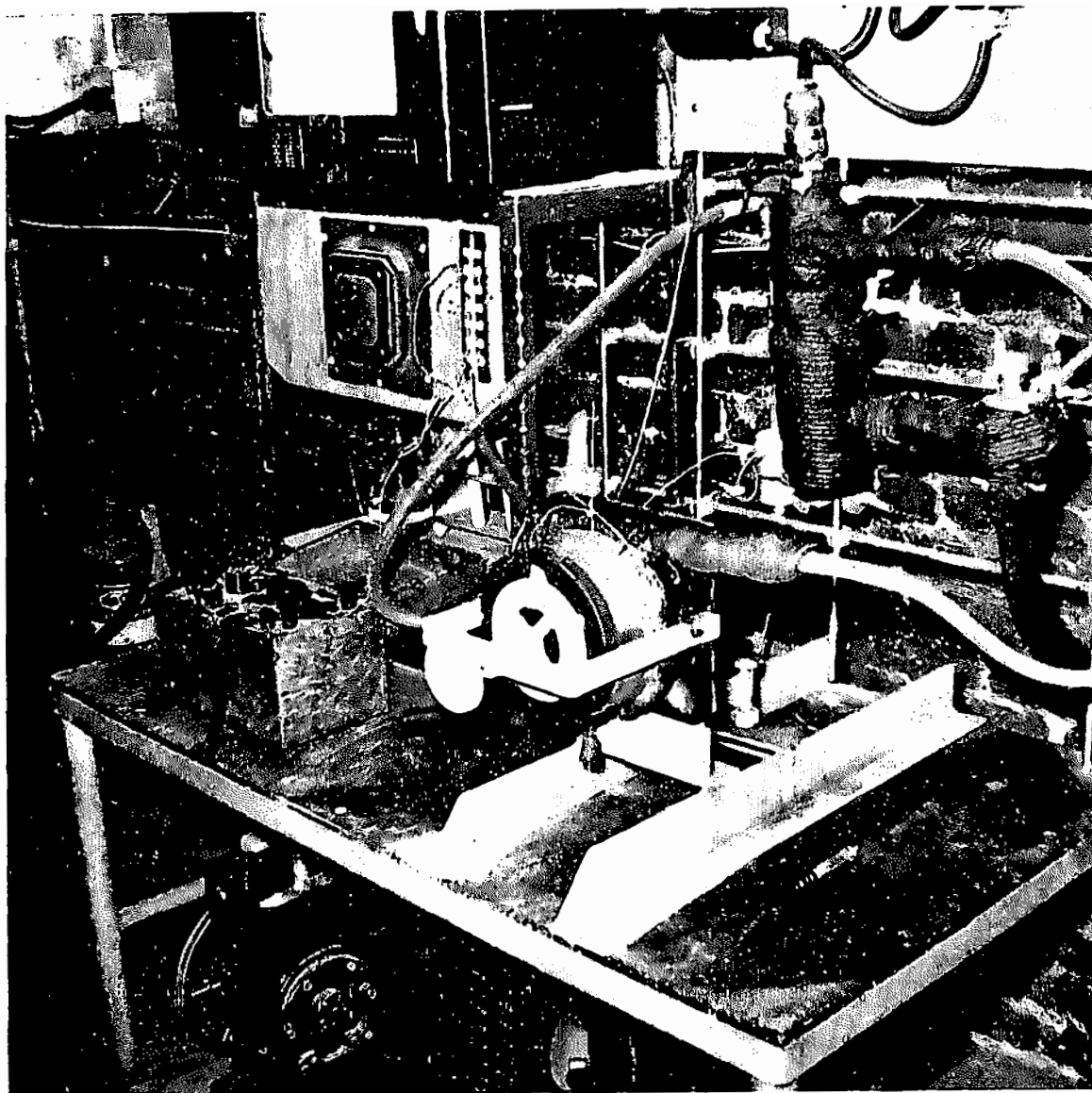


Figure 15. Photograph of the Apparatus with the Cell Tilted.

inch, and measured 5-3/4 inches in outside diameter and 4 inches in inside diameter. The three sections were clamped together. All of the "differential" liquid between the membrane and the end of the cell constituted a sample, which was removed from the cell by tipping the cell, opening the sample ports, and drawing the liquid into a hypodermic syringe.

## II. HEATING AND COOLING FACILITIES

The upper copper section housed a 375 watt "pancake" electric heater. Two copper-constantan thermocouples in the volume between the membrane and the hot wall monitored the temperature for a Leeds and Northrup Micromax controller. Provisions were also made for the simultaneous check of the thermocouple signal to the controller, using a Leeds and Northrup portable potentiometer.

The lower copper section incorporated a hollowed portion through which flowed the refrigerant, Freon-12. The refrigeration system was of a standard 1/2 HP, 6000 BTU/hr type. Two copper-constantan thermocouples were installed in the space between the membrane and the cold wall, with the emf signals read on the portable potentiometer.

## III. EXPERIMENTAL PROCEDURE

A run consisted in tipping the clamped cell vertically, filling the cell by inserting a hypodermic needle filled with

solution into the lower sample port of each section and injecting solution till it overflowed out of the upper sample port of each section. After the sample ports were closed, the cell was returned to a horizontal condition and the heating and cooling begun. At the conclusion of the run, the copper sections' sample ports were opened, the empty hypodermic needle inserted, the cell tipped and the sample drawn out. A steady state was achieved in about 24 hours.

The cellophane membrane was du Pont PT-600 which had been soaked in distilled water to remove the plasticizer. The membrane life was about one month under constant operation, so that the cell had to be dismantled only once a month. Wire mesh screens provided support for the membrane in the cell.

The analysis for the  $\text{CuSO}_4\text{-H}_2\text{O}$ ,  $\text{CoSO}_4\text{-H}_2\text{O}$ , and  $\text{CuSO}_4\text{-CoSO}_4\text{-H}_2\text{O}$  systems was made with a Beckman model DU spectrophotometer. The calculation of concentrations from the original spectrophotometer readings is shown in the Appendix, Part III-B, along with the governing equations and necessary absorbancy indices. In Long's thesis (21), the treatment of spectrophotometric data is dealt with in more detail.

## PART III

### CHAPTER II

#### DISCUSSION OF RESULTS

The experimental results are summarized in Figures 16-20 and Tables VI and VII. In Figures 16 and 17, the separations obtained in single salt and mixed salt experiments are plotted for 100°F temperature differences: 140°-40°F, and 159°-59°F. A straight line was drawn to represent these data by the usual least squares method and the standard deviation determined from this. The details are given in the Appendix, Part III-C. Tolerance limits of plus or minus two standard deviations are indicated by the dotted lines above and below the regression lines. It was found that all the data fell within the two standard deviation limit. Thus it can be asserted that if the regression line represents the data, and if it is assumed that the data are distributed normally about this line, then it would be expected that 95 per cent of the data points would fall within the two standard deviation limits. The data do conform to this specification. It is recognized that the sample consists of only twelve points and any conclusions drawn from this must be couched very conservatively.

It is noted from Figure 19 that the Soret coefficient increases with increasing concentration. These experimental

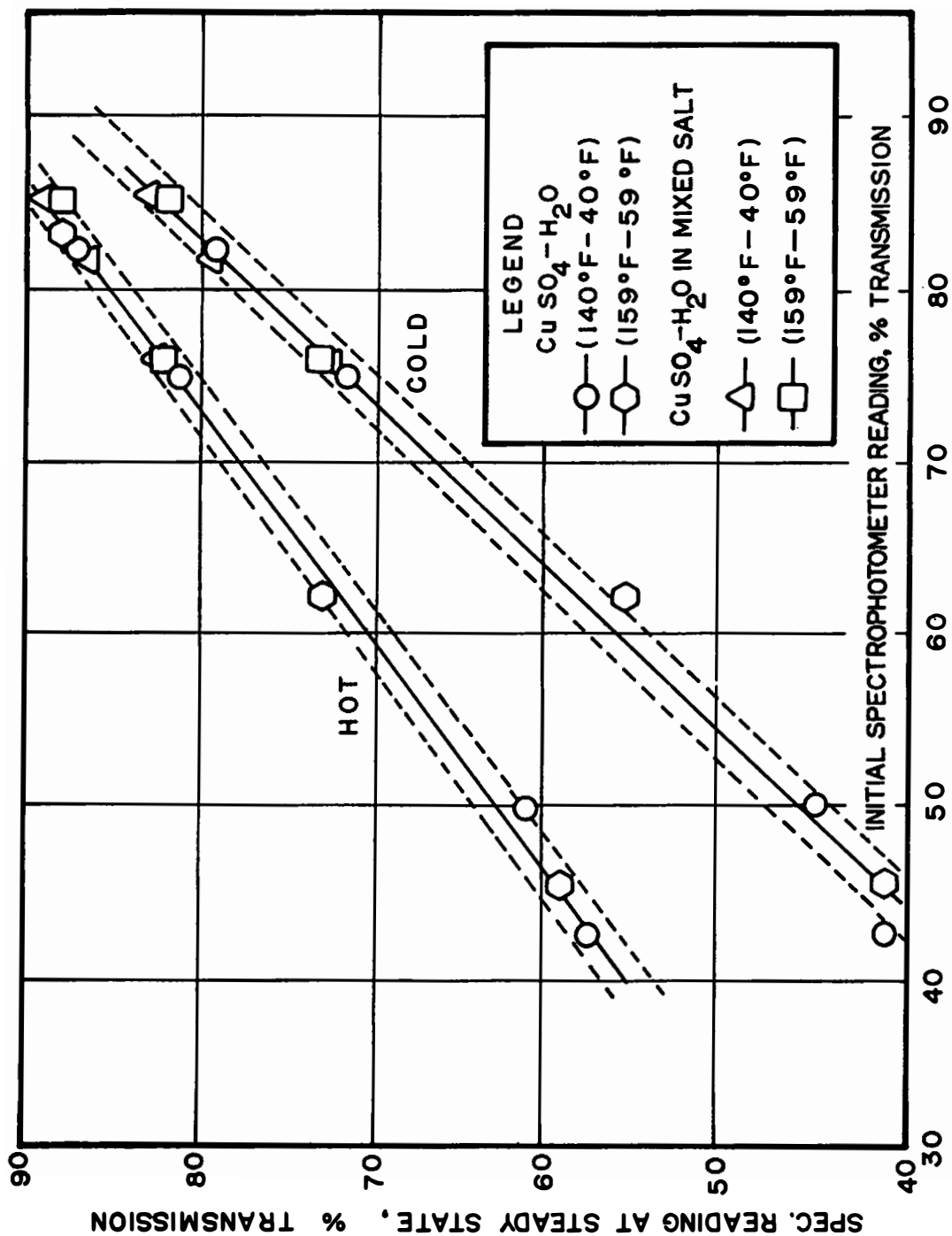


Figure 16. Spectrophotometer Reading at Steady State versus Initial Reading for  $\text{CuSO}_4\text{-H}_2\text{O}$



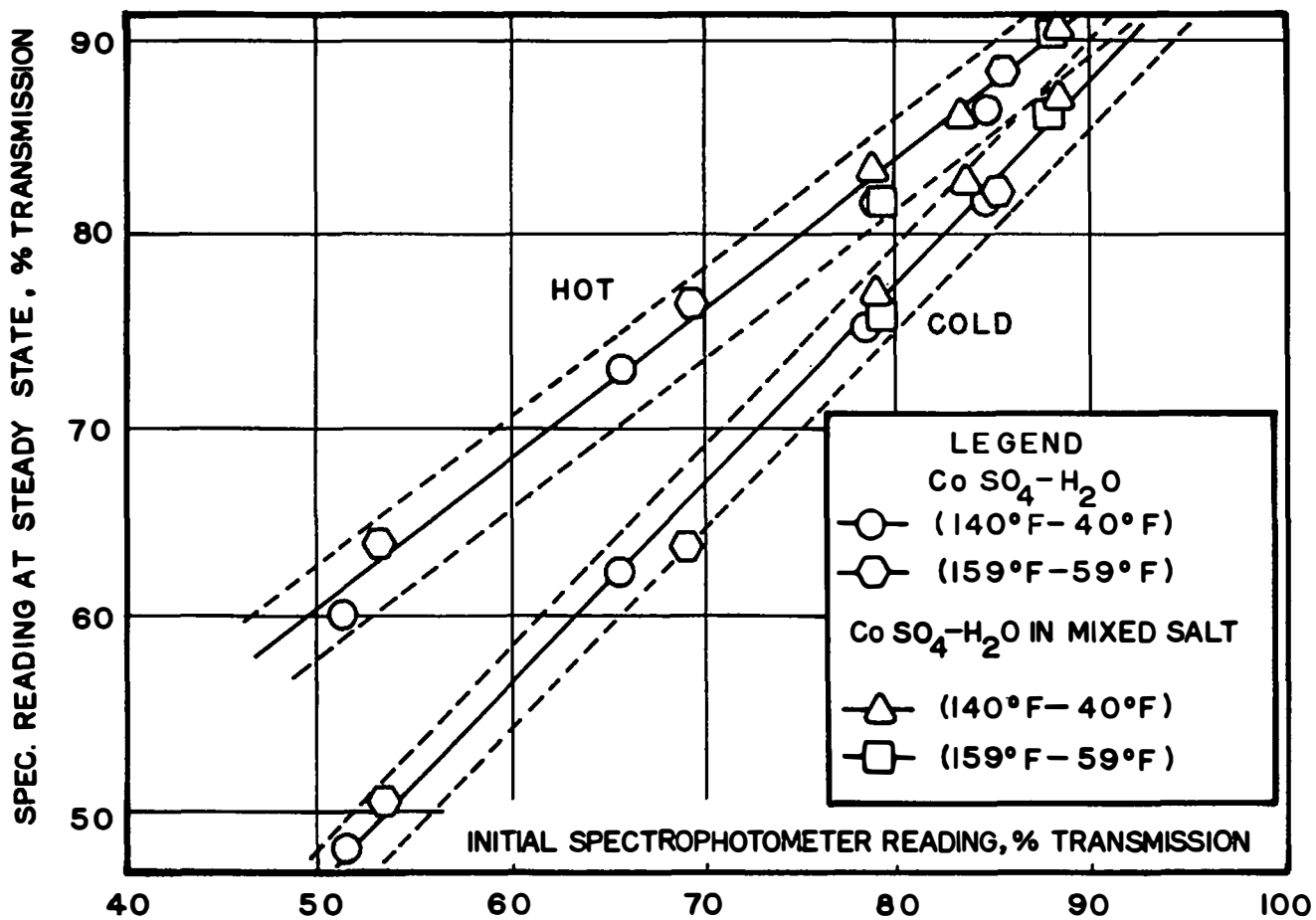


Figure 17. Spectrophotometer Reading at Steady State versus Initial Reading for  $\text{CoSO}_4 \cdot \text{H}_2\text{O}$

