

A Kinetic and Thermodynamic Study of Fast Reactions in  
Mixed Aqueous Solvents by the Pressure Jump Technique

A Dissertation  
Presented to the  
Faculty of the Department of Chemistry  
College of Arts and Sciences  
University of Houston

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

by  
David R. Underdown

August, 1972

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An Abstract

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## ABSTRACT

The change in the rate constants and stability constants of the one-to-one nickel(II) malonate complex was studied as a function of changing structure and macroscopic properties of the solvent at different temperatures. The favorable equilibrium constant, forward rate constant and entropy change of the nickel(II) malonate system allowed the use of the pressure jump technique to study the solvent effect on the thermodynamic and kinetic properties of the system. Small amounts of dioxane were used to vary the solvent properties because of its complete miscibility with water, low dielectric constant, and neutral nature. The variations in the kinetic and thermodynamic parameters of the nickel(II) malonate system in the various water-dioxane solvent systems are explained on the basis of the solvent structure promotion and breaking ability of dioxane. The equilibrium constants of nickel(II) malonate at different temperatures and in the various water-dioxane systems were determined from spectrophotometric data.

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# I

## INTRODUCTION

## INTRODUCTION

Results of investigations of the factors which influence the rates of complex formation indicate that the formation rate is strongly dependent upon the nature of the metal ion under investigation. These investigations also indicate a dependency of the rate of complex formation upon the number and nature of the ligands bound to the metal ion, the ionic charges of both reagents, steric effects, and solvent effects.

Eigen and his associates (1-4) proposed what now is generally accepted as the mechanism for complex formation between a metal ion and a bidentate ligand as shown in Figure 1. The mechanism is represented by the following equations:

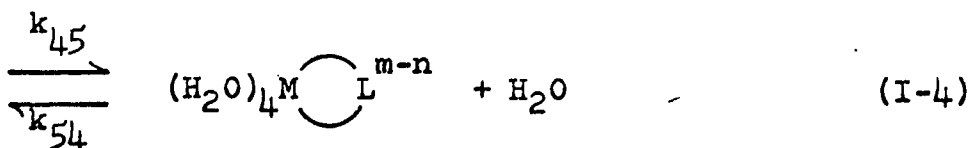
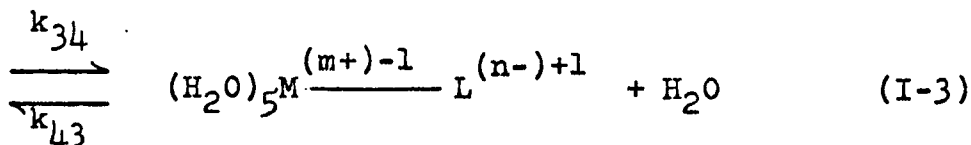
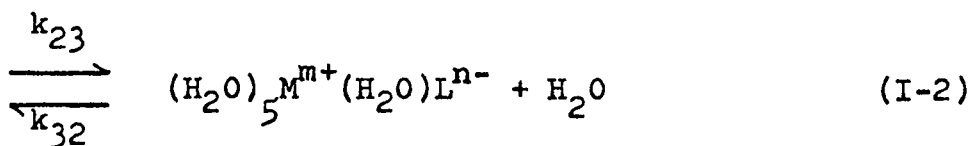
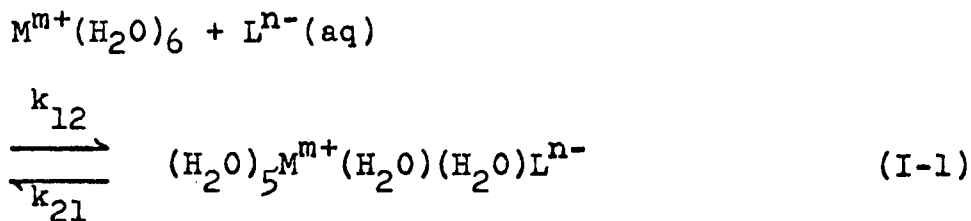
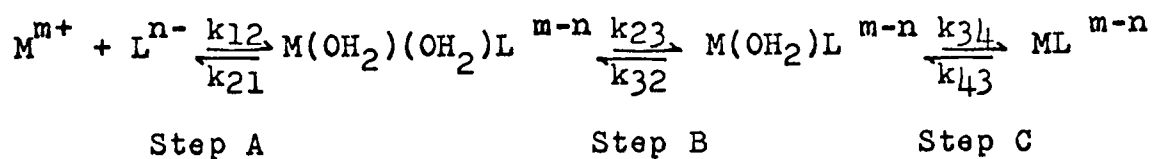


FIGURE 1

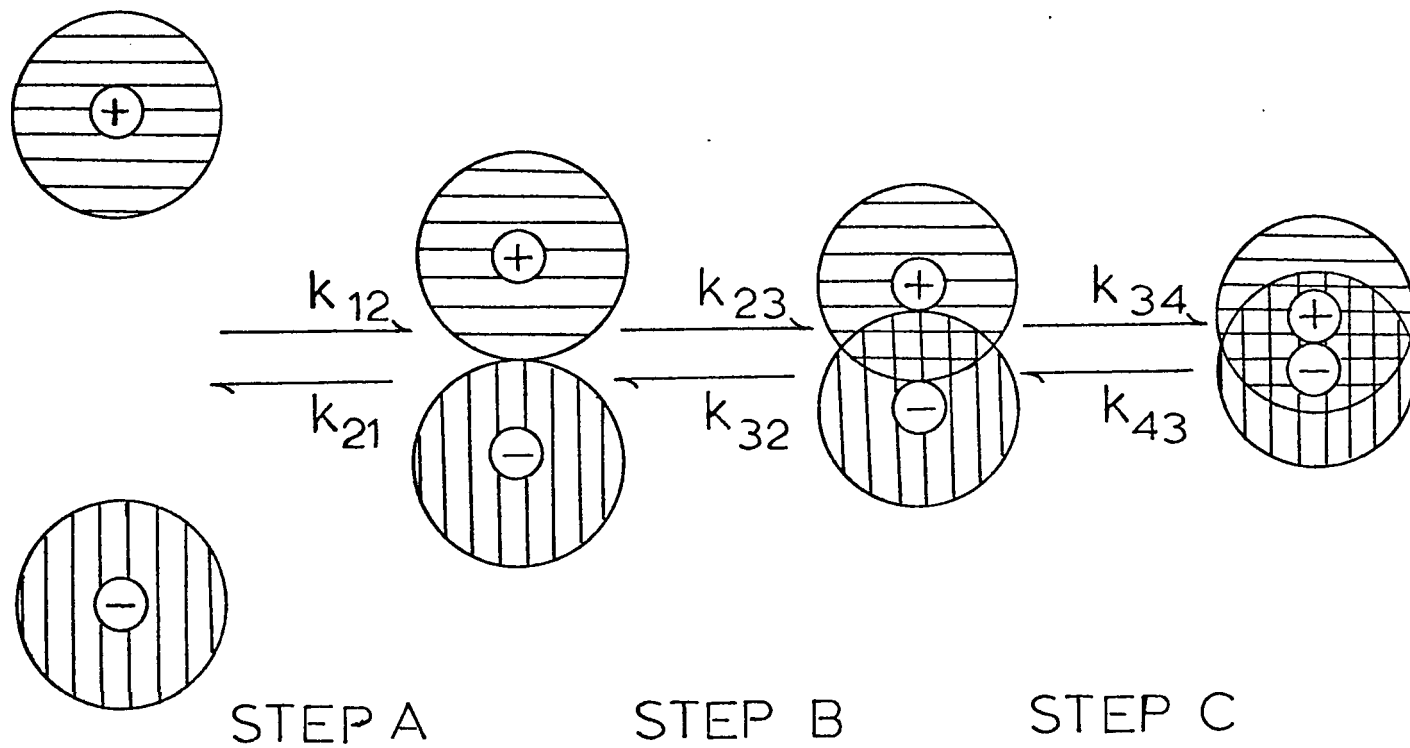
## MULTIPLE STEP COMPLEX FORMATION MECHANISM



Step A = Formation of Bjerrum Ion Pair

Step B = Formation of Outer-Sphere Coordination Complex

Step C = Formation of Inner-Sphere Coordination Complex



Step A is the diffusion controlled formation of the Bjerrum ion pair where the ions are separated by the water molecules which form the inner hydration sphere of each ion. Step B is the formation of the outer sphere coordination complex where the ions are separated by only the inner hydration sphere of the metal ion. Step C is the formation of the inner sphere coordination complex, i.e., formation of the first metal ligand bond and loss of a water molecule from the coordination sphere of the metal ion. Step D is the formation of the second metal ligand bond to form the fully chelated complex. This mechanism has been shown to quantitatively explain the relaxation effects observed in kinetic studies of weak polyvalent electrolyte systems (2,4). The development of such techniques as stopped flow, ultrasonic absorption, temperature jump and pressure jump for the study of fast reactions has resulted in a large accumulation of data supporting the mechanism for complex formation as proposed by Eigen. The results of the investigations of these systems has been reviewed by Kustin and Swinehart (5) and by Hewkin and Prince (6). Hexaaquonickel(II) has been a favorite for the study of fast reactions in solution because the rates of reaction are favorable for the use of the mentioned techniques and its behavior is typical of a large class of aquometal ions.

In recent years, fast reactions have been investigated in mixed aqueous and non-aqueous solvent systems (7-10) using

various techniques. These studies have shown that the rate of solvent exchange between the coordination sphere of metal ions and the bulk solvent depend upon: (1) metal ligand bond energies, (2) solvation differences between ground and transition states, and (3) steric requirements of different ligands.

To date, a great amount of information has been gathered concerning the factors governing the rate of complex formation in solution. In order to investigate the role of the solvent in the mechanism of complex formation, the solvent composition is varied and the changes in the kinetic and thermodynamic reaction parameters observed. The study by Pearson and Ellgen (7) of the rates of reaction of nickel(II) ions with 2,2'-bipyridyl, thiocyanate ion, and the dithio-oxalate ion ( $C_2O_2S_2^{2-}$ ) in methanol-water mixtures show agreement with the proposed mechanism. Their study showed that for uncharged ligands the variation in the rates of complex formation is independent of Step A of the proposed mechanism; whereas, for charged ligands the variation in the rate of complex formation is related to the variation in Step A. The results of their studies are explained on the basis of dependence of Step A upon dielectric constant of the solvent. It was concluded that small amounts of water should increase the second order rate irrespective of the charge of the ligands. The uncharged ligands are expected to form ion-dipole pairs to an extent independent of dielectric constant. Thus the effect on Step C should be

small and the substitution rate should rise smoothly but progressively less rapid with increasing water content. For charged ligands, small amounts of water will again increase the rate, but eventually the increasing dielectric constant must cause the rate of complex formation to decrease. The rate is expected to go through a maximum. Bennetto, Bulmer, and Caldin (11) have done a kinetic and thermodynamic study of the interaction of nickel(II) with 2,2'-bipyridyl by means of the stopped flow technique in a series of methanol-water mixtures. This study gave similar results to that of Pearson and Ellgen (7). Bennetto and Caldin (11) concluded that any theory which considers the role of the solvent in ligand substitution or solvent exchange at bivalent transition metal cations must give an interpretation of: (a) the general correlation of  $\Delta H^*$  and  $\Delta S^*$ , where the compensation suggests a considerable effect of solvation; and (b) the correlations which show that the kinetic differences between ligand and solvent substitution at a given cation are sensitive to structural properties of the solvents. Bennetto and Caldin (11) put forth a "first-order" theory based on an extension of Frank and Wen's (12) well established model for ions in water. This theory states: (a) that the dissociative step requires an enthalpy which is much the same from one solvent to another, and an entropy change which is small compared to the overall variation in  $\Delta S^*$ ; (b) that the molecules in the disordered region around the ion are in a

quasi-gaseous state; and ( c ) the effect of an added solute on the solvent structure is related to the difference between the enthalpies of evaporation of the two species. Casazza and Cefola (13) reported a kinetic and thermodynamic study of the rates of reaction of nickel(II) with acetylacetone in a series of 2-propanol-water solvent systems using a stopped flow technique. The study was made to clarify the role of the solvent in complexation reactions. The results showed that second order rate constants are a linear function of the inverse of the dielectric constant of the solvent system over a narrow range of dielectric constants. Outside this range, the change in slope is attributed to changes in the coordination sphere of nickel(II). The energy of activation in the region of linear relationship was separated into an energy of activation at constant dielectric and energy of activation at constant temperature. The data obtained implied that the temperature dependent activation energy was of major importance.

Water-dioxane mixtures have been a favorite solvent system in which to study solvent effects upon kinetic and thermodynamic parameters of a reaction system. This is because dioxane is completely miscible with water, it has a neutral nature, and the dielectric constants of water-dioxane mixtures vary over a large range as a result of dioxane's low dielectric constant. However, in such studies it is important to know if the observed changes in reaction parameters are

a result of decreasing dielectric constant or to a change in solvent-ion or solvent-solvent interaction.

Investigations by Clemett (14) and Feakins (15) indicate that small amounts of dioxane (<10%) in water produce a more structured solvent system. Winstein and Fainburg (16) have reported a minimum in activation parameters between 0.75 and 0.95 mole fraction of water as general phenomena for all sorts of reactions in all sorts of mixed aqueous solvents. Atkinson and Kor (8) studied the kinetics of ion association of manganese sulfate in water-dioxane and methanol-water mixtures using ultrasonic techniques. They found that the rates of complex formation in water-methanol mixtures increased linearly with increased mole fraction methanol; whereas, in water-dioxane mixtures the forward rate constants drastically increased at small mole fractions dioxane and then tends to level off. They did not give any explanation to the observed trends. The present study was initiated by an interest in the trend observed for the rate of complex formation in the water rich region of the water-dioxane solvent system.

The purpose of this study is to investigate the kinetics and thermodynamic parameters of nickel(II) malonate formation in the water-rich region of water-dioxane mixtures in order to learn more about the role of the solvent in the mechanism for the multiple-step association process.

## II

### THEORY

## THEORY

### 1. The Relaxation Time and the Rate Constant

In the discussion of step function perturbations for a one step equilibrium, the conventional rate equation describes the system after the perturbation is complete. The one step mechanism



can be described by:

$$\frac{d(AB)}{dt} = -\frac{d(A)}{dt} = -\frac{d(B)}{dt} = k_f(A)(B) - k_r(AB) \quad (\text{II-2})$$

If the system is initially at equilibrium when the equilibrium conditions are suddenly perturbed, the new equilibrium concentrations of the species present may be described as  $(A)'$ ,  $(B)'$  and  $(AB)'$  where

$$(A)' = (A)_{eq} + \Delta(A) \quad (\text{II-3})$$

$$(B)' = (B)_{eq} + \Delta(B) \quad (\text{II-4})$$

$$(AB)' = (AB)_{eq} + \Delta(AB) \quad (\text{II-5})$$

where the subscript eq designates equilibrium concentrations and  $\Delta$  represent deviations from the equilibrium concentrations.

From the stoichiometric relationship we know

$$\Delta(C) = \Delta(AB)' = -\Delta(A)' = -\Delta(B)' \quad (\text{II-6})$$

After the perturbation has occurred, equation (II-2) may be rewritten as

$$\frac{d\Delta(C)}{dt} = k_f(A)'(B)' - k_r(AB)' \quad (\text{II-7})$$

Using equations (II-3) through (II-6), equation (II-7) becomes

$$\begin{aligned} \frac{d\Delta(C)}{dt} = & \left[ k_{12} (A)_{eq} + \Delta(A) \right] \left[ (B)_{eq} + \Delta(B) \right] \\ & - k_{21} \left[ (AB)_{eq} + \Delta(AB) \right] \end{aligned} \quad (\text{II-8})$$

which may be rewritten as

$$\begin{aligned} \frac{d\Delta(C)}{dt} = & k_{12} \left[ (A)_{eq}(B)_{eq} - \Delta C(B)_{eq} - \Delta C(A)_{eq} + \Delta C^2 \right] \\ & - k_{21} \left[ (AB)_{eq} - \Delta C \right] \end{aligned} \quad (\text{II-9})$$

Upon rearrangement, equation (II-9) becomes

$$\begin{aligned} -\frac{d\Delta(C)}{dt} = & C \left\{ k_{12} \left[ (A)_{eq} + (B)_{eq} \right] + k_{21} \right\} + k_{21}(AB)_{eq} \\ & - k_{12}(A)_{eq}(B)_{eq} - k_{12}(\Delta C)^2 \end{aligned} \quad (\text{II-10})$$

Since

$$\frac{k_{12}}{k_{21}} = \frac{(AB)_{eq}}{(A)_{eq}(B)_{eq}} \quad (\text{II-11})$$

and at near equilibrium  $(\Delta C)^2$  is negligible, equation (II-10) becomes

$$\frac{d\Delta(C)}{dt} = -\Delta C \left\{ k_{12}[(A)_{eq} + (B)_{eq}] + k_{21} \right\} \quad (II-12)$$

The quantity in brackets is independent of time; therefore, integration of equation (II-12) gives

$$\frac{\Delta(C)}{\Delta C} = e^{-\left\{ k_{12}[(A)_{eq} + (B)_{eq}] + k_{21} \right\} t} \quad (II-13)$$

where  $\Delta C$  is the value of the concentration immediately after the chemical perturbation. Equation (II-13) implies that after a time period such that

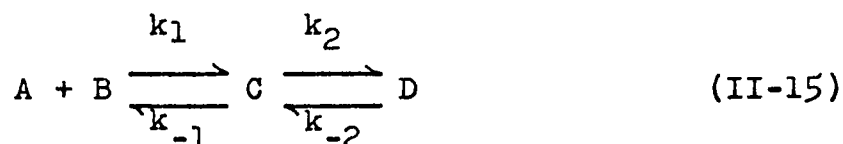
$$\left\{ k_{12}[(A)_{eq} + (B)_{eq}] + k_{21} \right\} t = 1$$

$\Delta(C)/\Delta C = 1/e$ ; i.e., the difference between the actual concentration and equilibrium concentrations has been reduced to  $1/e$  of the original. This time period has been denoted as  $\tau$ , the relaxation time. From a series of experimentally determined relaxation times at various concentrations, a plot of  $1/\tau$  against  $f_{\pm}^2 [(A)_{eq} + (B)_{eq}]$  yields a straight line. The slope of the plot is the forward rate constant ( $k_f$ ) and the intercept is the reverse rate constant ( $k_r$ ). The relationship between the relaxation time,  $k_f$  and  $k_r$  is shown in equation (II-14)

$$1/\tau = k_f f_{\pm}^2 [(A)_{eq} + (B)_{eq}] + k_r \quad (\text{II-14})$$

where  $f_{\pm}^2$  is the mean activity coefficient.

Most mechanisms are really a series of coupled reactions such as illustrated by equation (II-15)



The differential equations which describe such mechanisms may be set up as follows:

$$-\frac{d(A)}{dt} = k_1(A)(B) - k_{-1}(C) =$$

$$k_1 [(A)_{eq} + (B)_{eq}] \Delta(A) - k_{-1} \Delta(C) \quad (\text{II-16})$$

$$-\frac{d(D)}{dt} = k_2(C) + k_{-2}(D) = k_2 \Delta(C) + k_{-2} \Delta(D) \quad (\text{II-17})$$

Using stoichiometric mass balance, equations (II-16) and (II-17) become

$$-\frac{d\Delta(A)}{dt} = k_{-1} [-\Delta(A) - \Delta(D)] =$$

$$\left\{ k_1 [(A)_{eq} + (B)_{eq}] \right\} \Delta(A) + k_{-1} \Delta(D) \quad (\text{II-18})$$

$$-\frac{d\Delta(D)}{dt} = k_2 \Delta(A) + [k_{-1} + k_2] \Delta(D) \quad (\text{II-19})$$

For the coupled mechanism considered, there are n independent concentration variables and n independent rate equations. Near equilibrium, all these are linear first order differential equations of the form:

$$-\frac{d\Delta(C)_i}{dt} = \sum_{j=1}^n a_{ij} \Delta(C)_j \quad (\text{II-20})$$

where the  $a_{ij}$ 's are functions of the rate constants and equilibrium concentrations. The solution of such a system of equations requires use of matrix methods. These equations may be solved using:

$$\{C(t)\} = e^{-\{A\}t} \{C(0)\} \quad (\text{II-21})$$

where  $\{C\}$  is the column matrix  $(C_1, C_2, \dots, C_n)$  and  $\{A\}$  is a N by N matrix.

In the particular mechanism described by equation (II-15), if we let

$$A_{11} = k_1 (A)_{eq} + (B)_{eq} + k_{-1}$$

$$A_{12} = k_{-1}$$

$$A_{21} = k_2$$

$$A_{22} = k_{-2} + k_2$$

equations (II-16) and (II-17) become

$$-\frac{d\Delta(A)}{dt} = A_{11}\Delta(A) + A_{12}\Delta(D) \quad (\text{II-22})$$

$$-\frac{d\Delta(D)}{dt} = A_{21}\Delta(A) + A_{22}\Delta(D) \quad (\text{II-23})$$

The relaxation times of the system are then found by solving the following determinant:

$$\begin{vmatrix} A_{11} - 1/\tau & A_{12} \\ A_{21} & A_{22} - 1/\tau \end{vmatrix} = 0$$

which results in the following quadratic equation:

$$\frac{1}{\tau_1, \tau_2} = \frac{(A_{11} + A_{22}) \pm \sqrt{(A_{11} + A_{22})^2 - 4(A_{12}A_{21} - A_{11}A_{22})}}{2} \quad (\text{II-24})$$

Substituting the rate constants into equation (II-24) and rearranging we obtain:

$$\frac{1}{\tau_1, \tau_2} = \frac{1}{2} \left\{ k_1 [(A)_{eq} + (B)_{eq}] + k_{-1} + k_2 + k_{-2} \right\} - \left[ 1 \pm \left( \frac{4k_1k_2 [(A)_{eq} + (B)_{eq}] + k_1k_2 [(A)_{eq} + (B)_{eq}] + k_{-1}k_2}{\{k_1 [(A)_{eq} + (B)_{eq}] + k_{-1} + k_2 + k_{-2}\}^2} \right)^{\frac{1}{2}} \right] \quad (\text{II-25})$$

Expanding the square root term in a series allows you to drop all squared terms. Assuming  $k_1 [(A)_{eq} + (B)_{eq}] + k_{-1} \gg k_{-2} + k_2$ , equation (II-25) results in the following:

$$1/\tau_1 = k_1 [(A)_{eq} + (B)_{eq}] + k_{-1} \quad (II-26)$$

$$1/\tau_2 = k_{-2} + \frac{k_1 k_2 [(A)_{eq} + (B)_{eq}]}{k_1 [(A)_{eq} + (B)_{eq}] + k_{-1}} \quad (II-27)$$

assuming  $k_1/k_{-1} = K_1$  and letting

$$k_2 = \frac{K_1 k_2}{1 + K_1 [(A)_{eq} + (B)_{eq}]} \quad (II-28)$$

equation (II-27) becomes

$$1/\tau_2 = k_2 [(A)_{eq} + (B)_{eq}] + k_{-2} \quad (II-29)$$

where  $\tau_1$  and  $\tau_2$  refer to the relaxation times for step I and II respectively.

The above treatment shows that rate constants depend upon ionic concentration of free ions and the stability constants for ion pair formation.

## 2. Stability Constant of the Outer Sphere Complex

Ion pairing and the stability constant of the outer sphere complex is related to the association which occurs as a result of purely electrostatic attraction between oppositely charged ions. This concept which was introduced by Bjerrum soon after Debye and Huckel proposed their theory for ionic solutions where long-range electrostatic forces were taken into account (17) has proved helpful in interpreting the behavior of a large class of electrolyte solutions.

Generally the values of  $K_o$  must be estimated, although they may be experimentally determined in a few cases. The following equations have been derived by Fuoss (18) on the basis of a statistical argument and by Eigen (19) on the basis of a solution from the theory of diffusion controlled reactions:

$$K_o = K_o^0 e^b \quad (\text{II-30})$$

where

$$K_o^0 = \frac{4\pi Na^3}{3000} \quad (\text{II-31})$$

$$b = \frac{Z_1 Z_2 e^2}{aDkT} \quad (\text{II-32})$$

In the above equations,  $K_o^0$  is the association constant for uncharged particles, the term  $e^b$  is the ratio of the electrostatic energy to the thermal energy, and the rest of the symbols have the usual significance. The values of  $K_o$  obtained by using the above equations have been shown to be within a factor of 3 or 4 of the experimental value (20).

The association constants of magnesium(II) sulfate in various water-organic systems are given in Table 1 (21,22,23). Inspection of these data indicate a wide range of values for the association constants. It can be seen that the variation of  $K_o$  not only depends upon the water-organic solvent system, but also on the percent composition within any one of the

TABLE I  
ION PAIR CONSTANTS AT 25°C FOR A 2-2 ELECTROLYTE IN  
VARIOUS WATER-ORGANIC SOLVENT SYSTEMS,  $\mu \rightarrow 0$

| SOLVENT SYSTEM | % ORGANIC SOLVENT | $K_o$ |
|----------------|-------------------|-------|
| methanol-water | 0.0               | 133   |
|                | 10.0              | 237   |
|                | 20.0              | 439   |
|                | 30.0              | 881   |
| acetone-water  | 9.94              | 275   |
|                | 19.83             | 750   |
|                | 29.91             | 1750  |
|                | 40.17             | 5600  |
| dioxane-water  | 0.0               | 133   |
|                | 5.0               | 201   |
|                | 10.0              | 242   |
|                | 15.0              | 409   |
|                | 20.0              | 804   |
|                | 25.0              | 1156  |

specific water-organic solvent system. For this reason, a standard value of  $K_o$  was not used, as was done by other workers (24), in the calculation of the thermodynamic and kinetic parameters for the study done in the present work. The  $K_o$  values used in the present study were calculated using equations (II-30,31 and 32). The results of the calculations are presented later in the discussion on the results of the present study.

### 3. Conversion to Infinite Dilution

The stability constants used in this study were corrected to infinite dilution using the Bronsted-Bjerrum-Christiansen form of the Debye-Huckel equation(25):

$$\ln K_o = \ln K - \frac{2A(\pi Z - \pi Z')\sqrt{\mu}}{1 + \beta\sqrt{\mu}} \quad (\text{II-33})$$

where primes denote products,  $\beta$  is approximately unity, and

$$A = \frac{1.82 \times 10^6}{(DT)^{3/2}}$$

The rate constants were corrected to infinite dilution using a form of the above equation.

### III

#### EXPERIMENTAL

## EXPERIMENTAL

### 1. Nature of the Pressure-Jump Method

Studies done on electrolyte solutions using the pressure-jump technique involves the use of the pressure-step technique to study association processes in solution, containing various polyvalent ions. The pressure-step technique will affect the mobilities of the ions and the density of the solution in both cells of the pressure-step apparatus; the ionic concentration of the partially associated electrolyte in the solution under investigation will be changed indirectly because of the change in the density of the solution.

The pressure-jump technique deals mainly with the change of the specific conductance of the solution under investigation,  $\Delta L/L$ , where  $L$  represents the specific conductance ( $\text{ohm}^{-1} \text{ cm}^{-1}$ ). The electrolyte to be studied will determine the magnitude and concentration dependence of the relative change in specific conductance with a pressure change. For weak electrolytes and for electrolytes where a great deal of ion association occurs, the change in specific conductance is greatly concentration dependent; whereas,  $\Delta L/L$  is virtually independent of concentration for a change in pressure or temperature for strong electrolytes where there is little ion association. It should be noted here that for electrolyte

solutions which do show a change in the specific conductance with pressure or temperature the relaxation portion of the specific conductance change (i.e., the portion brought about by the change in the equilibrium constant) may be very small even though the total conductance change may be two tens to six tens percent for a given applied pressure.

