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A Spectrophotometric study on neodymium nitrate complexation in aqueous methanol

Sabariah Ismail
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in aqueous methanol**

Ismail, Sabariah, M.S.

San Jose State University, 1989

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**A SPECTROPHOTOMETRIC STUDY ON NEODYMIUM NITRATE
COMPLEXATION IN AQUEOUS METHANOL**

**A Thesis
Presented To
The faculty of the Department of Chemistry
San Jose State University**

**In Partial Fulfillment
of the Requirements for the Degree
Master of Science**

**by
Sabariah Ismail
August, 1989**

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ABSTRACT

A SPECTROPHOTOMETRIC STUDY ON NEODYMIUM NITRATE COMPLEXATION IN AQUEOUS METHANOL

by Sabariah Ismail

An investigation of the complexation reactions between neodymium(III) and nitrate ions in aqueous methanol was carried out using visible spectroscopy. Successive complexation occurs as :

where $n = 1$ or 2 depending upon conditions. Only the mono-complex exists above X (water mole fraction) $= 0.36$, below that the bis-complex forms. The equilibrium constants were determined for each of the complexes formed at $15, 20, 25$ and 37°C at an ionic strength of 3.0 and at varying water mole fractions. Using these values, the thermodynamic parameters, the enthalpy and entropy of the complexation reactions were calculated. The enthalpy and entropy are positive for the formation of the mono-complex; the reverse is true for the formation of the bis-complex. Using Choppin's arguments, the mono-complex is predominantly inner sphere and the bis-complexes are predominantly outer-sphere.

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1. INTRODUCTION

In aqueous solution the tripositive lanthanide ions show strong hydrolysis with a definite decrease in the pH value when the salts of these elements are dissolved in water.¹ Formation of aquo complex $[\text{Ln}(\text{OH}_2)_n]^{3+}$ where n is larger than 6, maybe 8 or 9 occurs.¹

This aquo complex with the "cloud of water molecules"¹ surrounding the central ion has a definite structure. The "cloud" or the hydration shell has its own geometry which separates it from the rest of the water; only ligands with strong structure-breaking influence can break into it.¹

Various methods have been applied to examine the structure and stability of lanthanide complexes in solution. Among the many methods, spectrophotocchemical methods have been most frequently employed. These methods are based on the change in the intensity or shape of the absorption bands when the water in the hydration shell of the lanthanide ion is replaced by other ligands.²

The bands which occurred due to the low-lying 4f orbitals are few, sharp, and highly characteristic.³ This is due to electronic transitions (Laporte forbidden) within the f^n configuration.⁴ It was postulated that the bands' intensity and shape would not be affected by ions complexing with the absorbing lanthanide ions since it was expected that only the outer (5d, 6s) valence shells would be influenced by such association.⁴ However, it is not so. The absorption spectra observed in simple aqueous solutions do change either in intensity or shape due to the formation of a complex.⁴ In this

spectrophotometric study, a small change in the intensity of the absorption band is observed when the neodymium ion complexes with the nitrate anions. However, the change is sufficient for studying the changes in the near environment of the ions.⁵

Several factors influence the formation of the lanthanide complexes. The nature of the lanthanide and the ligand are undoubtedly two of the most important ones, but the environmental factors like the temperature, and solvent are also significant.¹ It is therefore of interest to see how solvent and temperature affect the interaction between the lanthanides and the ligands.

Studies on the effects of other organic solvents on the complexation of the lanthanide ions were first initiated by Freed⁶ who had used spectroscopic methods to study the symmetry of lanthanide ions in solution, especially that around Eu(III) ions in ethanol and water. He found that the structures of the europium salts in ethanol are different from those in water. In recent years, there has been an emergence of various spectrophotometric techniques to investigate the complexation reactions. One of them is by Hamze and co-workers⁷ who have utilized a spectrophotometric method for the investigation of lanthanide halides in methanolic solutions to determine the effects of the solvent and solvation on the stability, electronic spectra, and structures of individual lanthanide complexes. Several thousand experimental optical density data covering all absorption ranges in the UV, visible and near IR were numerically treated. From this data, they discovered that the presence of water in the mixed methanol-water solvents leads to a decrease in the number and stabilities of the

lanthanide chloro-complexes.