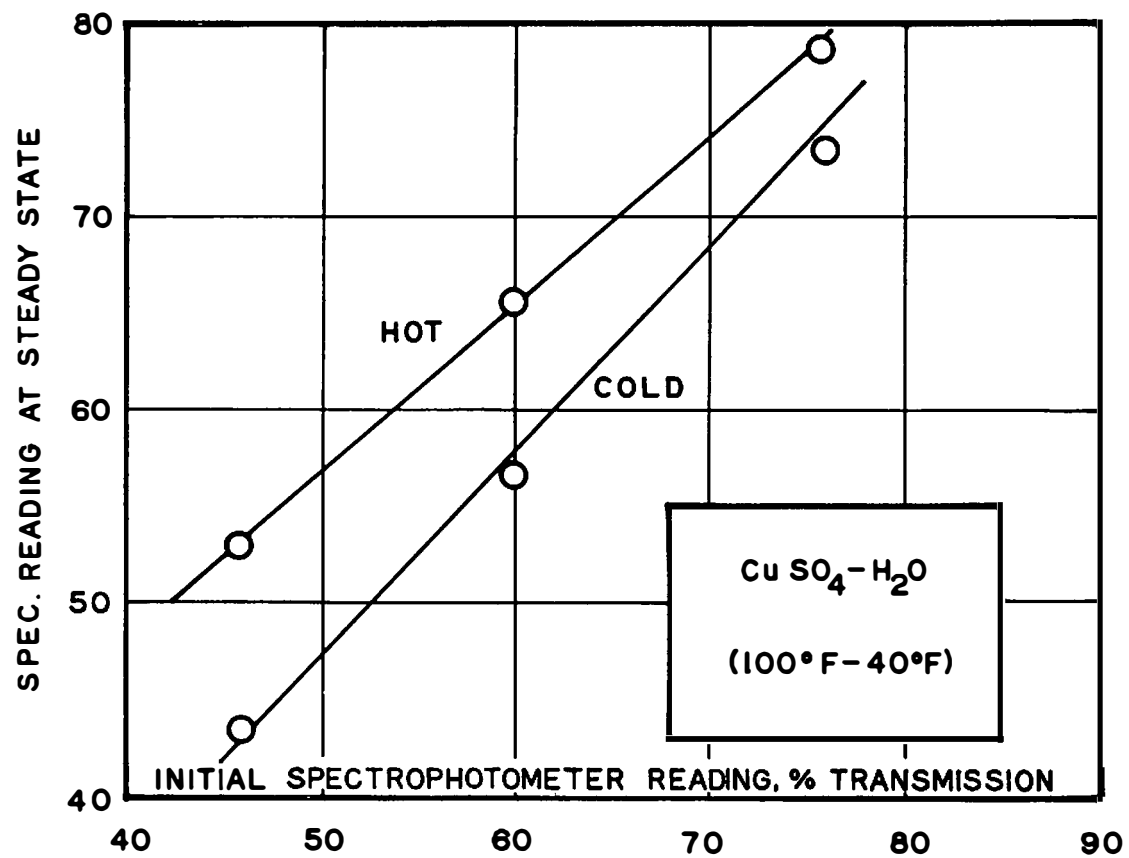


Figure 18. Spectrophotometer Reading at Steady State versus Initial Reading for  $\text{CuSO}_4\text{-H}_2\text{O}$

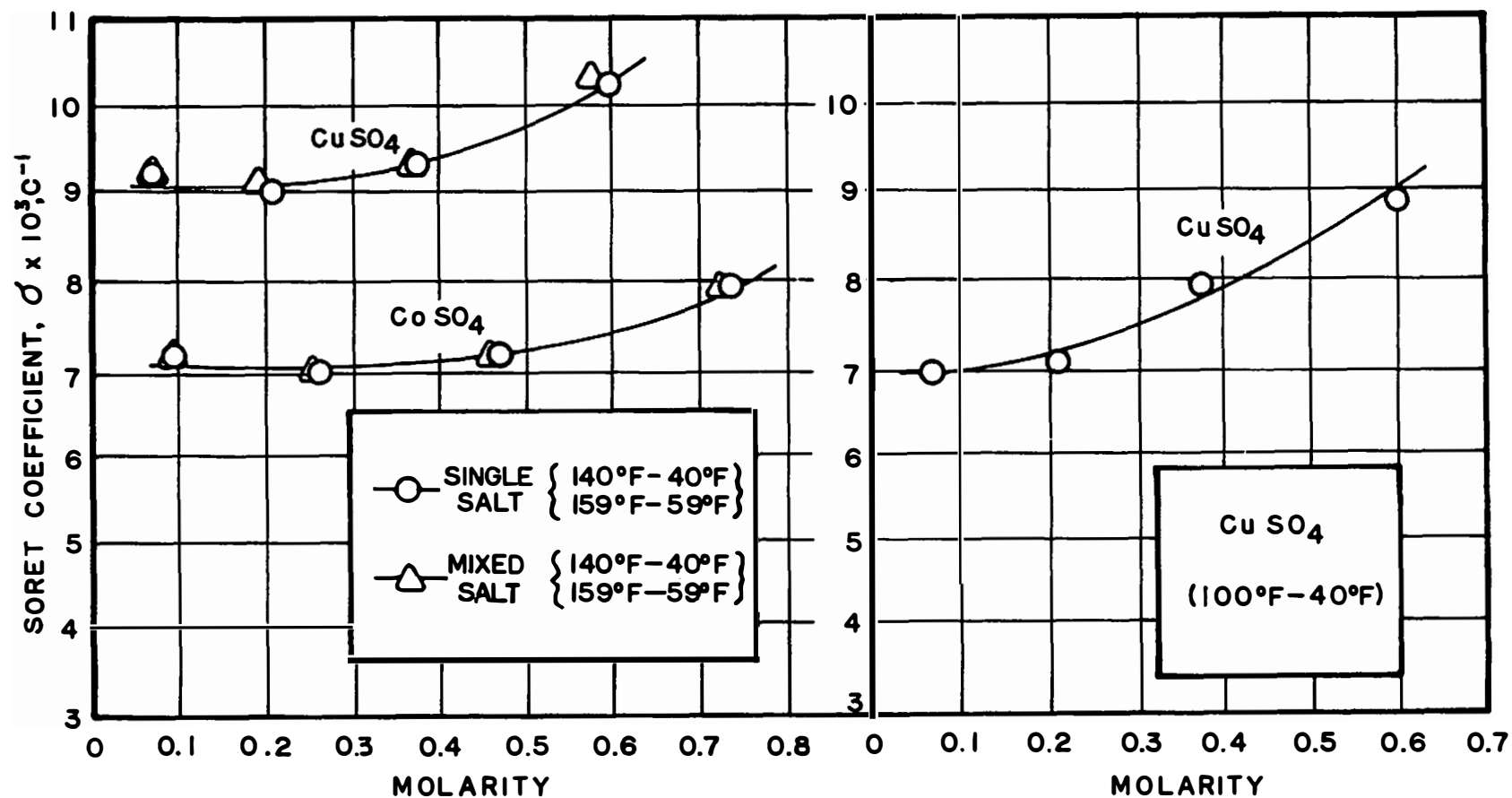


Figure 19. Soret Coefficients versus Concentration for  $\text{CuSO}_4$  and  $\text{CoSO}_4$  in Aqueous Solution

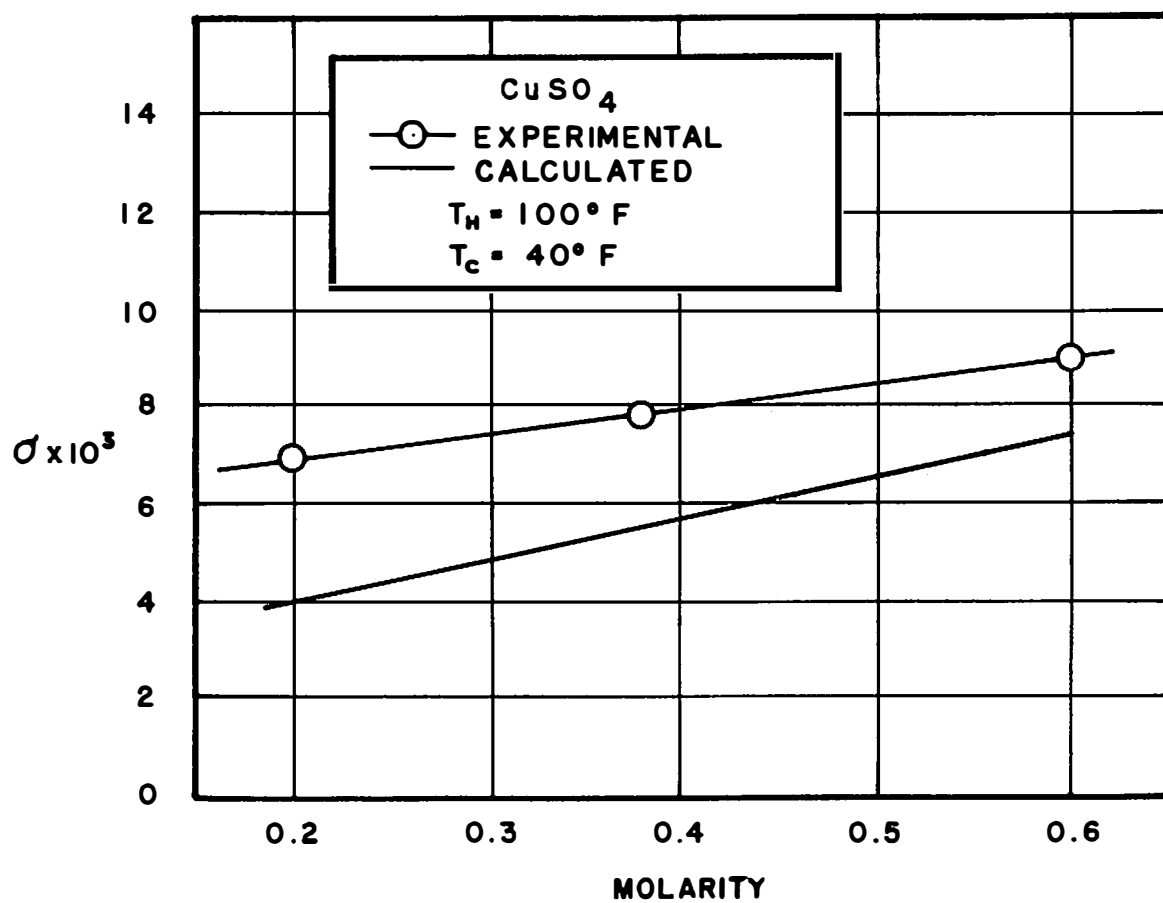


Figure 20. Soret Coefficient versus Concentration for  $\text{CuSO}_4$  Solution

TABLE VI  
SUMMARY OF THE CALCULATIONS OF THE SORET COEFFICIENTS  
FOR  $\text{CuSO}_4\text{-CoSO}_4\text{-H}_2\text{O}$  SYSTEM

Spectrophotometer R'd'g . % Transmission			Molarity			Soret Coeff. $\sigma \times 10^3$ $(^\circ\text{C})^{-1}$	System
Initial	Hot	Cold	Initial	Hot	Cold		
45	52.0	41.9	.598	.485	.654	8.87	
60	65.2	57.5	.376	.313	.407	7.87	$\text{CuSO}_4\text{-H}_2\text{O}$
75	78.3	73.4	.208	.177	.224	7.05	(100°-40°F)
90	91.2	89.1	.0753	.0654	.0824	6.88	
45	58.8	39.8	.598	.392	.695	10.2	
60	70.0	55.5	.376	.259	.435	9.27	$\text{CuSO}_4\text{-H}_2\text{O}$
75	81.3	71.2	.208	.149	.246	8.99	(159°-59°F)
90	92.4	87.7	.0753	.0562	.0939	9.21	(140°-40°F)
45	56.3	40.8	.733	.527	.822	7.91	
60	68.1	56.5	.469	.352	.524	7.10	$\text{CoSO}_4\text{-H}_2\text{O}$
75	80.0	72.0	.264	.205	.301	6.92	(159°-59°F)
90	91.7	87.9	.0965	.0799	.118	7.09	(140°-40°F)

**TABLE VII**  
**SUMMARY OF THE CALCULATIONS OF THE SORET COEFFICIENTS**  
**OF  $\text{CuSO}_4$  AND  $\text{CoSO}_4$  IN MIXED AQUEOUS SOLUTIONS**

Spectrophotometer Reading (% Transmission)					Molarity						Soret Coeff. $\sigma \times 10^3$ (°C) <sup>-1</sup>	
Initial	Hot Side		Cold Side		$\text{CuSO}_4$			$\text{CoSO}_4$			$\text{CuSO}_4$	$\text{CoSO}_4$
	$\text{CuSO}_4$	$\text{CoSO}_4$	$\text{CuSO}_4$	$\text{CoSO}_4$	Init	Hot	Cold	Init	Hot	Cold		
45	58.8	56.3	39.8	40.8	.579	.378	.674	.724	.521	.812	10.3	7.90
60	70.0	68.1	55.5	56.5	.364	.250	.422	.463	.348	.518	9.33	7.07
75	81.3	80.0	71.2	72.0	.202	.144	.239	.261	.202	.298	9.05	6.89
90	92.4	91.7	87.7	87.9	.0729	.0543	.0909	.0954	.0709	.117	9.26	7.07

results are compared with values calculated by the methods described previously and are shown in Figure 20. It is obvious that the experimental concentration dependence is adequately described by the calculated values.

Figure 21 is a plot of the temperature dependence of the experimental  $\text{CuSO}_4$  Soret coefficients. On this same figure calculated coefficients are also plotted. Note that at the higher temperature the experimental curve is horizontal, confirming the prediction of a small dependence of Soret coefficient upon temperature. However, at lower temperatures the Soret coefficient decreases, indicating perhaps an increasing complexity of the liquid structure. It can be stated, therefore, that it should be possible to predict separations to be expected for aqueous electrolyte solutions solely from non-experimental information, perhaps with the exception of low temperature conditions where the fluid deviates most strongly from the simple model postulated in the mathematical development.

For the  $100^\circ\text{F}$  gradient, the experimental coefficients were about 10 per cent higher than the corresponding results of Bosanquet (2). He used a cell partitioned in two equal halves, separated by a cellophane membrane. Arithmetic average values of concentration and temperature were assumed for each half.