The general equation for the specific conductance of a dilute electrolyte solution is as follows:

$$L = \frac{F}{1000} \sum C_n |Z_n| u_n = \frac{pF}{1000} \sum m_n |Z_n| u_n \quad (\text{III-1})$$

where  $F$  is the Faraday constant,  $C_n$  the molar concentration of the  $n^{\text{th}}$  conducting species,  $Z_n$  the charge on the  $n^{\text{th}}$  conducting species,  $p$  the density of the solution,  $m_n$  the molal concentration of the  $n^{\text{th}}$  conducting species and  $u_n$  the mobility. If the small changes in mobility, molality, and density are denoted by  $\delta u_n$ ,  $\delta m_n$  and  $\delta p$ , it follows, by neglecting second order terms, that:

$$\begin{aligned} \Delta L = \frac{F}{1000} \left[ \sum_n |Z_n| u_n p \delta m_n + \right. \\ \left. \sum_n |Z_n| m_n p \delta u_n + \sum_n |Z_n| u_n m_n \delta p \right] \quad (\text{III-2}) \end{aligned}$$

In equation (III-2), the first term represents the chemical process of relaxation; in other words, the portion caused by

a change in the number of ions in solution. The second term represents the conductance change due to a pressure change and the third term represents the change in concentration of the species in solution due to a change in the volume of the solution. The term which arises from the relaxation of the ionic atmosphere (4,26) is an additional time dependent term which contributes to the change in conductance with pressure, but the time constant for such a process (  $10^{-9}$  -  $10^{-7}$  sec ) is very short compared to the relaxation time measured by the pressure jump technique. The time constant of the relaxation of the ionic atmosphere is included in the term for the change in mobility with pressure. The second and third terms of equation (III-2) follow the pressure change almost instantaneously; therefore, they may be neglected. If we let  $i$  = reactants,  $j$  = products and  $n$  = total species, equation (III-2) becomes:

$$\Delta L/L = \frac{\sum_i |z_i| u_i \delta C_i + \sum_j |z_j| u_j \delta C_j}{\sum_n |z_n| u_n C_n} \quad (\text{III-3})$$

Equation (III-3) shows the chemical contribution to the change in conductance where the denominator includes the contribution to the total conductivity by all ionic species present in the solution and the numerator shows only the ionic species involved in the pressure sensitive equilibria.

From equation (III-3), it can be seen that at high concentrations the term  $\sum |z_n| u_n |c_n|$  will be very large; this would result in a loss of sensitivity in the pressure-jump apparatus. The pressure-jump technique is limited in the systems which may be studied because the system must contain ions in solution at a concentration of  $10^{-3} - 10^{-4}$  M, the system must have an equilibrium constant of  $10^4 - 10^5$  and the reverse rate constant must be small compared to the forward rate constant. The relaxation times which can be measured by the pressure-jump technique are limited by the diffusion rate of the gas being used to apply the pressure to the solution.

## 2. Thermodynamic Aspects of the Pressure-Jump Technique

There will be a temperature change which accompanies a rapid pressure change because a pressure change is essentially adiabatic. The change in temperature which results from the pressure change can be calculated from the following equation:

$$\left( \frac{\partial T}{\partial P} \right)_S = T \left( \frac{\alpha_P}{p \bar{C}_P} \right) \quad (\text{III-4})$$

where  $\alpha_P$  is the thermal coefficient of expansion at pressure  $P$ ,  $p$  the density,  $\bar{C}_P$  the specific heat at constant pressure. A 30-atm pressure step is accompanied by a temperature change of about  $0.05^\circ\text{C}$ . Usually the concentration change caused by

such a small temperature change is very small when compared to the concentration change caused by the pressure-jump and may be neglected.

Considering the total conductance change which results from a perturbation by a pressure-step as a function of the displacement of the system from the system ( $\theta$ ), we get the following expression:

$$\Delta L/L = \frac{\sum_i |z_i| u_i \nu_i - \sum_j |z_j| u_j \nu_j}{\sum_n |z_n| u_n c_n} \frac{\partial \theta}{\partial \ln K} \left[ \left( \frac{\partial \ln K}{\partial P} \right)_T + \left( \frac{\partial \ln K}{\partial T} \right)_P \left( \frac{\partial T}{\partial P} \right)_S \right] \delta P e^{-t/\tau} \quad (\text{III-5})$$

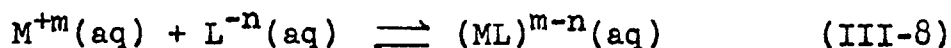
where  $\nu$  is the stoichiometric coefficient. From thermodynamics

$$\left( \frac{\partial \ln K}{\partial P} \right)_T = - \frac{\Delta V^\circ}{RT} \quad (\text{III-6})$$

$$\left( \frac{\partial \ln K}{\partial T} \right)_P = \frac{\Delta H^\circ}{RT^2} \quad (\text{III-7})$$

where  $\Delta V^\circ$  and  $\Delta H^\circ$  are the standard volume and enthalpy changes respectively.

For a real equilibrium situation such that:



where  $(\text{ML})^{m-n}(\text{aq})$  is an inner sphere complex,  $K_{\text{eq}}$  for the

system can be expressed in terms of concentrations and activity coefficients ( $f_i$ ) as follows:

$$K_{eq} = \frac{f_{ML} C_{ML}}{C_M^{+m} C_L^{-nf_M + mf_L - n}} \quad (III-9)$$

The following equation is obtained assuming a 1:1 electrolyte and  $t = 0$  immediately after a pressure-step perturbation:

$$\Delta L/L = \frac{\sum_i |z_i| u_i c_i - \sum_j |z_j| u_j c_j}{\sum_n |z_n| u_n c_n} \frac{C_0}{RT} \left[ \frac{2 - \alpha}{\alpha(1 - \alpha)} + \frac{\partial \ln f_{\pm}^2}{\partial \alpha} + \frac{\partial \ln f_{ML}}{\partial \alpha} \right]^{-1}$$

$$\left[ \Delta V^0 - \Delta H^0 \frac{\partial \alpha_P}{p \bar{C}_P} \right] \delta P \quad (III-10)$$

where  $\alpha$  is a function of the overall concentration ( $C_0$ ) which exists in the form of the free ion,  $f_{\pm}$  is the mean activity coefficient for the ML complex. Since it is known that the mean activity coefficient for ions does not change to any great extent with  $\alpha$  at low concentrations, the following terms may be dropped out of equation (III-10):

$$\frac{\partial \ln f_{\pm}^2}{\partial \alpha} + \frac{\partial \ln f_{ML}}{\partial \alpha}$$

Assuming that  $\Delta T$  and  $\Delta H^0$  are very small as compared to  $\Delta V^0$ , the following term may be dropped from equation (III-10):

$$\frac{\Delta H^{\circ} \alpha_p}{p \bar{C}_p}$$

When  $C_o = C_{M+m} = C_{L-n}$ , equation (III-10) becomes:

$$\Delta L/L = \frac{\sum_i |Z_i| u_i - \sum_j |Z_j| u_j}{\sum_n |Z_n| u_n C_n} \frac{C_o}{RT} \left[ \left( \frac{2-\alpha}{\alpha(1-\alpha)} \right)^{-1} \Delta V^{\circ} \right]_{\delta P} \quad (\text{III-11})$$

For a 1:1 system  $Z_i = Z_j$  and equation (III-11) becomes:

$$\frac{|Z_M| (u_M + u_L)}{|Z_n| C_M (u_M + u_L)} \frac{C_o}{RT} \left[ \frac{\alpha(1-\alpha)}{2-\alpha} \Delta V^{\circ} \right]_{\delta P} \quad (\text{III-12})$$

Assuming  $\alpha \ll 1$ , equation (III-12) becomes:

$$\Delta L/L = - \left( \frac{1}{\alpha C_o} \right) \left( \frac{C_o \Delta V^{\circ}}{RT} \right)_{\delta P} \left( \frac{\alpha(1-\alpha)}{2-\alpha} \right) =$$

$$- \frac{\Delta V^{\circ}}{2RT} \delta P \quad (\text{III-13})$$

Equation (III-13) describes what actually happens in a pressure-jump system. In an actual system two cells are used to cancel out the ionic mobility and  $\Delta p$ .

### 3. Apparatus

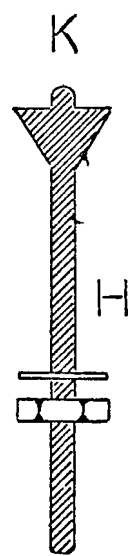
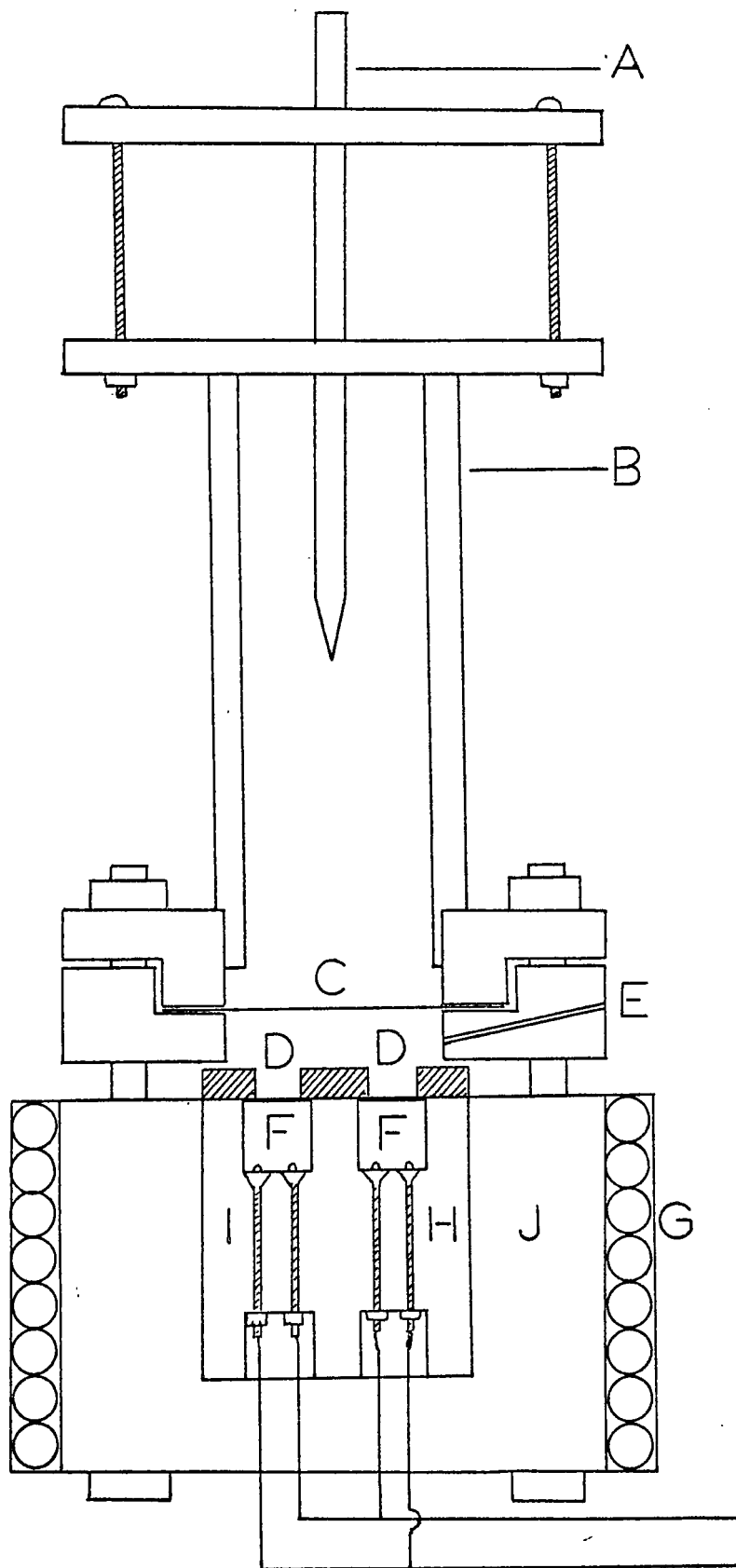
The pressure-jump apparatus (see Figure 2) used in this study is similar to that described by Hoffmann, Stushr, and Yeager (27). The main modifications were in the pressure-jump cell. The cell was a dual conductance cell constructed of Delrin rod. In order to overcome the problem of glueing the electrodes in the cell so that no leakage or movement is observed, the electrodes for the pressure-jump apparatus were constructed with a conical stem (see Figure 2) so as to increase the seal of the electrodes with the cell with an increase of pressure. No leak or movement was observed up to 30 atm . One cell of the pressure-jump apparatus contains the electrolyte solution under investigation while the other contains an electrolyte which has approximately the same conductance but exhibits no relaxation effects at times greater than  $10^{-6}$  seconds. After the sudden release of pressure by the bursting of the beryllium-copper alloy foil by a plunger, the relaxation effects are followed by means of a conductivity bridge (see Figure 3) with two cells in separate arms of the bridge.

A Hewlett-Packard sine wave generator, Model-200S, was used to provide a 200 kHz signal across the conductivity bridge. The bridge was coupled to the generator as well as the bridge detector system by means of a transformer especially made to provide maximum signal at the specified 200 kHz setting of the

## FIGURE 2

## SCHEME OF PRESSURE JUMP CELL

- A = Steel Plunger
- B = Muffler
- C = Copper-Beryllium Foil
- D = Diaphragms
- E = Pressure Capillary
- F = Conductivity Cells
- G = Thermostat Jacket
- H = Stainless Steel Electrodes
- I = Delrin Case
- J = Stainless Steel Holder
- K = Enlargement of Electrodes



## FIGURE 3

## SCHEME OF ELECTRICAL CIRCUIT

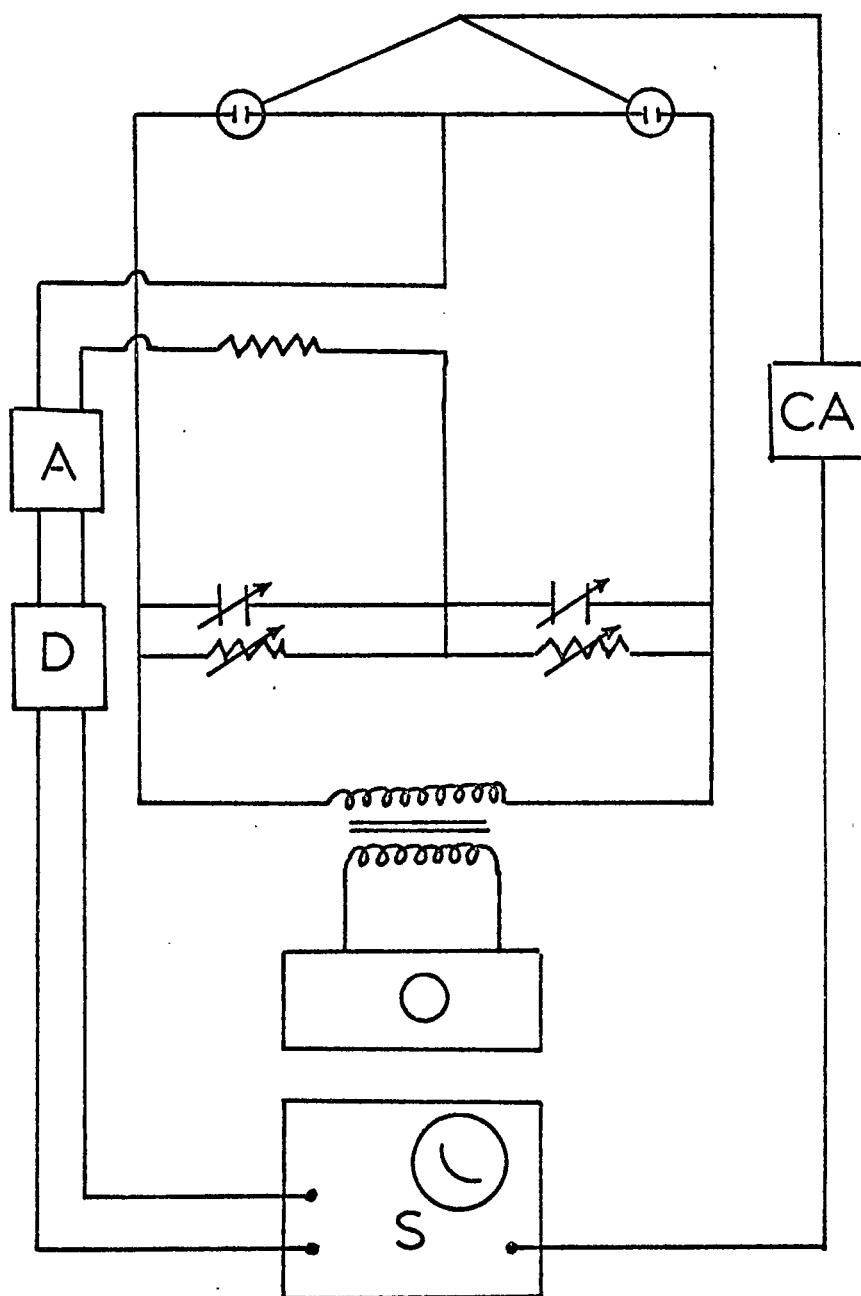
A = Differential Amplifier

D = Detector

O = Oscillator

S = Oscilloscope

CA = Charge Amplifier



sine wave generator (see Figure 4). It was unnecessary to shield the transformer because of its construction. The bridge was constructed of strip resistors variable from 0.01 ohm to 10 kohm connected in parallel with capacitors variable from 15 pF to 0.01 uF. The A.C. signal was displayed on a Tektronic dual gun cathode ray oscilloscope, Model 547, and amplified by a Tektronic differential amplifier, Model D. The oscilloscope was triggered internally by means of a D.C. signal. The oscilloscope curve of the re-equilibrium was photographed by a Polaroid camera mounted on the instrument.

#### 4. Preparation of the Solutions

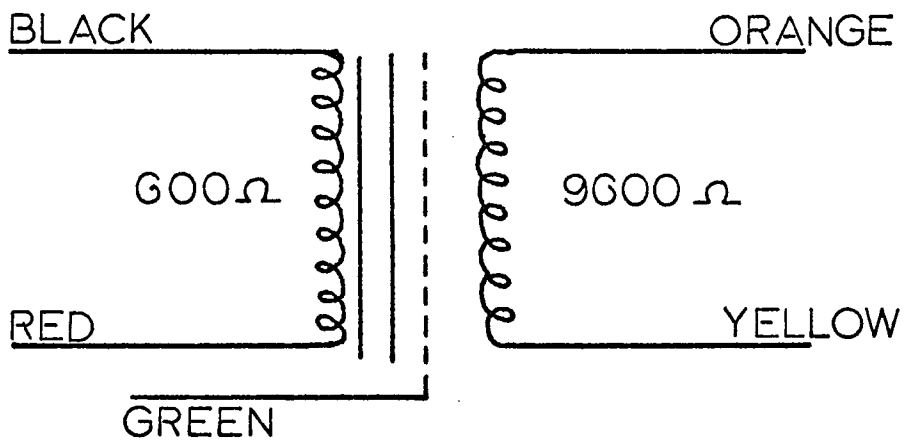
Nickel(II) malonate was prepared by mixing stoichiometric amounts of nickel(II) sulfate with malonic acid and then titrating with a standard solution of barium hydroxide until all the sulfate ions have precipitated as barium sulfate. The pH of the nickel(II) malonate solutions containing various mole fractions of dioxane were kept at least one pH unit above the  $pK_2$  of malonic acid for each of the respective mole fractions of dioxane. This was done to assure that most of the ligand molecules in the respective solutions are present in the anionic form. All compounds were reagent grade and were used without further purification. Reagent grade dioxane obtained from the Matheson Coleman and Company was used without further purification.

The concentrations of the nickel(II) ion, acid anion, and complex for each solution was calculated from stability

FIGURE 4

ELECTRICAL SCHEME OF TRANSFORMER

1 : 4



constants which were experimentally determined. In all cases the concentrations were corrected for changes in activity according to the following semi-empirical equation given by Davies (28):

$$\log f_i = -0.5Z_i^2 \left( \frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I \right) \quad (\text{III-14})$$

where  $f_i$  is the activity coefficient,  $Z_i$  is the charge of the  $i^{\text{th}}$  ion, and  $I$  is the ionic strength of the solution. This equation has been found to give activity coefficients reliable to  $\pm 2\%$  up to an ionic strength of 0.035 for virtually all electrolytes to which it has been applied.

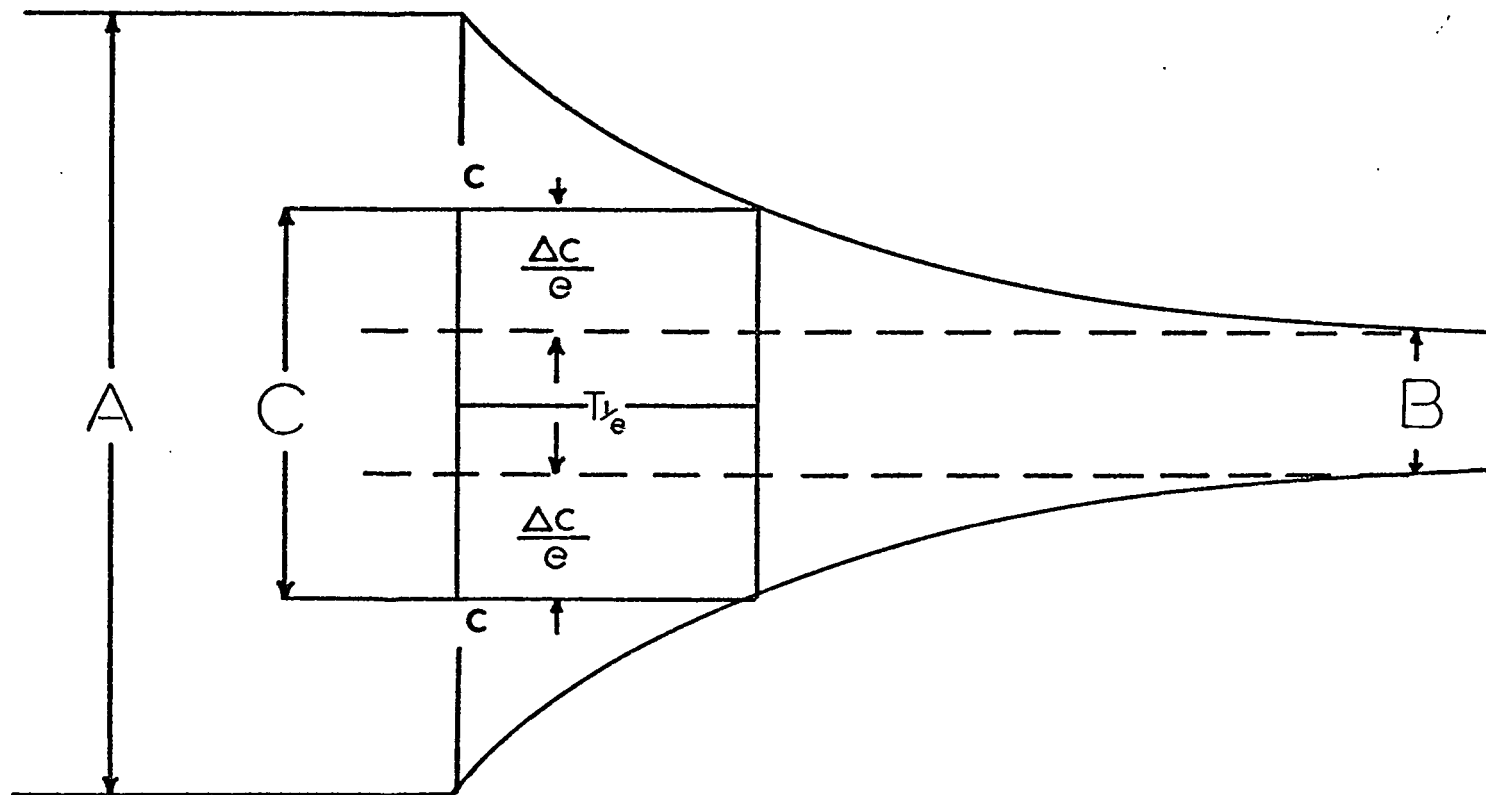
## 5. Kinetic Measurements

The nickel(II) malonate solutions were prepared immediately before use in order to prevent the formation of insoluble nickel(II) hydroxide and carbonates. The conductance of each solution was measured and a potassium chloride solution of identical conductance and solvent composition was prepared as a reference. All the solutions exhibited a relaxation which was characterized by a single relaxation step.

The relaxation time is measured as shown in Figure 5. The quantities A and B are proportional to the equilibrium concentrations in the cell at two different sets of conditions. The difference between A and B is equal to  $2\Delta C$ . Adding  $2\Delta C/C$  to B results in C, where the term  $2\Delta C/C$  corresponds to the

FIGURE 5

MEASUREMENT OF THE RELAXATION TIME  
FROM THE OSCILLOGRAM PATTERN



concentration difference which is reduced to  $1/e$  of the original deviation,  $2\Delta C$ . The relaxation time,  $T_{1/e}$ , can then be measured directly from the oscillogram.

Typical examples of the chemical relaxation process of nickel(II) malonate are shown in Figures 6-13. The rise time for the pressure-jump instrument was determined to be  $36 \pm 4$  microseconds; therefore, no correction was made in the measured relaxation time for the rise time of the instrument.