Silber and co-workers have studied the effects of methanol on the complexation of lanthanide nitrates using visible spectroscopy.^{8,9} These studies show that the equilibrium properties of the lanthanide salts are different in different solvent compositions. Silber and Strozier⁷ found that with Eu^{3+} and NO_3^- , both mono and bis-complexes are formed in water, but when methanol is added, the tris-complex also formed. With Er^{3+} and NO_3^- , only the mono-complex is formed in water. When methanol is added, from 20% methanol and up to 80% methanol, the bis-complexes are formed. Above 80% methanol or below X (water mole fraction) = 0.40 the tris-complexes are formed.⁸ Preliminary work with Nd^{3+} and NO_3^- in water indicated that only the mono-complex exists with $K_1 = 0.9$ at 25°C .¹⁰ It is therefore of interest to investigate the Nd(III) system in aqueous methanol so that the effects of methanol on the complexation reactions can be evaluated.

Besides visible spectroscopy, Silber et al. have applied the ultrasonic relaxation technique as a spectroscopic and kinetic probe to examine the complexation of lanthanide nitrates in aqueous solutions.¹¹ The use of this as a kinetic technique permits the separation of outer and inner sphere contributions, since lanthanide complexation follows a modified Eigen complexation mechanism.¹²

where $M^{m+}(S)$ and $L^{n-}(S)$ represent solvated metal and ligand; $M^{m+}(S)_y L^{n-}$ is an outer sphere solvent separated ion-pair, and $ML^{m-n}(S)$ is an inner sphere or contact ion pair formed by cation solvent loss combined with cation ligand bond formation.¹¹

Ultrasonic absorption measurements in water and aqueous organic solvents can differentiate between the two types of complexes, because step 12 is faster (occurs at higher frequency) than step III. If there are no inner sphere complexes in lanthanide systems, a small difference in sound absorption, α/f^2 (where f is the frequency) is observed between the salt solution and the solvent. When inner sphere complexes exist, a large difference is seen in the sound absorption between the test solution and the solvent. From the variation of absorption with frequency, it is usually possible to separate the data into both inner and outer sphere contributions.

Ultrasonic absorption measurements on 0.200 M $Nd(NO_3)_3$ solutions had been conducted in water and 50% methanol and the results were interpreted in terms of two forms of inner-sphere complexes which differ in solvation number.¹³ Since the ultrasound technique is unable to characterize the species in equilibrium, the present spectrophotometric study is necessary to better understand the system.

There have been several other spectrophotometric studies of the lanthanide nitrates in aqueous solutions. Using a differential spectrophotometric technique, Anagnostopoulos and Sakellaridis¹⁴ have studied these systems: $Pr^{3+} - NO_3^-$, $Sm^{3+} - NO_3^-$ and $Er^{3+} - NO_3^-$ in aqueous solutions. They found that $PrNO_3^{2+}$, $SmNO_3^{2+}$

and ErNO_3^{2+} are the only complexes formed with absorption maxima at 444.2 nm, 403.8 nm and 378.0 nm, respectively.

In an attempt to unravel any possible systematic effects connected with inner- and outer sphere complex formation, the "hypersensitive" transition in $\text{Nd}^{3+}(\text{aq})$ for $\text{Nd}(\text{NO}_3)_3$, NdCl_3 and $\text{Nd}(\text{ClO}_4)_3$ has been studied by Choppin, Henrie and Buijs¹⁵. By comparing the absorption spectra of the lanthanide ions with various ligands, it is found that in the case of the nitrates, the shape of the band is completely different. They explained that this is due to a small concentration of the inner-sphere neodymium nitrate complex in equilibrium with a much larger concentration of the outer sphere complex. They also suggested that covalent effects are important for lanthanide complexes, since the ligands within each group share certain chemical and physical characteristics. Formation of covalent bonds between NO_3^- and Ln^{3+} ions has also been discovered by Katzin¹⁶ who has investigated the spectra of $\text{Pr}(\text{NO}_3)_3$, $\text{Nd}(\text{NO}_3)_3$ and $\text{Er}(\text{NO}_3)_3$ solutions in tri-n-butylphosphate.

Abrahamer and Marcus⁵ suggested that depending on the solvent and on the concentrations, both inner- and outer sphere nitrate complexes of the lanthanides are indeed formed in solution. From studies of the density and molar absorptivity of erbium nitrate solutions and the chemical shift of ^{17}O -enriched water in the presence of Er and LiNO_3^- , $\text{Er}(\text{III})$ was found to form inner sphere complexes with the nitrate ions. They deduced from the data that the nitrate ligand replaced water in the inner coordination sphere (hydration shell) of the $\text{Er}(\text{III})$ ion. Since the average ligand number in

the inner sphere is lower than the total ligand number, they proposed that some outer-sphere coordination also occurs for all the lanthanides in nitrate solutions.