Temperature control on the hot and cold sides was

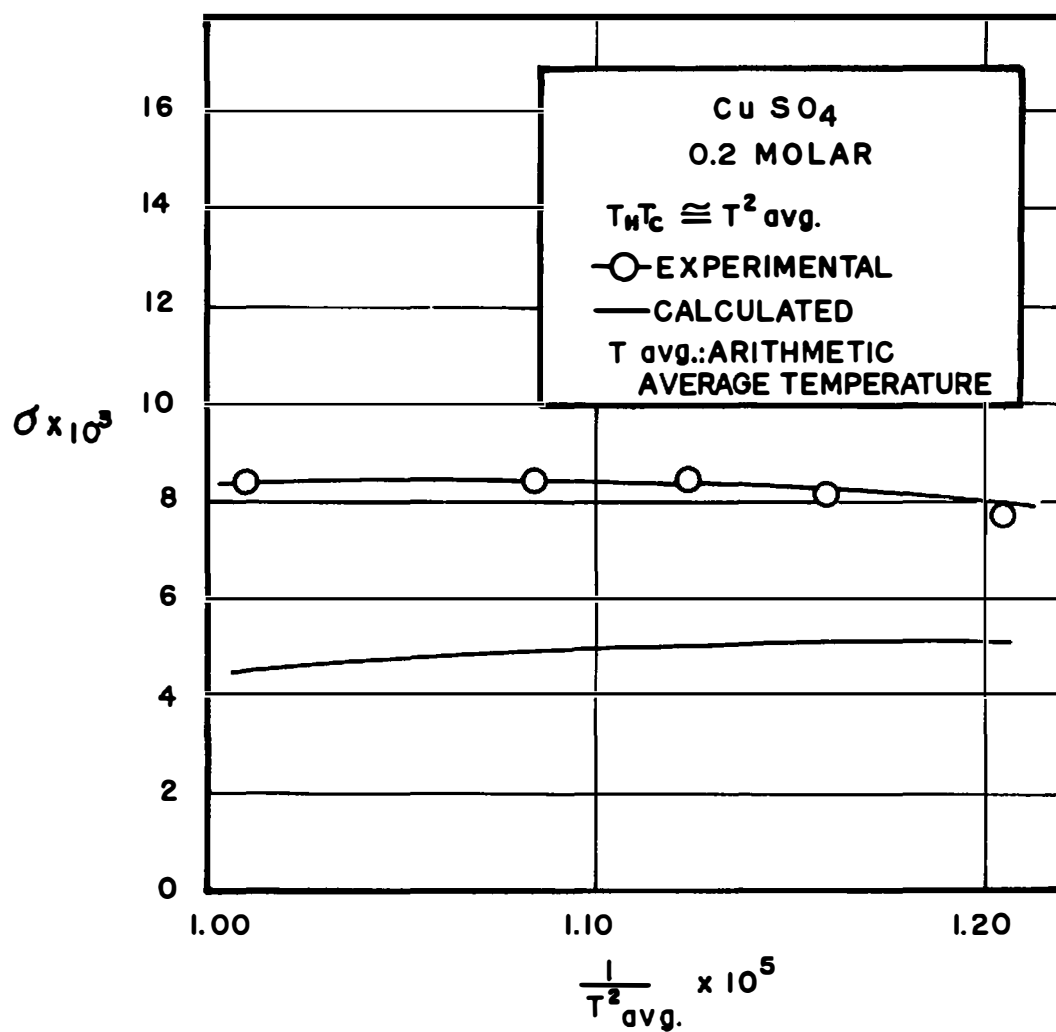


Figure 21. Soret Coefficient versus the Reciprocal of the Square of the Average Temperature for  $\text{CuSO}_4$



maintained at approximately  $\pm 1$  degree. The spectrophotometer was reproducible,  $\pm 0.5$  per cent transmission. Before making a run, the cell was always flushed with a portion of the solution that was about to be used, eliminating any significant residual errors. The two thermocouples in each sample zone were always within about two degrees of each other and hence an arithmetic average seemed reasonable. There was no measurement which appeared to introduce an unwarrantable degree of uncertainty.

## PART III

### CHAPTER III

#### CONCLUSIONS AND RECOMMENDATIONS

A Soret cell has been designed which allows the removal of a sample from the hot and cold ends of the cell without disrupting the rest of the contents. Soret coefficients increased monotonically from  $9.0-10.3 \times 10^{-3} \text{ } ^\circ\text{C}^{-1}$  over a 0.1-0.6 molarity range for  $\text{CuSO}_4$  and  $7.0-7.4 \times 10^{-3} \text{ } ^\circ\text{C}^{-1}$  for  $\text{CoSO}_4$  over the same molarity range. For the mixed salt system, no significant change in Soret coefficient of each component was detected as a result of the mixing.

At higher temperatures the Soret coefficient for  $\text{CuSO}_4$  was essentially constant but at the lower temperatures the Soret coefficient decreased with decreasing arithmetic average temperature. The high temperature behavior is generally in accord with the predicted behavior based on the development given in Part II.

A more durable membrane should be found and integrated into the design of the cell used in this investigation.

It is recommended that a thorough investigation be launched to study the effect of the membrane on Soret coefficients.

Soret coefficient data, as a function of temperature

difference, mean temperature and concentration need to be gathered so that a more satisfactory statistical analysis can be undertaken.

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## LIST OF REFERENCES

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## **APPENDICES**

### **PART II**



## APPENDIX A

### SAMPLE CALCULATIONS

#### 1. Calculation of Per Cent Separation of Neon-Argon

The trial and error solution of Equations 30-32, and 33a will be shown for a 50 per cent mixture.

From Equations 30, 30a-30c, with

$$T_H = 293.1^\circ\text{K}; \quad \alpha = 4.34$$

$$T_C = 90.2^\circ\text{K}; \quad N_2/N_1 = 1$$

$$C = \ln \frac{293.1}{90.2} = 1.18$$

$$B = \frac{293.1 - 90.2}{(293.1)(90.2)} = .00769^\circ\text{K}^{-1}$$

$$A = \frac{N_1}{N_1 + \alpha N_2} = \frac{1}{5.34} = 0.187$$

and

$$H^* = -125r + 96.3 + \frac{28.8}{r}$$

If  $r$  is varied, corresponding values of  $H^*$  can be calculated. A summary is given below.

(1)	(2)	(3)	(4)	(5)
<u>r</u>	<u><math>\frac{28.8}{r}</math></u>	<u>(2)+96.3</u>	<u>125 r</u>	<u><math>H^*=(3)-(4)</math></u>
0.5	57.6	153.9	62.5	91.4
0.6	48.0	144.3	75.0	69.3
0.7	41.2	137.5	87.5	50.0
0.8	36.0	132.3	100.0	32.3
0.9	32.0	128.3	112.5	15.8

From Equation 28,

$$T_o = \frac{293.1-90.2}{\ln \frac{2931}{902}} = 172.1^\circ\text{K}$$

With Equation 31 and  $r=0.5$ ;  $H^*=91.4$ , the result is

$$1 = \frac{\frac{172.1}{T_A} (1+4.34)}{1+(4.34)(0.5)e^{91.4/T_A}}$$

A trial and error solution is  $T_A=211.6^\circ\text{K}$ . Similarly for  $r=0.7$  and  $r=0.9$ , trial and error methods are employed.

For  $r=0.5$ ,  $H^*=91.4$ , Equation 32 becomes

$$1 = \frac{\frac{172.1}{T_B}(1+4.34)(0.5 e^{91.4/T_B})}{1+(4.34)(0.5) e^{91.4/T_B}}$$

It is necessary to again resort to trial and error methods of evaluating  $T_B$ . The solution is  $T_B=167.7^\circ\text{K}$ . Again values of  $T_B$  are determined for  $r=0.7$  and  $r=0.9$ . The results are given in the following table.

$N_1 = N_2$			
$r$	$H^*$	$T_A$	$T_B$
0.5	91.4	211.6	167.7
0.7	50.0	185.0	170
0.9	15.8	174.3	171.8

If Equation 33a is written in function notation as

$$1 = f(r, H^*, T_A, T_B)$$

and the three sets of values  $r$ ,  $H^*$ ,  $T_A$ ,  $T_B$  substituted into 33a, it is found that

$$f(0.5, 91.4, 211.6, 167.7) = 0.980$$

$$f(0.7, 50.0, 185.0, 170) = 0.995$$

$$f(0.9, 15.8, 174.3, 171.8) = 1.005$$

Interpolation yields

$$r = 0.80$$

$$H^* = 32.3$$

The separation is defined as

$$\begin{aligned} \text{Separation} &\equiv \left( \frac{\eta_2}{\eta_1 + \eta_2} \right)_C - \left( \frac{\eta_2}{\eta_1 + \eta_2} \right)_H \\ &= \frac{(\eta_2/\eta_1)_C}{1 + (\eta_2/\eta_1)_C} - \frac{(\eta_2/\eta_1)_H}{1 + (\eta_2/\eta_1)_H} \times 100 \\ &= \frac{(\eta_2/\eta_1)_C [1 + (\eta_2/\eta_1)_H] - (\eta_2/\eta_1)_H [1 + (\eta_2/\eta_1)_C]}{[1 + (\eta_2/\eta_1)_C] [1 + (\eta_2/\eta_1)_H]} \\ \text{Separation} &= \frac{(\eta_2/\eta_1)_C - (\eta_2/\eta_1)_H}{[1 + (\eta_2/\eta_1)_C] [1 + (\eta_2/\eta_1)_H]} \end{aligned}$$

From Equation 21, with  $r=0.80$ ,  $H^*=32.3$ , the separation is calculated below.

$$\begin{aligned} \text{Separation} &= \frac{0.8e^{32.3/90.2} - 0.8e^{32.3/293.1}}{(1 + 0.8e^{32.3/90.2})(1 + 0.8e^{32.3/293.1})} \\ &= \frac{0.8(1.430 - 1.116)}{[1 + (0.8)(1.430)][1 + (0.8)(1.116)]} \end{aligned}$$

$$= .0617$$

The separation is therefore 6.17 per cent.

## 2. A Calculation "Short Cut" for Liquids

For the calculations involving the liquids, a short cut was employed. This short cut involved the recognition that in most cases the heavier component usually migrates down the temperature gradient. Therefore, if initially  $N_2/N_1=3$ , where  $N_2$  and  $N_1$  refer to the number of atoms of the heavy and light components, respectively, then at steady state it would be expected that:

$$\left(\frac{\eta_2}{\eta_1}\right)_{\text{cold}} > 3 \quad \text{and} \quad \left(\frac{\eta_2}{\eta_1}\right)_{\text{hot}} < 3$$

Schematically, this is indicated in Figure 22, below.

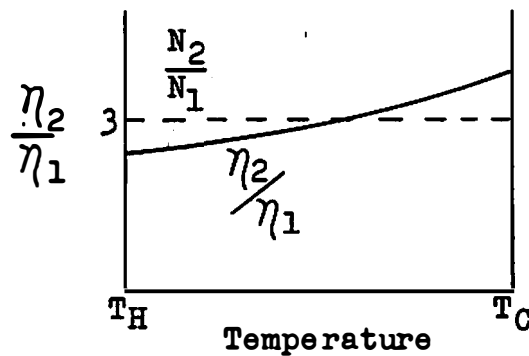


Figure 22. Concentration Ratio versus Temperature at Steady State.

If in Equation 30L various corresponding values of  $H^*$  and

$r$  are obtained so that curves such as in Figure 23 can be plotted from Figure 22, then it is possible to avoid trial

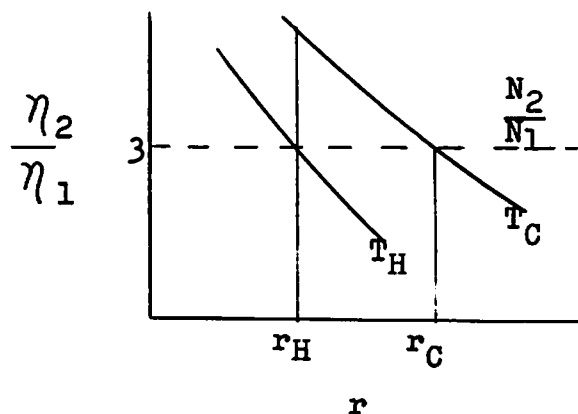


Figure 23. Concentration Ratio versus  $r$  at Steady State.

and error methods by utilizing the implications of Figures 22 and 23.

If  $\left(\frac{\eta_2}{\eta_1}\right)_{\text{cold}} > 3$ , then from Figure 23, the lower limit of the  $T_C$  curve is given by  $r=r_C$ . Similarly, if  $\left(\frac{\eta_2}{\eta_1}\right)_{\text{hot}} < 3$ , the indicated upper limit of the  $T_H$  curve is given by  $r=r_H$ . Thus  $r_H < r < r_C$  represents the permissible range of  $r$ . If corresponding values of  $(\eta_2/\eta_1)_{\text{hot}}$  and  $(\eta_2/\eta_1)_{\text{cold}}$  are determined from Figure 23 for  $r$  equal to  $r_H$ ,  $r_C$ , and intermediate values, Soret coefficients can be calculated from these  $\eta_2/\eta_1$  pairs. The values of the Soret coefficient by this method for the organic liquid pairs varied

only slightly over the range of  $r$  so that an arithmetic average could be confidently used. The result was a Soret coefficient for a fixed temperature gradient and  $N_2/N_1$ . This procedure in detail is presented in the section 3 of this appendix. The calculations showing the conversion of a  $(\eta_2/\eta_1)_{\text{hot}}$  and  $(\eta_2/\eta_1)_{\text{cold}}$  pair to a Soret coefficient is also shown.

For the aqueous electrolyte calculations, the above procedure was utilized to determine the allowable  $r$  range. The calculations proceeded, governed by the equations developed in Part II, Chapter I of this report.

### 3. The Calculation of Soret Coefficients from Equation 30L

The following procedure obviates the tedious trial and error procedure outlined in section 1. All calculations involving liquids, including electrolytes, followed the "short cut" procedure. Let  $N_2/N_1 = .040$  (3.85%);  $T_H = 312.1^\circ\text{K}$ ;  $T_C = 298.1^\circ\text{K}$ . The heavier component is denoted as component 2. For  $\alpha = 100$ , with Equations 30L, 30L-a—30L-c,

$$A = \frac{N_1}{N_1 + \alpha N_2} = 1 + \frac{1}{4} = 0.20$$

$$\frac{C}{B} = \frac{312.1 - 298.1}{\ln \frac{312.1}{298.1}} = 305$$

Equation 30L becomes

$$H^* = 305 \left[ -20r + .600 + \frac{.008}{r} \right]$$

If the heavier component is assumed to migrate down the temperature gradient, then, at steady state,  $(\eta_2/\eta_1)_C > .040$  and  $(\eta_2/\eta_1)_H < .040$ . Corresponding values of  $H^*$  and  $r$  will be calculated, so that  $\eta_2/\eta_1$  values (from  $\eta_2/\eta_1 = re^{H^*/T}$ ) straddle the allowable range. A summary of such calculations is given below.