## 6. Determination of Stability Constants

### a. Malonic acid

An adaption of the spectrophotometric method used by Jones and Stock (29) was used to determine the primary and secondary thermodynamic dissociation constants of malonic acid in the various water-dioxane solvent systems. Conductimetric and electrometric methods have been the main methods used to determine the dissociation constants of various compounds in mixed aqueous solvent systems (23,30,31). Even though these two methods give better accuracy than the spectrophotometric method, the difficulties involved in overcoming the uncertainties introduced by the existence of liquid-junction potentials and of the standardization of the pH scale causes the spectrophotometric method to be easier to use. In the present study the difficulties mentioned above have been overcome by using the spectrophotometric method. The

## FIGURE 6

EXPERIMENTAL RELAXATION CURVE  
OF NICKEL(II) MALONATE

Temperature = 15°C

Nickel(II) Malonate =  $8.0 \times 10^{-3} \text{ M}$ Solvent Composition = 100% H<sub>2</sub>O

Relaxation Time = 4.24 msec

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## FIGURE 7

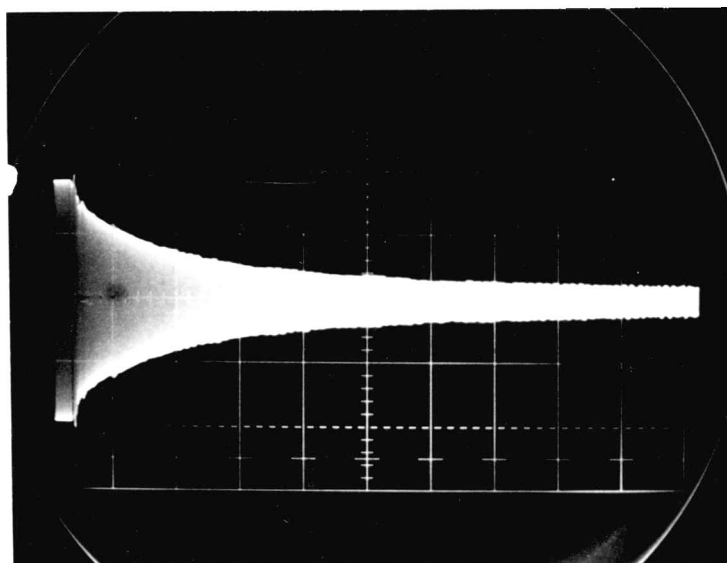
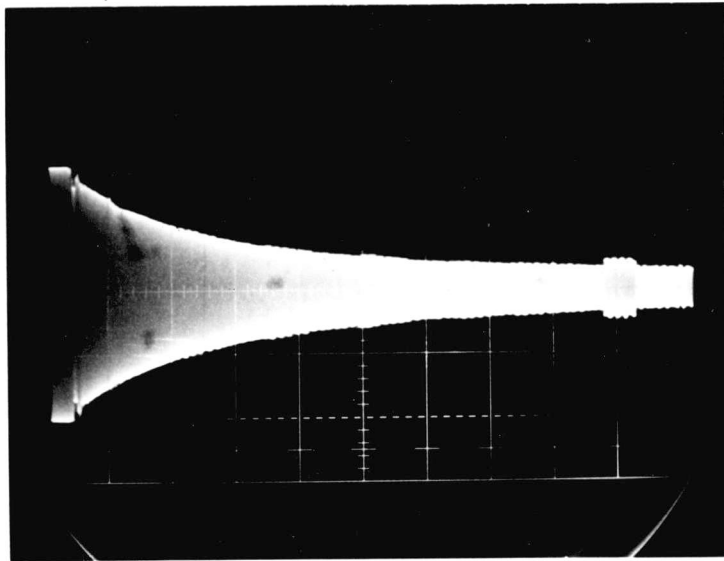
EXPERIMENTAL RELAXATION CURVE  
OF NICKEL(II) MALONATE

Temperature = 15°C

Nickel(II) Malonate =  $8.0 \times 10^{-3} \text{ M}$ 

Solvent Composition = 0.02 Mole Fraction Dioxane

Relaxation Time = 2.97 msec



## FIGURE 8

EXPERIMENTAL RELAXATION CURVE  
OF NICKEL(II) MALONATE

Temperature = 15°C

Nickel(II) Malonate =  $8.0 \times 10^{-3} \text{M}$ 

Solvent Composition = 0.042 Mole Fraction Dioxane

Relaxation Time = 1.94 msec

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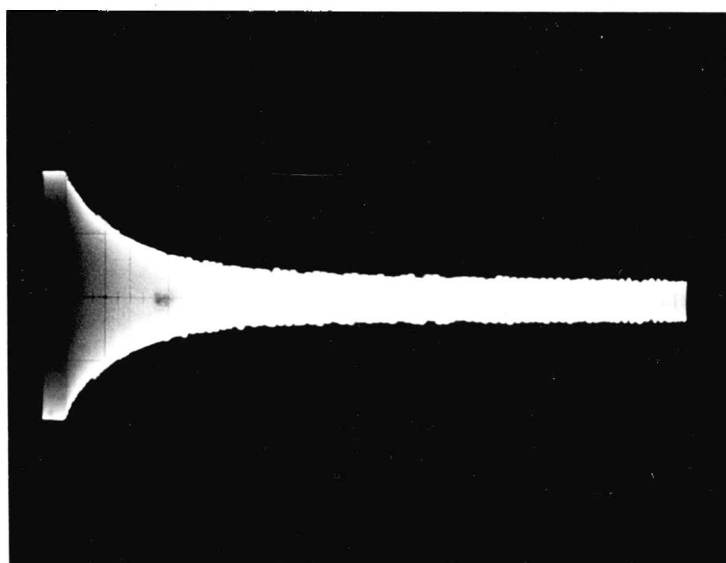
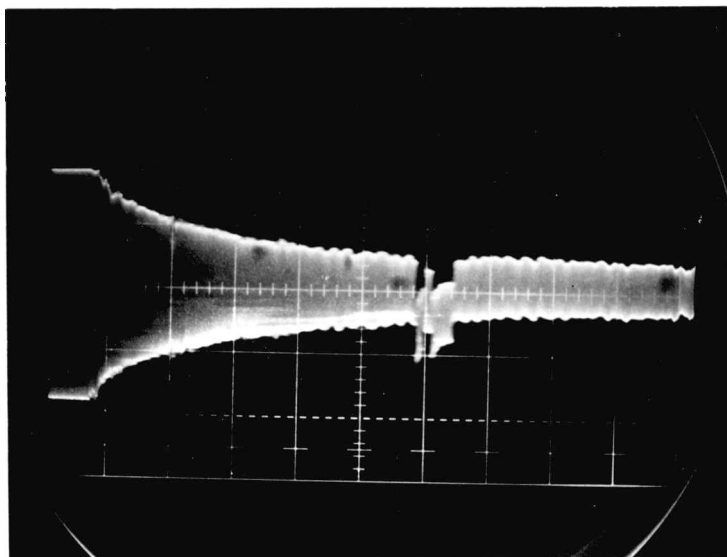
## FIGURE 9

EXPERIMENTAL RELAXATION CURVE  
OF NICKEL(II) MALONATE

Temperature = 25°C

Nickel(II) Malonate =  $8.0 \times 10^{-3} \text{M}$ Solvent Composition = 100% H<sub>2</sub>O

Relaxation Time = 2.00 msec



## FIGURE 10

EXPERIMENTAL RELAXATION CURVE  
OF NICKEL(II) MALONATE

Temperature = 25°C

Nickel(II) Malonate =  $4.0 \times 10^{-4} \text{M}$ Solvent Composition = 100% H<sub>2</sub>O

Relaxation Time = 2.42 msec

-----

## FIGURE 11

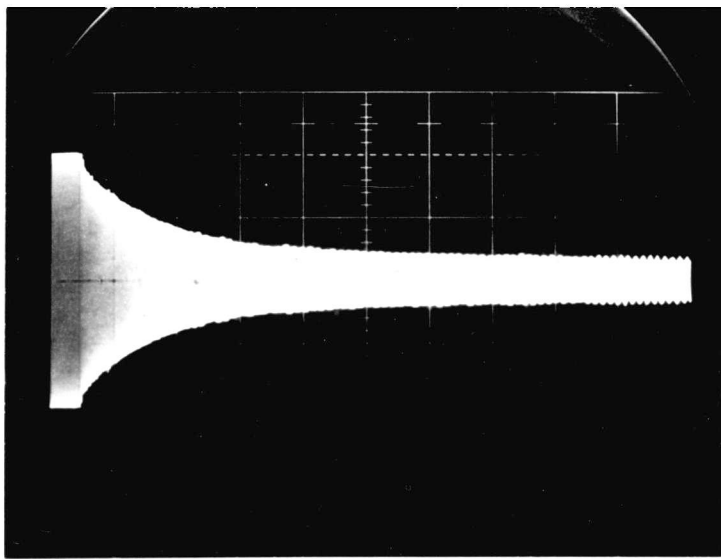
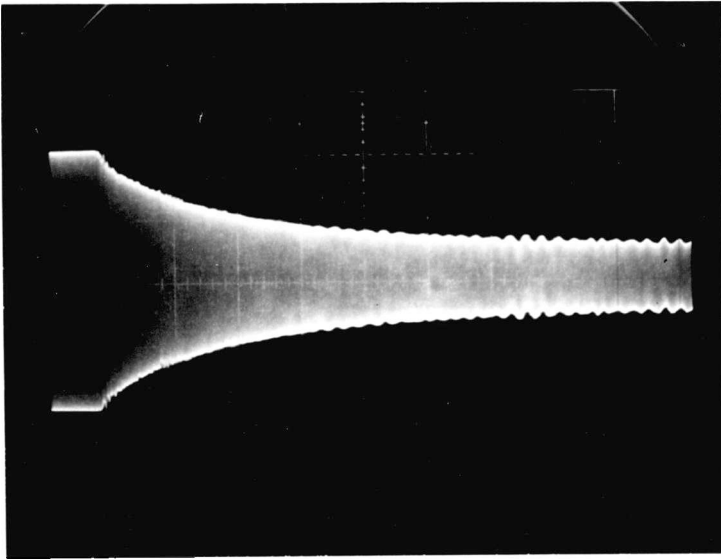
EXPERIMENTAL RELAXATION CURVE  
OF NICKEL(II) MALONATE

Temperature = 25°C

Nickel(II) Malonate =  $4.0 \times 10^{-3} \text{M}$ 

Solvent Composition = 0.02 Mole Fraction Dioxane

Relaxation Time = 1.94 msec



## FIGURE 12

## EXPERIMENTAL RELAXATION CURVE

## OF NICKEL(II) MALONATE

Temperature = 25°C

Nickel(II) Malonate =  $4.0 \times 10^{-3} \text{M}$

Solvent Composition = 0.042 Mole Fraction Dioxane

Relaxation Time = 1.57 msec

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## FIGURE 13

## EXPERIMENTAL RELAXATION CURVE

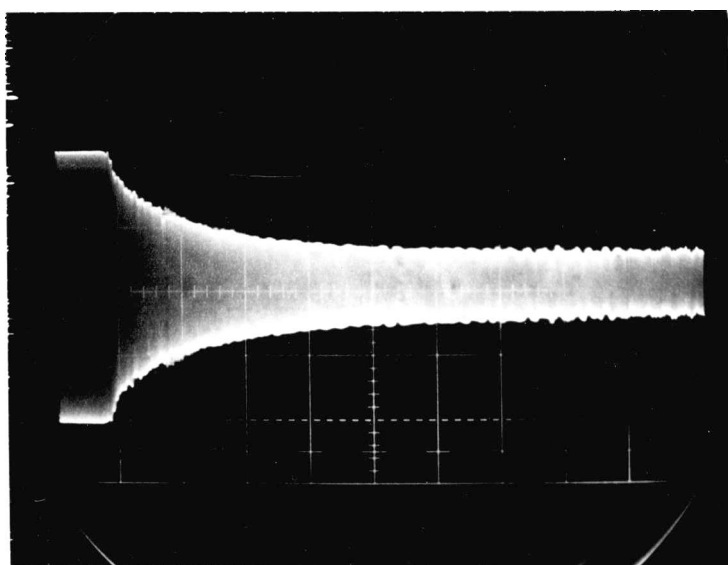
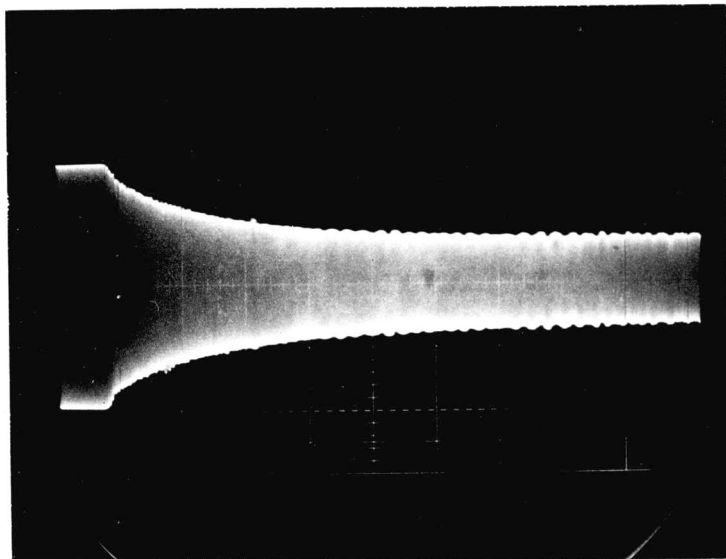
## OF NICKEL(II) MALONATE

Temperature = 25°C

Nickel(II) Malonate =  $4.0 \times 10^{-3} \text{M}$

Solvent Composition = 0.064 Mole Fraction Dioxane

Relaxation Time = 0.940 msec



method involves the use of a buffer solution made up of partially neutralized solutions of a monobasic weak acid. The hydrogen ion concentrations were calculated very accurately from known dissociation constants of the monobasic acid in the water-dioxane solutions used.

Since spectrophotometric and electrometric methods measure different functions of the hydrogen ion concentration, minor modifications were made in the method of computing the thermodynamic dissociation constants of a dibasic acid,  $H_2A$ , as described by Speakman (32).

If pH is defined in terms of hydrogen ion activity as follows:

$$pH = -\log a_{H^+} \quad (III-15)$$

the pH measured by electrometric methods is a direct measure of  $f(H^+)$  where  $f$  is the activity coefficient of a univalent ion and  $(H^+)$  is the molar concentration of hydrogen ions. In the case of spectrophotometric determination of pH, two solutions in which the color and concentration of an indicator are the same do not have the same pH value unless they have the same ionic strength (32). For the sulphonaphthalein indicator used, bromophenol blue,:

$$K = \frac{f_H + f_B = (H^+)(B^-)}{f_{HB} - (HB^-)} \quad (III-16)$$

For a sulphonephthalein indicator in a buffered solution, the color of the buffered solution is governed by  $(B^-)/(HB^-)$  since the main color change of a sulphonephthalein indicator is known to be associated with the ionization of a phenolic hydrogen atom in the singly charged carboxylate ion (33,34). From the above it can be seen that if two solutions containing the same concentration of indicator have the same color then the following is the same in each solution:

$$\frac{f_H + f_{B^-}(H^+)}{f_{HB^-}}$$

If the activity coefficients of the two univalent ions are taken to be equal, and that of the bivalent ion to be  $f_2$ , equality of color of two solutions with identical concentrations of indicator identity the quantity:

$$pf_2(H^+) = -\log f_2(H^+) \quad (III-17)$$

The thermodynamic dissociation constants of a dibasic acid,  $H_2A$ , may be described by the following equations:

$$K_1 = \frac{(H^+)(HA^-)f_1^2}{(H_2A)f_0} \quad (III-18)$$

$$K_2 = \frac{(H^+)(A^{2-})f_2}{(HA^-)} \quad (III-19)$$

where  $f_0$  is the activity coefficient of the non-charged particle and  $f_1$  is the activity coefficient of the univalent ion. In a solution of a weak dibasic acid the total acid molar concentration (a) is as follows:

$$a = (H_2A) + (HA^-) + (A^{=}) \quad (III-20)$$

When a strong monoacidic base such as sodium hydroxide is added to give a final molar concentration of base (b), the following equation is true:

$$b = (HA^-) + 2(A^{=}) + (H^+) + (OH^-) \quad (III-21)$$

Defining the following as:

$$L = b + (H^+) - (OH^-) = (HA^-) + 2(A^{=}) \quad (III-22)$$

$$M = a - b - (H^+) + (OH^-) = (H_2A) - (A^{=}) \quad (III-23)$$

$$N = 2a - b - (H^+) + (OH^-) = 2(H_2A) + (HA^-) \quad (III-24)$$

it can be shown that:

$$\frac{(H^+)^2 f_1^2 f_2 L}{N f_0} = K_1 \frac{(H^+) f_2 M}{N f_1} + K_1 K_2 \quad (III-25)$$

If we let

$$Y = \frac{(H^+)^2 f_1^2 f_2 L}{N f_0} \quad (III-26)$$

$$X = \frac{(H^+)f_2M}{Nf_1} \quad (III-27)$$

equation (III-25) may be rewritten as:

$$Y = K_1X + K_1K_2 \quad (III-28)$$

In determining X and Y, certain approximations must be made; however, these can be shown to have no serious affect on the accuracy of conclusions drawn from the above equations. First, at the pH's below 7 the hydroxyl ion concentration can be neglected. Second, at ionic strengths less than 0.035 the activity coefficient of the uncharged particles are approximately equal to unity.

In the present study the ionic strength of the buffer solutions were kept at 0.035 and the ionic strength of the test solutions were kept at 0.01 or greater with potassium chloride. Davies' activity equation (28) was used to evaluate the activity coefficient of the various solutions. By assigning an approximate value of ionic strength for the test solution the value of  $f_1$  and  $f_2$  were calculated then values of  $(H^+)$ , X and Y. From the resulting plots, the values of  $K_1$  and  $K_2$  were obtained and hence  $(H_2A)$ ,  $(HA^-)$  and  $(A^{=})$ . From these values a new value of the ionic strength was calculated. After successive approximations, constant values of  $K_1$  and  $K_2$  for malonic acid were obtained for the various water-dioxane solvent systems.

The procedure described above was used to determine the primary and secondary dissociation constants of malonic acid in the various solvent systems at  $15^{\circ}$ ,  $25^{\circ}$  and  $35^{\circ}\text{C} \pm 0.05^{\circ}\text{C}$ . The reagents used were reagent grade and were used without further purification. The indicator used was bromophenol blue and was made up to a final concentration of 0.04% according to the method described by Clark and Lubs (35). Bromophenol blue was determined to have a wavelength of maximum absorbance of 594 nm in all of the systems in which it was used.

The color standards used to prepare the calibration curves were prepared from partially neutralized benzoic acid-sodium benzoate buffer solutions. The dissociation constants of benzoic acid in the various solvent systems are known very accurately from conductivity investigations (36) and this allowed the accurate determination of ionic strength and hydrogen ion concentration of each system. The test solutions and the comparison standards contained the same amount of indicator.

The color comparisons were made on a Cary Model-14 spectrophotometer using 1 cm quartz cells at  $15^{\circ}$ ,  $25^{\circ}$  and  $35^{\circ}\text{C}$ . The absorption curves measured were accurate to within  $\pm 2\%$ . The percentage transmission of each solution was measured at the wavelength of maximum absorbance and a graph was constructed of the percentage transmission against  $\text{pf}_2(\text{H}^+)$  for each solvent system. From these graphs, the range of absorbance

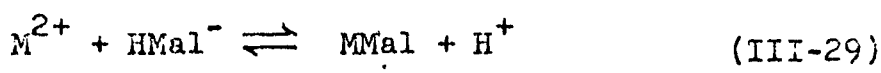
which was linear with respect to  $\text{pf}_2(\text{H}^+)$  was determined.

The malonic acid solutions used to determine the dissociation constants were prepared by adding fixed amounts of indicator solution and neutralizing the acid solutions to various stages of neutralization ranging from 20% to 80% using standard sodium hydroxide solution. Each solution was made up to a final total acid concentration which was maintained constant at 0.005 M. The  $\text{pf}_2(\text{H}^+)$  values were then determined as described above, by comparison with the standard buffer solution of the proper solvent composition in which the  $\text{pf}_2(\text{H}^+)$  values were accurately known.

b. Nickel(II) malonate

The stability constants of nickel(II) malonate in various water-dioxane solvent systems were determined by the method described in the determination of the stability constants of malonic acid. Malonic acid, sodium hydroxide, nickel(II) chloride, and standard amounts of indicator were used to prepare the solutions. The color of each nickel(II) malonate solution at each solvent composition was matched to a color of the standard benzoic acid-sodium benzoate buffer of the same solvent composition, thus determining the value of  $\text{pf}_2(\text{H}^+)$  for the solution and an approximate value of the ionic strength. The effect of adding the bivalent metal chloride to the half neutralized malonic acid solutions is to increase the hydrogen ion concentration of the malonate buffer solution by 20-fold

in some cases, such as copper (34). The increase of the hydrogen ion concentration is due to the following reaction:



The amount of complexed metal malonate and thus the stability constant of the metal malonate is calculated from the knowledge of the concentrations of  $Na^{+}$ ,  $Cl^{-}$ ,  $M^{2+}$ ,  $MMal$ ,  $Mal^{-}$ ,  $HMal^{-}$ ,  $H_2Mal$ ,  $H^{+}$ ,  $OH^{-}$  and possibly  $MHMal^{+}$ . The species,  $Na_2Mal$  and  $KCl_2$ , are known to be highly dissociated. Of the species listed above, the concentrations of  $Na^{+}$  and  $Cl^{-}$  are known,  $OH^{-}$  is negligible in acidic solutions, and the concentration of  $MHMal^{+}$  is unlikely to be large enough to be considered. With knowledge of the above concentrations, the other six unknowns may be calculated by successive approximations from (a) the  $pf_2(H^{+})$ ; (b) the equation of electroneutrality; (c) the known total concentration of malonate radical; (d) the known total concentration of bivalent metal; and (e) and (f)  $K_1$  and  $K_2$  of malonic acid in the various solvent systems. The association constants of the nickel(II) malonate were calculated from the following equation:

$$K_{eq} = \frac{f_2^2(M^{2+})(Mal^{-})}{(MMal)} \tag{III-30}$$

The value obtained in this experiment for 100% water at 25°C was within experimental error of those obtained from conductivity experiments (34,37,38).

#### IV

#### RESULTS AND DISCUSSION

## RESULTS AND DISCUSSION

### 1. Thermodynamic Section

The stability constants for complex formation must be known in order to study a reaction by fast reaction techniques. It is known that the stability constant of a complex will change with solvent composition (39). The stability constants for nickel(II) malonate have been measured in 100% water at various temperatures, but the stability constants have not been determined in water-dioxane solvent systems.

To determine the stability constants for nickel(II) malonate in the various water-dioxane solvent systems considered in this study, it was necessary to know the primary ( $K_1$ ) and secondary ( $K_2$ ) stability constants for malonic acid in the various solvent systems. The previously described spectrophotometric technique was used to determine  $K_1$  and  $K_2$  for malonic acid in 100% water, 0.02, 0.042, and 0.064 mole percent dioxane at three different temperatures. The parameters used to determine the standards of absorption for the sulphonephthalein indicator, bromophenol blue, used in the determination of the stability constants of malonic acid and nickel(II) malonate are given in Tables II - V. The change in the absorption of each standard line was checked as a function of temperature and found to vary less than 2% over the temperature range of 15° to 35°C; therefore, the values of

TABLE II

PARAMETERS FOR BENZOIC ACID-SODIUM BENZOATE BUFFER CALIBRATION CURVE IN 100% WATER

pKa BENZOIC ACID = 4.20, IONIC STRENGTH = 0.035, TEMPERATURE = 25°C, BPB =

BROMOPHENOL BLUE

| HA(M)<br>X 10 <sup>2</sup> | NaA(M)<br>X 10 <sup>3</sup> | KCl(M)<br>X 10 <sup>3</sup> | ml BPB<br>0.04% | Volume<br>(ml ) | pH   | pf <sub>2</sub> (H <sup>+</sup> ) | Absorbance<br>±2% |
|----------------------------|-----------------------------|-----------------------------|-----------------|-----------------|------|-----------------------------------|-------------------|
| 1.48                       | 25.9                        | 9.10                        | 1.0             | 50.0            | 3.30 | 3.60                              | 0.20              |
| 1.48                       | 8.25                        | 26.6                        | 1.0             | 50.0            | 3.44 | 3.74                              | 0.26              |
| 1.48                       | 2.59                        | 3.24                        | 1.0             | 50.0            | 3.91 | 4.21                              | 0.46              |
| 1.48                       | 1.44                        | 3.35                        | 1.0             | 50.0            | 4.42 | 4.72                              | 0.67              |

TABLE III

PARAMETERS FOR BENZOIC ACID-SODIUM BENZOATE BUFFER CALIBRATION CURVE IN 0.02 MOLE FRACTION DIOXANE,  $pK_a$  BENZOIC ACID = 4.45, IONIC STRENGTH = 0.035, TEMPERATURE = 25°C, BPB = BROMOPHENOL BLUE

| HA(M)<br>$\times 10^2$ | NaA(M)<br>$\times 10^3$ | KCl(M)<br>$\times 10^3$ | ml. BPB<br>0.04% | Volume<br>(ml ) | Dioxane<br>(ml ) | pH   | $pf_2(H^+)$ | Transmittance<br>Percent<br>$\pm 2\%$ | Absorbance<br>$\pm 2\%$ |
|------------------------|-------------------------|-------------------------|------------------|-----------------|------------------|------|-------------|---------------------------------------|-------------------------|
| 1.95                   | 1.23                    | 3.38                    | 1.5              | 38.8            | 3.40             | 3.25 | 3.55        | -----                                 | -----                   |
| 1.64                   | 1.83                    | 3.30                    | 1.5              | 38.8            | 3.40             | 3.50 | 3.80        | 44                                    | 0.35                    |
| 1.62                   | 5.14                    | 3.00                    | 1.5              | 38.8            | 3.40             | 4.00 | 4.30        | 23                                    | 0.64                    |
| 1.30                   | 8.20                    | 2.68                    | 1.5              | 38.8            | 3.40             | 4.25 | 4.55        | 12                                    | 0.92                    |
| 0.97                   | 30.8                    | 0.42                    | 1.5              | 38.8            | 3.40             | 4.50 | 4.80        | 3                                     | 1.47                    |

TABLE IV

PARAMETERS FOR BENZOIC ACID-SODIUM BENZOATE BUFFER CALIBRATION CURVE IN 0.042 MOLE FRACTION DIOXANE,  $pK_a$  BENZOIC ACID = 4.76, IONIC STRENGTH = 0.035, TEMPERATURE = 25°C, BPB = BROMOPHENOL BLUE

| HA(M)<br>$\times 10^2$ | NaA(M)<br>$\times 10^3$ | KCl(M)<br>$\times 10^3$ | ml. BPB<br>0.04% | Volume<br>(ml ) | Dioxane<br>(ml ) | pH   | $pf_2(H^+)$ | Absorbance<br>$\pm 2\%$ |
|------------------------|-------------------------|-------------------------|------------------|-----------------|------------------|------|-------------|-------------------------|
| 1.82                   | 1.00                    | 3.39                    | 1.5              | 41.54           | 7.16             | 3.50 | 3.80        | 0.24                    |
| 1.52                   | 2.65                    | 3.23                    | 1.5              | 41.54           | 7.16             | 4.00 | 4.30        | 0.50                    |
| 1.21                   | 3.76                    | 3.13                    | 1.5              | 41.54           | 7.16             | 4.25 | 4.55        | 0.71                    |
| 1.21                   | 6.66                    | 2.83                    | 1.5              | 41.54           | 7.16             | 4.50 | 4.80        | 0.93                    |
| 1.21                   | 21.1                    | 1.39                    | 1.5              | 41.54           | 7.16             | 5.00 | 5.30        | 1.30                    |

TABLE V

PARAMETERS FOR BENZOIC ACID-SODIUM BENZOATE BUFFER CALIBRATION CURVE IN 0.064 MOLE  
 FRACTION DIOXANE,  $pK_a$  BENZOIC ACID = 5.09, IONIC STRENGTH = 0.035, TEMPERATURE =  
 25°C, BPB = BROMOPHENOL BLUE

| HA(M)<br>$\times 10^2$ | NaA(M)<br>$\times 10^3$ | KCl(M)<br>$\times 10^3$ | ml. BPB<br>0.04% | Volume<br>(ml ) | Dioxane<br>(ml ) | pH   | $pf_2(H^+)$ | Transmittance<br>Percent<br>$\pm 2\%$ | Absorbance<br>$\pm 2\%$ |
|------------------------|-------------------------|-------------------------|------------------|-----------------|------------------|------|-------------|---------------------------------------|-------------------------|
| 1.41                   | 0.36                    | 3.46                    | 1.5              | 44.54           | 10.9             | 3.50 | 3.80        | 63                                    | 0.19                    |
| 1.41                   | 0.51                    | 3.46                    | 1.5              | 44.54           | 10.9             | 3.75 | 4.05        | 60                                    | 0.23                    |
| 1.70                   | 1.40                    | 3.37                    | 1.5              | 44.54           | 10.9             | 4.00 | 4.30        | 45                                    | 0.34                    |
| 1.41                   | 2.10                    | 3.30                    | 1.5              | 44.54           | 10.9             | 4.25 | 4.55        | 32                                    | 0.50                    |
| 1.41                   | 3.65                    | 3.14                    | 1.5              | 44.54           | 10.9             | 4.50 | 4.80        | 20                                    | 0.69                    |
| 1.13                   | 9.21                    | 2.58                    | 1.5              | 44.54           | 10.9             | 5.00 | 5.30        | 7.9                                   | 1.1                     |

the absorptions measured at 25°C were used to determine the stability constants at 15°, 25°, and 35°C. A typical set of pH and  $\text{pf}_2(\text{H}^+)$  values as a function of absorption of the standard indicator is shown in Figure 14. An example of a plot from which  $K_1$  and  $K_2$  for malonic acid were determined is shown in Figure 15. The parameters used in the determination of  $K_1$  and  $K_2$  of malonic acid in the various binary solvent systems are shown in Tables VI-IX. The values of  $K_1$  and  $K_2$  for malonic acid in the various solvent compositions and temperatures are given in Table X.

The stability constants for nickel(II) malonate were determined in 100% water, 0.02, 0.042, and 0.064 mole per cent dioxane at three different temperatures as previously described. The parameters for the determination of the stability constants determined are given in Table XI. The stability constants for nickel(II) malonate as a function of solvent composition are shown in Figure 16.