Coward and Kiser¹⁷ have previously studied the complexation of Nd^{3+} and NO_3^- ions in aqueous solutions using a differential spectrophotometric technique. Their results at 579 nm indicate that $\text{Nd}(\text{NO}_3)_2^{2+}$ is the only important absorbing species other than $\text{Nd}^{3+}(\text{aq})$ with an equilibrium constant of 0.77 at an ionic strength of 4.2. Foos, Kertes and Peleg have recorded the absorption spectra of neodymium in $\text{LiNO}_3\text{-KNO}_3$ eutectic and its mixtures with water or chloride ions in the temperature range between 80 – 350 °C.¹⁸ They discovered that the molar absorptivities of some of the bands are sensitive to the environment.

Barinow and Tebieliew¹⁹ have studied the influence of HNO_3 concentration and some of its salts on the absorption spectrum of 0.05 M $\text{Nd}(\text{NO}_3)_3$ in water and found that both the mono and the bis-complexes are formed. Recently, Majdan and Sadowski² have investigated the visible absorption of $\text{Nd}(\text{NO}_3)_3$ in a 90:10 methanol-water mixture. They found the equilibrium constants to be $K_1 = 3.6$ and $K_2 = 1.0$ for $\text{Nd}(\text{MeOH})_x\text{NO}_3^{2+}$ and $\text{Nd}(\text{MeOH})_x(\text{NO}_3)_2^+$. Using the stepwise equilibrium constants ratio as the basis for analysis, they found that these are inner sphere complexes. Although this study is similar to our work, the method that we proposed to use to calculate the equilibrium constants is quite different.

In our study, the program developed by Gaizer was used to calculate the log of the equilibrium constants (log beta's). Recently,

this program was modified and re-written in QBASIC which makes the calculation much faster. The existence of one or more complexes of the type M_pL_q with β defined as:

$$\beta = [M_pL_q] / [M]^p[L]^q \quad (2)$$

is assumed in the Gaizer program. At each wavelength, Beer's Law is presumed to be valid, and that the deviation from Beer's Law is due to the formation of at least one complex. Therefore, the absorbance A is equal to the sums of the absorbances of each species, given by :

$$A = A_M + A_L + \sum_1^{p,q} A_{M_pL_q} \quad (3)$$

If quartz cells with one cm pathlength are used in the spectral measurements; absorbance in the 1 cm cells becomes

$$A = \epsilon_M[M] + \epsilon_L[L] + \sum_1^{p,q} \epsilon_{M_pL_q}[M_pL_q] \quad (4)$$

To use this program, the following data need to be entered; the total metal concentration $[M]$, the total ligand concentration $[L]$, the number of wavelengths used, and the absorbance of each solution at each wavelength, the number of complexes and first estimates of the logarithms of the overall complexation constant (β) and the molar extinction coefficients (ϵ). Initially, the program utilizes the first estimates at each wavelength independently to come up with the best set of molar extinction coefficients. It then uses the set of molar extinction coefficients and the concentrations of the free and complexed species to calculate the absorbances. Then, it applies the calculated data at all of the wavelengths to find the best equilibrium

constants. The final values beginning with the inputs are then printed along with the square of the differences between the measured and the calculated absorbances (square of the residuals (U)). A new set of equilibrium constants is then entered and the process is repeated until a minimum value is found in the square of the residuals. This minimum value is found by plotting the log of equilibrium constants (log beta's) versus the square of the residuals. Theoretically, the result would be a V shaped curve, but in practice, a U shaped curve is obtained. The best value of log beta is the minimum on the curve.

The $\ln \beta$, is related to the change in free energy (ΔG^0) for the overall complexation process as

$$\Delta G^0 = -RT \ln \beta_n \quad (5)$$

where β_n is the overall complexation constant. $\beta_n = K_1 K_2 \dots K_n$, based on the following definitions for K (the stepwise equilibrium constant) and β :

β_1 is similar since

but K_n and β_n differ because

whereas

From these equations it is clear that $\beta_n = K_1 K_2 \dots K_n$.

Since the Gaizer program calculates the results in terms of β_n , the results are first separated into K_n , the successive equilibrium constants. By determining each of these individual equilibrium

constants (K) as a function of temperature, it is possible to calculate ΔH^0 (the enthalpy of complexation) and ΔS^0 (the entropy of complexation) since :

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (10)$$

Combination of equation (10) with equation (5) gives equation (11)

$$\ln K = - \Delta H^0/RT + \Delta S^0/R \quad (11)$$

Thus, a plot of $\ln K$ vs. $1/T$ would give a slope which is equal to $-\Delta H^0/R$ and an intercept equals to $\Delta S^0/R$.