(1) $r$	.01	.005	.003
(2) $20r$	.200	.100	.060
(3) $.008/r$	.800	1.60	2.67
(4) $.600-(2)$	.400	.500	.540
(5) $(3)+(4)$	1.20	2.10	3.21
(6) $H^*=305(5)$	366	640	979
(7) $(\eta_2/\eta_1)_H$	.0323	.0389	.0692
(8) $(\eta_2/\eta_1)_C$	.0341	.0428	.0801

In Figure 24,  $(\eta_2/\eta_1)_C$  and  $(\eta_2/\eta_1)_H$  values are plotted as functions of  $r$ , with the allowable range for  $\eta_2/\eta_1$  marked off. Three values of  $r$ , .0040, .0052, and .0056, represent the extremities and the mid-point of the allowable range. The corresponding values of  $\eta_2/\eta_1$  from Figure 24 are tabulated below.

$r$	$(\eta_2/\eta_1)_C$	$(\eta_2/\eta_1)_H$
.0048	.0438	.0400
.0052	.0410	.0381
.0056	.0400	.0367

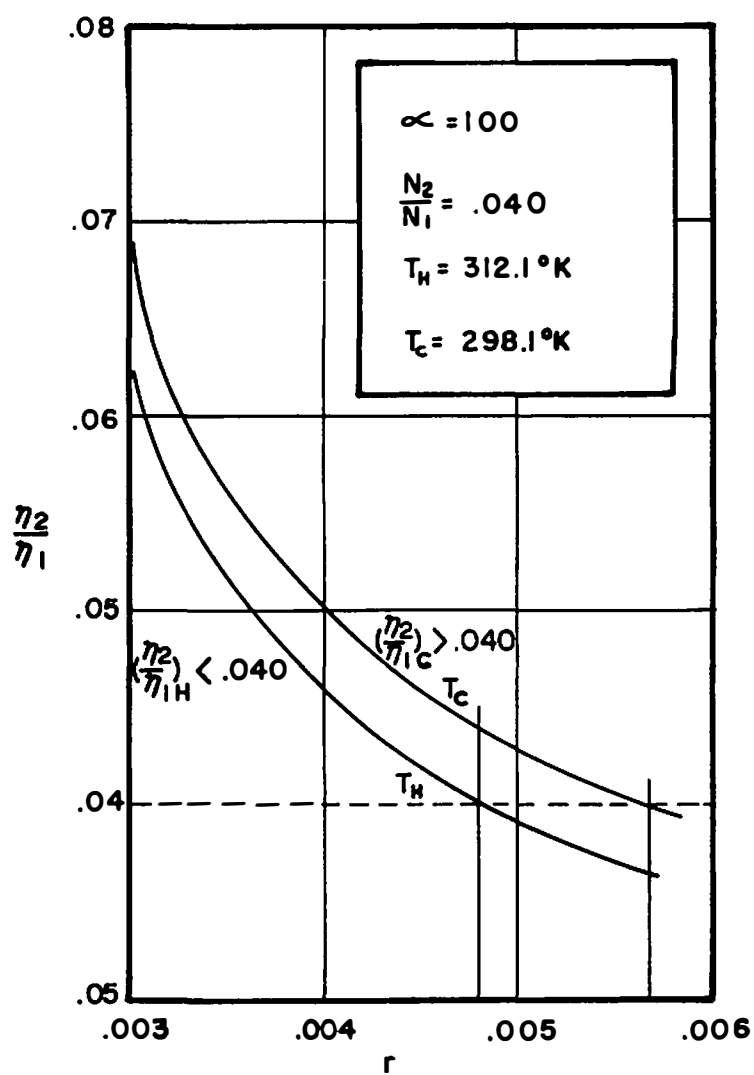


Figure 24. Concentration Ratio versus  $r$  for Liquids



Since  $\eta$  represents atoms per volume,  $\frac{\eta_2/N}{\eta_1/N}$  represents mole ratio, with  $N$  equal to Avogadro's number. Therefore mole fraction is equal to  $\frac{\eta_2/\eta_1}{1+\eta_2/\eta_1}$ . The Soret coefficient is defined by

$$\sigma = \frac{1}{T_H - T_C} \ln \frac{(\text{mole fraction})_C}{(\text{mole fraction})_H}$$

where component 2 is the component of interest and represents the electrolyte. Therefore,

$$r=.0048: \quad \sigma = \frac{1}{14} \ln \frac{.0438/1.0438}{.0400/1.040} = .00622$$

$$r=.0052 \quad \sigma = .00635$$

$$r=.0056 \quad \sigma = .00589$$

Hence

$$\sigma_{\text{avg}} \times 10^3 = 6.15$$

#### 4. Derivation of Figure 5

For an atom to be in its ground state, each electron of the atom must be in its orbital ground state. The energy of each electron is then the energy required to remove the electron from its orbit to infinity. This energy is called the ionization potential. In Figure 4, the ionization potential is plotted as a function of atomic number,  $z$ , for various orbits. The sum of the ionization potentials of all the electrons in an atom is defined as the electronic energy

of the atom.

As an example of how the points were determined for Figure 5, consider carbon ( $Z=6$ ) in its ground state.

Carbon:  $Z=6$

Ground State				Ionization Potential (electron volts)
$1s^2$	$2s^2$	$2p^2$	$3P_0$	11.3
$1s^2$	$2s^2$	$2p$	$2P_{\frac{1}{2}}^0$	24.4
$1s^2$	$2s^2$	$1S_0$		47.9
$1s^2$	$2s$	$2S_{\frac{1}{2}}$		64.5
$1s^2$	$1S_0$			392.0
$1s$	$2S_{\frac{1}{2}}$			<u>489.8</u>
				1029.9

Carbon:  $Z^2 = 36$ ; I.P. = 1029.9 EV.

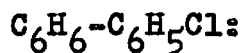
### 5. The Calculation of $\alpha$ for Some Systems

Three representative systems will be selected to illustrate how  $\alpha$  was calculated.

<u>Neon-Argon:</u>	<u>From Figure 5</u>	
	I.P.	$\alpha = \frac{E_2}{E_1}$
*Component 2: Argon ( $Z=18$ )	16,700	4.34
Component 1: Neon ( $Z=10$ )	3,850	

---

\*Component 2 is always the heavier one.



In dealing with molecules, the calculation of the electronic energy of each species becomes considerably more uncertain. However, if it is assumed that in the formation of a molecule from its elements, the energy change involves only the outer electrons, and then only on the order of magnitude of the heat of formation, the calculation method becomes more rational. For example, the ionization potential of the outer electron of carbon is seen to be 11.3 EV. The heat of formation of  $C_6H_6(L)$  is 11,600 calories per mole, or about 1/2 electron volt per molecule. In section 4 of this appendix the electronic energy of carbon was found to be 1,029.9 electron volts. Noting the possible energy changes introduced by carbon-hydrogen, carbon-carbon, and the benzene ring formation, it would seem reasonable to neglect these effects and proceed to calculate  $\alpha$  by adding the contribution of each atom in the molecule. For the  $C_6H_6-C_6H_5Cl$  system,

From Figure 5

	I.P.
Carbon ( $Z=6$ )	1030
Hydrogen ( $Z=1$ )	13.6
Chlorine ( $Z=17$ )	13,053

and

$$\begin{aligned}
 \text{Electronic Energy, } C_6H_6 &= 6(1030)+6(13.6)=6,260 \text{ EV} \\
 \text{Electronic Energy, } C_6H_5Cl &= 6(1030)+5(13.6)+13,053 \\
 &= 19,300 \text{ EV}
 \end{aligned}$$

Therefore,

$$\alpha = \frac{19,300}{6,260} = 3.08$$

H<sub>2</sub>O-CdSO<sub>4</sub>:

Ionization of an electrolyte in aqueous solution is usually assumed to affect the outer, or valence, electrons of an atom. It has been noted previously that the contribution of the outer electrons to the total electronic energy of an atom is very small. Therefore, the error introduced by ignoring the ionization when determining the electronic energy of the atom should be negligible.

The salt will be assumed to be completely ionized in solution. Any deviation from this will be corrected for by introducing a correction factor,  $\frac{\nu}{i}$ , where  $\nu$  is the number of ions produced at infinite dilution and  $i$  is the van't Hoff Factor. The use of the correction factor is illustrated in section 6 of this appendix. Since electroneutrality is a necessary condition, it will be assumed that statistically the salt migrates as a neutral molecule (or ion-associated complex). Therefore,

From Figure 5

I.P.

Cadmium	(Z=48)	170,000 EV
Sulfur	(Z=16)	12,000
Oxygen	(Z=8)	2,300
Hydrogen	(Z=1)	13.6

$$\begin{aligned}\text{Electronic Energy, CdSO}_4 &= 170,000 + 12,000 + 4(2,300) \\ &= 191,000 \text{ EV}\end{aligned}$$

$$\begin{aligned}\text{Electronic Energy, H}_2\text{O} &= 2(13.6) + 2,300 \\ &= 2,330 \text{ EV}\end{aligned}$$

and

$$\alpha = \frac{191,000}{2,330} = 82.0$$

#### 6. The Calculation of $\alpha$ Using the Correction Factor, $\frac{\nu}{i}$

From Robinson and Stokes (26),  $\frac{\nu}{i} = \frac{1}{\phi} = \phi^{-1}$ , where  $\phi$  is the molal osmotic coefficient. Since the deviation of the electrolyte from ideality has been imputed to an apparent atomic number greater than the literature value, the correction is applied as indicated below.

$\text{H}_2\text{O}-(\text{CdSO}_4)^*$

$$\text{Cd}^* = \phi^{-1} \text{ Cd}$$

$$\text{S}^* = \phi^{-1} \text{ S}$$

$$\text{O}^* = \phi^{-1} \text{ O}$$

For a 0.5 molal solution,  $\phi = .466$ , or  $\phi^{-1} = \frac{1}{.466} = 2.1$

Specifically,

		<u>From Figure 5</u>
	Z	I.P.
$\text{Cd}^* = 2.1(48)$	100.8	1,000,000
$\text{S}^* = 2.1(16)$	33.6	70,000
$\text{O}^* = 2.1(8)$	16.8	4(14,000)
		<hr/> 1,126,000

---

\*Denotes apparent behavior.

and

$$\alpha = \frac{1,126,000}{2,330} = 483$$

### 7. The Calculation of the "Hershey" Correction Factor

The Hershey factor is defined as the correction to the atomic number of the electrolyte so that the coordinates  $(\sigma, \alpha)$  of each electrolyte, fall on the calculated line determined from Equation 30L. The Soret coefficient,  $\sigma$ , is the experimental value.

#### H<sub>2</sub>O-CdSO<sub>4</sub>:

The Soret coefficient for a 0.50 molal solution (0.89 mol per cent) is given by Tanner (30) as  $\sigma \times 10^3 = 6.85$ . From Figure 10,  $\alpha = 345$  is required for the data point to fall on the calculated line. Since

$$\alpha = \frac{E_2^*}{E_1} = \frac{E_{\text{CdSO}_4}^*}{E_{\text{H}_2\text{O}}} = \frac{E_{\text{CdSO}_4}^*}{2300} = 345$$

it follows that

$$E_{\text{CdSO}_4}^* = 793,000$$

$$Z^* = HZ, \text{ or } \text{Cd}^* = H|\text{Cd}| = H(48)$$

$$S^* = H|S| = H(16)$$

$$O^* = H|\text{O}| = H(8)$$

To the nearest tenth, it was found that  $H = 1.8$

---

\*Denotes apparent behavior.

The calculations are shown below.

		<u>From Figure 5</u>
	Z	I.P.
Cd* = 1.8(48)	86.4	720,000
S* = 1.8(16)	28.8	50,000
O* = 1.8(8)	14.4	<u>4(10,000)</u>
		810,000

The Hershey factor = 1.8

---

\*Denotes apparent behavior.

## APPENDIX B

### DERIVATION OF EQUATIONS 30 AND 30L FROM A TAYLOR EXPANSION OF THE INTEGRANDS OF EQUATIONS 29 AND 29L

#### 1. Perfect Gas, Equation 29

$$\frac{N_1}{N_1 + \alpha N_2} \ln \frac{T_H}{T_C} = \int_{1/T_H}^{1/T_C} \frac{dz}{z(1 + \alpha r e^{H^* z})}$$

$$\text{Let } f(z) = \frac{1}{(1 + \alpha r e^{H^* z})} ; \quad f(0) = \frac{1}{(1 + \alpha r)}$$

$$f'(z) = - \frac{\alpha r H^* e^{H^* z}}{(1 + \alpha r e^{H^* z})^2} ; \quad f'(0) = - \frac{\alpha r H^*}{(1 + \alpha r)^2}$$

Neglect second order and higher terms. (The error introduced by neglecting second order and higher terms will be approximated at the end of Appendix B.) Therefore,

$$\frac{f(z)}{z} = \frac{1}{z(1 + \alpha r e^{H^* z})} \approx \left( \frac{1}{1 + \alpha r} \right) \frac{1}{z} - \frac{\alpha r H^*}{(1 + \alpha r)^2}$$

and from Equation 29

$$\frac{N_1}{N_1 + \alpha N_2} \ln \frac{T_H}{T_C} = \left( \frac{1}{1 + \alpha r} \right) \int_{1/T_H}^{1/T_C} \frac{dz}{z} - \frac{\alpha r H^*}{(1 + \alpha r)^2} \int_{1/T_H}^{1/T_C} dz \quad (\text{B-1})$$



If the integration is performed and the limits substituted, the result is

$$\frac{N_1}{N_1 + \alpha N_2} \ln \frac{T_H}{T_C} = \left( \frac{1}{1 + \alpha r} \right) \ln \frac{T_H}{T_C} - \frac{\alpha r H^*}{(1 + \alpha r)^2} \left[ \frac{T_H - T_C}{T_H T_C} \right] \quad (B-2)$$

$$\text{Let } A = \frac{N_1}{N_1 + \alpha N_2}$$

$$B = \frac{T_H - T_C}{T_H T_C}$$

$$C = \ln \frac{T_H}{T_C}$$

$$x = \alpha r$$

$$1 + x = 1 + \alpha r$$

and substitute these quantities into Equation B-2. With some rearrangement, Equation B-3 can be obtained,

$$\left[ A - \frac{1}{(1+x)} \right] C = - \left[ \frac{x H^*}{(1+x)^2} \right] B \quad (B-3)$$

and finally,

$$H^* = \frac{\frac{C}{B} \left[ \frac{1}{(1+x)} - A \right]}{\left[ \frac{x}{(1+x)^2} \right]}$$

$$H^* = \frac{C}{B} \left[ \frac{(1+x)}{x} - \frac{(1+x)^2 A}{x} \right]$$

$$H^* = \frac{C}{B} \left[ \frac{(1-A) + (1-2A)x - Ax^2}{x} \right]$$

$$H^* = \frac{C}{B} \left[ -A\alpha r + (1-2A) + \frac{(1-A)}{\alpha r} \right] \quad (30)$$