The free energies for complex formation were calculated using the following equation:

$$\Delta G^\circ = -RT \ln K_{\text{eq}} \quad (\text{IV-1})$$

The enthalpies for complex formation were determined using the following equation:

$$\log K_{\text{eq}} = - \frac{\Delta H^\circ}{2.303R} \frac{1}{T} + \text{constant} \quad (\text{IV-2})$$

FIGURE 14

CALIBRATION CURVE OF BENZOIC ACID-SODIUM  
BENZOATE BUFFER IN 0.042 MOLE FRACTION  
DIOXANE, IONIC STRENGTH = 0.035  
INDICATOR = 0.04% BROMOPHENOL BLUE  
TEMPERATURE = 25°C

A = pH

B =  $\text{pf}_2(\text{H}^+)$

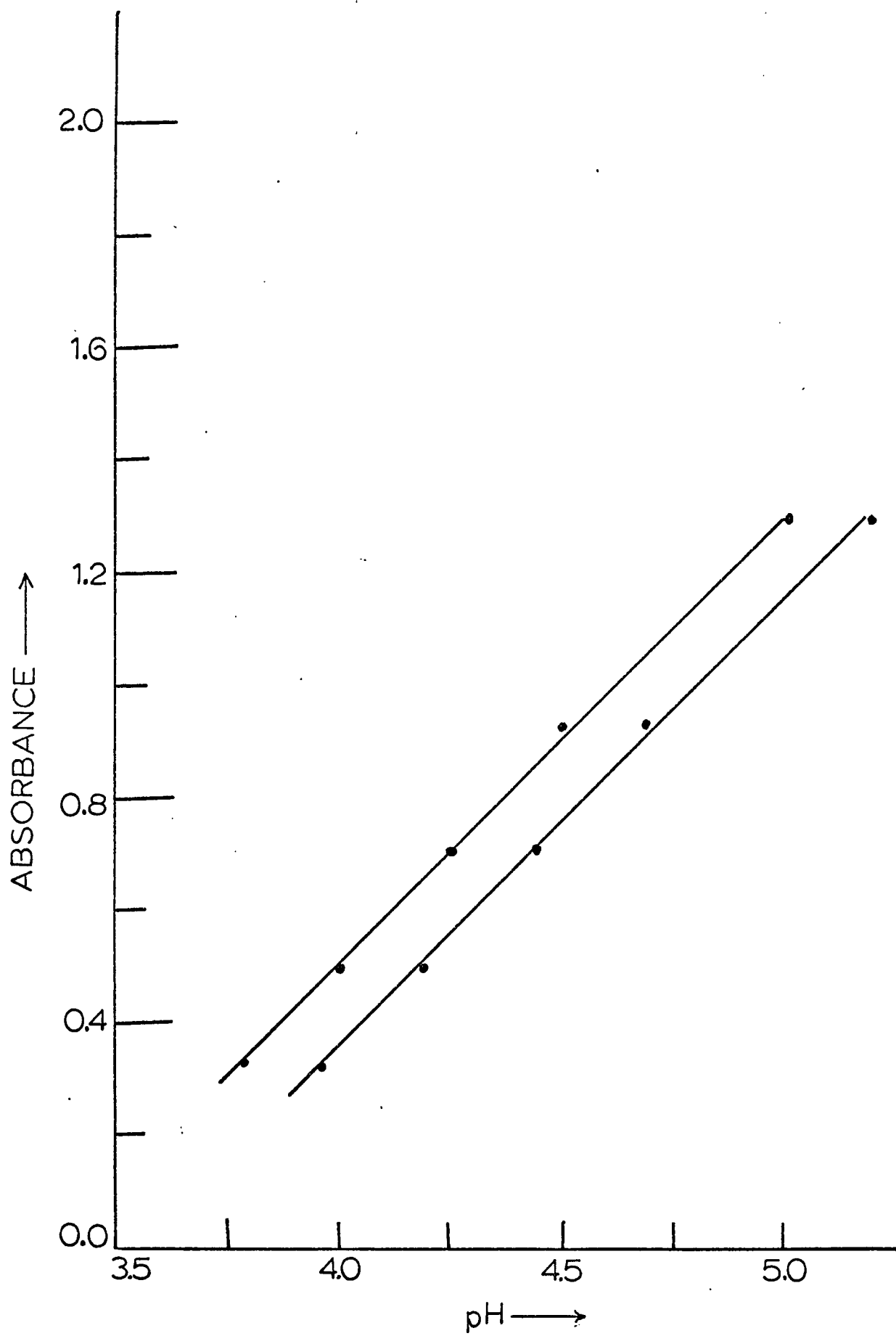


FIGURE 15

DETERMINATION OF  $K_1$  AND  $K_2$   
OF MALONIC ACID

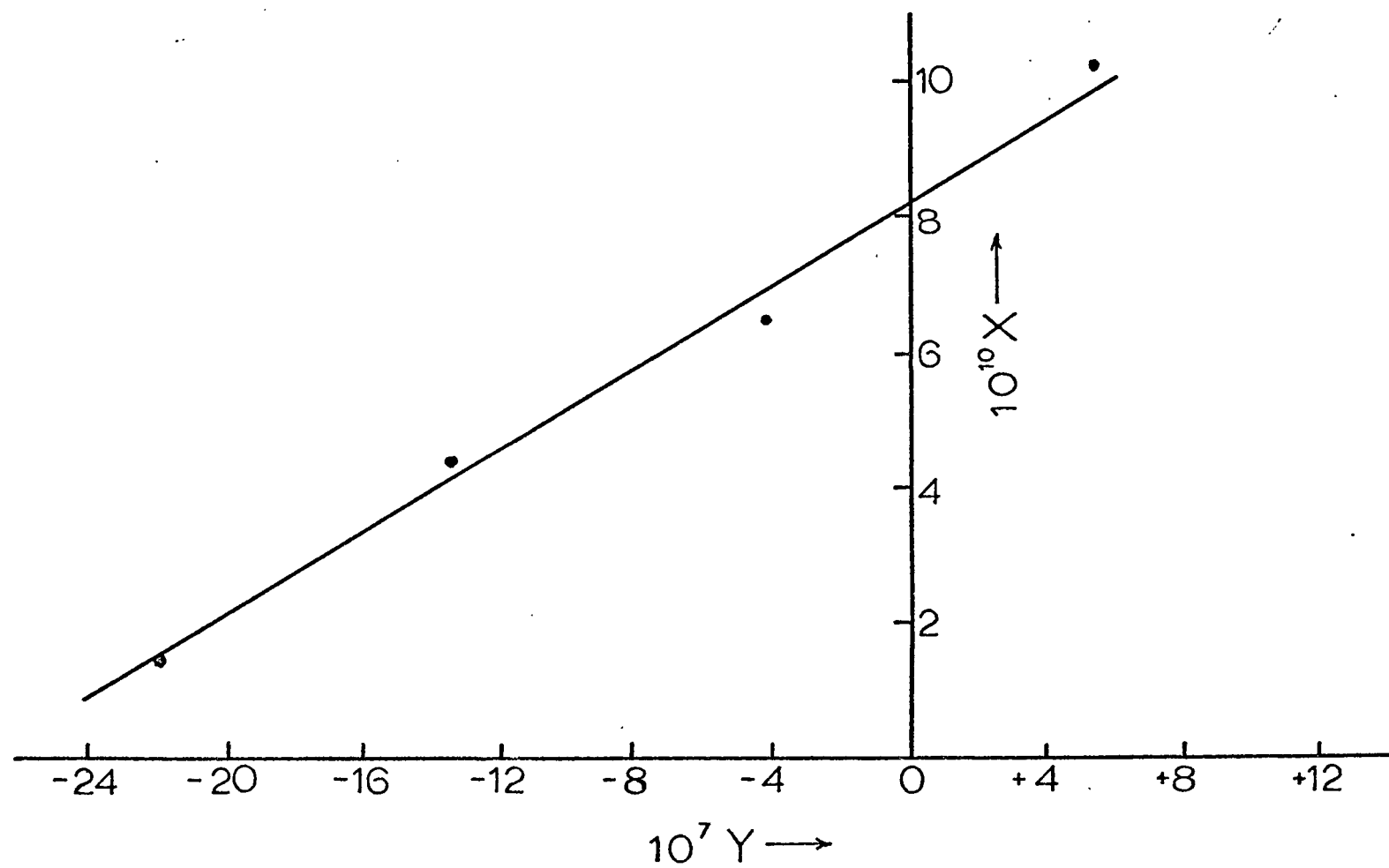


TABLE VI

PARAMETERS FOR THE DETERMINATION OF  $K_1$  AND  $K_2$   
OF MALONIC ACID IN 100% WATER  
TEMPERATURE = 25°C, BPB = BROMOPHENOL BLUE

| $H_2MaL(M)$<br>$\times 10^3$ | $NaOH(M)$<br>$\times 10^3$ | ml. BPB<br>0.04% | Volume<br>(ml ) | pH   | Absorbance<br>$\pm 2\%$ |
|------------------------------|----------------------------|------------------|-----------------|------|-------------------------|
| 5.0                          | 3.96                       | 1.0              | 50.0            | 3.52 | 0.21                    |
| 5.0                          | 4.48                       | 1.0              | 50.0            | 3.80 | 0.34                    |
| 5.0                          | 4.86                       | 1.0              | 50.0            | 4.15 | 0.54                    |
| 5.0                          | 5.13                       | 1.0              | 50.0            | 4.57 | 0.69                    |
| 5.0                          | 5.33                       | 1.0              | 50.0            | 4.85 | 0.82                    |

TABLE VII

PARAMETERS FOR THE DETERMINATION OF  $K_1$  AND  $K_2$  OF  
MALONIC ACID IN 0.02 MOLE FRACTION DIOXANE  
TEMPERATURE = 25° C, BPB = BROMOPHENOL BLUE

| $H_2MaL(M)$<br>$\times 10^3$ | $NaOH(M)$<br>$\times 10^3$ | ml BPB<br>0.04% | Dioxane<br>(ml ) | Volume<br>(ml ) | pH   | Absorbance<br>$\pm 2\%$ |
|------------------------------|----------------------------|-----------------|------------------|-----------------|------|-------------------------|
| 5.0                          | 4.15                       | 1.5             | 3.40             | 38.8            | 3.81 | 0.48                    |
| 5.0                          | 4.52                       | 1.5             | 3.40             | 38.8            | 4.18 | 0.74                    |
| 5.0                          | 4.78                       | 1.5             | 3.40             | 38.8            | 4.35 | 0.95                    |
| 5.0                          | 4.96                       | 1.5             | 3.40             | 38.8            | 4.45 | 1.17                    |

TABLE VIII

PARAMETERS FOR THE DETERMINATION OF  $K_1$  AND  $K_2$  OF  
MALONIC ACID IN 0.042 MOLE FRACTION DIOXANE  
TEMPERATURE = 25°C, BPB = BROMOPHENOL BLUE

| $H_2MaL(M)$<br>$\times 10^3$ | $NaOH(M)$<br>$\times 10^3$ | ml. BPB<br>0.04% | Dioxane<br>(ml ) | Volume<br>(ml ) | pH   | Absorbance<br>$\pm 2\%$ |
|------------------------------|----------------------------|------------------|------------------|-----------------|------|-------------------------|
| 5.0                          | 3.86                       | 1.5              | 7.16             | 41.54           | 3.85 | 0.33                    |
| 5.0                          | 4.64                       | 1.5              | 7.16             | 41.54           | 4.37 | 0.76                    |
| 5.0                          | 4.90                       | 1.5              | 7.16             | 41.54           | 4.70 | 1.02                    |
| 5.0                          | 4.98                       | 1.5              | 7.16             | 41.54           | 4.78 | 1.32                    |

TABLE IX

PARAMETERS FOR THE DETERMINATION OF  $K_1$  AND  $K_2$  OF  
 MALONIC ACID IN 0.064 MOLE FRACTION DIOXANE  
 TEMPERATURE = 25°C, BPB = BROMOPHENOL BLUE

| $H_2MaL(M)$<br>$\times 10^3$ | $NaOH(M)$<br>$\times 10^3$ | ml BPB<br>0.04% | Dioxane<br>(ml ) | Volume<br>(ml ) | pH   | Absorbance<br>$\pm 2\%$ |
|------------------------------|----------------------------|-----------------|------------------|-----------------|------|-------------------------|
| 5.0                          | 4.20                       | 1.5             | 10.9             | 44.54           | 4.14 | 0.38                    |
| 5.0                          | 4.44                       | 1.5             | 10.9             | 44.54           | 4.32 | 0.51                    |
| 5.0                          | 4.59                       | 1.5             | 10.9             | 44.54           | 4.48 | 0.64                    |
| 5.0                          | 4.77                       | 1.5             | 10.9             | 44.54           | 4.72 | 0.83                    |
| 5.0                          | 5.00                       | 1.5             | 10.9             | 44.54           | 4.98 | 1.04                    |

TABLE X

$K_1$  AND  $K_2$  OF MALONIC ACID AT VARIOUS MOLE  
FRACTIONS DIOXANE

TEMPERATURE = 25°C, IONIC STRENGTH = 0

| Mole Fraction<br>Dioxane | $K_1 \times 10^4$ | $K_2 \times 10^7$ |
|--------------------------|-------------------|-------------------|
| 0.000                    | 13.5              | 12.5              |
| 0.020                    | 7.48              | 2.82              |
| 0.042                    | 4.55              | 2.56              |
| 0.064                    | 3.45              | 2.40              |

$K_1 = \pm 2\%$

$K_2 = \pm 15\%$

TABLE XI

DETERMINATION OF STABILITY CONSTANTS OF NICKEL(II) MALONATE  
IN VARIOUS MOLE FRACTIONS DIOXANE

| Mole<br>Fraction<br>Dioxane | Temperature<br>(°C) | $\bar{C}_{H^+}$<br>$\times 10^4 M$ | $\bar{C}_{H_2Mal}$<br>$\times 10^4 M$ | $\bar{C}_{HMal^-}$<br>$\times 10^3 M$ | $\bar{C}_{Mal^-}$<br>$\times 10^5 M$ | $\bar{C}_{Ni^{+2}}$<br>$\times 10^3 M$ | $\bar{C}_{NiMal}$<br>$\times 10^4 M$ | $K_{eq} \times 10^4$<br>$\mu \rightarrow 0$ |
|-----------------------------|---------------------|------------------------------------|---------------------------------------|---------------------------------------|--------------------------------------|----------------------------------------|--------------------------------------|---------------------------------------------|
| 0.000                       | 15                  | 2.57                               | 7.98                                  | 4.18                                  | 2.04                                 | 8.76                                   | 5.25                                 | .926                                        |
| 0.000                       | 25                  | 2.75                               | 8.46                                  | 4.14                                  | 1.88                                 | 8.71                                   | 5.71                                 | 1.06                                        |
| 0.000                       | 35                  | 2.88                               | 8.79                                  | 4.10                                  | 1.78                                 | 8.68                                   | 6.03                                 | 1.15                                        |
| 0.020                       | 15                  | 1.38                               | 7.78                                  | 4.21                                  | 0.86                                 | 6.16                                   | 5.26                                 | 2.56                                        |
| 0.020                       | 25                  | 1.55                               | 8.56                                  | 4.14                                  | 0.75                                 | 6.09                                   | 6.04                                 | 3.21                                        |
| 0.020                       | 35                  | 1.73                               | 9.41                                  | 4.05                                  | 0.66                                 | 6.00                                   | 6.88                                 | 4.07                                        |
| 0.042                       | 15                  | 0.95                               | 8.66                                  | 4.12                                  | 1.11                                 | 4.17                                   | 6.27                                 | 2.80                                        |
| 0.042                       | 25                  | 1.05                               | 9.34                                  | 4.06                                  | 0.99                                 | 4.11                                   | 6.94                                 | 3.26                                        |
| 0.042                       | 35                  | 1.15                               | 10.1                                  | 3.99                                  | 0.89                                 | 4.04                                   | 7.65                                 | 4.05                                        |
| 0.064                       | 15                  | 0.63                               | 7.72                                  | 4.21                                  | 1.16                                 | 3.05                                   | 5.28                                 | 2.07                                        |
| 0.064                       | 25                  | 0.71                               | 8.50                                  | 4.14                                  | 1.41                                 | 2.98                                   | 6.04                                 | 2.62                                        |
| 0.064                       | 35                  | 0.77                               | 9.17                                  | 4.07                                  | 1.26                                 | 2.91                                   | 6.69                                 | 2.80                                        |

$\bar{C}$  = equilibrium concentration       $K_{eq} = \pm 7\%$

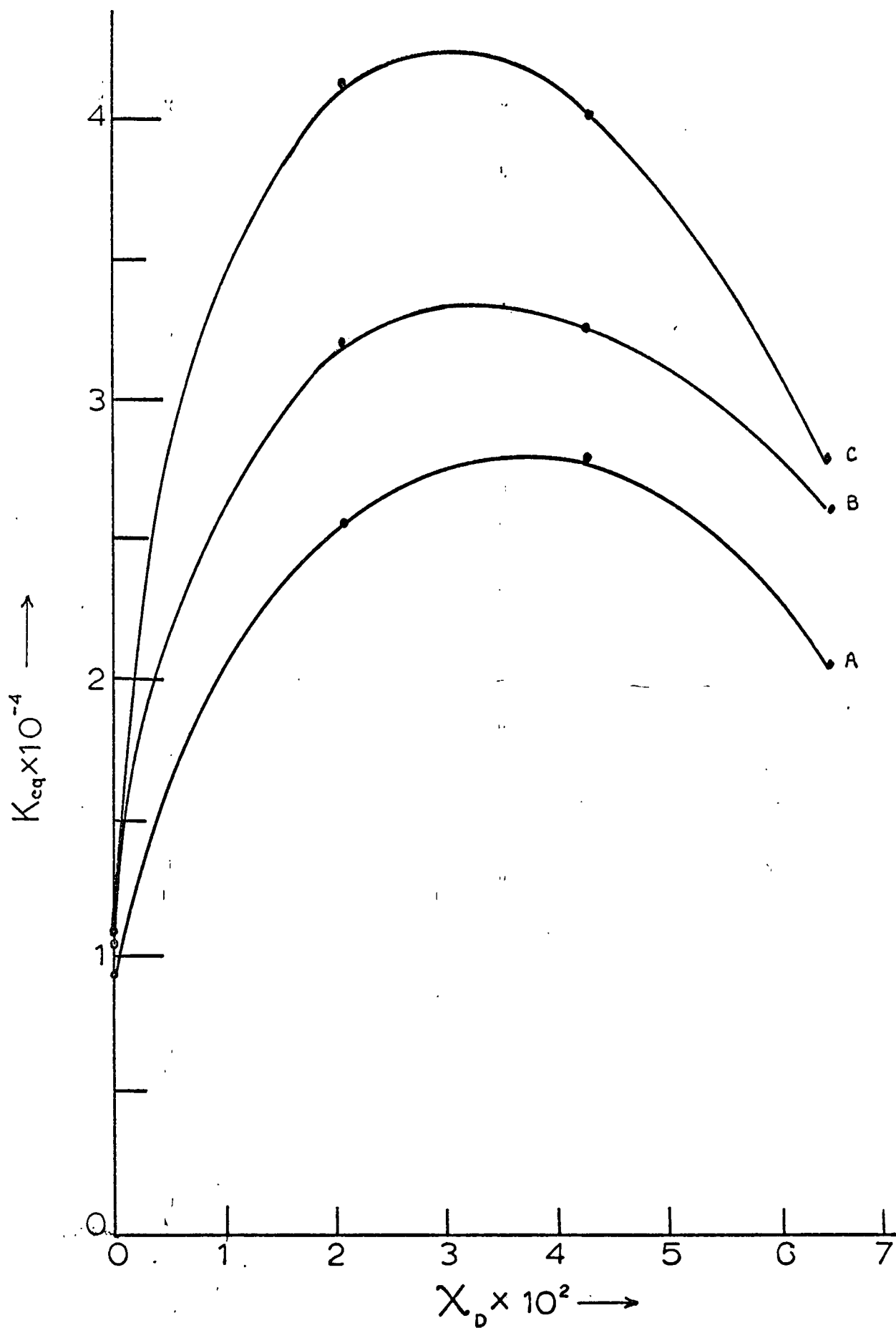
FIGURE 16

STABILITY CONSTANTS OF NICKEL(II) MALONATE  
(  $K_{eq}$ ,  $\text{MOLE}^{-1}$  ) AS A FUNCTION OF  
MOLE FRACTION DIOXANE AND TEMPERATURE,  $\mu \rightarrow 0$

$$A = 15^{\circ}\text{C}$$

$$B = 25^{\circ}\text{C}$$

$$C = 35^{\circ}\text{C}$$



A plot of  $\log K_{eq}$  vs.  $1/T$  gives a straight line with a slope equal to  $-\Delta H^\circ/2.303R$ . The entropies for complex formation were calculated using the following equation :

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \quad (IV-3)$$

The experimentally determined values of  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $T\Delta S^\circ$  are given in Tables XII-XIV respectively. The experimentally determined values of  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $T\Delta S^\circ$  are shown as a function of solvent composition in Figures 17-19.

The trends observed for  $\Delta H^\circ$ ,  $T\Delta S^\circ$ , and  $\Delta G^\circ$  as a function of solvent composition seem to fit the trend set by the solvation of the species involved in the reaction. The enthalpies of transfer ( $\delta\Delta H_g$ ) for the  $Ni^{2+}$  ion and the  $Mal^-$  ion have been determined in the water-rich region of the water-dioxane solvent system (40). The enthalpies of transfer which have been determined for the  $Ni^{2+}$  ion and the  $Mal^-$  ion are given in Tables XV.

Relative to water being zero, Figure 20 shows  $\Sigma\delta\Delta H_g$  and  $\delta\Delta H^\circ$  plotted as a function of solvent composition. As can be seen, it is apparent that the trend of  $\delta\Delta H^\circ$  for nickel(II) malonate follows closely the trend set by  $\Sigma\delta\Delta H_g$ . This implies that the values obtained for  $\Delta H^\circ$ ,  $T\Delta S^\circ$ , and  $\Delta G^\circ$  are very dependent upon the solvation of the reacting species present in the system. This could account for the

TABLE XII

FREE ENERGY OF REACTION ( $\Delta G^\circ$ , KCAL MOLE<sup>-1</sup> )  
FOR THE NICKEL(II) MALONATE SYSTEM AS A FUNCTION  
OF MOLE FRACTION DIOXANE AND TEMPERATURE, ( $\mu \rightarrow 0$  )

| Mole Fraction<br>Dioxane | 15°C  | 25°C  | 35°C  |
|--------------------------|-------|-------|-------|
| 0.000                    | -5.22 | -5.49 | -5.72 |
| 0.020                    | -5.81 | -6.14 | -6.50 |
| 0.042                    | -5.86 | -6.15 | -6.49 |
| 0.064                    | -5.68 | -6.02 | -6.27 |

$$\Delta G^\circ = \pm 6\%$$

FIGURE 17

FREE ENERGIES OF REACTION ( $\Delta G^\circ$ , KCAL MOLE<sup>-1</sup> )  
FOR THE NICKEL(II) MALONATE SYSTEM AS A FUNCTION  
OF MOLE FRACTION DIOXANE AND TEMPERATURE,  $\mu \rightarrow 0$

$$A = 15^\circ\text{C}$$

$$B = 25^\circ\text{C}$$

$$C = 35^\circ\text{C}$$

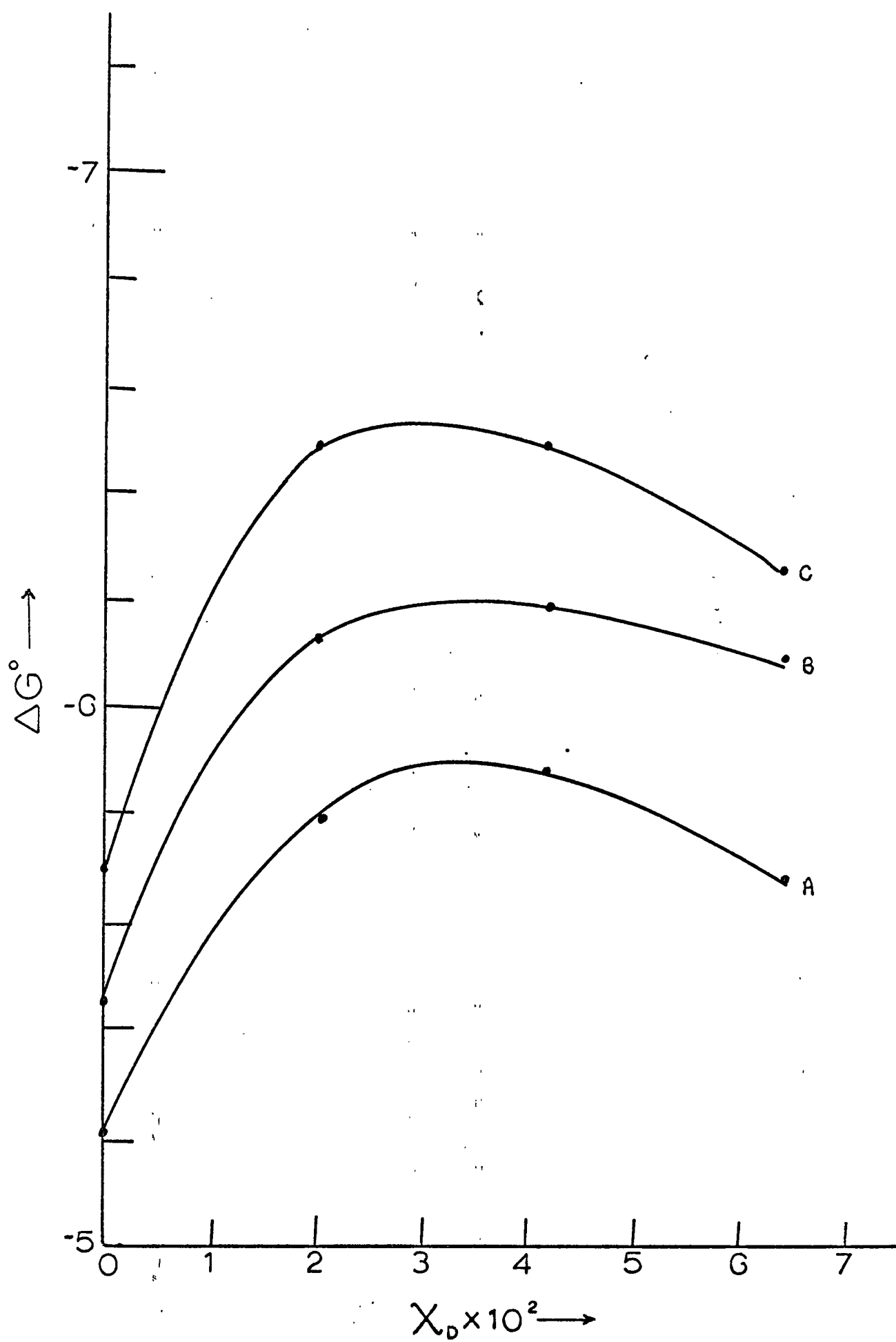


TABLE XIII

ENTHALPIES OF REACTION (  $\Delta H^\circ$ , KCAL. MOLE<sup>-1</sup> )  
FOR THE NICKEL(II) MALONATE SYSTEM  
AS A FUNCTION OF MOLE FRACTION DIOXANE,  $\mu \rightarrow 0$

| Mole Fraction<br>Dioxane | $\Delta H^\circ$ |
|--------------------------|------------------|
| 0.000                    | 2.09             |
| 0.020                    | 4.15             |
| 0.042                    | 3.48             |
| 0.064                    | 3.06             |

$$\Delta H^\circ = \pm 2.5\%$$

FIGURE 18

ENTHALPIES OF REACTION (  $\Delta H^\circ$ , KCAL MOLE<sup>-1</sup> )  
FOR THE NICKEL(II) MALONATE SYSTEM  
AS A FUNCTION OF MOLE FRACTION DIOXANE,  $\mu \rightarrow 0$

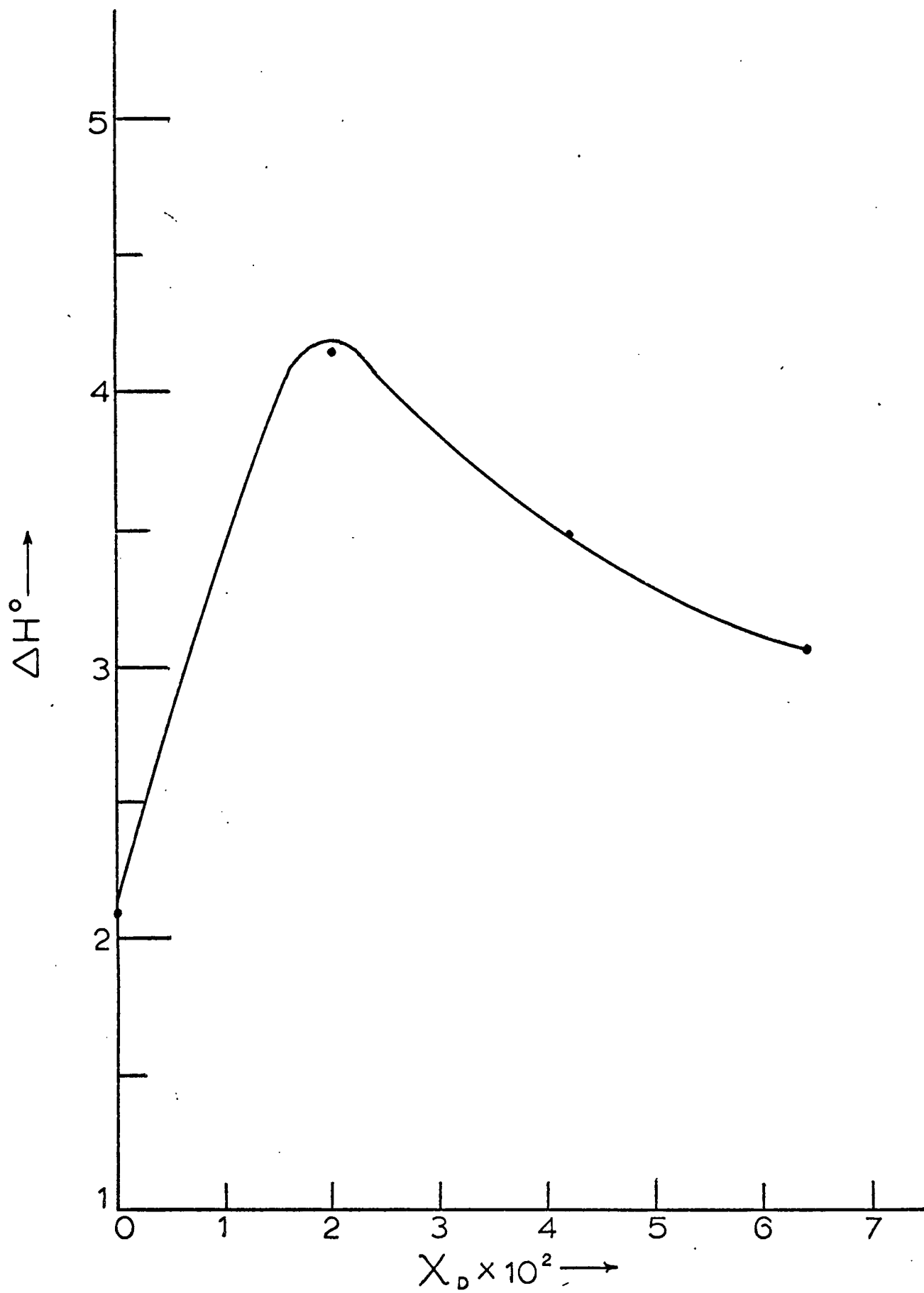


TABLE XIV

ENTROPIES OF REACTION (  $T\Delta S^\circ$ , KCAL. MOLE<sup>-1</sup> )