To summarize, a study on the complexation reactions of $\text{Nd}^{3+}(\text{aq})$ with $\text{NO}_3^-(\text{aq})$ in aqueous methanol will be carried out as a function of solvent composition and temperature. The equilibrium constants (K) obtained from this study will then be used to determine the enthalpy and the entropy of complexation.

2. EXPERIMENTAL

The neodymium perchlorate and the neodymium nitrate stock solutions were made from the dried anhydrous oxide (Nd_2O_3) obtained from Molycorp Inc., by adding in the appropriate inorganic acids. Distilled water was mixed in before dropping in the acid. While adding the acid, the mixture was also gently heated so as to hasten the reaction. The stock solutions were made either in water, or in methanol (E.M. Science), depending upon the kind of solvent composition needed. The high water mole fraction stock solutions were made in water, and methanol was subsequently added. The low water mole fraction stock solutions were made in methanol, and water is added later by volume into the working solutions. The water in the methanolic stock was removed at low pressure and 60°C several times using the Buchi 011 Rotavapor after first removing the methanol and the methanol-water mixture. Methanol was then added to the anhydrous mixture in order to make the methanolic stock. The water content was determined by Karl Fischer automatic titrations utilizing a Metrohm Automat E547 with an electronic buret. The sodium perchlorate stock solution was made by reacting sodium bicarbonate with concentrated perchloric acid :

Working solutions were prepared by diluting the stock in 10 ml volumetric flasks. A buret was used to add the stock solution into the flasks. Sodium nitrate was the source of the ligand and sodium

perchlorate was required to maintain the ionic strength at 3.0. For the low water mole fraction solutions, lithium nitrate (J. T. Baker Chemicals) and lithium perchlorate (Alfa Products, anhydrous 99.5 %) were used because they were more soluble than the sodium salts in this solvent. Even though Na^+ and Li^+ ions often cause different effects, the differences are negligible in this study because of the approximate similarity in the activity coefficient values. At an ionic strength of 0.1, the activity coefficient for Li^+ is 0.8 and for Na^+ it is 0.78.²¹ At higher ionic strength, the ions (Li^+ and Na^+) lose some of their effectiveness and their activity coefficients decrease. Therefore, by maintaining a high ionic strength, the differences in the activity coefficients are kept at a minimum value. It is also essential to keep the ionic strength constant, since at constant ionic strength the activity coefficients remain unchanged in the mass law equations.

A small computer program was written in BASIC in order to calculate the concentration of ClO_4^- required to keep the ionic strength at 3.0 for given concentrations of Nd^{3+} and NO_3^- ions. The formula for ionic strength is given by equation (13)

$$I = 1/2 (m_1 z_1^2 + m_2 z_2^2 + \dots) \quad (13)$$

where $m_1, m_2, \dots$ represent the molar concentrations of the various ions in the solution and z_1, z_2 are their respective charges.²¹

Assuming that only the mono-complex forms,

$$I = 3.0 = 1/2 \{ [\text{Nd}^{3+}]3^2 + [\text{NdNO}_3^{2+}]2^2 + [\text{Na}^+] + [\text{ClO}_4^-] + [\text{NO}_3^-] \} \quad (14)$$

$$3 = 1/2 \{ (a-x)9 + 4x + (c+b) + (b+3a) + (c-x) \}$$

$$b = 3 + 3x + -6a - c \quad (15)$$

where $a = [\text{Nd}(\text{ClO}_4)_3]$

$$b = [\text{NaClO}_4]_3$$

$$c = [\text{NaNO}_3]$$

$$x = [\text{NdNO}_3^{2+}] \text{ (the amount of mono-complex formed)}$$

then the complex formation is given by

The equilibrium constant is :

$$K_1 = [\text{NdNO}_3^{2+}] / [\text{Nd}^{3+}][\text{NO}_3^-] \quad (17)$$

which can be written as

$$K_1 = x / (a-x)(c-x) \quad (18)$$

In order to have a program that will calculate $[\text{NaClO}_4]$ in moles per liter with $[\text{Nd}(\text{ClO}_4)_3]$ and $[\text{NaNO}_3]$ as the inputs. For a 1:2 complex,

several modifications were made :

$$\text{free } [\text{Nd}^{3+}] = z = a - x - y \quad (19)$$

$$\text{free } [\text{NO}_3^-] = d = c - x - 2y \quad (20)$$

(16) then becomes

$$K_1 = x / (a-x-y)(c-x-2y) = x / [z][c] \quad (21)$$

$$K_2 = [\text{Nd}(\text{NO}_3)_2^+] / [\text{NdNO}_3^{2+}][\text{NO}_3^-] \quad (22)$$