## 2. Liquids, Equation 29L

$$\frac{N_1}{N_1 + \alpha N_2} (T_H - T_C) = \int_{1/T_H}^{1/T_C} \frac{dz}{z^2 (1 + \alpha r e^{H^* z})}$$

As done previously, if second order and higher terms are neglected,

$$\frac{N_1}{N_1 + \alpha N_2} (T_H - T_C) = \frac{1}{(1 + \alpha r)} \int_{1/T_H}^{1/T_C} \frac{dz}{z^2} - \frac{\alpha r H^*}{(1 + \alpha r)^2} \int_{1/T_H}^{1/T_C} \frac{dz}{z} \quad (B-4)$$

or

$$\frac{N_1}{N_1 + \alpha N_2} (T_H - T_C) = \left( \frac{1}{1 + \alpha r} \right) (T_H - T_C) - \frac{\alpha r H^*}{(1 + \alpha r)^2} \ln \frac{T_H}{T_C} \quad (B-5)$$

With

$$A = \frac{N_1}{N_1 + \alpha N_2}$$

$$B = \ln \frac{T_H}{T_C}$$

$$C = T_H - T_C$$

$$x = \alpha r$$

$$1+x = 1+\alpha r$$

and Equation B-5, the result is:

$$AC = \left(\frac{1}{1+x}\right) C - \frac{H^*x}{(1+x)^2} B$$

$$H^* = C\left(\frac{1}{1+x} - A\right) / \frac{xB}{(1+x)^2}$$

$$H^* = \frac{C(1-A-Ax)(1+x)}{xB}$$

$$H^* = \frac{C}{B} \left[ -Ax + (1-2A) + \frac{1-A}{x} \right]$$

or finally

$$H^* = \frac{C}{B} \left[ -A\alpha_r + (1-2A) + \frac{(1-A)}{\alpha_r} \right] \quad (30L)$$

Error Introduced by Neglecting Second Order and Higher Terms in the Derivation of Equations 30 and 30L

Given:

$$f(z) = \frac{1}{(1+\alpha_r e^{H^*z})} ; \quad f(0) = \frac{1}{1+\alpha_r} \quad (B-6)$$

Then

$$f'(z) = \frac{-H^*\alpha_r e^{H^*z}}{(1+\alpha_r e^{H^*z})^2} ; \quad f'(0) = \frac{-H^*\alpha_r}{(1+\alpha_r)^2} \quad (B-7)$$

$$\begin{aligned} f''(z) &= \frac{df'(z)}{dz} = \frac{d}{dz} (-H^*\alpha_r) \left[ e^{H^*z} (1+\alpha_r e^{H^*z})^{-2} \right] \\ &= (-H^*\alpha_r) \left[ e^{H^*z} (-2)(1+\alpha_r e^{H^*z})^{-3} (\alpha_r e^{H^*z}) \right. \\ &\quad \left. + (1+\alpha_r e^{H^*z})^{-2} (H^*) e^{H^*z} \right] \end{aligned}$$

$$\begin{aligned}
&= (-H^* \alpha_r) (1 + \alpha_{re}^{H^* z})^{-2} (H^* e^{H^* z}) \left[ \frac{-2 \alpha_{re}^{H^* z}}{(1 + \alpha_{re}^{H^* z})} + 1 \right] \\
&= \frac{-(H^*)^2 \alpha_{re}^{H^* z}}{(1 + \alpha_{re}^{H^* z})^2} \left[ \frac{-2 \alpha_{re}^{H^* z} + 1 + \alpha_{re}^{H^* z}}{(1 + \alpha_{re}^{H^* z})} \right] \\
f''(z) &= \frac{-(H^*)^2 \alpha_{re}^{H^* z} (1 - \alpha_{re}^{H^* z})}{(1 + \alpha_{re}^{H^* z})^3} \quad (B-8)
\end{aligned}$$

The Taylor series expansion about zero with the LaGrange form of the remainder is given by

$$f(z) = f(0) + f'(0)z + R_2 \quad (B-9)$$

where

$$R_2 = \frac{f''(X)}{2!} z^2 \sim \frac{f''(z)}{2!} z^2$$

since  $z_{hot} \sim z_{cold}$ .

From Equations B-9, B-8, B-7, and B-6,

$$\begin{aligned}
\left| \frac{R_2}{f(0) + f'(0)z} \right| &= \left| \frac{\frac{-z^2}{2} (H^*)^2 \alpha_{re}^{H^* z} (1 - \alpha_{re}^{H^* z}) / (1 + \alpha_{re}^{H^* z})^3}{\left( \frac{1}{(1 + \alpha_r)} - \frac{H^* \alpha_r z}{(1 + \alpha_r)^2} \right)} \right| \\
&= \left| \frac{-z^2 (H^*)^2 (\alpha) (re^{H^* z}) (1 - \alpha_{re}^{H^* z})}{2 \left[ \frac{(1 + \alpha_r) - H^* \alpha_r z}{(1 + \alpha_r)^2} \right] (1 + \alpha_{re}^{H^* z})^3} \right| \\
&= \left| \frac{-z^2 (H^*)^2 (\alpha) (re^{H^* z}) (1 - \alpha_{re}^{H^* z}) (1 + \alpha_r)^2}{2 \left[ 1 + \alpha_r (1 - H^* z) \right] (1 + \alpha_{re}^{H^* z})^3} \right| \quad (B-10)
\end{aligned}$$

As an example of the possible error involved in neglecting  $R_2$ , consider the following:

$$\alpha \sim 5 \times 10^2$$

$$r \sim 10^{-3}$$

$$re^{H^*z} \sim 10^{-4}$$

$$H^* \sim 4 \times 10^2$$

and

$$\left| \frac{R_2}{f(0) + f'(0)z} \right| \sim \left| \frac{(10^{-5})(16 \times 10^4)(5 \times 10^2) [1 - (5 \times 10^2)(10^4)] [1 + .5^2]}{2 [1 + (5 \times 10^2)(10^4)]^3 [1 + .5(1 - 1.3)]} \right|$$

$$\sim .05$$

That is, the remainder is approximately 5 per cent of the first two terms.

## APPENDIX C

### DERIVATION OF EQUATION 33A FROM 33

Starting with

$$(\eta_1)_{T_B} + (T_A - T_B) \left( \frac{d\eta_1}{dT} \right)_{T_B} \cong \frac{N_1}{V} \quad (33)$$

and

$$\eta_1 = \frac{T_0}{T} \left[ \frac{N_1 + \alpha N_2}{V} \right] / (1 + \alpha r e^{H^*/T}) \quad (22)$$

Let

$$A = T_0 \left( \frac{N_1 + \alpha N_2}{V} \right)$$

$$B = \alpha r$$

Equation 22 becomes

$$\eta_1 = \frac{A}{T(1 + B e^{H^*/T})}$$

and

$$\begin{aligned} \frac{d\eta_1}{dT} &= A \left\{ \frac{- \left[ T - \left( \frac{H^* B e^{H^*/T}}{T^2} \right) + (1 + B e^{H^*/T}) \right]}{T^2 (1 + B e^{H^*/T})^2} \right\} \\ \frac{d\eta_1}{dT} &= \frac{A}{T(1 + B e^{H^*/T})} \left[ \frac{B e^{H^*/T} (H^* - T) - T}{T^2 (1 + B e^{H^*/T})} \right] \quad (C-1) \end{aligned}$$

If Equations 33 and C-1 are combined, the result is

$$\frac{A}{T_B(1+Be^{H^*/T_B})} \left\{ 1 + (T_A - T_B) \left[ \frac{Be^{H^*/T_B} (H^* - T_B) - T_B}{T_B^2(1+Be^{H^*/T_B})} \right] \right\} = \frac{N_1}{V}$$

Simplifying this result,

$$\frac{A \left[ Be^{H^*/T_B} [2T_B^2 + H^*T_A - H^*T_B - T_A T_B] + [2T_B^2 - T_A T_B] \right]}{T_B^3(1+Be^{H^*/T_B})^2} = \frac{N_1}{V}$$

whereby the final equation is obtained if A and B are replaced by their defined quantities and the result divided by  $\frac{N_1}{V}$  :

$$1 = \frac{T_0(1+\alpha \frac{N_2}{N_1}) \left[ \alpha re^{H^*/T_B} [2T_B^2 + H^*(T_A - T_B) - T_A T_B] + [2T_B^2 - T_A T_B] \right]}{T_B^3(1+\alpha re^{H^*/T_B})^2} \quad (33A)$$

## APPENDIX D

### DERIVATION OF EQUATION 36

From Equation 35,

$$\frac{\eta_2}{\eta_1} = re^{H^*/T_H} = \frac{(\eta_2)_{T_H}}{(\eta_1)_{T_H}} = \frac{(\eta_2)_{T_A} + \left( \frac{d\eta_2}{dT} \right)_{T_A} (T_H - T_A)}{(\eta_1)_{T_A} + \left( \frac{d\eta_1}{dT} \right)_{T_A} (T_H - T_A)} \quad (D-1)$$

with

$$\eta_1 = \frac{N_1 + \alpha N_2}{V} / (1 + \alpha re^{H^*/T}) \quad (22)$$

and

$$\frac{\eta_2}{\eta_1} = re^{H^*/T} \quad (21)$$

the following development is obtained:

$$\left( \frac{d\eta_1}{dT} \right)_{T_A} = \frac{(\eta_1)_{T_A} \alpha r H^* e^{H^*/T_A}}{T^2 (1 + \alpha re^{H^*/T_A})} \quad (D-2)$$

$$\left( \frac{d\eta_2}{dT} \right)_{T_A} = \frac{-r(\eta_1)_{T_A} H^* e^{H^*/T_A}}{T_A^2 (1 + \alpha re^{H^*/T_A})} \quad (D-3)$$

$$\eta_2 = (\eta_1)_{T_A} re^{H^*/T_A} \quad (D-4)$$

Combining Equations D-1, D-4, 21 and 22, with some simplification, Equation 36 results:



$$1 = \frac{e^{H^*/T_A} [T_A^2(1 + \alpha_{re}^{H^*/T_A}) - H^*(T_H - T_A)]}{e^{H^*/T_H} [T_A^2(1 + \alpha_{re}^{H^*/T_A}) + H^* \alpha_{re}^{H^*/T_A} (T_H T_A)]} \quad (36)$$

## APPENDIX E

### THE DETERMINATION OF OSMOTIC COEFFICIENTS

#### WHERE NO DATA ARE AVAILABLE

For electrolytes where no osmotic coefficients are available, Prutton and Maron (27) state that it is possible to approximate these data by classifying the electrolyte. For example, with  $\nu$  and  $C$  representing the number of ions produced at infinite dilution ( $\nu_{\text{K}_2\text{SO}_4}=3$ ) and molar concentration, respectively, and  $\phi$  the osmotic coefficient, a plot of  $(1-\phi)$  versus  $\nu C$  yields a family of curves. It is found that uni-univalent electrolytes generally coincide, di-divalent salts likewise behave similarly, and so on for other combinations. It is thus possible to find osmotic coefficients for  $\text{Zr}(\text{NO}_3)_4$  and  $\text{Hf}(\text{NO}_3)_4$  from the data of  $\text{Th}(\text{NO}_3)_4$ .

TABLE VIII  
OSMOTIC COEFFICIENTS,  
REF. (26)  
(25°C.)\*

Salt	Mol % Heavy Comp.	$\phi$	Salt	Mol % Heavy Comp.	$\phi$
KCl	0.89	.899	CoSO <sub>4</sub>	0.89	—
	1.77	.897		1.77	—
	3.85	.918		3.85	—
NaCl	0.89	.921	CuSO <sub>4</sub>	0.89	.469
	1.77	.936		1.70	.461
	3.85	.990		—	—
KBr	0.89	.904	MgSO <sub>4</sub>	0.89	.522
	1.70	.907		1.79	.525
	3.85	.934		3.85	.723
KI	0.89	.917	NiSO <sub>4</sub>	0.89	.475
	1.76	.926		1.92	.459
	3.85	.965		3.85	.649
NaI	0.89	.952	ZnSO <sub>4</sub>	0.89	.483
	1.77	.991		1.80	.478
	3.85	1.104		3.85	.659
NaBr	0.89	.933	Na <sub>2</sub> SO <sub>4</sub>	0.89	.690
	1.77	.958		1.76	.642
	3.85	1.048		3.85	.628
BaCl <sub>2</sub>	0.89	.864	AgNO <sub>3</sub>	0.89	.811
	1.78	.934		1.77	.742
	3.85	1.160		3.85	1.169
SrCl <sub>2</sub>	0.89	.899	Pb(NO <sub>3</sub> ) <sub>2</sub>	0.89	.606
	1.77	1.009		1.77	.533
	3.85	1.373		3.85	—
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	0.89	.677	KNO <sub>3</sub>	0.89	.817
	1.80	.640		1.77	.756
	3.85	.624		3.85	.650
CdSO <sub>4</sub>	0.89	.466	NaNO <sub>3</sub>	0.89	—
	1.79	.452		1.77	—
	3.85	.591		3.85	—

\*There is a slight variation with temperature.

## APPENDIX F

JUSTIFICATION OF THE USE OF AN "AVERAGE" VALUE OF  $H^*$   
OVER THE FINITE INTERVAL,  $T_H, T_C$  IN  $\frac{\eta_2}{\eta_1} = \text{re}^{H^*/T}$

From the experimental data shown in Figure 12, it appears that a suitable equation describing the linearity of the data is

$$\begin{aligned}\sigma &= \frac{a}{T_H T_C} + b, \quad \text{or} \\ &= \frac{a + b T_H T_C}{T_H T_C} = \frac{H^*}{T_H T_C}\end{aligned}\tag{F-1}$$

This suggests

$$\frac{\eta_2}{\eta_1} = \text{re}^{H^*/T} = \text{re}^{a-bT^2/T}\tag{F-2}$$

which can be shown to yield (F-1):

$$\begin{aligned}\frac{\left(\frac{\eta_2}{\eta_1}\right)_C}{\left(\frac{\eta_2}{\eta_1}\right)_H} &= \frac{\text{re}^{\frac{a-bT_C^2}{T_C}}}{\text{re}^{\frac{a-bT_H^2}{T_H}}} = e^{\frac{a}{T_C} - \frac{a}{T_H} - bT_C + bT_H} \\ &= e^{\frac{a(T_H - T_C)}{T_H T_C} + b(T_H - T_C)}\end{aligned}$$

$$\sigma = \frac{1}{\Delta T} \ln \frac{x_2}{x_1} \approx \frac{1}{\Delta T} \ln \frac{(\eta_2/\eta_1)_C}{(\eta_2/\eta_1)_H} = \frac{a}{T_H T_C} + b$$

or

$$\sigma = \frac{a + b T_H T_C}{T_H T_C} = \frac{H^*}{T_H T_C} \quad (\text{F-1})$$

which confirms the choice of  $H^*$  in Equation F-2.