FOR THE NICKEL(II) MALONATE SYSTEM

AS A FUNCTION OF MOLE FRACTION DIOXANE AND TEMPERATURE,  $\mu \rightarrow 0$ 

| Mole Fraction<br>Dioxane | 15°C | 25°C | 35°C |
|--------------------------|------|------|------|
| 0.000                    | 7.31 | 7.58 | 7.81 |
| 0.020                    | 9.96 | 10.3 | 10.7 |
| 0.042                    | 9.34 | 9.63 | 9/97 |
| 0.064                    | 8.74 | 9.08 | 9.33 |

 $T\Delta S^\circ = \pm 5.3\%$

## FIGURE 19

ENTROPIES OF REACTION (  $T\Delta S^\circ$ , KCAL MOLE<sup>-1</sup> )

FOR THE NICKEL(II) MALONATE SYSTEM

AS A FUNCTION OF MOLE FRACTION DIOXANE

TEMPERATURE = 25°C,  $\mu \rightarrow 0$

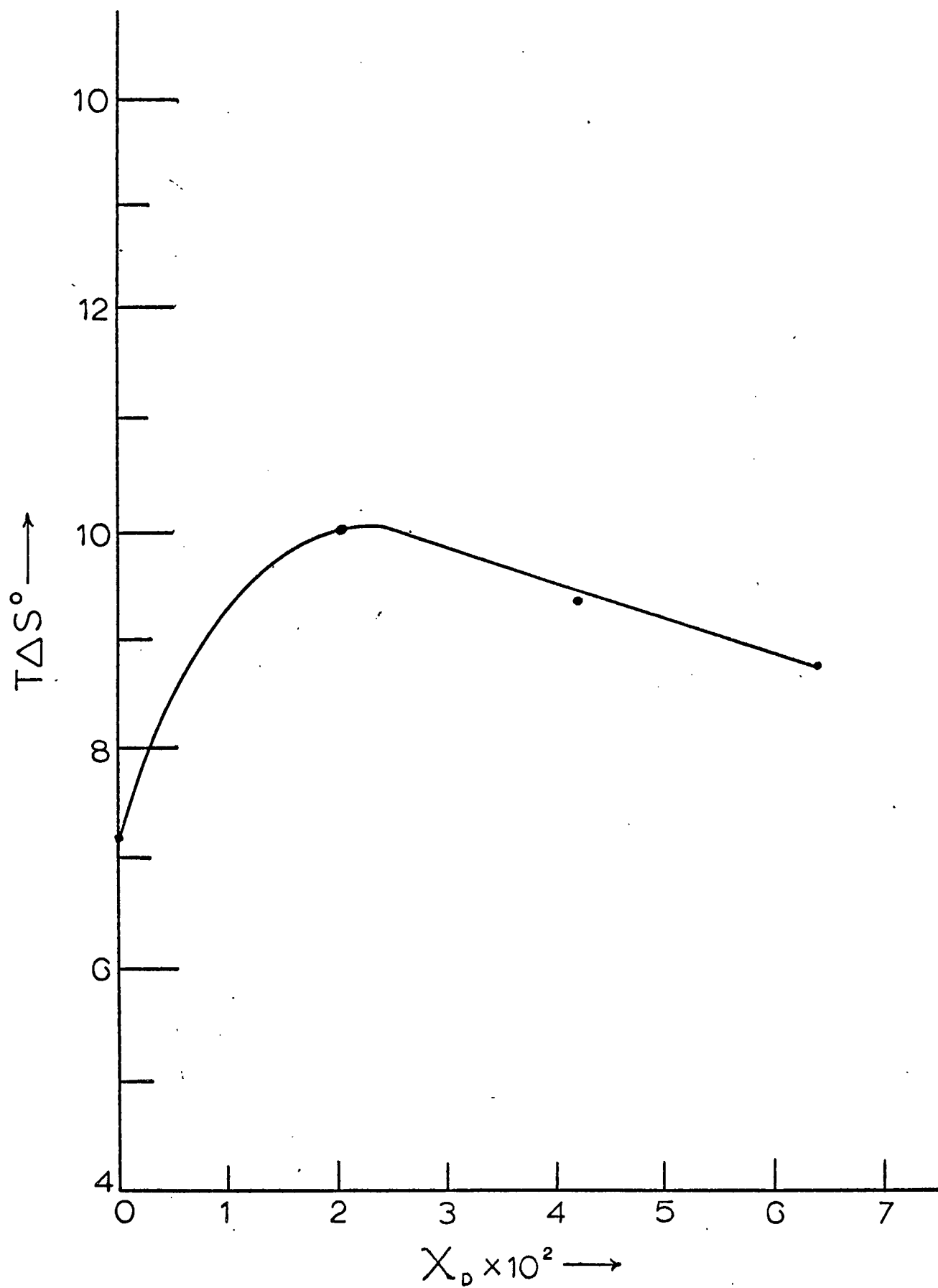


TABLE XV

SINGLE ION ENTHALPIES OF TRANSFER ( $\delta\Delta H_g$ , KCAL MOLE<sup>-1</sup>)  
FROM WATER TO AQUEOUS BINARY MIXTURES OF DIOXANE

| Mole Fraction Dioxane |       | $\delta\Delta H_g$ | $\delta\Delta H_g$ | $\Sigma\delta\Delta H_g$ |
|-----------------------|-------|--------------------|--------------------|--------------------------|
| From                  | To    | Ni <sup>+2</sup>   | Mal <sup>=</sup>   |                          |
| 0.000                 | 0.020 | +1.71              | +0.29              | +2.00                    |
| 0.000                 | 0.042 | +0.62              | +0.98              | +1.60                    |
| 0.000                 | 0.064 | -0.40              | +1.83              | +1.43                    |

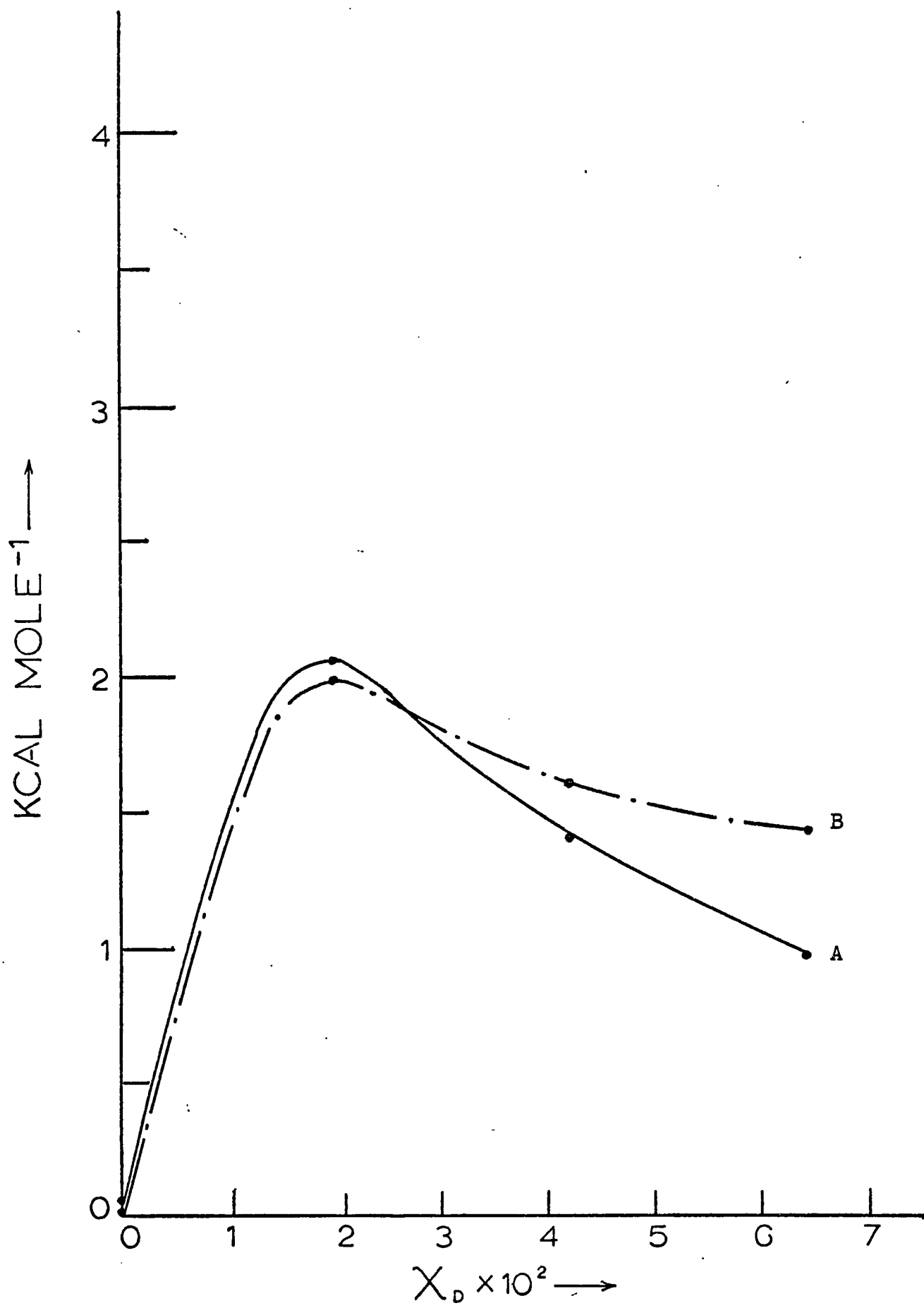
$$\delta\Delta H_g = \pm 0.05$$

## FIGURE 20

ENTHALPIES OF TRANSFER AS A FUNCTION  
OF MOLE FRACTION DIOXANE

$$A = \delta \Delta H^{\circ}$$

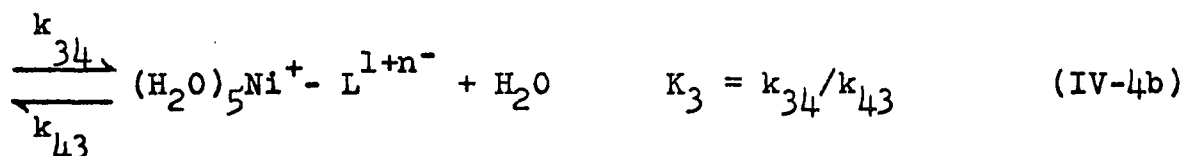
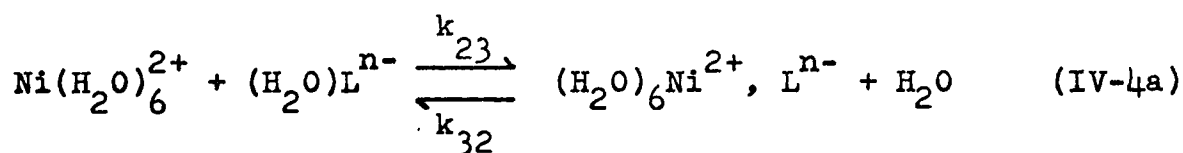
$$B = \sum \delta \Delta H_g$$



trends observed in the thermodynamic parameters of the nickel (II) malonate system in the water rich region of the water-dioxane solvent systems.

## 2. Kinetic Section

According to the mechanism put forth by Eigen for the reaction of a metal ion and a bidentate ligand in solution, the reaction scheme for the formation of a bidentate complex with hexaaquonickel(II) may be written



where the first step is the formation of the ion pair in which the ions are separated by the strongly bonded water molecules of the inner hydration sphere. The second step is the rate determining step which involves the loss of a water molecule from the first coordination sphere of the metal ion and the formation of a metal-ligand bond. The third step is

the formation of the second metal-ligand bond to form the fully chelated species.

According to the above mechanism, the rate of formation of the nickel(II) malonate complex can be expressed as follows:

$$\frac{d[(H_2O)_4Ni \text{---} L]}{dt} = k_{45} [(H_2O)_5Ni^{+-} L^{1+n-}] - k_{54} [(H_2O)_4Ni \text{---} L] \quad (IV-5)$$

Assuming  $K_3 \gg K_4$  so that

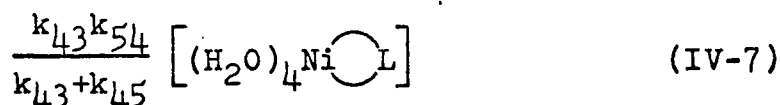
$$\frac{d[(H_2O)_5Ni^{+-} L^{1+n-}]}{dt} = 0$$

equation (IV-5) becomes

$$\frac{d[(H_2O)_4Ni \text{---} L]}{dt} = \frac{k_{34}k_{45}}{k_{43}+k_{45}} [(H_2O)_5Ni^{2+}, (H_2O)L^{n-}] - \frac{k_{43}k_{54}}{k_{43}+k_{45}} [(H_2O)_4Ni \text{---} L] \quad (IV-6)$$

If the ion pair formation step is faster than either the second or third step and it is at equilibrium all through the reaction, equation (IV-6) becomes

$$\frac{d[(H_2O)_4Ni \text{---} L]}{dt} = \frac{K_0k_{34}k_{45}}{k_{43}+k_{45}} [Ni(H_2O)_6^{2+}][L^{n-}] -$$



From equation (IV-7) it can be seen that the rate constants for the formation and dissociation of the bidentate complex may be represented by the following equations respectively:

$$k_f = K_o \left\{ \frac{k_{34}k_{45}}{k_{43}+k_{45}} \right\} \quad (\text{IV-8})$$

$$k_r = \frac{k_{43}k_{54}}{k_{43}+k_{45}} \quad (\text{IV-9})$$

If the rate determining step in the mechanism as proposed by Eigen is the loss of one water molecule from the first coordination sphere of the nickel(II) ion, the reaction parameters for the formation of the bidentate nickel(II) complex in mixed water-dioxane solvent systems should be a function of the degree of solvation of the nickel(II) ion in the different solvents.

The forward rate constants for the reaction ( $k_f$ ) at each fixed solvent composition and temperature were determined by measuring the relaxation times for several different concentrations at a fixed solvent composition and temperature using the following equation:

$$1/\tau = k_f \left[ \bar{C}_{\text{Ni}^{2+}} + \bar{C}_{\text{Mal}^-} \right] + k_r \quad (\text{IV-10})$$

where  $\bar{C}$  indicates equilibrium concentrations. Since ionic interactions can be described in terms of activity coefficients, equation (IV-10) can be rewritten in the general form

$$1/\gamma = k_f f(c) + k_r \quad (\text{IV-11})$$

where the concentration dependent term  $f(c)$  is given by

$$f(c) = f_{\pm}^2 \left\{ \bar{C}_+ \left( 1 + \frac{\partial \ln f_+}{\partial \ln C_+} \right) + \bar{C}_- \left( 1 + \frac{\partial \ln f_-}{\partial \ln C_-} \right) \right\} \quad (\text{IV-12})$$

where  $f_+$  and  $f_-$  are the activity coefficients of the free ions. The  $\partial \ln f_i / \partial \ln C_i$  terms may be calculated from experimental data after allowance for ion association equilibria or from a theoretical equation based on the Debye-Huckel theory (41)

$$\frac{\partial \ln f_+}{\partial \ln C_+} = \frac{\partial \ln f_-}{\partial \ln C_-} = - \frac{\Gamma Z_i^2 \bar{C}_i^2 (Z_+ + Z_-)}{4(1 + \mu^{1/2}) \mu^{1/2}} \quad (\text{IV-13})$$

In this equation  $\mu$  is the ionic strength of the solution and  $\Gamma$  is given by

$$\Gamma = \frac{7.91 \times 10^5}{(DT)^{3/2}} \quad (\text{IV-14})$$

Values of  $\Gamma$  were calculated for each solvent system and used to calculate  $\partial \ln f_i / \partial \ln C_i$  which in turn were used to calculate values of  $f(c)$ . Plots of  $f(c)$  vs  $1/\gamma \times 10^{-2}$  gave values of  $k_f$  used in this study. The parameters in Tables XIV-XXVII were

TABLE XVI

NICKEL(II) MALONATE IN 100% WATER  
 TEMPERATURE = 15°C, IONIC STRENGTH  $\rightarrow 0$

| $C_{Ni^{+2}} = C_{Mal} (M)$ | $\bar{C}_{NiMal} (M)$ | $1/\tau \times 10^{-2}$<br>sec <sup>-1</sup> (ave.) | $f_2$ | $f_2 ( \bar{C}_{Ni^{+2}} + \bar{C}_{Mal} ) (M)$ |
|-----------------------------|-----------------------|-----------------------------------------------------|-------|-------------------------------------------------|
| $1.0 \times 10^{-2}$        | $9.01 \times 10^{-3}$ | 3.00                                                | 0.766 | $1.13 \times 10^{-3}$                           |
| $8.0 \times 10^{-3}$        | $7.12 \times 10^{-3}$ | 2.43                                                | 0.777 | $1.03 \times 10^{-3}$                           |
| $6.0 \times 10^{-3}$        | $5.25 \times 10^{-3}$ | 2.20                                                | 0.790 | $9.19 \times 10^{-4}$                           |
| $1.0 \times 10^{-3}$        | $7.21 \times 10^{-4}$ | 1.14                                                | 0.863 | $4.10 \times 10^{-4}$                           |

$\tau = \pm 5\%$

TABLE XVII

NICKEL(II) MALONATE IN 0.02 MOLE FRACTION DIOXANE

TEMPERATURE = 15°C, IONIC STRENGTH  $\rightarrow 0$ 

| $C_{Ni^{+2}} = C_{Mal} (M)$ | $\bar{C}_{NiMal} (M)$ | $1/\tau \times 10^{-2}$<br>sec <sup>-1</sup> (ave.) | $f_2$ | $f_2 (\bar{C}_{Ni^{+2}} + \bar{C}_{Mal} = ) (M)$ |
|-----------------------------|-----------------------|-----------------------------------------------------|-------|--------------------------------------------------|
| $1.0 \times 10^{-2}$        | $9.39 \times 10^{-3}$ | 5.42                                                | 0.808 | $7.72 \times 10^{-4}$                            |
| $8.0 \times 10^{-3}$        | $7.46 \times 10^{-3}$ | 3.48                                                | 0.818 | $7.05 \times 10^{-4}$                            |
| $6.0 \times 10^{-3}$        | $5.54 \times 10^{-3}$ | 3.43                                                | 0.829 | $6.25 \times 10^{-4}$                            |
| $1.0 \times 10^{-3}$        | $8.21 \times 10^{-4}$ | 1.49                                                | 0.888 | $2.78 \times 10^{-4}$                            |

 $\tau = \pm 5\%$

TABLE XVIII

NICKEL(II) MALONATE IN 0.042 MOLE FRACTION DIOXANE

TEMPERATURE = 15°C, IONIC STRENGTH  $\rightarrow 0$ 

| $C_{Ni^{+2}} = C_{Mal} (M)$ | $\bar{C}_{NiMal} (M)$ | $1/\tau \times 10^{-2}$<br>sec. <sup>-1</sup> (ave ) | $f_2$ | $f_2 ( \bar{C}_{Ni^{+2}} + \bar{C}_{Mal} ) (M)$ |
|-----------------------------|-----------------------|------------------------------------------------------|-------|-------------------------------------------------|
| $1.0 \times 10^{-2}$        | $9.42 \times 10^{-3}$ | 5.32                                                 | 0.812 | $7.43 \times 10^{-4}$                           |
| $8.0 \times 10^{-3}$        | $7.48 \times 10^{-3}$ | 5.15                                                 | 0.821 | $6.78 \times 10^{-4}$                           |
| $6.0 \times 10^{-3}$        | $5.55 \times 10^{-3}$ | 4.35                                                 | 0.832 | $6.01 \times 10^{-4}$                           |
| $1.0 \times 10^{-3}$        | $8.28 \times 10^{-4}$ | 1.86                                                 | 0.890 | $2.68 \times 10^{-4}$                           |

 $\tau = \pm 5\%$

TABLE XIX

NICKEL(II) MALONATE IN 0.064 MOLE FRACTION DIOXANE

TEMPERATURE = 15°C, IONIC STRENGTH  $\rightarrow 0$ 

| $C_{Ni^{+2}} = C_{Mal} (M)$ | $\bar{C}_{NiMal} (M)$ | $1/\tau \times 10^{-2}$<br>sec <sup>-1</sup> (ave ) | $f_2$ | $f_2 ( \bar{C}_{Ni^{+2}} + \bar{C}_{Mal} ) (M)$ |
|-----------------------------|-----------------------|-----------------------------------------------------|-------|-------------------------------------------------|
| $1.0 \times 10^{-2}$        | $9.33 \times 10^{-3}$ | 6.58                                                | 0.800 | $8.29 \times 10^{-4}$                           |
| $8.0 \times 10^{-3}$        | $7.40 \times 10^{-3}$ | 7.49                                                | 0.809 | $7.57 \times 10^{-4}$                           |
| $6.0 \times 10^{-3}$        | $5.49 \times 10^{-3}$ | 5.60                                                | 0.821 | $6.73 \times 10^{-4}$                           |

 $\tau = \pm 5\%$

TABLE XX

NICKEL(II) MALONATE IN 100% WATER  
 TEMPERATURE = 25°C, IONIC STRENGTH  $\rightarrow 0$

| $C_{Ni^{+2}} = C_{Mal^{=}}(M)$ | $\bar{C}_{NiMal}(M)$  | $1/\tau \times 10^{-2}$<br>sec. <sup>-1</sup> (ave.) | $f_2$ | $f_2(\bar{C}_{Ni^{+2}} + \bar{C}_{Mal^{=}})(M)$ |
|--------------------------------|-----------------------|------------------------------------------------------|-------|-------------------------------------------------|
| $1.0 \times 10^{-2}$           | $9.07 \times 10^{-3}$ | 5.60                                                 | 0.772 | $1.08 \times 10^{-3}$                           |
| $8.0 \times 10^{-3}$           | $7.18 \times 10^{-3}$ | 5.08                                                 | 0.782 | $9.84 \times 10^{-4}$                           |
| $6.0 \times 10^{-3}$           | $5.29 \times 10^{-3}$ | 4.65                                                 | 0.796 | $8.75 \times 10^{-4}$                           |
| $4.0 \times 10^{-3}$           | $3.43 \times 10^{-3}$ | 4.23                                                 | 0.813 | $7.38 \times 10^{-4}$                           |
| $2.0 \times 10^{-3}$           | $1.61 \times 10^{-3}$ | 3.65                                                 | 0.841 | $5.43 \times 10^{-4}$                           |
| $1.0 \times 10^{-3}$           | $7.34 \times 10^{-4}$ | 2.71                                                 | 0.866 | $3.90 \times 10^{-4}$                           |

$\tau = \pm 5\%$

TABLE XXI

NICKEL(II) MALONATE IN 0.02 MOLE FRACTION DIOXANE

TEMPERATURE = 25°C, IONIC STRENGTH  $\rightarrow 0$ 

| $C_{Ni^{+2}} = C_{Mal^{=}}(M)$ | $\bar{C}_{NiMal}(M)$  | $1/\tau \times 10^{-2}$<br>sec. <sup>-1</sup> (ave.) | $f_2$ | $f_2(\bar{C}_{Ni^{+2}} + \bar{C}_{Mal^{=}})(M)$ |
|--------------------------------|-----------------------|------------------------------------------------------|-------|-------------------------------------------------|
| $1.0 \times 10^{-2}$           | $9.46 \times 10^{-3}$ | -----                                                | 0.817 | $7.08 \times 10^{-4}$                           |
| $8.0 \times 10^{-3}$           | $7.52 \times 10^{-3}$ | 7.43                                                 | 0.826 | $6.46 \times 10^{-4}$                           |
| $6.0 \times 10^{-3}$           | $5.58 \times 10^{-3}$ | 6.27                                                 | 0.837 | $5.72 \times 10^{-4}$                           |
| $4.0 \times 10^{-3}$           | $3.66 \times 10^{-3}$ | 4.96                                                 | 0.851 | $4.80 \times 10^{-4}$                           |
| $2.0 \times 10^{-3}$           | $1.77 \times 10^{-3}$ | 4.41                                                 | 0.873 | $3.52 \times 10^{-4}$                           |
| $1.0 \times 10^{-3}$           | $8.38 \times 10^{-4}$ | 3.14                                                 | 0.893 | $2.54 \times 10^{-4}$                           |

 $\tau = \pm 5\%$

TABLE XXII

NICKEL(II) MALONATE IN 0.042 MOLE FRACTION DIOXANE

TEMPERATURE = 25°C, IONIC STRENGTH  $\rightarrow 0$ 

| $C_{Ni^{+2}} = C_{Mal^{=}}(M)$ | $\bar{C}_{NiMal}(M)$  | $1/\tau \times 10^{-2}$<br>sec <sup>-1</sup> (ave.) | $f_2$ | $f_2(\bar{C}_{Ni^{+2}} + \bar{C}_{Mal^{=}})(M)$ |
|--------------------------------|-----------------------|-----------------------------------------------------|-------|-------------------------------------------------|
| $1.0 \times 10^{-2}$           | $9.46 \times 10^{-3}$ | -----                                               | 0.818 | $7.01 \times 10^{-4}$                           |
| $8.0 \times 10^{-3}$           | $7.52 \times 10^{-3}$ | 9.17                                                | 0.826 | $6.39 \times 10^{-4}$                           |
| $6.0 \times 10^{-3}$           | $5.59 \times 10^{-3}$ | 8.23                                                | 0.837 | $5.67 \times 10^{-4}$                           |
| $4.0 \times 10^{-3}$           | $3.66 \times 10^{-3}$ | 6.37                                                | 0.851 | $4.76 \times 10^{-4}$                           |
| $2.0 \times 10^{-3}$           | $1.77 \times 10^{-3}$ | 5.15                                                | 0.874 | $3.49 \times 10^{-4}$                           |
| $1.0 \times 10^{-3}$           | $8.39 \times 10^{-4}$ | 3.73                                                | 0.893 | $2.52 \times 10^{-4}$                           |

 $\tau = \pm 5\%$

TABLE XXIII

NICKEL(II) MALONATE IN 0.064 MOLE FRACTION DIOXANE

TEMPERATURE = 25°C, IONIC STRENGTH  $\rightarrow 0$ 

| $C_{Ni^{+2}} = C_{Mal} (M)$ | $\bar{C}_{NiMal} (M)$ | $1/\gamma \times 10^{-2}$<br>sec <sup>-1</sup> (ave ) | $f_2$ | $f_2 ( \bar{C}_{Ni^{+2}} + \bar{C}_{Mal} = ) (M)$ |
|-----------------------------|-----------------------|-------------------------------------------------------|-------|---------------------------------------------------|
| $1.0 \times 10^{-2}$        | $9.40 \times 10^{-3}$ | 17.3                                                  | 0.809 | $7.58 \times 10^{-4}$                             |
| $8.0 \times 10^{-3}$        | $7.47 \times 10^{-3}$ | 17.8                                                  | 0.818 | $6.92 \times 10^{-4}$                             |
| $6.0 \times 10^{-3}$        | $5.54 \times 10^{-3}$ | 14.0                                                  | 0.830 | $6.14 \times 10^{-4}$                             |
| $4.0 \times 10^{-3}$        | $3.63 \times 10^{-3}$ | 10.8                                                  | 0.845 | $5.16 \times 10^{-4}$                             |
| $2.0 \times 10^{-3}$        | $1.74 \times 10^{-3}$ | 7.35                                                  | 0.868 | $3.79 \times 10^{-4}$                             |
| $1.0 \times 10^{-3}$        | $8.23 \times 10^{-4}$ | 4.00                                                  | 0.888 | $2.74 \times 10^{-4}$                             |