$$\text{where } y = [\text{Nd}(\text{NO}_3)_2^+] \text{ (the amount of bis-complexes formed)}$$

$$\text{thus, } K_2 = y / (x)(c-x-2y) = y / [x][c] \quad (23)$$

Rearranging (18) gives

$$a = z + x + y \quad (24)$$

Combining these equations gives :

$$a = z + K_1[z][c] + K_2[c][x]$$

$$a = z + K_1[z][c] + K_1K_2[z][c]^2$$

$$a = z(1 + K_1[c] + K_1K_2[c]^2)$$

Therefore :

$$z = a / 1 + K_1[c] + K_1K_2[c]^2 \quad (25)$$

in which :

$$x = K_1(c)(z) = [\text{NdNO}_3^{2+}] \quad (26)$$

$$y = K_1K_2(z)(c)^2 = [\text{Nd}(\text{NO}_3)_2^+] \quad (27)$$

The new ionic strength equation is :

$$2I = 9(\text{Nd}^{3+}) + 4(\text{NdNO}_3^{2+}) + [\text{Nd}(\text{NO}_3)_2^+] + [\text{Li}^+] + [\text{ClO}_4^-] \\ + [\text{NO}_3^-]$$

$$6 = (9a - 9x - 9y) + 4x + y + c + b + (3a + b) + (c - x - 2y)$$

$$6 = 12a - 6x - 10y + 2c + 2b$$

$$3 = 6a - 3x - 5y + c + b$$

$$b = 3 - 6a + 3x + 5y + c \quad (28)$$

where free $[\text{ClO}_4^-] = 3a + c$, since $[\text{Nd}(\text{ClO}_4)_3] = a$, $[\text{LiNO}_3^-] = c$ and

free $[\text{Li}^+] = c + b$, where b is the amount of $[\text{LiClO}_4]$ that is needed.

Examples of the programs are given in Appendix C.

Absorbance measurements were made using the Gilford Model 2600 UV-VIS single beam spectrophotometer. The temperature was

regulated using the Gilford Thermoset which measures and reproduces the temperature to within 0.1°C . The spectrometer was also interfaced to an Apple III computer; this allowed the storage of both the digital and the graphical output. The cell compartment of the spectrometer can hold up to four quartz cells, thus permitting one reference solution and three sample solutions to be measured at one run. The Gilford was programmed to function in the difference spectral mode; it subtracts the reference solution from each sample solution. The reference solution is either water, methanol, or water mixed with methanol; the choice is based on the solvent system being studied.

In order to choose the most sensitive wavelengths for making the absorbance measurements, a solution of $\text{Nd}(\text{NO}_3)_3$ at 0.3 M was made, and its absorbance minus the absorbance of 0.3 M solution of $\text{Nd}(\text{ClO}_4)_3$ was measured from 340 nm to 700 nm. From this difference spectrum of absorbance versus wavelength, four peaks with the highest maximum absorbances were chosen: 346.7 nm, 354.7 nm, 522.1 nm and 575.8 nm (Fig. 1).

Then, plots of the absorbance versus the ratio of the concentration of perchlorate ions to the constant $\text{Nd}(\text{III})$ ions concentration were made at the four wavelengths (Figs. 2 and 3). All the plots show horizontal straight lines, indicating that there is no change in the absorption due to the perchlorate ions. This probably indicates the absence of measurable complexation between the neodymium and the perchlorate ions, since in the analogous $\text{Er}(\text{III})$ ion

Figure 1. Difference spectrum of absorbance vs. wavelength.

Figure 2. Absorbance vs. [perchlorate ions]/[neodymium (III) ions]
at 521.7 nm

Figure 3. Absorbance vs. [perchlorate ions]/[neodymium (III) ions]
at 575.3 nm

system, perchlorate ion does change the absorption due to the formation of a complex. Further confirmation is obtained from Beer's Law plots of $\text{Nd}(\text{ClO}_4)_3$; all the plots obey Beer's Law (Figs. 4, 5).

Several solutions of $\text{Nd}(\text{NO}_3)_3$ at various concentrations were then made and their absorbances were measured at these four wavelengths. Beer's Law plots were constructed at these four wavelengths; all four show deviations from the Beer's Law. In order to select the most sensitive wavelengths, absorbance measurements were made from 520.5 to 523.5 nm and from 573.5 to 583.5 nm. Two wavelengths with the highest absorption intensity were selected (Figs. 6, 7). The wavelengths are 521.7 and 575.3 nm, and so absorbance data for the mole ratio plots were taken at these wavelengths, and also at four other wavelengths slightly higher and lower than the absorbance maxima. The six wavelengths are 521.2, 521.7, 522.2, 574.8, 575.3, and 575.8 nm.