With  $H^*$  a function of  $T$ , it was desirable to investigate the error involved in the integration of Equation 29-L

$$M' = \int_{1/T_H}^{1/T_C} \frac{dz}{z^2 (1 + \alpha \exp^{H^* z})} \quad (29-L)$$

where (1)  $H^*$  is not a function of temperature, and

$$(2) H^* = a - bT^2$$

Choose: for  $\text{CuSO}_4$

$$T_H = 333^\circ\text{K}; \quad z_H = \frac{1}{T_H} = 3.00 \times 10^{-3}$$

$$T_C = 277^\circ\text{K}; \quad z_C = \frac{1}{T_C} = 3.61 \times 10^{-3}$$

$$T_H T_C = 9.22 \times 10^4$$

So that from Figure 12,

$$\alpha = 480$$

$$\bar{r} = .0013$$

$$\sigma = 5.22 \times 10^{-3}$$

$$a = 338$$

$$H^* = 481$$

$$b = 15.2 \times 10^{-4}$$

$$(\eta_2/\eta_1)_C = \bar{r} e^{H^*/T_C} = r e^{\frac{a}{T_C} - bT_C}$$

$$(\eta_2/\eta_1)_H = \bar{r} e^{H^*/T_H} = r e^{\frac{a}{T_H} - bT_H}$$

From the above information:  $r = .00332$ .

By graphical integration, it will be shown that

$$M \cong M' , \text{ where}$$

$$M = \int_{1/T_H}^{1/T_C} \frac{dz}{z^2(1+\alpha \operatorname{Re}^{az-\frac{b}{z}})}$$

and

$$M' = \int_{1/T_H}^{1/T_C} \frac{dz}{z^2(1+\alpha \overline{\operatorname{Re}}^{H^*z})}$$

The calculations are shown in Table IX and the plot of the information appears in Figure 25. It is obvious that the error introduced is negligible.

TABLE IX  
SUMMARY OF GRAPHICAL INTEGRATION CALCULATIONS

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Z	Z <sup>2</sup>	H*	H*Z	$\frac{H*Z}{e}$	$\alpha r(5)$	1+(6)	(2)(7)	$\frac{1}{(8)}$
3.00 x 10 <sup>-3</sup>	9.00 x 10 <sup>-6</sup>	481	1.443	4.233	2.64	3.64	32.8 x 10 <sup>-6</sup>	3.05 x 10 <sup>4</sup>
3.1 "	9.61 "	481	1.491	4.442	2.77	3.77	36.2 "	2.76 "
3.2 "	10.2 "	481	1.539	4.660	2.91	3.91	39.8 "	2.51 "
3.3 "	10.9 "	481	1.587	4.889	3.05	4.05	44.1 "	2.27 "
3.4 "	11.6 "	481	1.635	5.13	3.20	4.20	48.7 "	2.05 "
3.5 "	12.2 "	481	1.684	5.39	3.36	4.36	53.2 "	1.88 "
3.61 "	13.0 "	481	1.736	5.67	3.54	4.54	59.0 "	1.69 "
$\alpha = 480$		$\bar{r} = .0013$		$\alpha \bar{r} = .624$				
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
$\frac{1}{Z}$	aZ	b( $\frac{1}{Z}$ )	(2)-(3)	$\frac{e}{(4)}$	$\alpha r(5)$	1+(6)	Z <sup>2</sup> (7)	$\frac{1}{(8)}$
333	1.014	.506	.508	1.662	2.64	3.64	32.8 x 10 <sup>-6</sup>	3.05 x 10 <sup>4</sup>
322	1.048	.489	.559	1.749	2.78	3.78	36.3 "	2.75 "
312	1.082	.474	.608	1.837	2.92	3.92	40.0 "	2.50 "
303	1.115	.460	.655	1.925	3.06	4.06	44.2 "	2.26 "
294	1.149	.447	.702	2.018	3.21	4.21	48.8 "	2.05 "
286	1.183	.435	.748	2.113	3.37	4.37	53.3 "	1.88 "
277	1.220	.421	.799	2.223	3.54	4.54	59.0 "	1.69 "
a=338		b=15.2 x 10 <sup>-4</sup>		$\alpha = 480$		r=.00332		
					$\alpha r=1.594$			

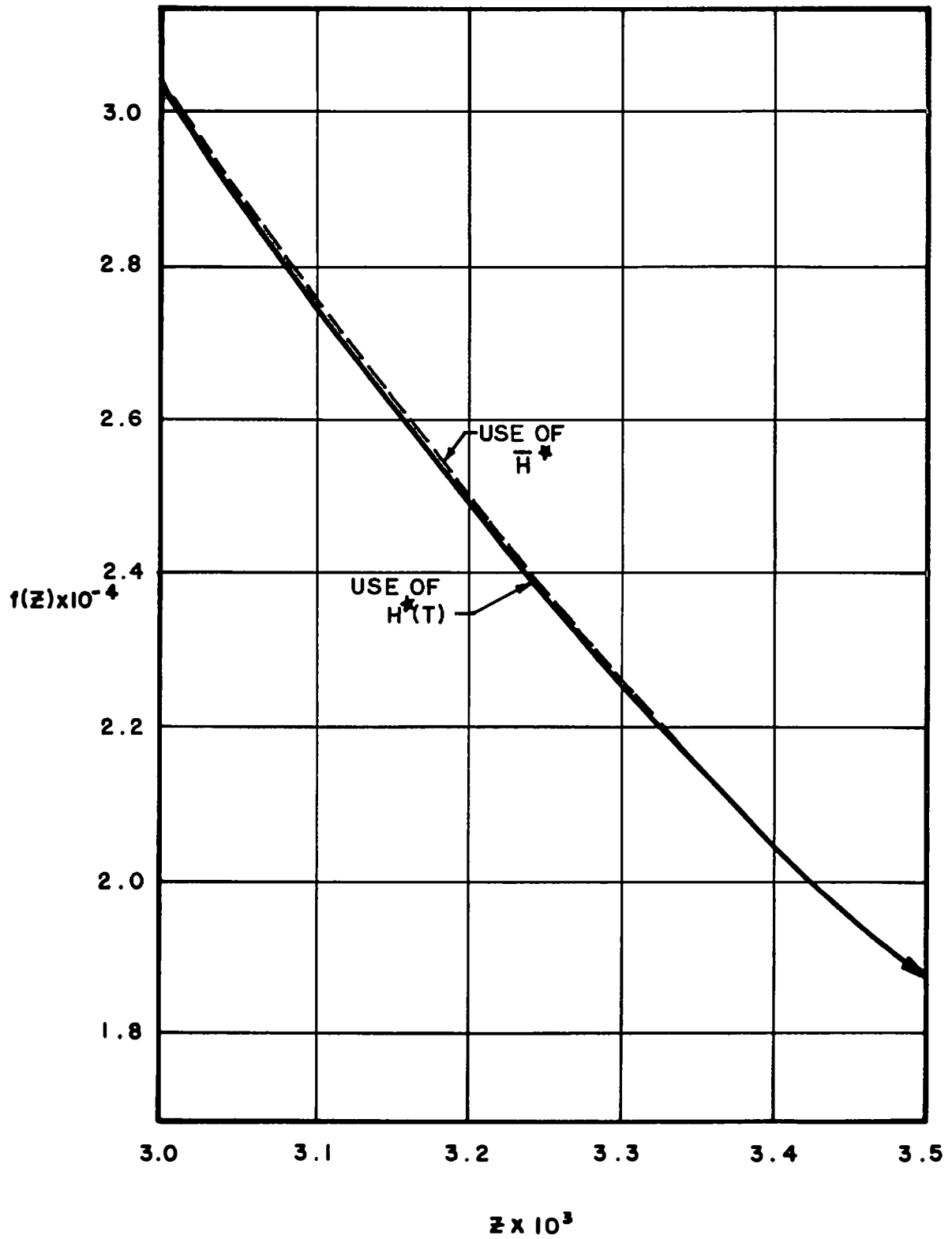


Figure 25. Graphical Integration Solution of Equation 29-L



## APPENDIX G

JUSTIFICATION OF THE ASSUMPTION THAT  $\frac{d\eta_2}{dT}$  AND  $\frac{d\eta_1}{dT}$  ARE CONSTANT OVER THE  $T_H, T_A$  INTERVAL

For dilute solutions, where  $\eta_2 \ll \eta_1$ ,

$$\frac{\eta_2}{\eta_1} \approx \frac{\eta_2}{N_1/V} \quad (G-1)$$

so that

$$\frac{d\eta_2}{dT} = \frac{N_1}{V} \frac{d\frac{\eta_2}{N_1/V}}{dT} \approx \frac{N_1}{V} \frac{d\left(\frac{\eta_2}{\eta_1}\right)}{dT} \quad (G-2)$$

Therefore, for

$$T_H = 289^\circ\text{K}; \quad T_C = 277^\circ\text{K}; \quad \frac{N_2}{N_1} = .00611$$

by the calculation procedure described in Chapter II,

$$(\eta_2/\eta_1)_C = .00641$$

$$(\eta_2/\eta_1)_H = .00598$$

$$T_A = 285^\circ\text{K}$$

$$\sigma \times 10^3 = 5.79$$

Figure 26 and Equation G-2 illustrate the reasonableness of the assumption made.

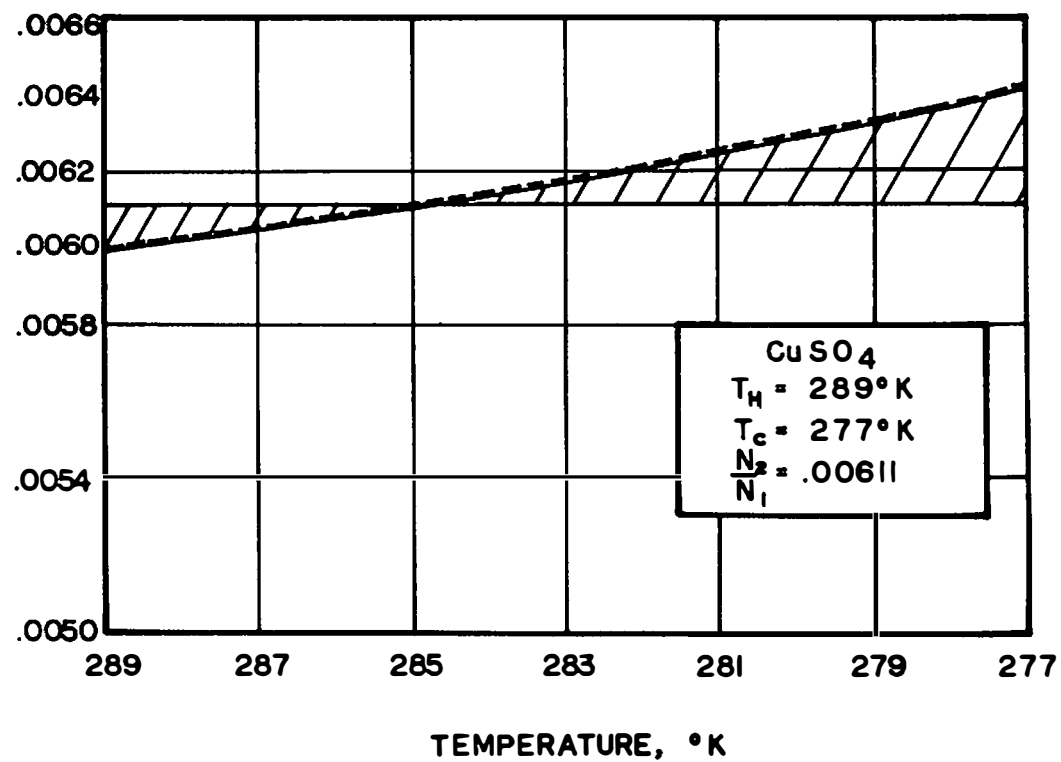


Figure 26. Concentration Ratio versus Temperature for  $\text{CuSO}_4$  (Calculated)

## APPENDIX H

### SPECULATION ON THE SIGNIFICANCE OF $\alpha = \frac{E_2^0}{E_1^0}$

The evaluation of  $\alpha$  from  $\alpha = \frac{P_1}{P_2} \frac{Q_2}{Q_1}$  was based on

the postulation that the total energy of an atom could be expressed as the linear sum of its various components of this energy, that is, translational, rotational, vibrational, electronic, etc. The further speculation as to the general form of the partition function corresponding to each energy term together with the equipartition principle led to

$$\alpha = \frac{E_2^0}{E_1^0}$$

where  $E^0$  is the electronic energy and the subscripts refer to a particular component. A question of the significance of electronic energy when dealing with transport processes is pertinent, particularly at the "ordinary" temperature with which thermal diffusion is concerned. An attempt will be made here to impute to  $\alpha$  some significance which is not readily apparent.

In general, the partition function for a gas atom is written as

$$P = P_{TR} P_{ROT} P_{VIB} P_{ELECT} \dots P_{NUC}$$

and at the usual temperatures,  $P_{ELECT}$  and  $P_{NUC}$  are dismissed

as irrelevant since the atom is assumed in its ground state as far as electronic and nuclear energies of the atom are concerned. By definition,

$$\begin{array}{ll} E_{\text{ELECT}} \equiv 0; & P_{\text{ELECT}} \equiv g \\ E_{\text{NUC}} \equiv 0; & P_{\text{NUC}} \equiv 1 \end{array}$$

where  $g$  is the degeneracy.

The question that naturally arises from this regards the validity of assigning a value of zero to these energy terms (electronic and nuclear) when one is dealing with a single specie in a system. In effect a zero point of energy is being defined for the atom,  $E \equiv 0$  when the atom is at rest (translation, rotation, etc.) and in its electronic and nuclear ground state. However, suppose there are two species of atoms in the system. How then does the zero point of energy for specie 2 compare with that of specie 1? What is the significance of assigning  $E_{\text{ELECT}} = 0$  for specie 1, when it is necessary to evaluate a quantity such as  $(E_{\text{ELECT}})_2 / (E_{\text{ELECT}})_1$ ? While pondering this problem, consider also that there is a relationship between intermolecular forces and electronic energies. Shouldn't, therefore, it be possible to express intermolecular forces and interactions in terms of electronic energies? In an attempt to rationalize what appears to be a confusing situation, a speculative mechanism for molecular interactions will be proposed below together with a consistent definition of the zero of energy.