 $\gamma = \pm 5\%$

TABLE XXIV

NICKEL(II) MALONATE IN 100% WATER  
 TEMPERATURE = 35°C, IONIC STRENGTH  $\rightarrow 0$

| $C_{Ni^{+2}} = C_{Mal} (M)$ | $\bar{C}_{NiMal} (M)$ | $1/\tau \times 10^{-2}$<br>sec. <sup>-1</sup> (ave ) | $f_2$ | $f_2 ( \bar{C}_{Ni^{+2}} + \bar{C}_{Mal} ) (M)$ |
|-----------------------------|-----------------------|------------------------------------------------------|-------|-------------------------------------------------|
| $1.0 \times 10^{-2}$        | $9.11 \times 10^{-3}$ | 12.2                                                 | 0.775 | $10.4 \times 10^{-4}$                           |
| $8.0 \times 10^{-3}$        | $7.21 \times 10^{-3}$ | 11.2                                                 | 0.786 | $9.55 \times 10^{-4}$                           |
| $6.0 \times 10^{-3}$        | $5.32 \times 10^{-3}$ | 9.85                                                 | 0.799 | $8.49 \times 10^{-4}$                           |
| $1.0 \times 10^{-3}$        | $7.45 \times 10^{-4}$ | 4.76                                                 | 0.868 | $3.79 \times 10^{-4}$                           |

$\tau = \pm 5\%$

TABLE XXV

NICKEL(II) MALONATE IN 0.02 MOLE FRACTION DIOXANE

TEMPERATURE = 35°C, IONIC STRENGTH  $\rightarrow 0$ 

| $C_{Ni^{+2}} = C_{Mal^{=}}(M)$ | $\bar{C}_{NiMal}(M)$  | $1/\tau \times 10^{-2}$<br>sec. <sup>-1</sup> (ave.) | $f_2$ | $f_2(\bar{C}_{Ni^{+2}} + \bar{C}_{Mal^{=}})(M)$ |
|--------------------------------|-----------------------|------------------------------------------------------|-------|-------------------------------------------------|
| $1.0 \times 10^{-2}$           | $9.52 \times 10^{-3}$ | 19.4                                                 | 0.826 | $6.45 \times 10^{-4}$                           |
| $8.0 \times 10^{-3}$           | $7.57 \times 10^{-3}$ | 14.0                                                 | 0.834 | $5.88 \times 10^{-4}$                           |
| $6.0 \times 10^{-3}$           | $5.63 \times 10^{-3}$ | 11.6                                                 | 0.844 | $5.20 \times 10^{-4}$                           |
| $1.0 \times 10^{-3}$           | $8.55 \times 10^{-4}$ | 7.46                                                 | 0.898 | $2.31 \times 10^{-4}$                           |

 $\gamma = \pm 5\%$

TABLE XXVI

NICKEL(II) MALONATE IN 0.042 MOLE FRACTION DIOXANE

TEMPERATURE = 35°C, IONIC STRENGTH  $\rightarrow 0$ 

| $C_{Ni^{+2}} = C_{Mal} (M)$ | $\bar{C}_{NiMal} (M)$ | $1/\tau \times 10^{-2}$<br>$sec^{-1} (ave)$ | $f_2$ | $f_2 ( \bar{C}_{Ni^{+2}} + \bar{C}_{Mal} = ) (M)$ |
|-----------------------------|-----------------------|---------------------------------------------|-------|---------------------------------------------------|
| $1.0 \times 10^{-2}$        | $9.52 \times 10^{-3}$ | 28.8                                        | 0.826 | $6.43 \times 10^{-4}$                             |
| $8.0 \times 10^{-3}$        | $7.57 \times 10^{-3}$ | 16.7                                        | 0.834 | $5.86 \times 10^{-4}$                             |
| $6.0 \times 10^{-3}$        | $5.63 \times 10^{-3}$ | 16.2                                        | 0.844 | $5.19 \times 10^{-4}$                             |
| $1.0 \times 10^{-2}$        | $8.55 \times 10^{-4}$ | 7.89                                        | 0.898 | $2.31 \times 10^{-4}$                             |

 $\gamma = \pm 5\%$

TABLE XXVII

NICKEL(II) MALONATE IN 0.064 MOLE FRACTION DIOXANE

TEMPERATURE = 35°C, IONIC STRENGTH  $\rightarrow 0$ 

| $C_{Ni^{+2}} = C_{Mal} (M)$ | $\bar{C}_{NiMal} (M)$ | $1/\tau \times 10^{-2}$<br>sec. <sup>-1</sup> (ave.) | $f_2$ | $f_2 (\bar{C}_{Ni^{+2}} + \bar{C}_{Mal} =) (M)$ |
|-----------------------------|-----------------------|------------------------------------------------------|-------|-------------------------------------------------|
| $1.0 \times 10^{-2}$        | $9.42 \times 10^{-3}$ | 27.5                                                 | 0.812 | $7.39 \times 10^{-4}$                           |
| $8.0 \times 10^{-3}$        | $7.48 \times 10^{-3}$ | 26.4                                                 | 0.821 | $6.74 \times 10^{-4}$                           |
| $6.0 \times 10^{-3}$        | $5.55 \times 10^{-3}$ | 18.6                                                 | 0.832 | $5.98 \times 10^{-4}$                           |
| $1.0 \times 10^{-3}$        | $8.28 \times 10^{-4}$ | 7.87                                                 | 0.890 | $2.67 \times 10^{-4}$                           |

 $\tau = \pm 5\%$

used to obtain  $k_f$  values for each solvent composition and temperature. The reverse rate constants for each reaction was found by using

$$k_r = \frac{k_f}{K_{eq}} \quad (IV-15)$$

where  $K_{eq}$  is the equilibrium constant for the monocomplex formation at a fixed solvent composition and temperature. The results of the experimentally determined  $k_f$  and  $k_r$  values are given in Tables XXVIII and XXIX. The forward rate constant for the rate determining step ( $k_{34}$ ) at a fixed solvent composition and temperature is calculated using

$$k_f = K_0 k_{34} \quad (IV-16)$$

In order to use equation (IV-16), it is necessary to obtain values of  $K_0$  for the nickel(II) malonate complex at zero ionic strength. Values of  $K_0$  were calculated using equations (II-30,31 and 32). The dielectric constants determined by Critchfield (42) in various mole fractions dioxane from 15°C to 35°C by conductance measurements were used in the calculation of  $K_0$ . The values used are given in Table XXX and are shown as a function of solvent composition in Figure 21. The  $K_0$  values calculated are given in Table XXXI and are shown in Figure 22 as a function of solvent composition. The values obtained are correct to within a

TABLE XXVIII

FORWARD RATE CONSTANT (  $K_f$  ) AS A FUNCTION OF  
MOLE FRACTION OF DIOXANE AND TEMPERATURE,  $\mu \rightarrow 0$

| Mole Fraction<br>Dioxane | 15° C              | 25° C              | 35° C              |
|--------------------------|--------------------|--------------------|--------------------|
| 0.000                    | $2.39 \times 10^5$ | $3.91 \times 10^5$ | $1.11 \times 10^6$ |
| 0.020                    | $6.73 \times 10^5$ | $1.92 \times 10^6$ | $2.45 \times 10^6$ |
| 0.042                    | $7.53 \times 10^5$ | $1.77 \times 10^6$ | $4.13 \times 10^6$ |
| 0.064                    | $6.74 \times 10^5$ | $2.94 \times 10^6$ | $4.23 \times 10^6$ |

$K_f = \pm 5\%$

TABLE XXIX

REVERSE RATE CONSTANT (  $K_r$  ) AS A FUNCTION OF  
MOLE FRACTION OF DIOXANE AND TEMPERATURE,  $\mu \rightarrow 0$

| Mole Fraction<br>Dioxane | 15°C | 25°C  | 35°C  |
|--------------------------|------|-------|-------|
| 0.000                    | 25.8 | 37.0  | 97.1  |
| 0.020                    | 26.2 | 59.9  | 60.2  |
| 0.042                    | 26.9 | 54.3  | 102   |
| 0.064                    | 32.5 | 112.2 | 105.5 |

$K_r = \pm 20\%$

TABLE XXX

DIELECTRIC CONSTANTS FOR WATER-DIOXANE SYSTEMS  
FROM 15°C TO 35°C

| Mole Fraction<br>Dioxane | Temperature<br>(°C) | Dielectric<br>Constant |
|--------------------------|---------------------|------------------------|
| 0.000                    | 15                  | 81.88                  |
| 0.000                    | 25                  | 78.48                  |
| 0.000                    | 35                  | 74.97                  |
| 0.020                    | 15                  | 74.00                  |
| 0.020                    | 25                  | 70.06                  |
| 0.020                    | 35                  | 67.50                  |
| 0.042                    | 15                  | 66.50                  |
| 0.042                    | 25                  | 63.75                  |
| 0.042                    | 35                  | 60.09                  |
| 0.064                    | 15                  | 60.03                  |
| 0.064                    | 25                  | 57.25                  |
| 0.064                    | 35                  | 54.63                  |

## FIGURE 21

DIELECTRIC CONSTANTS FOR WATER-DIOXANE  
SOLVENT SYSTEMS

$$A = 15^{\circ}\text{C}$$

$$B = 25^{\circ}\text{C}$$

$$C = 35^{\circ}\text{C}$$

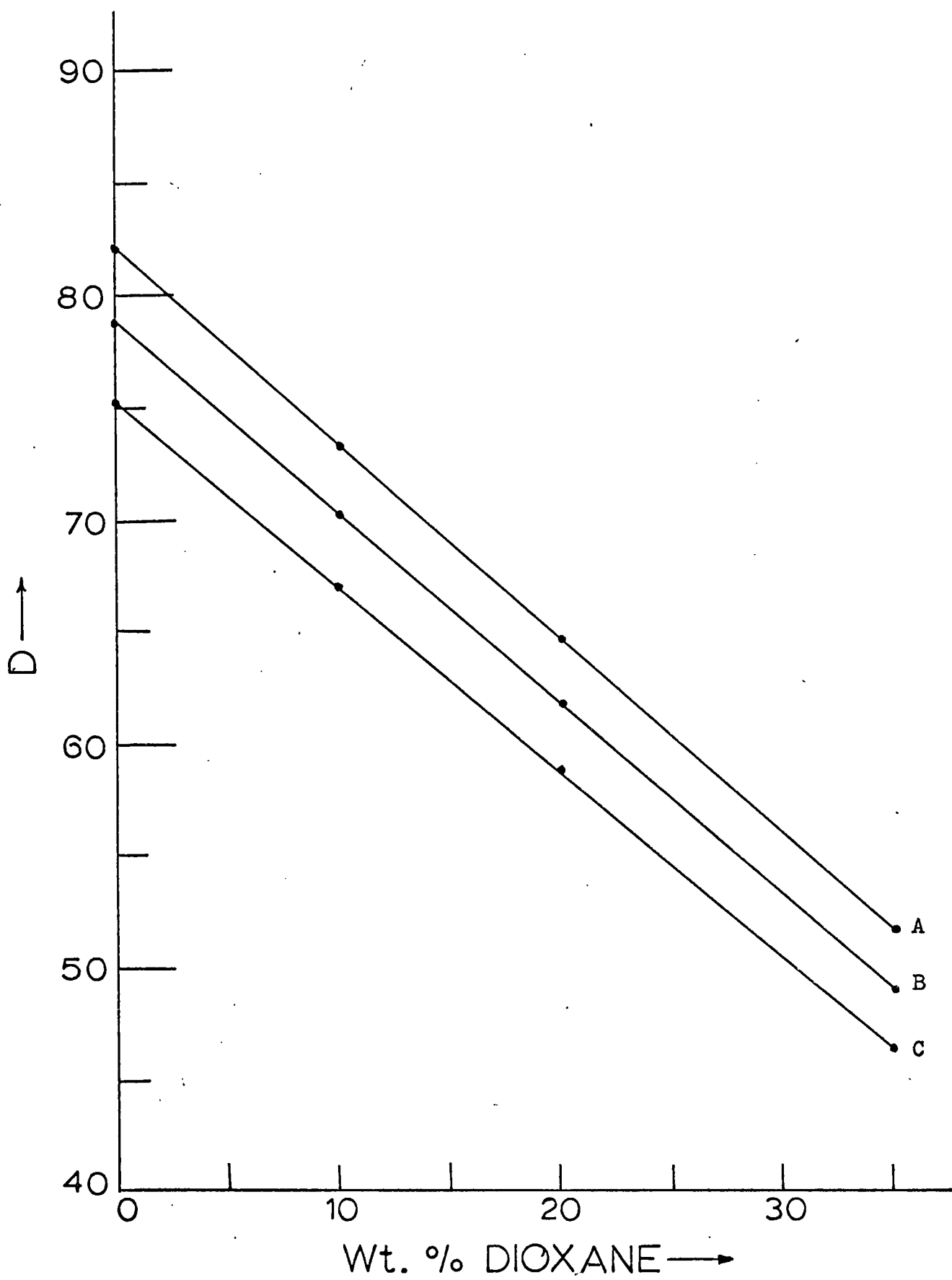


TABLE XXXI

ION PAIR STABILITY CONSTANTS (  $K_o$  ) FOR THE  
NICKEL(II) MALONATE SYSTEM AS A FUNCTION OF  
MOLE FRACTION DIOXANE AND TEMPERATURE,  $\mu \rightarrow 0$

| Mole Fraction<br>Dioxane | 15°C               | 25°C               | 35°C               |
|--------------------------|--------------------|--------------------|--------------------|
| 0.000                    | $2.72 \times 10^2$ | $2.85 \times 10^2$ | $3.07 \times 10^2$ |
| 0.020                    | $4.97 \times 10^2$ | $5.66 \times 10^2$ | $5.81 \times 10^2$ |
| 0.042                    | $1.01 \times 10^3$ | $1.07 \times 10^3$ | $1.28 \times 10^3$ |
| 0.064                    | $2.13 \times 10^3$ | $2.37 \times 10^3$ | $2.65 \times 10^3$ |

$K_o = \pm$  factor of 3 or 4

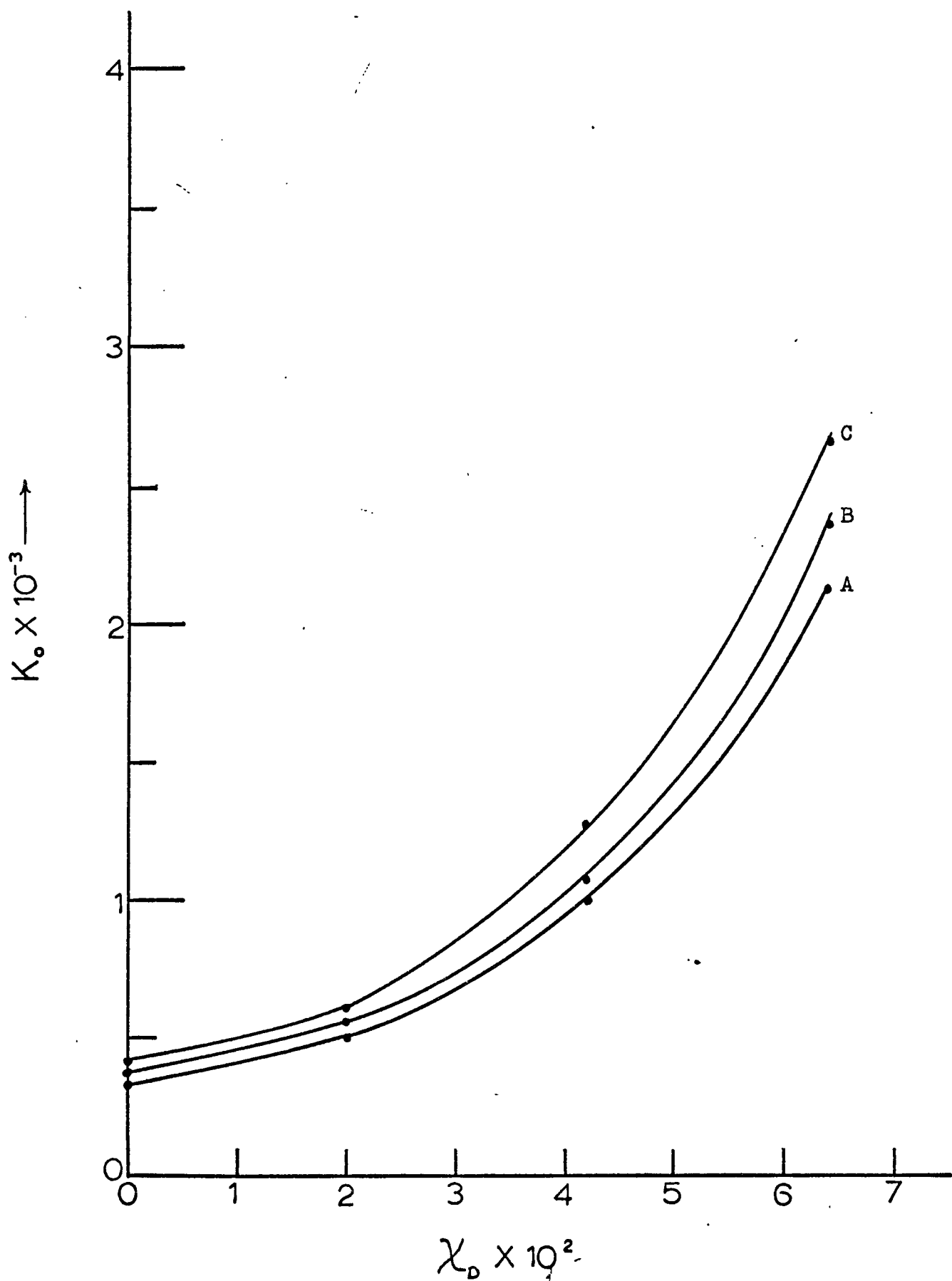
FIGURE 22

ION PAIR STABILITY CONSTANTS (  $K_o$ ,  $\text{MOLE}^{-1}$  ) FOR THE  
NICKEL(II) MALONATE SYSTEM AS A FUNCTION OF  
MOLE FRACTION DIOXANE AND TEMPERATURE,  $\mu \rightarrow 0$

$$A = 15^{\circ}\text{C}$$

$$B = 25^{\circ}\text{C}$$

$$C = 35^{\circ}\text{C}$$



factor of 3 or 4. The trend of  $K_o$  values obtained from these calculations are in good agreement with observed trends for 2-2 electrolytes in mixed aqueous solvent systems, as shown in Table I. The results of calculations of  $k_{34}$  values are given in Table XXXII and are shown as a function of solvent composition in Figure 23.

The enthalpy change in the formation of the ion pair was calculated using the following equation:

$$\Delta H_o = (-RT \ln K_o + T \Delta S_o) 10^{-3} \quad (\text{IV-17})$$

where  $\Delta S_o$  was assumed to be equal to  $-19.4 Z_+ Z_- / a$  (43,44) with  $a$ , the distance of closest approach of the ion pair, equal to  $5A$  and  $Z_i$  is the charge on the ion. The results of these calculations are given in Table XXXIII and are shown as a function of solvent composition in Figure 24.

The Arrhenius activation energies for the nickel(II) malonate systems were determined by plotting  $\log k_f$  vs  $1/T$  giving a slope equal to  $-E_a/4.574$ . The experimentally determined values of  $E_a$  are given in Table XXXIV and are shown as a function of solvent composition in Figure 25. The enthalpies, entropies, and free energies of activation for the nickel(II) malonate system in each solvent composition were determined using the following equations, respectively:

$$\Delta H_f^* = E_a - 1.986 \times 10^{-3} T \quad (\text{IV-18})$$

TABLE XXXII

FORWARD RATE CONSTANTS OF THE RATE DETERMINING STEP  
(  $k_{34}$  ) FOR THE NICKEL(II) MALONATE SYSTEM AS A  
FUNCTION OF MOLE FRACTION DIOXANE AND TEMPERATURE,  $\mu \rightarrow 0$

| Mole Fraction<br>Dioxane | 15°C               | 25°C               | 35°C               |
|--------------------------|--------------------|--------------------|--------------------|
| 0.000                    | $8.80 \times 10^2$ | $1.37 \times 10^3$ | $3.64 \times 10^3$ |
| 0.020                    | $1.36 \times 10^3$ | $3.39 \times 10^3$ | $4.22 \times 10^3$ |
| 0.042                    | $7.48 \times 10^2$ | $1.66 \times 10^3$ | $3.22 \times 10^3$ |
| 0.064                    | $3.16 \times 10^2$ | $1.25 \times 10^3$ | $1.59 \times 10^3$ |

$k_{34} = \pm 5\%$

## FIGURE 23

FORWARD RATE CONSTANTS OF THE RATE DETERMINING STEP  
(  $k_{34}$ , SEC<sup>-1</sup> ) FOR THE NICKEL(II) MALONATE SYSTEM  
AS A FUNCTION OF  
MOLE FRACTION DIOXANE AND TEMPERATURE,  $\mu \rightarrow 0$

$$A = 15^{\circ}\text{C}$$

$$B = 25^{\circ}\text{C}$$

$$C = 35^{\circ}\text{C}$$

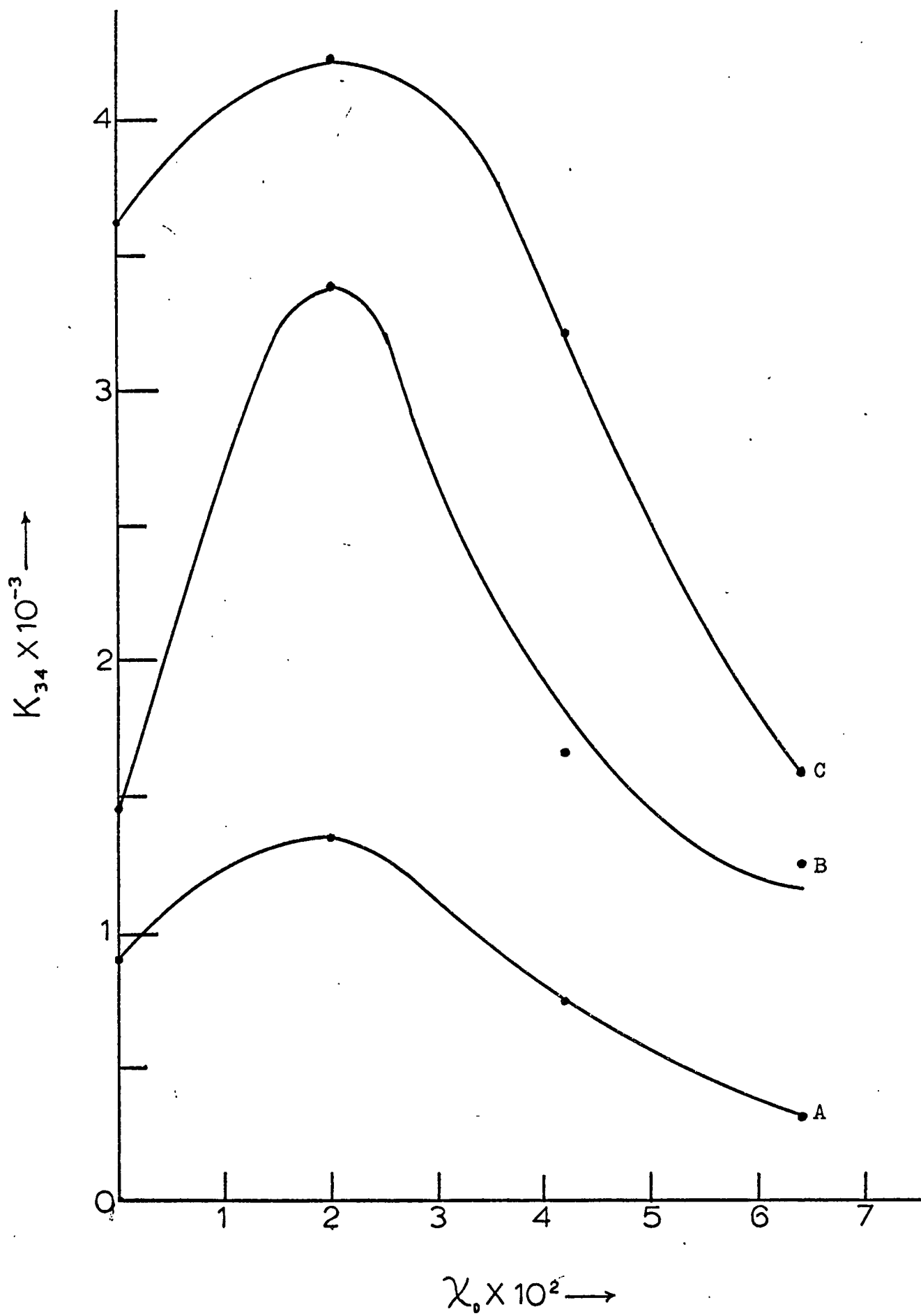


TABLE XXXIII

ENTHALPIES OF ION PAIR FORMATION ( $\Delta H_o$ , KCAL MOLE<sup>-1</sup> )  
FOR THE NICKEL(II) MALONATE SYSTEM AS A  
FUNCTION OF MOLE FRACTION DIOXANE AND TEMPERATURE,  $\mu \rightarrow 0$

| Mole Fraction<br>Dioxane | 15°C   | 25°C   | 35°C   |
|--------------------------|--------|--------|--------|
| 0.000                    | +1.113 | +1.123 | +1.116 |
| 0.020                    | +0.768 | +0.717 | +0.725 |
| 0.042                    | +0.363 | +0.343 | +0.240 |
| 0.064                    | -0.067 | -0.130 | -0.204 |