The solutions for the measurements at the six wavelengths had the same concentration of neodymium perchlorate, varying concentration of the ligand (NO_3^-), and calculated concentration of the perchlorate ions (using the ionic strength program). Mole ratio plots, which are plots of the absorbance vs. $[\text{NO}_3^-]/[\text{Nd(III)}]$, were then made in order to determine the number of complexes formed. The mole ratio plot (Fig. 8) shows the intersection of two straight lines. The point of intersection indicates the number of complexes formed. This information together with the absorption data, guessed log of equilibrium constants ($\log \beta$'s), the ϵ_M 's (extinction coefficients of

Figure 4. Beer's Law Plot for neodymium perchlorate at 521.7 nm

Figure 5. Beer's Law Plot of neodymium perchlorate at 575.3 nm.

Figure 6. Beer's Law Plot of neodymium (III) nitrate at 521.7 nm

Figure 7. Beer's Law Plot of neodymium (III) nitrate at 575.3 nm

Figure 8. Absorbance vs. $[Ligand]/[Nd(III)]$ for $X = 0.20$ at 25 C.

the metal), ϵ_{ML} 's (extinction coefficients of the complexes), and the ϵ_L 's (extinction coefficients of the ligands) were then entered into the Gaizer Multiple Wavelength Program. The ϵ_L 's are all equal to zero since there is no absorption from the ligand. The ϵ_M 's were determined from the slopes of the Beer's law plots in the region where no deviations from Beer's Law are found. The program then calculates the equilibrium constants and refines the extinction coefficients of the complexes; the extinction coefficients of the metals were fixed at the values obtained from the Beer's Law plots. The output of the program lists out the value of U which is the square of residuals. By plotting these values versus the refined $\log \beta$ values, a U-shaped curve is obtained. The best $\log \beta$ value is the minimum on the curve. Once the $\log \beta$'s were obtained, the next step was to plot the $\ln K$ (since $\beta_n = K_1 K_2 \dots K_n$) values versus $1/T$. Since $\Delta G^0 = \Delta H^0 - T\Delta S^0 = -RT \ln K$, we can divide both sides of the equations by RT , and get equation (11) below:

$$-\Delta H^0 / RT + \Delta S^0 / R = \ln K \quad (11)$$

The plot of $\ln K$ versus $1/T$ gives slope = $-\Delta H^0 / R$ and intercept = $\Delta S^0 / R$. Thus the enthalpy of complexation, ΔH^0 is equal to -slope multiplied by R and the entropy of complexation, ΔS^0 is equal to the intercept multiplied by R .

3. RESULTS AND DISCUSSION

in the aqueous system of Nd^{3+} , Na^+ or Li^+ , ClO_4^- and NO_3^- , it is important to consider the possibility of all the four different cation-anion interactions. This leads to the necessity of Beer's Law plots for $\text{Nd}(\text{ClO}_4)_3$. The plots at all the absorption peaks show a linear relationship between the absorbance and the concentration of the neodymium perchlorate. This is true in water and in water-methanol solutions in the absence of the nitrate ligand. An example of the plot is shown in Fig. 4. In Fig. 8, a plot of the absorbance as a function of the concentration ratio of $[\text{ClO}_4^-]/[\text{Nd}(\text{III})]$ at constant $[\text{Nd}(\text{III})]$ is shown for the data at 521.70 nm and at 25 °C and X (water mole fraction) = 0.20. The plot shows that there is no change in absorbance at constant $[\text{Nd}(\text{III})]$ with increasing $[\text{ClO}_4^-]$. Similar results were obtained at all the other five wavelengths used in this study at all solvent compositions and temperatures. There are two probable reasons for the results obtained. First, it could indicate that there is no complexation and second, it could mean that the peaks are not sensitive to complexation. However, when the absorbance is plotted against the $[\text{NO}_3^-]/[\text{Nd}(\text{III})]$ ratio under the same conditions as in the perchlorate system, deviation from a straight line occurs (Fig. 8). From this evidence, it is concluded that the perchlorate data indicates the absence of measurable complexation. This is also consistent with the results obtained by Coward and Kiser¹⁷; their

work shows that there is no association of the perchlorate anion with the neodymium cation. This behavior is similar to Eu(III) but different from Er(III) which forms complexes with the perchlorate anion in aqueous methanol.^{8, 22}