Consider a system composed of atoms of species 1 and 2. The zero point of energy will be defined as  $E=0$  when the atom is at rest (translation, rotation, etc.), is located at infinity with respect to its nearest neighbors and is in its electronic and nuclear ground state. Now allow two atoms to approach each other. It is proposed that the resulting interaction conforms to the "square well" type of diagram, as shown in Figure 27.

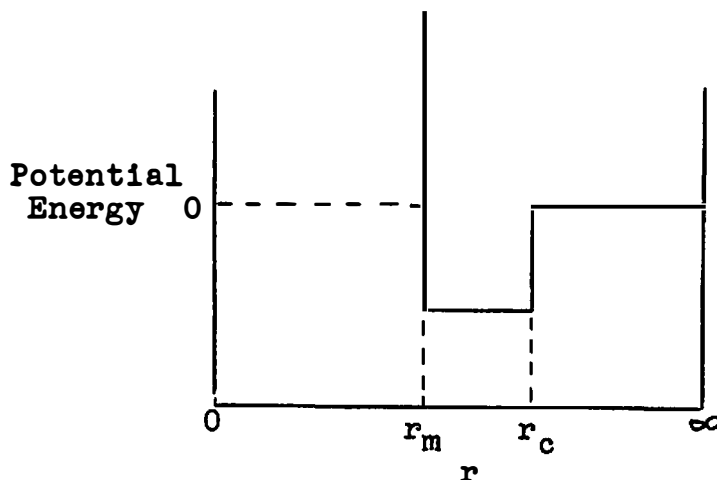


Figure 27. "Square Well" Interaction Between Two Atoms

At distances greater than  $r_c$ , the two atoms do not exert any influence upon each other and the total energy of each atom is given by the sum of its translation, vibration, and rotational components. However, at  $r_c$ , and until  $r_m$ , there is an interaction between atoms--an interaction which

is proportional to the electronic energy of each atom. The total energy of each atom is therefore given by

$$E = E_{TR} + E_{VIB} + E_{ROT} + E_{INTERACTION}$$

where

$$E_{INTERACTION} = k E_{ELECTRONIC}$$

If it is intuitively felt that  $E_{INTERACTION}$  should vary over the  $r_m, r_c$  range, then let it be asserted that this variation is small enough to allow an average value to be used over the  $r_m, r_c$  range.

It was on the basis of the above discussion that the final result,  $\alpha = \frac{E_2^0}{E_1^0}$ , was derived. It is proposed that

$\alpha$  be called an "interaction coefficient."

## **APPENDICES**

### **PART III**

### **PART III**

#### **APPENDIX A**

##### **ORIGINAL DATA**

Tables X and XI are tabulations of original data. They are compiled from pages 1251-1254 of the Original Record of Research, Volume V, Department of Chemical and Metallurgical Engineering, The University of Tennessee, Knoxville, Tennessee.



TABLE X  
TABULATION OF ORIGINAL DATA, SINGLE SALT

Run #	Initiated	Terminated	Spectrophotometer Reading (% Transmittancy)			System	Temperature (°F.)	
			Initial	Cold	Hot		Hot	Cold
1	June 7	June 9	50.3	44.0	—	CuSO <sub>4</sub> -H <sub>2</sub> O	139.0	40.0
2	June 9	June 10	49.8	43.5	—	"	139.5	40.0
3	June 10	June 11	50.0	44.0	60.0	"	140.0	40.5
4	June 11	June 12	50.0	45.0	62.0	"	140.5	40.5
5	June 12	June 12	50.5	48.0	59.0	"	140.5	40.0
6	June 14	June 14	50.5	47.5	60.5	"	140.0	40.0
7	June 14	June 15	42.5	40.0	57.5	"	140.0	40.0
8	June 18	June 19	82.5	79.0	83.0	"	140.0	40.0
9	June 19	June 20	84.0	85.5	—	"	140.0	40.0
10	June 20	June 21	51.5	48.0	60.0	CoSO <sub>4</sub> -H <sub>2</sub> O	140.5	40.0
11	June 21	June 22	79.0	75.0	81.5	"	"	"
12	June 22	June 24	85.0	81.5	86.5	"	"	"
13	June 24	June 25	66.0	62.5	73.0	"	"	"
14	June 25	June 26	75.0	71.5	81.0	CuSO <sub>4</sub> -H <sub>2</sub> O	"	"
15	June 26	June 27	82.5	79.0	87.0	"	"	"
22	July 1	July 2	46.0	43.5	53.0	"	100.0	40.0
23	July 2	July 3	60.0	56.5	65.5	"	"	"
24	July 3	July 4	76.0	73.0	78.5	"	"	"
25	July 4	July 6	45.5	40.0	59.0	"	159.0	59.0
26	July 6	July 7	62.5	55.0	73.0	"	"	"
27	July 7	July 8	83.5	78.5	88.0	"	"	"
28	July 8	July 9	53.0	50.5	64.0	CoSO <sub>4</sub> -H <sub>2</sub> O	"	"
29	July 9	July 10	69.5	63.5	76.5	"	"	"
30	July 10	July 11	85.5	82.0	88.5	"	"	"
35	July 15	July 16	78.0	74.5	81.0	CuSO <sub>4</sub> -H <sub>2</sub> O	119.0	40.0

TABLE XI  
TABULATION OF ORIGINAL DATA, MIXED SALTS

Run #	Initiated	Terminated	Initial	Spec. Reading (% Trans.)		Initial	Spec. Reading (% Trans.)		Temp. (°F.)
				Hot	Cold		Hot	Cold	
				CuSO <sub>4</sub>			CuSO <sub>4</sub>		
16	June 27	June 28	85.5	89.0	83.0	79.0	83.5	77.0	140°-40°
18	June 29	June 30	76.0	82.5	72.5	88.5	91.0	87.0	"
19	June 30	July 1	82.0	86.5	79.0	84.0	87.0	82.5	"
31	July 11	July 12	76.0	82.0	73.0	88.0	90.5	86.0	159°-59°
33	July 13	July 14	85.5	87.5	81.5	79.5	81.5	75.5	"

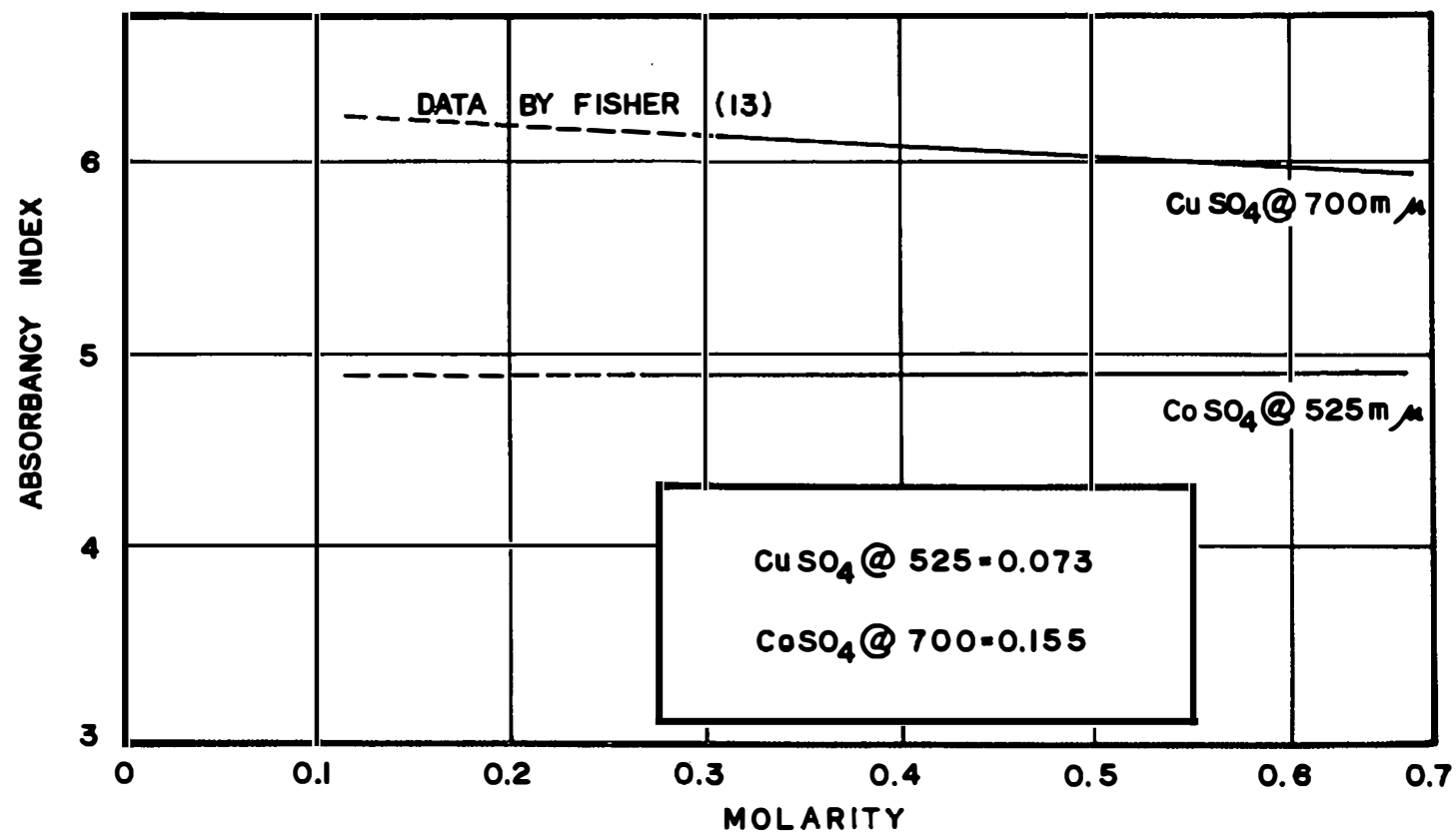


Figure 28. Absorbancy Indices versus Concentration for  $\text{CuSO}_4\text{-CoSO}_4\text{-H}_2\text{O}$

## APPENDIX B

### SAMPLE CALCULATIONS

#### 1. Calculation of the Soret Coefficient, $\sigma$ , for a Single Salt, $\text{CuSO}_4$

---

From original data on page 1270 of the Original Record  
of Research, Volume V,

- |  |  |
|--|--|
| (1) Initial reading, % transmittancy     | = 45.0   |
| (2) % transmittancy, cold wall           | = 39.8   |
| (3) % transmittancy, hot wall            | = 58.8   |
| (4) Temperature difference = 100°F       | = 55.6°C   |
| (5) Absorption cell thickness            | = 0.097 cm   |
| (6) Absorbancy coefficient,<br>hot wall  | = $\frac{\log_{10} \text{item (3)}}{\text{item (5)}}$<br>= 2.38  |
| (7) Absorbancy coefficient,<br>cold wall | = $\frac{\log_{10} \text{item (2)}}{\text{item (5)}}$<br>= 4.12  |
| (8) Salt concentration, hot wall         | = $\frac{\text{item (6)}}{\text{absorbancy index}}$<br>= $\frac{2.38}{6.07} = .392 \frac{\text{g.moles}}{\text{liter}}$                          |
| (9) Salt concentration, cold wall        | = $\frac{\text{item (7)}}{\text{absorbancy index}}$<br>= $\frac{4.12}{5.93} = .695 \frac{\text{g.moles}}{\text{liter}}$                          |
| (10) Mole fraction, hot wall             | = $\frac{\text{item (8)}}{\text{item (8)} + \frac{1000 \text{ g. H}_2\text{O}}{\text{mw H}_2\text{O}}}$<br>= $\frac{.392}{.392 + 55.6} = .00700$ |

$$\begin{aligned} (11) \text{ Mole fraction, cold wall} &= \frac{\text{item (9)}}{\text{item (9)} + \frac{1000 \text{ g. H}_2\text{O}}{\text{mw H}_2\text{O}}} \\ &= \frac{.695}{.695 + 55.6} \\ &= .0124 \end{aligned}$$

$$\begin{aligned} (12) \text{ Soret coefficient, } \sigma &= \frac{1}{\text{item (4)}} \ln \frac{\text{item (11)}}{\text{item (10)}} \\ &= \frac{1}{55.6} \ln \frac{.0124}{.00700} \\ &= 10.2 \times 10^{-3} \text{ } ^\circ\text{C}^{-1} \end{aligned}$$

## 2. Calculation of the Soret Coefficient, $\sigma$ , for $\text{CuSO}_4$ and $\text{CoSO}_4$ in a Mixed Salt Solution

From original data on page 1279 of the Original Record  
of Research, Volume V.