$\Delta H_o = \pm 10\%$

FIGURE 24

ENTHALPIES OF ION PAIR FORMATION (  $\Delta H_o$ , KCAL. MOLE<sup>-1</sup> )  
FOR THE NICKEL(II) MALONATE SYSTEM AS A  
FUNCTION OF MOLE FRACTION DIOXANE AND TEMPERATURE,  $\mu \rightarrow 0$

$$A = 15^{\circ}\text{C}$$

$$B = 25^{\circ}\text{C}$$

$$C = 35^{\circ}\text{C}$$

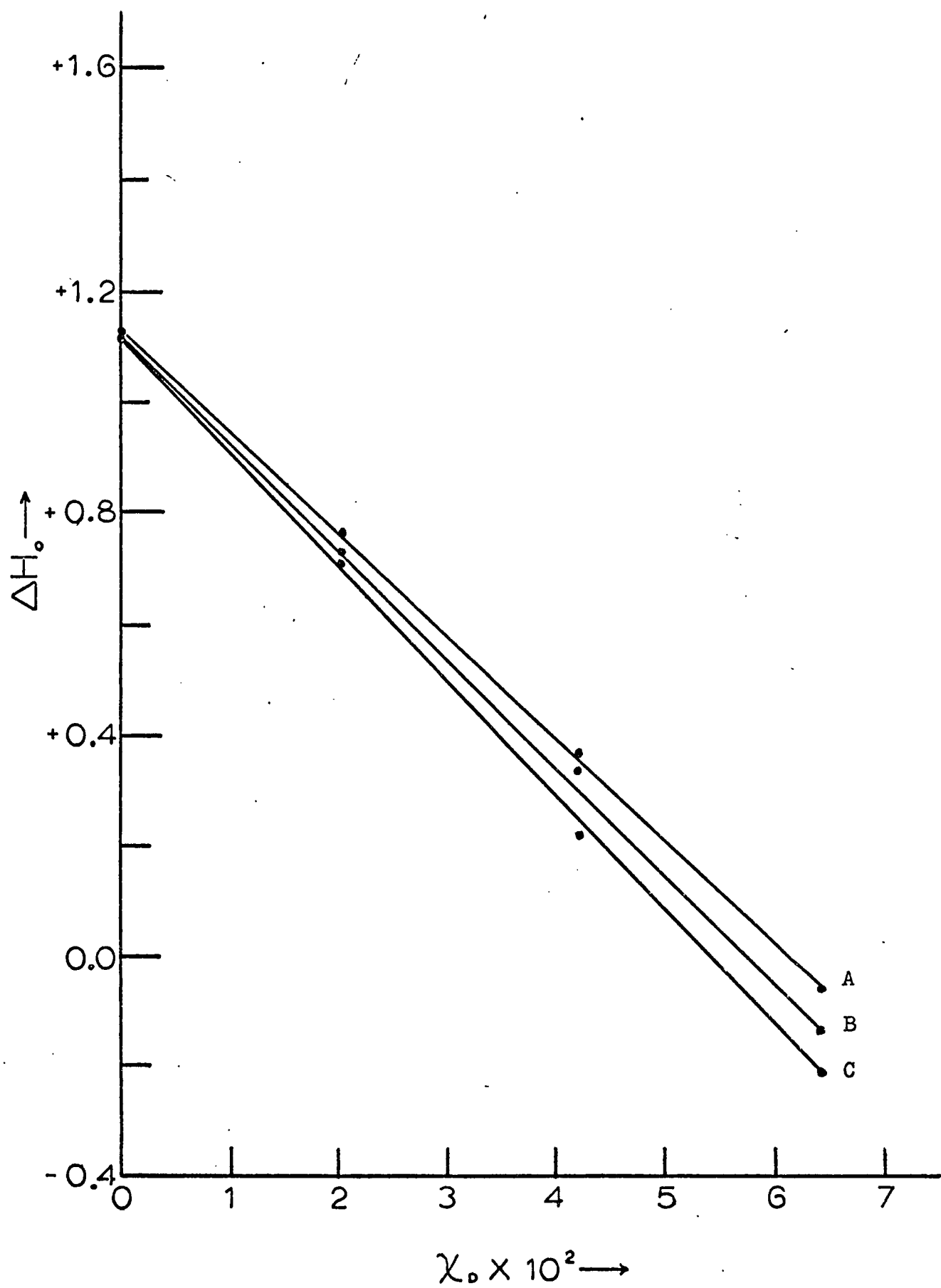


TABLE XXXIV

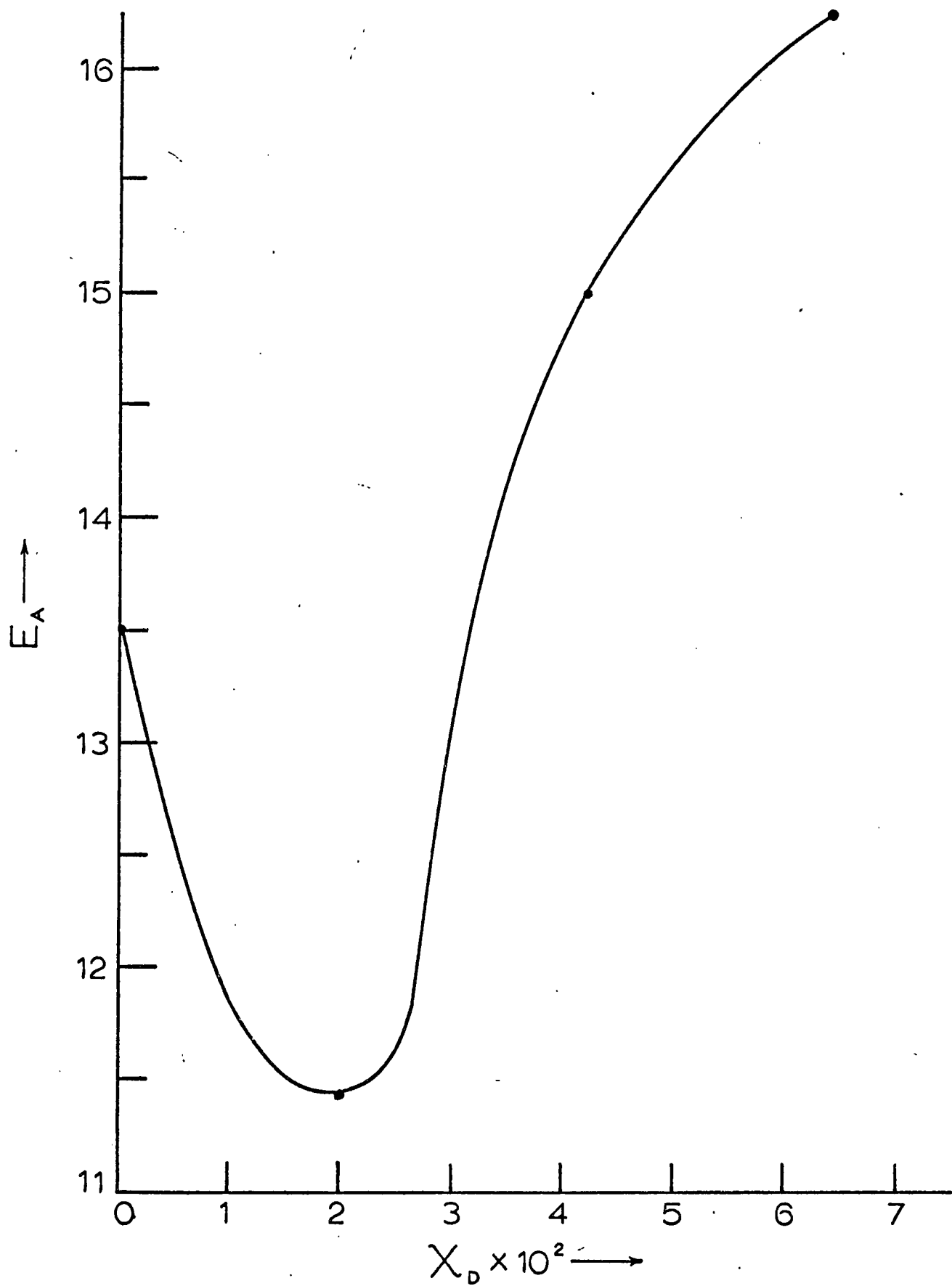
ENERGIES OF ACTIVATION (  $E_a$ , KCAL MOLE<sup>-1</sup> )  
FOR THE NICKEL(II) MALONATE SYSTEM  
AS A FUNCTION OF MOLE FRACTION DIOXANE,  $\mu \rightarrow 0$

| Mole Fraction<br>Dioxane | $E_a$ |
|--------------------------|-------|
| 0.000                    | 13.5  |
| 0.020                    | 11.5  |
| 0.042                    | 15.0  |
| 0.064                    | 16.3  |

$$E_a = \pm 6\%$$

## FIGURE 25

ENERGIES OF ACTIVATION (  $E_a$ , KCAL MOLE<sup>-1</sup> )  
FOR THE NICKEL(II) MALONATE SYSTEM  
AS A FUNCTION OF MOLE FRACTION DIOXANE,  $\mu \rightarrow 0$



$$\Delta S_f^* = 1.986(\ln A - 1 - \ln 2.085 \times 10^{10} T) \quad (\text{IV-19})$$

$$\Delta G_f^* = \Delta H_f^* - (T \Delta S_f^*) 10^{-3} \quad (\text{IV-20})$$

where  $\ln A$  is the intercept of the Arrhenius plot. The uncertainties in  $E_a$  and  $T \Delta S_f^*$  are about  $\pm 0.7$  kcal/mole and  $\pm 2.2$  kcal/mole, respectively. The results of the above calculations are given in Tables XXXV-XXXVII and Figures 26-28 show the results as a function of solvent composition.

According to most of the work published concerning fast ligand substitution reactions (45,46,1), it is assumed that in the mechanism proposed by Eigen,  $k_{34} \gg k_{45}$ . This assumption means that the rate determining step for the mechanism is the loss of the water molecule from the inner hydration sphere of the metal ion. By using this assumption and the relationship which results,  $k_f = K_o k_{34}$ , we have

$$\begin{aligned} \Delta H_f^* &= \frac{d \ln k_f}{dt} = \frac{d \ln K_o}{dt} + \frac{d \ln k_{34}}{dt} \\ &= \Delta H_o + \Delta H_{34}^* \end{aligned} \quad (\text{IV-21})$$

where  $\Delta H_f^*$  is the enthalpy of activation for the overall process,  $\Delta H_o$  is the enthalpy of ion pair formation, and  $\Delta H_{34}^*$  is the enthalpy of activation for the loss of the water molecule from the inner hydration sphere of the metal ion. The values of  $\Delta H_{34}^*$  for each solvent system was calculated using equation (IV-22).

TABLE XXXV

ENTHALPIES OF ACTIVATION ( $\Delta H_f^*$ , KCAL. MOLE<sup>-1</sup>)  
FOR THE NICKEL(II) MALONATE SYSTEM AS A  
FUNCTION OF MOLE FRACTION DIOXANE AND TEMPERATURE,  $\mu \rightarrow 0$

| Mole Fraction<br>Dioxane | 15°C | 25°C | 35°C |
|--------------------------|------|------|------|
| 0.000                    | 13.0 | 12.9 | 12.9 |
| 0.020                    | 10.9 | 10.9 | 10.8 |
| 0.042                    | 14.4 | 14.4 | 14.4 |
| 0.062                    | 15.7 | 15.7 | 15.7 |

$$\Delta H_f^* = \pm 5\%$$

## FIGURE 26

ENTHALPIES OF ACTIVATION (  $\Delta H_f^*$ , KCAL. MOLE<sup>-1</sup> )  
FOR THE NICKEL(II) MALONATE SYSTEM AS A  
FUNCTION OF MOLE FRACTION DIOXANE  
TEMPERATURE = 25°C,  $\mu \rightarrow 0$

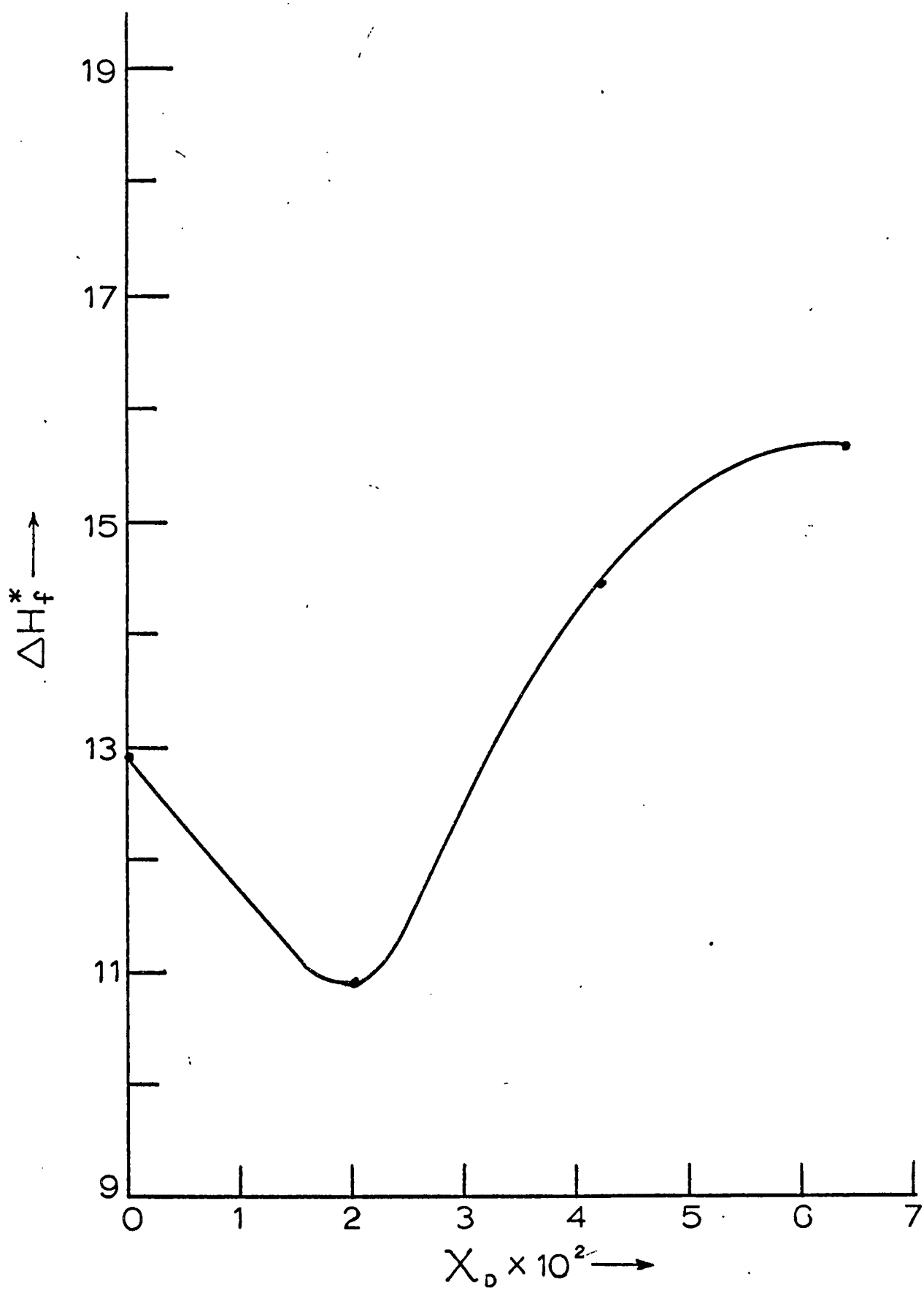


TABLE XXXVI

ENTROPIES OF ACTIVATION (  $T\Delta S_f^*$ , KCAL. MOLE<sup>-1</sup> )  
 FOR THE NICKEL(II) MALONATE SYSTEM AS A  
 FUNCTION OF MOLE FRACTION DIOXANE AND TEMPERATURE,  $\mu \rightarrow 0$

| Mole Fraction<br>Dioxane | 15°C | 25°C | 35°C |
|--------------------------|------|------|------|
| 0.000                    | 3.15 | 3.24 | 3.33 |
| 0.020                    | 1.80 | 1.84 | 1.89 |
| 0.042                    | 5.35 | 5.53 | 5.68 |
| 0.064                    | 6.64 | 6.85 | 7.06 |

$$T\Delta S_f^* = \pm 4\%$$

## FIGURE 27

ENTROPIES OF ACTIVATION (  $T\Delta S_f^*$ , KCAL. MOLE<sup>-1</sup> )  
FOR THE NICKEL(II) MALONATE SYSTEM AS A  
FUNCTION OF MOLE FRACTION DIOXANE  
TEMPERATURE = 25°C,  $\mu \rightarrow 0$

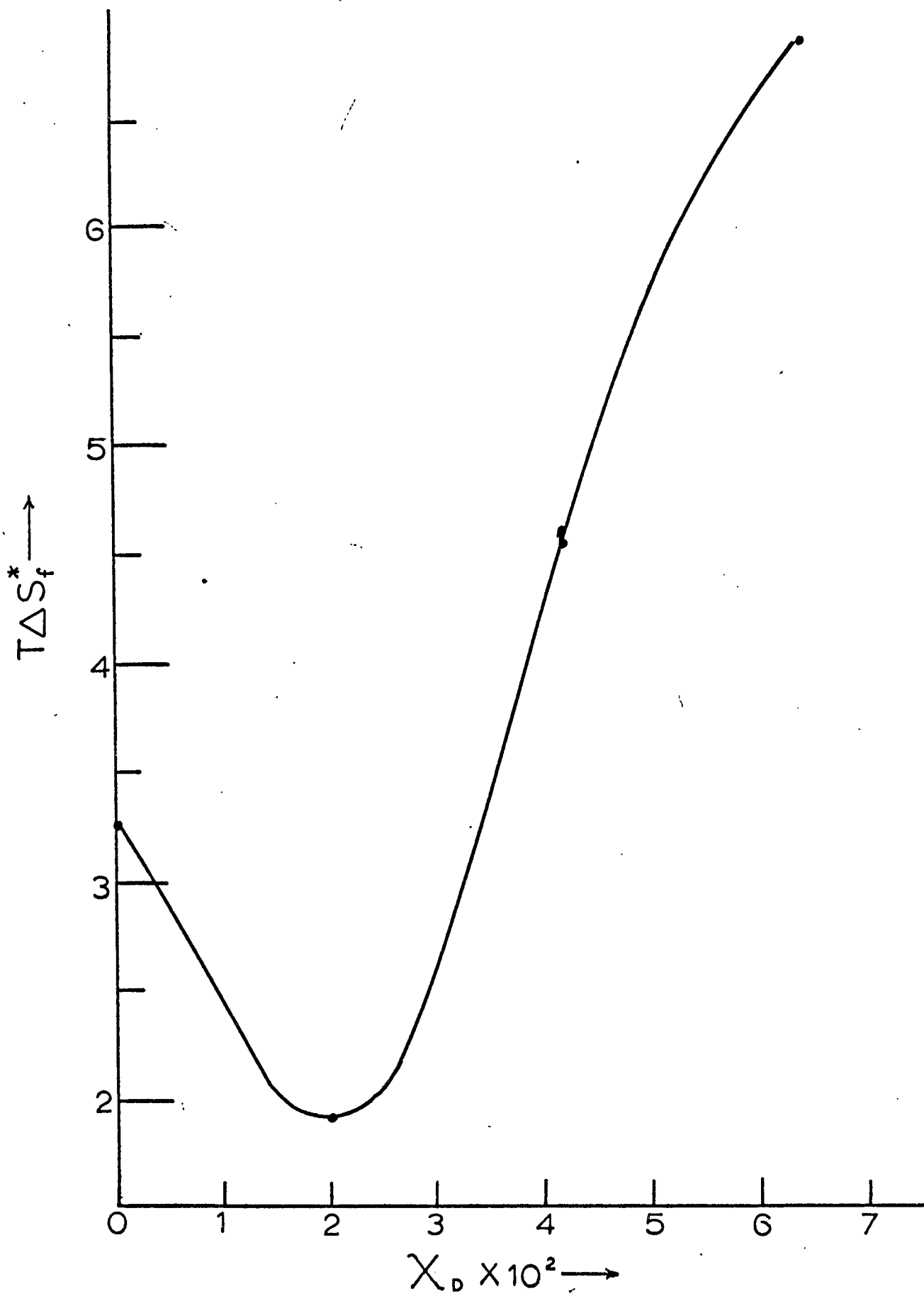


TABLE XXXVII

FREE ENERGIES OF ACTIVATION ( $\Delta G_f^*$ , KCAL MOLE<sup>-1</sup>)  
FOR THE NICKEL(II) MALONATE SYSTEM AS A  
FUNCTION OF MOLE FRACTION DIOXANE AND TEMPERATURE,  $\mu \rightarrow 0$

| Mole Fraction<br>Dioxane | 15°C | 25°C | 35°C |
|--------------------------|------|------|------|
| 0.000                    | 9.80 | 9.69 | 9.58 |
| 0.020                    | 9.08 | 9.02 | 8.96 |
| 0.042                    | 9.09 | 8.91 | 8.72 |
| 0.064                    | 9.05 | 8.82 | 8.59 |

$$\Delta G_f^* = \pm 5\%$$

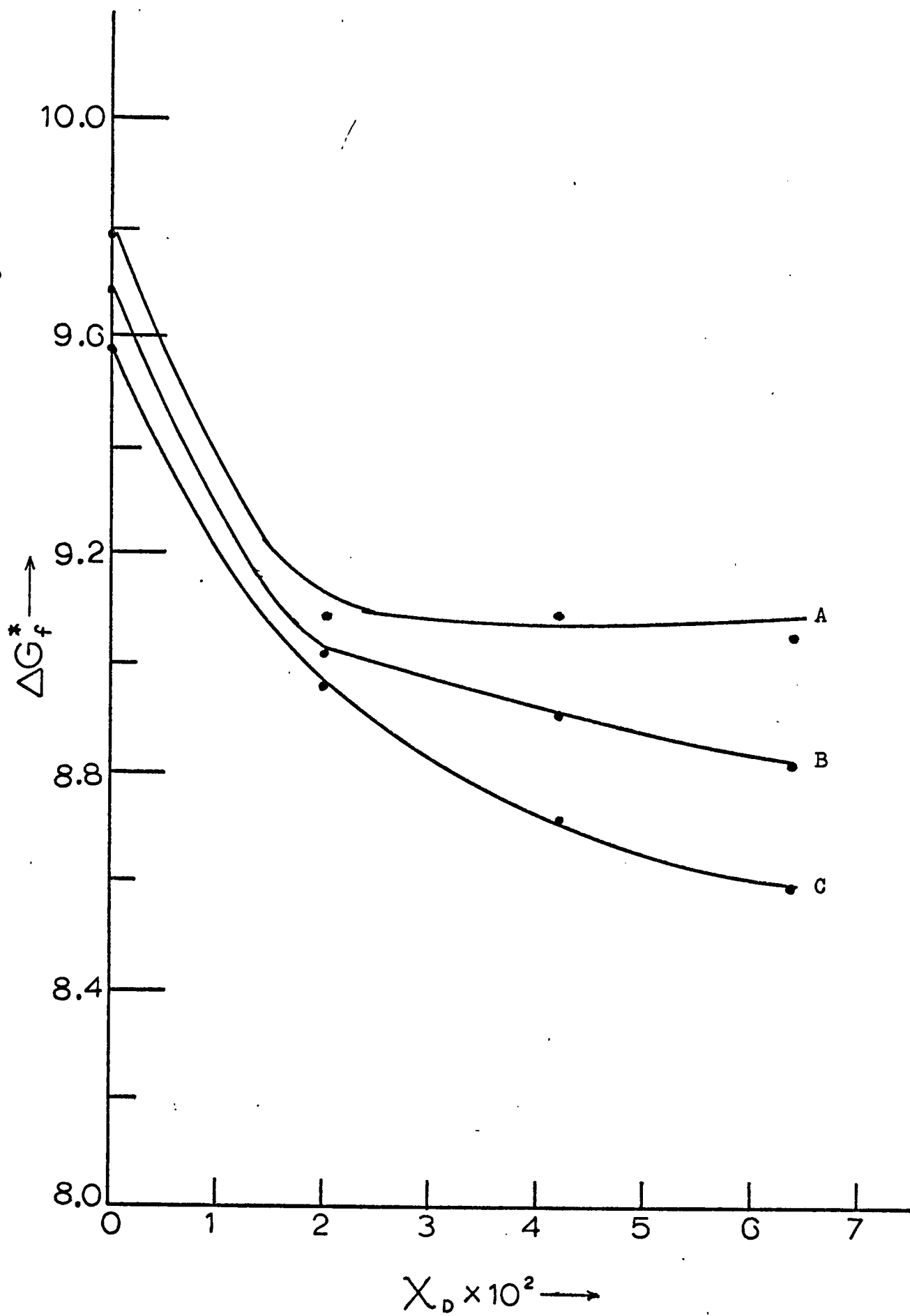
FIGURE 28

FREE ENERGIES OF ACTIVATION ( $\Delta G_f^*$ , KCAL MOLE<sup>-1</sup> )  
FOR THE NICKEL(II) MALONATE SYSTEM AS A  
FUNCTION OF MOLE FRACTION DIOXANE AND TEMPERATURE,  $\mu \rightarrow 0$

$$A = 15^{\circ}\text{C}$$

$$B = 25^{\circ}\text{C}$$

$$C = 35^{\circ}\text{C}$$



$$\Delta H_{34}^* = \Delta H_f^* - \Delta H_o \quad (IV-22)$$

The other activation parameters for the rate determining step were obtained using the following equations:

$$\Delta S_{34}^* = \Delta S_f^* - \Delta S_o \quad (IV-23)$$

$$\Delta G_{34}^* = \Delta H_{34}^* - T\Delta S_{34}^* (10^{-3}) \quad (IV-24)$$

The results of the calculations are given in Tables XXXVIII-XL and the variations as a function of solvent composition are shown in Figures 29-31.

It has been recognized for a number of years (47,48,49) that the reaction medium has a tremendous effect on reaction parameters such as reaction rates and equilibria. In order to obtain a real understanding of reactions in solution, it is necessary to understand the role of the medium surrounding the reacting molecules in the reaction. A considerable amount of information concerning the role of the medium can be obtained if it is known how the energies of molecules, ions, and transition states change as a function of solvent composition.

It is accepted by most workers in solution chemistry that water has a three demensional ice-like structure. The addition of a non-aqueous co-solvent to water might be expected to disrupt the very ordered structure of water. This breaking down of the water structure would be expected to start at the

TABLE XXXVIII

ENTHALPIES OF ACTIVATION OF THE RATE DETERMINING STEP  
 (  $\Delta H_{34}^*$ , KCAL MOLE<sup>-1</sup> ) FOR THE NICKEL(II) MALONATE SYSTEM  
 AS A FUNCTION OF MOLE FRACTION DIOXANE AND TEMPERATURE,  $\mu \rightarrow 0$

| Mole Fraction<br>Dioxane | 15°C | 25°C | 35°C |
|--------------------------|------|------|------|
| 0.000                    | 11.8 | 11.8 | 11.8 |
| 0.020                    | 10.1 | 10.1 | 10.1 |
| 0.042                    | 14.1 | 14.1 | 14.1 |
| 0.064                    | 15.8 | 15.8 | 15.9 |

$$\Delta H_{34}^* = \pm 3\%$$

## FIGURE 29

ENTHALPIES OF ACTIVATION OF THE RATE DETERMINING STEP  
(  $\Delta H_{34}^*$ , KCAL MOLE<sup>-1</sup> ) FOR THE NICKEL(II) MALONATE SYSTEM  
AS A FUNCTION OF MOLE FRACTION DIOXANE  
TEMPERATURE = 25°C,  $\mu \rightarrow 0$

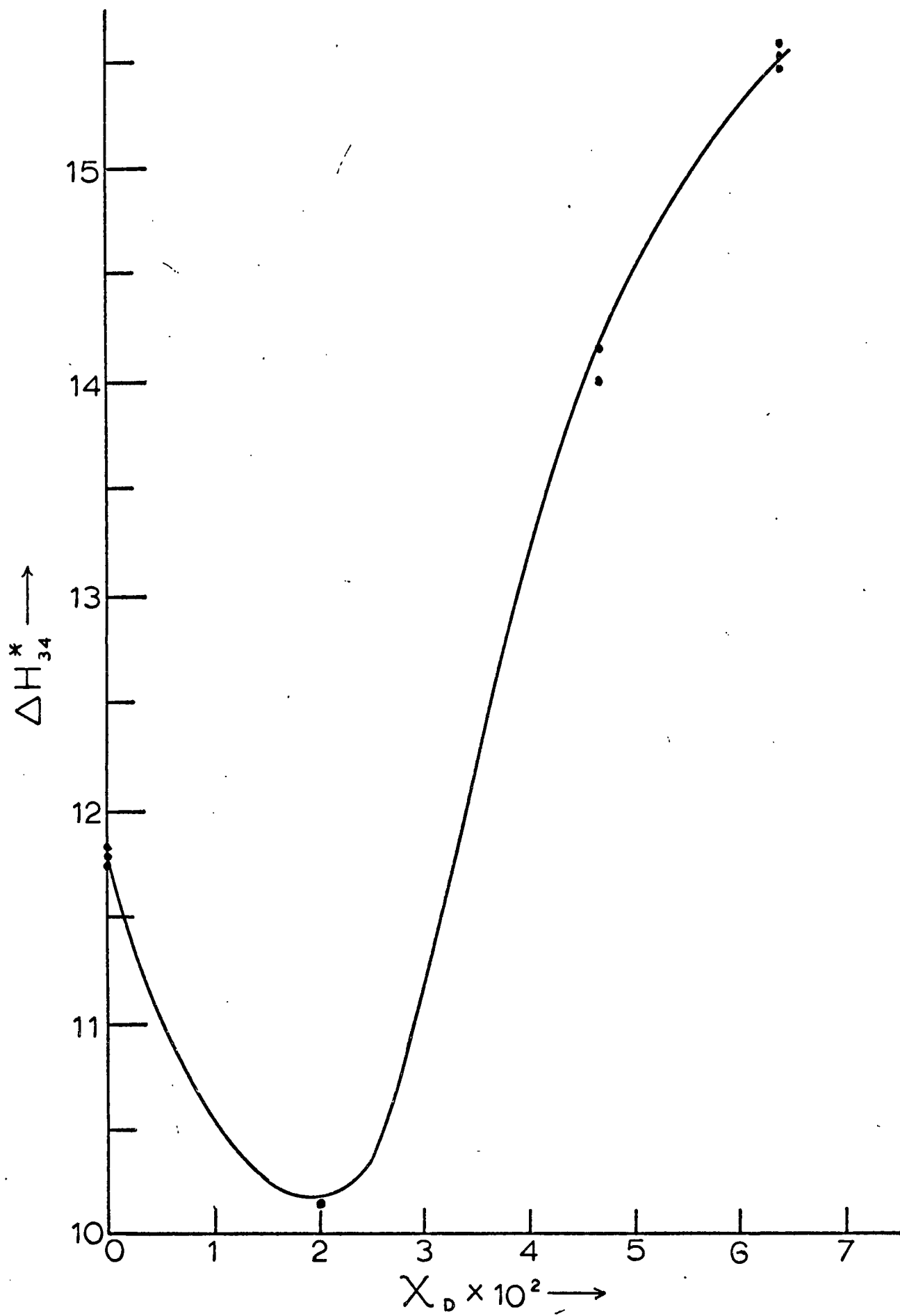


TABLE XXXIX

ENTROPIES OF ACTIVATION OF THE RATE DETERMINING STEP  
 (  $T\Delta S_{34}^*$ , KCAL MOLE<sup>-1</sup> ) FOR THE NICKEL(II) MALONATE SYSTEM  
 AS A FUNCTION OF MOLE FRACTION DIOXANE AND TEMPERATURE,  $\mu \rightarrow 0$

| Mole Fraction<br>Dioxane | 15°C  | 25°C  | 35°C  |
|--------------------------|-------|-------|-------|
| 0.000                    | -1.18 | -1.25 | -1.31 |
| 0.020                    | -2.53 | -2.64 | -2.74 |
| 0.042                    | +1.01 | +1.03 | +1.04 |
| 0.064                    | +2.30 | +2.36 | +2.42 |

$$T\Delta S_{34}^* = \pm 3\%$$

## FIGURE 30

ENTROPIES OF ACTIVATION OF THE RATE DETERMINING STEP  
(  $T\Delta S_{34}^*$ , KCAL MOLE<sup>-1</sup> ) FOR THE NICKEL(II) MALONATE SYSTEM  
AS A FUNCTION OF MOLE FRACTION DIOXANE  
TEMPERATURE = 25°C,  $\mu \rightarrow 0$