To determine the number of complexes formed between the Nd^{3+} and the NO_3^- ions, mole ratio plots were made. Lines in these plots were generated using a linear regression computer program which was able to calculate the lines of the best fit for a given mole ratio plot as well as the intersection point of those lines. The plots at both the 521.7 and 575.3 nm for all the water mole fractions at the four temperatures (15, 20, 25, and 37⁰ C) are included in (Appendix A), Figs. 24 to 47. The mole ratio plot for water shows that only the mono-complex forms.¹⁰ The trend continues down to $X = 0.36$ (80% methanol). At that water mole fraction and below, two complexes are formed (Figs. 36–39). Our results agree with those of Majdan's² who found two complexes at 90% methanol.

Ultrasonic measurements by Silber et al. on 0.200 M $\text{Nd}(\text{ClO}_4)_3$ as a function of water composition show that at least two relaxation processes exist.¹³ The two relaxations were correlated with the two reaction steps shown below, which are analogous to the results in water for the nitrates.

The relaxations in water and in 50% methanol are interpreted in terms of two forms of inner sphere complexes which differ in solvation number.¹³ Fig. 9 shows a plot of $\mu_{\max}$ (excess absorption maxima) vs. X (water mole fraction) for $\text{Er}(\text{NO}_3)_3$, $\text{Eu}(\text{NO}_3)_3$ and $\text{Nd}(\text{NO}_3)_3$ in aqueous methanol solutions. $\mu_{\max}$ is given by equation 29

$$\mu_{\max} = A f v / 2 \quad (29)$$

where A and f are the relaxation amplitude and the frequency, respectively, and v is the solution sound velocity. $\mu_{\max}$ is also proportional to the concentration of the reacting species times the reaction volume change squared. Therefore, $\mu_{\max}$ acts as a probe to detect coordination number changes in solution.²³ From the plot, it can be seen that $\mu_{\max}$ is higher for Eu(III) ions than for the corresponding Er(III) and Nd(III) salts. In addition, all three form measurable amounts of inner sphere complexes. In water, the amplitude of $\mu_{\max}$ corresponds to the relative values of the equilibrium constants which increase from Nd(III) to Er(III) to Eu(III). K_1 for $\text{Nd}(\text{NO}_3)_2^{2+} = 3.81$ and $K_1 = 8.6$ for $\text{Er}(\text{NO}_3)_2^{2+}$, $\text{Eu}(\text{NO}_3)_2^{2+}$ and $\text{Eu}(\text{NO}_3)_2^{+}$ exist with $K_1 = 5.7$, $K_2 = 1.8$ ($\beta_2 = 10.26$) at 25 °C and at an ionic strength of 3.0.^{10, 24, 8}

When methanol is added to aqueous solutions of all the three lanthanides, $\mu_{\max}$ increases until it reaches a maximum. Since the addition of methanol lowers the dielectric constant and increases

Figure 9. $\mu_{\max}$ vs. X (water mole fraction) for lanthanide nitrates.

complexation, the initial increase in $\mu_{\max}$ is expected.²³ It is believed that a coordination number change takes place as the solvent composition changes, judging from the existence of a maximum in each of these curves.²³ For Er(III) and Nd(III) the maximum occurs at $X = 0.4$; for Eu(III) ions the maximum takes place at $X = 0.6$. The equilibrium measurements for Eu(III) ions reveal that the mono, bis and tris complexes exist in aqueous methanol at $X = 0.87$ and below.⁸ This shows that the maximum at $X = 0.6$ is not an indication of a higher complex forming. For Er(III) ions only the mono and bis-complex exist above $X = 0.40$.⁹ Below $X = 0.40$, the tris-complex becomes stable for Er. Therefore, for Er(III) ions the maximum occurs in the region where a third nitrate adds and this is thought as the mechanism that induces a coordination number change.²³ The present work for Nd(III) ions shows that only the mono-complex exists above $X = 0.40$. Below $X = 0.40$, the bis complex also forms. Thus, the Nd(III) ions system is like the Er(III) ions system, the maximum at 0.4 reflects the formation of a higher complex, in this case the bis-complex.

Equilibrium constants for the formation of complexes in solution were determined using the modified Gaizer²⁰ program for multiple wavelengths. Tables 5-28 in Appendix B show the absorbance data for all the water mole fractions at the four temperatures which are used in the program for the determination of the equilibrium constants and the extinction coefficients of the mono-, and bis-complexes. The program was able to yield a good minimum in the square of the residuals in all cases of solvent

composition at each of the four temperatures. A plot of the square of the residuals versus log beta obtained from the refinement process of log betas used to calculate the equilibrium constants is shown in Fig. 10. The equilibrium constants and the extinction coefficients of both the aqueous metal ions and the complexes are listed in Tables 29 -34 in Appendix B.