- (1) Initial reading, % transmittancy = 60.0
- (2) % transmittancy,  $\text{CuSO}_4$ , hot wall = 70.0
- (3) % transmittancy,  $\text{CuSO}_4$ , cold wall = 55.5
- (4) % transmittancy,  $\text{CoSO}_4$ , hot wall = 68.1
- (5) % transmittancy,  $\text{CoSO}_4$ , cold wall = 56.5
- (6) Temperature difference =  $100^\circ\text{F}$  =  $55.6^\circ\text{C}$
- (7) Absorption cell thickness = 0.097 cm
- (8) Absorbancy coefficient,  $\text{CuSO}_4$   
hot wall 
$$= \frac{\log_{10} \frac{100}{\text{item (2)}}}{\text{item (7)}}$$
$$= 1.60$$
- (9) Absorbancy coefficient,  $\text{CuSO}_4$   
cold wall 
$$= \frac{\log_{10} \frac{100}{\text{item (3)}}}{\text{item (7)}}$$

$$(10) \text{ Absorbancy coefficient, } \text{CoSO}_4 \text{ hot wall} = \frac{2.64}{\frac{\log_{10} \frac{100}{\text{item (4)}}}{\text{item (7)}}}$$

$$(11) \text{ Absorbancy coefficient, } \text{CoSO}_4 \text{ cold wall} = \frac{\log_{10} \frac{100}{\text{item (5)}}}{\text{item (7)}} = 2.56$$

(12) Salt concentration,  $\text{CuSO}_4$ , hot wall:

$$\begin{aligned} & \frac{\text{abs. index } \text{CoSO}_4 @ 525\mu \times \text{item (8)} - \text{abs. index } \text{CoSO}_4 @ 700\mu \times \text{item (10)}}{\text{abs. index } \text{CuSO}_4 @ 700\mu \times \text{abs. index } \text{CoSO}_4 @ 525\mu - \text{abs. index } \text{CoSO}_4 @ 700\mu \times \text{abs. index } \text{CuSO}_4 @ 525\mu} \\ &= \frac{(4.88)(1.60) - (.155)(1.72)}{(6.16)(4.88) - (.155)(.073)} = .250 \frac{\text{g.moles}}{\text{liter}} \end{aligned}$$

(13) Salt concentration,  $\text{CuSO}_4$ , cold wall:

$$\begin{aligned} & \frac{\text{abs. index } \text{CoSO}_4 @ 525\mu \times \text{item (9)} - \text{abs. index } \text{CoSO}_4 @ 700\mu \times \text{item (11)}}{\text{abs. index } \text{CuSO}_4 @ 700\mu \times \text{abs. index } \text{CoSO}_4 @ 525\mu - \text{abs. index } \text{CoSO}_4 @ 700\mu \times \text{abs. index } \text{CuSO}_4 @ 525\mu} \\ &= \frac{(4.88)(2.64) - (.155)(2.56)}{(6.06)(4.88) - (.155)(.073)} = .422 \frac{\text{g.moles}}{\text{liter}} \end{aligned}$$

(14) Salt concentration,  $\text{CoSO}_4$ , hot wall:

$$\begin{aligned} & \frac{\text{abs. index } \text{CuSO}_4 @ 700\mu \times \text{item (10)} - \text{abs. index } \text{CuSO}_4 @ 525\mu \times \text{item (8)}}{\text{abs. index } \text{CuSO}_4 @ 700\mu \times \text{abs. index } \text{CoSO}_4 @ 525\mu - \text{abs. index } \text{CoSO}_4 @ 700\mu \times \text{abs. index } \text{CuSO}_4 @ 525\mu} \\ &= \frac{(6.16)(1.72) - (.073)(1.60)}{(6.16)(4.88) - (.155)(.073)} = .348 \frac{\text{g.moles}}{\text{liter}} \end{aligned}$$

(15) Salt concentration,  $\text{CoSO}_4$ , cold wall:

$$\begin{aligned} & \frac{\text{abs. index } \text{CuSO}_4 @ 700\mu \times \text{item (11)} - \text{abs. index } \text{CuSO}_4 @ 525\mu \times \text{item (9)}}{\text{abs. index } \text{CuSO}_4 @ 700\mu \times \text{abs. index } \text{CoSO}_4 @ 525\mu - \text{abs. index } \text{CoSO}_4 @ 700\mu \times \text{abs. index } \text{CuSO}_4 @ 525\mu} \end{aligned}$$

$$= \frac{(6.06)(2.56) - (.073)(2.64)}{(6.06)(4.88) - (.155)(.073)} = .518 \frac{\text{g.moles}}{\text{liter}}$$

(16) Mole fraction,  $\text{CuSO}_4$ , hot wall:

$$= \frac{\text{item (12)}}{\text{item (12)} + \text{item (14)} + \frac{1000 \text{ g.H}_2\text{O}}{\text{mw H}_2\text{O}}}$$

$$= \frac{.250}{.250 + .348 + 55.6} = .00445$$

(17) Mole fraction,  $\text{CuSO}_4$ , cold wall:

$$= \frac{\text{item (13)}}{\text{item (13)} + \text{item (15)} + \frac{1000 \text{ g.H}_2\text{O}}{\text{mw H}_2\text{O}}}$$

$$= \frac{.422}{.422 + .518 + 55.6} = .00748$$

(18) Mole fraction,  $\text{CoSO}_4$ , hot wall:

$$= \frac{\text{item (14)}}{\text{item (14)} + \text{item (12)} + \frac{1000 \text{ g.H}_2\text{O}}{\text{mw H}_2\text{O}}}$$

$$= \frac{.348}{.348 + .250 + 55.6} = .00620$$

(19) Mole fraction,  $\text{CoSO}_4$ , cold wall:

$$= \frac{\text{item (15)}}{\text{item (15)} + \text{item (13)} + \frac{1000 \text{ g.H}_2\text{O}}{\text{mw H}_2\text{O}}}$$

$$= \frac{.518}{.518 + .422 + 55.6} = .00917$$

(20) Soret coefficient,  $\text{CuSO}_4 = \frac{1}{\text{item (6)}} \ln \frac{\text{item (17)}}{\text{item (16)}}$

$$= \frac{1}{55.6} \ln \frac{.00748}{.00445}$$

$$= 9.33 \times 10^{-3} \text{ } ^\circ\text{C}^{-1}$$

$$\begin{aligned} (21) \text{ Soret coefficient, } \text{CoSO}_4 &= \frac{1}{\text{item (6)}} \ln \frac{\text{item (19)}}{\text{item (18)}} \\ &= \frac{1}{55.6} \ln \frac{.00917}{.00620} \\ &= 7.07 \end{aligned}$$



## APPENDIX C

### CALCULATIONS INVOLVED IN THE LINEAR CORRELATIONS OF FIGURES 16 AND 17

#### 1. Linear Correlation of $\text{CuSO}_4$ Data of Figure 16

Let

$x$  = initial spectrophotometer reading, % transmission

$y$  = hot side                      "                      "                      "

$z$  = cold side                      "                      "                      "

The following equations are given by Croxton (9)

$$\text{I: } \sum y = Na + b \sum x \quad (\text{C-1})$$

$$\text{II: } \sum xy = a \sum x + b \sum x^2 \quad (\text{C-2})$$

$$\text{I': } \sum Z = Na' + b' \sum X \quad (\text{C-3})$$

$$\text{II': } \sum x Z = a' \sum x + b' \sum x^2 \quad (\text{C-4})$$

where

$$y = a + bx \quad (\text{C-5})$$

$$Z = a' + b'x \quad (\text{C-6})$$

The standard deviation is defined by

$$s_{y.x} = \sqrt{\frac{\sum y^2 - (a \sum y + b \sum xy)}{N}} \quad (\text{C-7})$$

The following table summarizes the calculations.

TABLE XII  
SUMMARY OF LINEAR CORRELATION CALCULATIONS,  $\text{CuSO}_4$

Run No.	Temp. Range (°F.)	x	y	z	xy	x <sup>2</sup>	y <sup>2</sup>	z <sup>2</sup>	xz
1-6	140°-40°	50.0	61.0	44.0	3050.0	2500.0	3721.0	1936.0	2200.0
7	"	42.5	57.5	40.0	2443.8	1806.2	3306.2	1600.0	1700.0
14	"	75.0	81.0	71.5	6075.0	5625.0	6561.0	5112.2	5362.5
15	"	82.5	87.0	79.0	7177.5	6806.2	7569.0	6241.0	6517.5
*16	"	85.5	89.0	83.0	7609.5	7310.2	7921.0	6889.0	7096.5
*18	"	76.0	82.5	72.5	6270.0	5776.0	6806.2	5256.2	5510.0
*19	"	82.0	86.5	79.0	7093.0	6724.0	7482.2	6241.0	6478.0
25	159°-59°	45.5	59.0	40.0	2684.5	2070.2	3481.0	1600.0	1820.0
26	"	62.5	73.0	55.0	4562.5	3906.2	5329.0	3025.0	3437.5
27	"	83.5	88.0	78.5	7348.0	6972.2	7744.0	6162.2	6554.8

\*Mixed salt

$$\sum x = 685.0 \qquad \sum x y = 54,313.8 \qquad \sum x^2 = 49,496.2$$

$$\sum y = 764.5 \qquad \sum x z = 46,676.8 \qquad \sum y^2 = 59,920.6$$

$$\sum z = 642.5 \qquad N = 10 \qquad \sum z^2 = 44,062.6$$

If Equations C-1 and C-2 are solved simultaneously, the result is

$$y = 24.7 + 0.756 x \qquad \text{(C-8)}$$

Similarly, C-3 and C-4 yield

$$z = -6.69 + 1.04 x \qquad \text{(C-9)}$$

The standard deviation  $S_{y.x}$  is calculated from C-7 with a and b values from C-8 and  $N=10$ . In Equation C-7, if y, a and b are replaced in C-7 by z,  $a'$  and  $b'$  and C-9 is used to obtain  $a'$  and  $b'$ , Equation C-7 will yield  $S_{z.x}$ . These results are summarized below:

$$S_{y.x} = 0.678$$

$$S_{z.x} = 1.33$$

## 2. Linear Correlation of $\text{CoSO}_4$ Data of Figure 17

Equations C-1 - C-7 are applicable. The method of calculation is exactly as before. The results are summarized in Table XIII.

TABLE XIII  
SUMMARY OF LINEAR CORRELATION CALCULATIONS,  $\text{CoSO}_4$

Run No.	Temp. Range (°F.)	x	y	z	xy	xz	$x^2$	$y^2$	$z^2$
10	140°-40°	51.5	60.0	48.0	3090.0	2472.0	2652.2	3600.0	2304.0
11	"	79.0	81.5	75.0	6438.5	5925.0	6241.0	6642.2	5625.0
12	"	85.0	86.5	81.5	7352.5	6927.5	7225.0	7482.2	6642.2
13	"	66.0	73.0	62.5	4818.0	4125.0	4356.0	5329.0	3906.2
*16	"	79.0	83.5	77.0	6596.5	6083.0	6241.0	6972.2	5929.0
*18	"	88.5	91.0	87.0	8053.5	7699.5	7832.2	8281.0	7569.0
*19	"	84.0	87.0	82.5	7308.0	6930.0	7056.0	7570.0	6806.2
28	159°-59°	53.0	64.0	50.5	3392.0	2676.5	2809.0	4096.0	2550.2
29	"	69.5	76.5	63.5	5316.8	4413.2	4830.2	5852.2	4032.2
30	"	85.5	88.5	82.0	7566.8	7011.0	7310.2	7832.2	6724.0

\*Mixed salt

$$\sum x = 741.0$$

$$\sum x y = 59,932.6$$

$$\sum x^2 = 56,552.8$$

$$\sum y = 791.5$$

$$\sum x z = 54,262.7$$

$$\sum y^2 = 63,657.0$$

$$\sum z = 709.5$$

$$N = 10$$

$$\sum z^2 = 52,088.0$$

$$y = 21.4 + 0.780 x$$

$$z = -5.13 + 1.03 x$$

$$s_{y.x} = 1.15$$

$$s_{z.x} = 1.04$$

## **LIST OF SYMBOLS**

## LIST OF SYMBOLS

A	Variable defined in Equation 25a and 25 L-a
B	Variable defined in Equation 25b and 25 L-b
C	Variable defined in Equation 25c and 25 L-c
$D_1'$	Coefficient of thermal diffusion of the $i^{\text{th}}$ component, Equation 1.
$D_i$	Coefficient of ordinary diffusion of the $i^{\text{th}}$ component, Equation 1.
$E_r, E_s$	Energy of atoms in states r and s respectively, Equation 3.
$E_{ij}$	Energy of an atom of component, i, in energy level, j.
E	Total energy of the system
$E_1^0, E_2^0$	Electronic energy of components 1 and 2 respectively
F	Repulsive force between gas atoms
$H^*$	Defined by Equation 21
$J_i$	Diffusive flux of the $i^{\text{th}}$ component, Equation 1.
L	Length of the cell along temperature gradient
$N_1, N_2$	Mol fraction at cold and hot side respectively, Equation 2.
$N_r/N_s$	Ratio of the number of atoms in energy states r and s, Equation 3.
$N_1, N_1, N_2$	Total number of atoms of component 1, 1, 2 respectively.
$P_i$	Partition function for $i^{\text{th}}$ component, Equation 7
$\Delta P$	Vapor pressure change
$Q_1$	$-\frac{\partial}{\partial \beta} P_1$
S	Cross sectional area of the cell

$S_{y.x}$	Standard deviation of $y$ as a function of $x$ , Equation E-7
$T$	Temperature, Equation 1
$T_H, T_C$	Temperature of hot and cold sides respectively
$T_0$	Initial temperature of the system
$T_A, T_B$	Intermediate temperatures between $T_H$ and $T_C$
$\Delta T_b$	Boiling point change
$\Delta T$	Temperature gradient, Equation 2
$\Delta T_f$	Freezing point change
$V$	Volume of the cell
$X$	Linear distance along the cell; mol fraction
$Z$	Atomic number
$a, a'$	Constants, Equations 16, 32-36
$b, b'$	Constants, Equations 16, 32-36
$c, c'$	Constants, Equations 32-36
$d$	Derivative
$e$	Base of natural logarithms, Equation 3
$f$	Functional notation
$g_r, g_s$	Statistical weights of energy levels $r$ and $s$ , Equation 3
$h$	Planck's constant
$i$	van't Hoff Factor
$k$	Boltzmann constant
$m$	Mass; molality
$\vec{n}$	Unit normal vector, Equation 1
$r$	Intermolecular distance; constant, Equation 16
$r, r', r'', r'''$	Constants, Equations 46-50

$s, s', s'', s'''$	Constants, Equations 46-50
$t_s$	Time of implementation of the temperature gradient
$t_f$	Time at steady state
$t, t', t'', t'''$	Constants, Equations 46-50
$x$	Linear dimension along temperature gradient
$x$	Initial spectrophotometer reading
$y$	Hot side spectrophotometer reading at steady state
$z$	$\frac{1}{T}$
$z$	Cold side spectrophotometer reading at steady state
$\alpha$	$\frac{P_1 Q_2}{P_2 Q_1} = \frac{E_2^0}{E_1^0}$ Ratio electronic energies of two components
$\beta$	Reciprocal of $kT$
$\eta_1, \eta_2$	Atoms per unit volume of components 1 and 2 respectively
$\eta_{ij}$	Number of atoms of component, $i$ , at energy level, $j$ , per unit volume
$\eta_{in}$	Number of atoms of component, $i$ , at energy level, $n$ , per unit volume
$K, K'$	Constants
$\nu, \nu'$	Constants
$\nu$	Number of atoms produced by electrolyte at infinite dilution
$\xi_i$	Mol fraction of the $i$ th component, Equation 1
$\pi$	Osmotic pressure
$\rho$	Molar Density, Equation 1
$\sigma$	Soret coefficient, Equation 2
$\Sigma$	Summation
$\phi, \phi^{-1}$	Osmotic coefficient and its reciprocal respectively



Tr	Translation
Rot	Rotation
Vib	Vibration
Elect	Electronic
Misc	Miscellaneous
$1s^2S_{\frac{1}{2}}$	Electron orbit
I. P.	Ionization potential
EV	Electron volts

**VITA**

## VITA

Daniel Hershey was born in New York City on February 12, 1931. He attended the New York public and high schools, graduating with a Bachelor's degree in chemical engineering from the Cooper Union in 1953. After a year and one-half of industrial experience he was drafted into the Army. Immediately upon discharge, he entered The University of Tennessee, where he received his M.S. degree, with a major in chemical engineering, during December, 1958. He will be awarded a Ph.D. in chemical engineering during June, 1961.