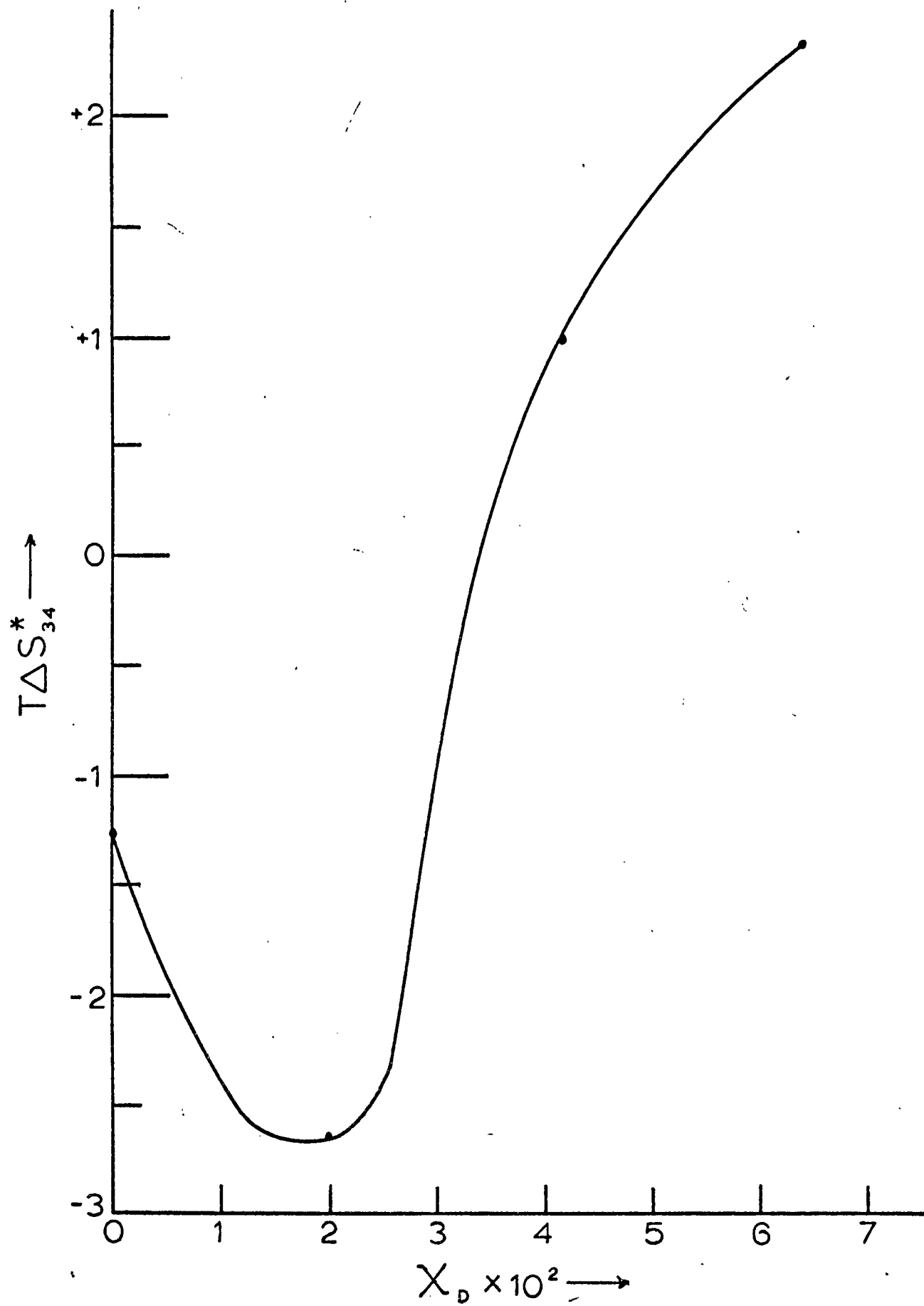


TABLE XL

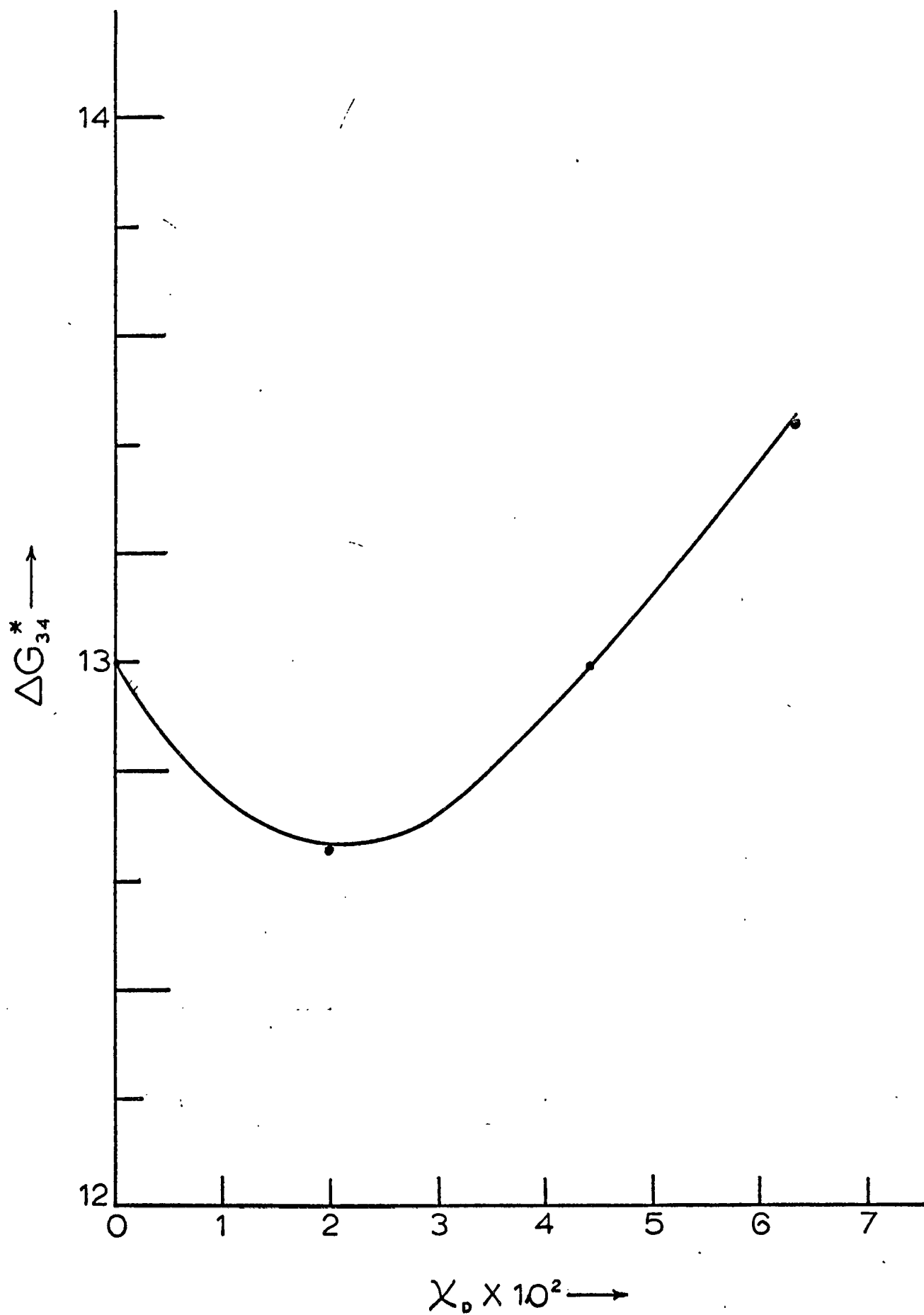
FREE ENERGIES OF ACTIVATION OF THE RATE DETERMINING STEP  
 (  $\Delta G_{34}^*$ , KCAL MOLE<sup>-1</sup> ) FOR THE NICKEL(II) MALONATE SYSTEM  
 AS A FUNCTION OF MOLE FRACTION DIOXANE AND TEMPERATURE,  $\mu \rightarrow 0$

| Mole Fraction<br>Dioxane | 15°C | 25°C | 35°C |
|--------------------------|------|------|------|
| 0.000                    | 13.0 | 13.0 | 13.1 |
| 0.020                    | 12.7 | 12.7 | 12.8 |
| 0.042                    | 13.0 | 13.1 | 13.1 |
| 0.064                    | 13.4 | 13.6 | 13.5 |

$$\Delta G_{34}^* = \pm 3\%$$

## FIGURE 31

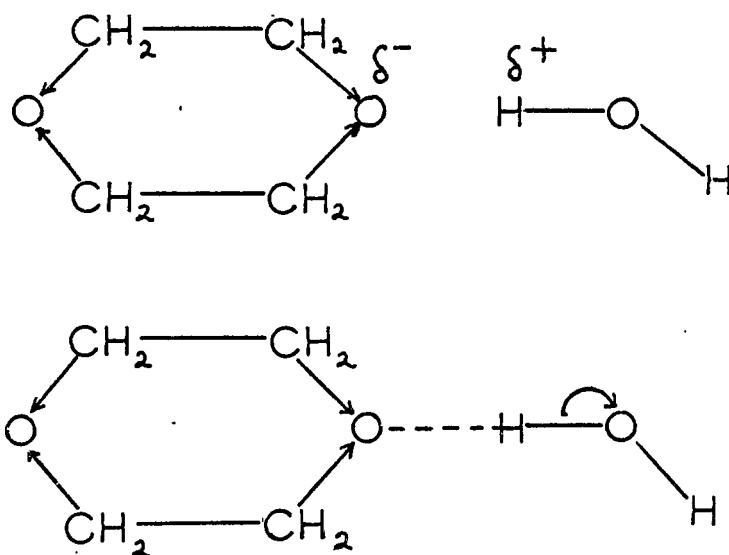
FREE ENERGIES OF ACTIVATION OF THE RATE DETERMINING STEP  
(  $\Delta G_{34}^*$ , KCAL MOLE<sup>-1</sup> ) FOR THE NICKEL(II) MALONATE SYSTEM  
AS A FUNCTION OF MOLE FRACTION DIOXANE  
TEMPERATURE = 25°C,  $\mu \rightarrow 0$



very beginning of the addition of the co-solvent. In an extensive review of aqueous mixed solvents, Franks (50,51) shows that initially a reduction in the structure of water is not observed upon the addition of the first increments of an organic co-solvent to water. Rather, an increase in the degree of order of the solvent system up to 10 mole-% organic co-solvent is observed. Beyond this composition, the highly ordered solvent structure begins to collapse and the system behaves like an ordinary binary solvent mixture. It has been argued (52) that in the region of inflection the co-solvent has exhausted the structure-making properties of water. Franks pointed out that when alcohols are the co-solvent there appears to be a great deal of long-range solvent structuring. However, the extent of long-range solvent structuring appears to decrease if the non-aqueous co-solvent contains two separated hydrogen bonded sites, such as in 1,4-dioxane. In the case of the 1,4-dioxane-water solvent system, there appear to be two distinct intermolecular hydrogen bonded complexes (53). It would appear that in contrast to alcohols, the dipolar nature of dioxane does not bring about an enhancement of long-range order in aqueous mixtures as well as hydrocarbon segments of a polar molecule (54). Conclusive proof that dioxane in dilute solutions of water does not interact strongly with water, i.e., does not form strong bonds with water molecules, was determined by Clemett (56) in a study of the spin-lattice relaxation time

of dioxane in water. This implies that the increased structure in water observed upon the addition of 1-10 mole per cents of dioxane is the result of enhanced hydrogen bonding between water molecules by dioxane.

Because of the inductive effect of the methylene groups in dioxane, the oxygen atoms have a higher charge density than the oxygen atoms in a water molecule. In other words, dioxane is more "basic" than water. It would then be expected that in a water-dioxane mixture the dioxane molecules would induce a charge displacement in a water molecule adjacent to it. This would result in the water molecules being more "basic" in a water-dioxane mixture as compared to pure water.



It would be expected that this effect would be felt over a large chain or group of water molecules. The result of the addition of the dioxane to water would be an enhancement of

the solvent structure by enlarging the water clusters. The results of Clemett (14) shows that in the 5-20 mole percent range the structure of the solvent mixture decreases. An explanation for this could be that at large mole percent of dioxane the competition between dioxane molecules for the water molecules results in a break down of the water-water and water-dioxane clusters.

Atkinson and Kor (8) observed by an ultrasonic technique that for mixed aqueous solvent systems containing up to 5 mole percent of dioxane there was a drastic increase in the forward rate constant for the three step association equilibrium between  $Mn^{2+}$  and  $SO_4^{=}$ . They did not attempt to explain the observed results, even though a number of treatments (47,48,49) have been developed from classical electrostatic equations for the behavior of ions or dipoles in continuous dielectric in an effort to describe the effect of changing medium on the rates of various kinds of reactions.

According to the three step association mechanism as described by Eigen (1), the rate determining step is the loss of a water molecule from the first coordination sphere of the metal ion. Considering the variation in the water-dioxane interaction, the rate of the associative reaction should increase with the addition of dioxane up to approximately 10 mole percent and then decrease as more dioxane is added. This

trend, if the idea presented concerning the structure making and breaking ability of dioxane is true, should also be reflected in the activation parameters for the associative reaction.

Over the past twenty years a great amount of energy and effort has been devoted by several groups to determine the effects of solvent variation on the activation parameters of a number of classical reactions. The results of Winstein and Fainburg (16) are a dramatic example of the effect of solvent change on  $\Delta H^*$  and  $\Delta S^*$  in highly aqueous media. Winstein and Fainburg (16) found extrema in  $\Delta H^*$  for the heats of solution between 0.75 and 0.95 mole fraction water in a large number of reactions in mixed aqueous solvent systems. The exact position and size of the minimum varies with the substrate, the organic co-solvent, and temperature. Caldin (11) found that the changes in the rate constants for the reaction of nickel(II) with 2,2'-bipyridyl in water-methanol mixtures are a resultant of much larger changes in the activation parameters  $\Delta H^*$  and  $\Delta S^*$ . Large compensating values of  $\Delta H^*$  and  $\Delta S^*$  are characteristic of reactions involving changes in solvation. Maxima or minima are commonly encountered when such reactions take place in water-organic solvent mixtures.

In order to attempt an explanation of the effect of the solvent on the mechanism for the three step association reaction as described by Eigen (1), it is necessary to give an

explanation to the effect of the solvent on the factors which determine the rate and the activation parameters of an associative reaction. According to Eigen's mechanism, the rate is independent of the ligand. This has been shown to be true in a majority of the fast reaction studies. Assuming this to be true, the contribution to the mechanism by the cation is of major importance. When a cation is added to a water solvent system, the cation will have a structuring effect upon the solvent molecules (57). Immediately around the ion the solvent molecules are oriented such that the negatively charged oxygen atoms are pointed toward the cation. Beyond the first coordination sphere, the charge from the metal ion is still strong enough to orient a sphere of solvent molecules a few molecules thick with the negative end of the dipole pointed toward the ion. This region of oriented solvent molecules is called the secondary solvation sphere. In this region the cation can only "see" a structureless dipole. In a water-dioxane solvent system it has been shown by preferential solvation studies in mixed solvents using nmr methods (58) that nickel(II) and cobalt(II) do not have any dioxane molecules in the coordination sphere; however, dioxane molecules may or may not be in the secondary solvation sphere. The presence of dioxane in the secondary solvation sphere or in the proximity of the secondary solvation sphere could cause the secondary solvation sphere to be more ordered as a result of intermolecular

hydrogen bonded water molecules. This ordering of water molecules by intermolecular hydrogen bonding has been shown by Clemett (55) to increase up to  $\leq 10$  mole percent of dioxane and then decrease upon addition of more dioxane. Since the secondary solvation sphere is only a few water molecules thick at most, the water molecules in the coordination sphere would feel, to a small extent, the effect of the hydrogen bonding in the secondary solvation sphere. Up to approximately 10 mole percent dioxane, this interaction would result in a weakening of the interaction between the metal ion and the water molecules in the primary coordination sphere. This weakened interaction would result in less energy being required to remove a water molecule from the primary coordination sphere, in other words, a decrease in  $\Delta H_{34}^*$ . When the mole percent dioxane exceeds 10 mole percent, the hydrogen bonded water system is broken down and the decreased interaction in the bulk solvent would cause the value of  $\Delta H_{34}^*$  to increase (see Figure 29).

The same type of trend as observed by Atkinson and Kor (8) is observed for the three step association of nickel(II) malonate in water-rich water-dioxane solvent systems. The thermodynamic and kinetic data obtained in this study are given in Tables XII-XIV, XXVIII, XXIX, XXXII-XXXIX. These data are shown as a function of solvent composition in Figures 17-19, 23-31. As can be seen from the Figures, there are

extrema in each of the parameters in the water-rich region. Considering the sharp trough in the activation parameters in the neighborhood of 0.02-0.042 mole fraction dioxane, this suggests some special type of interaction between the transition state and the two components of the medium. The works of Robertson, Hyne, and Tommila (59-65) shows that a number of reactions with different transition states show behavior similar to the ones observed in this study.

From Table XXXII it can be seen that the contribution of  $\Delta H_o$  to the total  $\Delta H_f^*$  is very small; therefore,  $\Delta H_{34}^*$  is the most important enthalpy factor to be considered. Using the same argument,  $T\Delta S_{34}^*$  is the most important entropy factor to be considered. The trend observed in  $k_{34}$  is then easily interpreted as being a result of the variation in  $\Delta H_{34}^*$  and  $T\Delta S_{34}^*$  from 0.0 to 0.02 mole fraction dioxane. Results show that  $T\Delta S_{34}^*$  and  $\Delta H_{34}^*$  are negative in value. Above 0.02 mole fraction dioxane both parameters begin a positive trend and finally become positive in value.

The magnitude and sign of the enthalpy of activation for the rate determining step,  $\Delta H_{34}^*$ , is a measure of the amount of energy needed to remove a water molecule from the primary coordination sphere. If it is assumed that the mechanism is a  $S_N1$  process, the magnitude and sign of  $\Delta H_{34}^*$  will not be affected by the ligand. Therefore, any variation in  $\Delta H_{34}^*$  is a result of some type of solvent effect. One possible

explanation for the observed trend in  $\Delta H_{34}^*$  is the structure promotion and breaking ability of dioxane in water-rich media as explained previously.

The variation in  $\Delta H_{34}^*$  does not clarify the question as to whether or not the mechanism which is being observed is  $S_N1$  or  $S_N2$  or some mechanism between the two. Comparing  $\Delta H_{34}^*$  for the  $S_N2$  and  $S_N1$  mechanism,  $\Delta H_{34}^*$  for the  $S_N2$  mechanism should be smaller. The smaller  $\Delta H_{34}^*$  for a  $S_N2$  mechanism would result from a partial neutralization of the nickel(II) effective charge by the incoming ligand. This would make the removal of the inner sphere water molecule easier.

The variation in  $T\Delta S_{34}^*$  gives some insight into the answer to the question. The variation of  $T\Delta S_{34}^*$  as a function of solvent composition is given in Table 31. If the mechanism is  $S_N1$ , in every solvent composition there would be a  $-T\Delta S_{34}^*$  contribution in going from  $Ni(H_2O)_6^{2+}$  to  $Ni(H_2O)_5^{2+}$ . The  $-T\Delta S_{34}^*$  would result from the increased effective charge of  $Ni(H_2O)_5^{2+}$  as compared to  $Ni(H_2O)_6^{2+}$ . The increase in effective charge on nickel(II) would result in more arrangement and enlargement of the secondary solvation sphere. Any variation in  $-T\Delta S_{34}^*$  would have to come from some source other than the desolvation of  $Ni(H_2O)_6^{2+}$ . It has already been pointed out that as small mole percents of dioxane are added to water there is an initial structuring effect by dioxane which results

from the promotion of intermolecular hydrogen bonding between the water molecules. Therefore, upon the addition of small mole fractions of dioxane there is a  $-T\Delta S$  contribution to the system which would be followed by a  $+T\Delta S$  contribution as more and more dioxane is added. It is reasonable to think that the addition of one more water molecule to the secondary or bulk solvent would not contribute very much of a  $+T\Delta S$  effect upon the system. Considering these facts, it would be reasonable to think that the  $T\Delta S_{34}^*$  values would be relatively small and would vary as the structuredness of the solvent system varies.

If the mechanism is a  $S_N2$  type of mechanism you would expect the  $T\Delta S_{34}^*$  values to follow a trend set by  $\Delta H_{34}^*$  for the system. Since the trend of  $\Delta H_{34}^*$  represents the trend of the solvation of the metal ion, it also represents the effective positive charge of the metal ion. With the change in the effective charge of the metal ion, there would be a corresponding change in the attraction between the cation and the ligand which would result in a  $T\Delta S_{34}^*$  contribution to the system exactly opposite to that set by  $\Delta H_{34}^*$ . Since it is observed that the trend of  $\Delta H_{34}^*$  and  $T\Delta S_{34}^*$  are identical, this indicates that the mechanism of the three step association process as proposed by Eigen (1) is truly  $S_N1$  in nature.

Upon examination of the information obtained, the following are generalities which seem to hold for the system

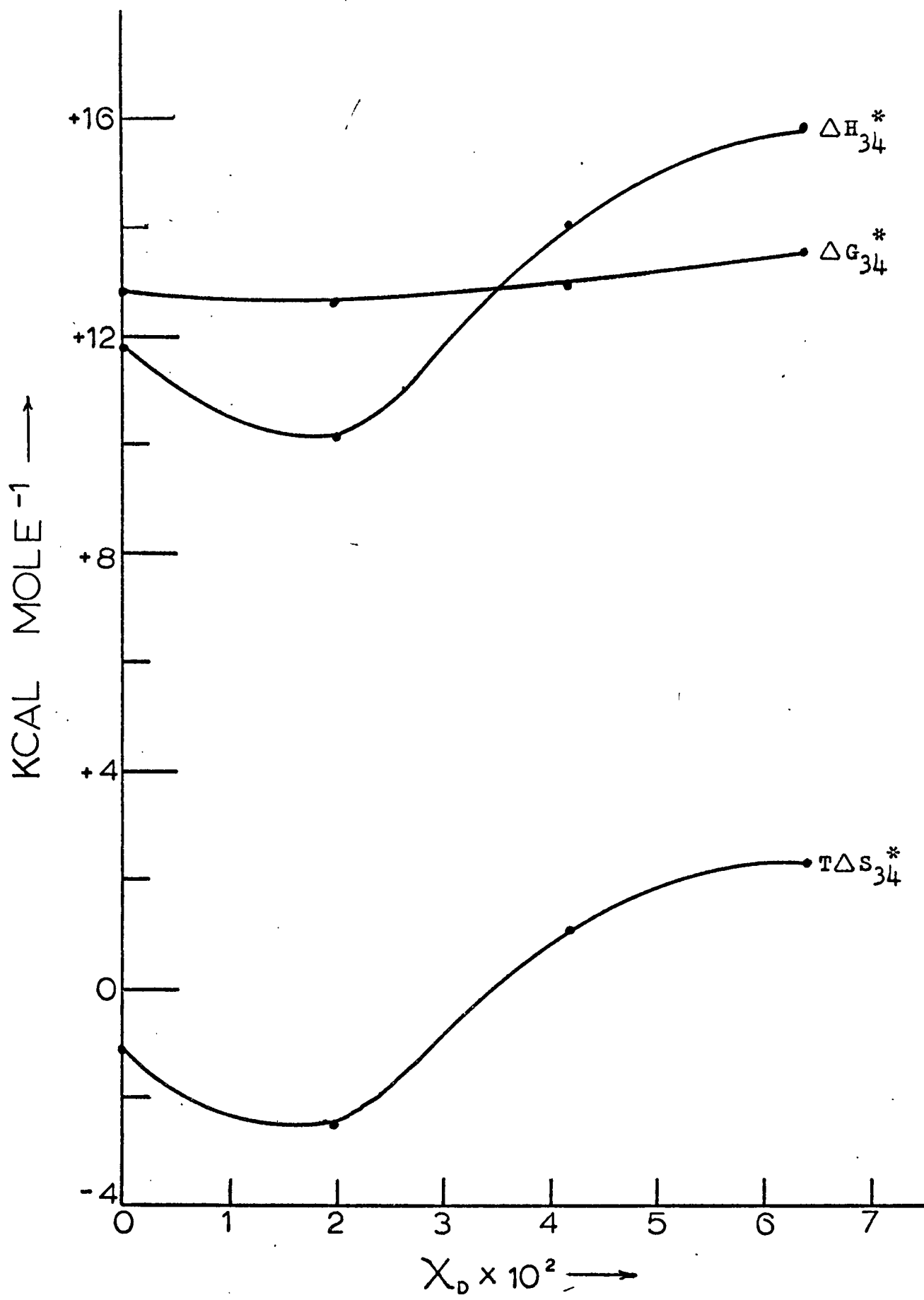
studied: (a) Enthalpies and entropies of activation show extrema in highly aqueous binary solvents which result in extrema in the observed rate constants; (b) A number of physical properties show changes indicating that the solvent goes through a maximum degree of structuredness in the same region where enthalpies and entropies of activation give extrema; (c) Free energies of activation do not reflect the sudden variations described above (see Figure 32) since  $\Delta H^*$  and  $T\Delta S^*$  are related to  $\Delta G^*$  as derivatives and would be expected to show sharper fluctuations.

The parameter variations observed for the nickel(II) malonate system in aqueous dioxane solvents follow the pattern suggested by Franks and Evans' theory (57). - reaction parameters are strongly influenced by solvent structure. Hydrogen bonding being mainly responsible for the increased structuredness within a mixed aqueous solvent system. It appears, however, that only a small amount of "extra structure" is gained by addition of the organic co-solvent. This is reflected in the small but distinct variation in the activation parameters. The microscopic act which could account for the observed variations is probably akin to building clathrate cages (12, 66) around the organic co-solvent.

From the observations made in this study, it appears that the mechanism for the associative process as proposed by Eigen (1) is correct in mixed aqueous solvents for charged

FIGURE 32

COMPARISON OF  $\Delta H_{34}^*$ ,  $T\Delta S_{34}^*$ , AND  $\Delta G_{34}^*$  AT 25°C  
AS A FUNCTION OF SOLVENT COMPOSITION



cations and ligands. There is some question (67) as to whether or not this mechanism for the substitution of a ligand at a solvated metal ion is valid for a neutral ligand. It is evident that much more research is needed to find out the role of mixed aqueous solvents on reaction mechanisms.

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