There was an increase in the values of the extinction coefficient of the aqueous metal ions (ϵ_M) with increased concentration of methanol or decreased concentration of water in the medium. This is also observed in the study done by Abrahamer and Marcus⁵ on lanthanide nitrates in aqueous methanol. They conclude that the low dielectric constant of methanol produces a high local concentration of nitrate anions around the neodymium cation so that penetration into the first coordination sphere becomes more likely, and the lower basicity of methanol compared with water facilitates its replacement by the nitrate.⁵

Accordingly, there was an increase in the value of the equilibrium constants from the higher to the lower water mole fractions (X) for both complexes. The equilibrium constants, K_1 and K_2 , as a function of water mole fractions and temperature are shown in Table 1. A plot of K_1 vs. X at 25 °C is presented in Fig. 11. In Fig. 12, plots of K_1 vs. X for $\text{Er}(\text{NO}_3)_3$, $\text{Eu}(\text{NO}_3)_3$ and $\text{Nd}(\text{NO}_3)_3$ at 25 °C are shown. Similar plots for K_2 are shown in Figs.13-14. The increase in the values of the equilibrium constants as the water mole

Figure 10. U vs. $\log \beta$ for $X=0.90$ at 15°C

Table 1

Equilibrium constants of the complexes as a function of temperature and water mole fractions

Temp. (Celcius)	15	20	25	37
X _w = 0.90				
K1	10.09 ± 1.2	16.23 ± 1.3	20.67 ± 1.2	28.86 ± 1.2
X _w = 0.77				
K1	22.29 ± 1.2	27.08 ± 1.2	34.32 ± 1.2	63.10 ± 1.2
X _w = 0.60				
K1	23.17 ± 1.2	30.09 ± 1.2	45.98 ± 1.3	90.16 ± 1.2
X _w = 0.36				
K1	25.53 ± 1.7	39.28 ± 1.6	62.34 ± 1.4	166.73 ± 1.5
K2	7.33 ± 1.4	6.49 ± 1.3	4.12 ± 1.1	2.09 ± 1.1
X _w = 0.20				
K1	27.26 ± 1.5	45.12 ± 1.3	72.43 ± 1.8	176.32 ± 1.5
K2	7.55 ± 1.0	7.03 ± 1.05	5.07 ± 1.1	2.48 ± 1.5
X _w = 0.04				
K1	31.72 ± 1.3	54.85 ± 2.0	83.12 ± 1.4	210.91 ± 1.5
K2	8.13 ± 1.0	7.94 ± 1.0	5.56 ± 1.0	3.75 ± 1.0

Figure 11. K_1 for neodymium nitrate vs. X at 25°C

Figure 12. Lanthanide nitrate mono-complexes at 25 ° C

Figure 13. K_2 vs. X for neodymium nitrate at 25 C

Figure 14. Lanthanide nitrate bis-complexes at 25 ° C

fraction gets lower is expected because the dielectric constant decreases with decreasing water mole fractions. As the dielectric constant decreases, the medium becomes less able to support ions and complexation becomes more favorable, the situation is similar for the bis-complexes. All the three systems--Er(III) ions, Eu(III) ions and Nd(III) ions--show an increase in the equilibrium constants from the higher to the lower water mole fractions.

Even though an exact comparison between our results and Majdan's² results cannot be done since Majdan did not specify the temperature and ionic strength, we did try to fit our absorbance values at 25°C in 90% methanol with his equilibrium constants ($K_1 = 3.6$ and $K_2 = 1$) using the Gaizer program. The square of the residuals obtained using Majdan's values is larger ($.0315 \pm 0.018$) than the one obtained using our values ($.0294 \pm 0.018$). In addition, the Gaizer program had refined the ϵ_{ML1} (extinction coefficient of the first complex) at 521.2 nm to zero, an unlikely value for the ϵ_{ML1} . Furthermore, the ϵ_{ML2} 's errors obtained using their K_1 and K_2 values are large compared with the ϵ_{ML2} 's errors using our values. The data are summarized in Table 2. We had also calculated the standard deviations for the differences between the measured and the calculated absorbances ($A_{\text{meas.}} - A_{\text{calc.}}$) from the output of the Gaizer programs at all of the six wavelengths. Table 3 shows the standard deviation calculated for both of the programs. When the data are compared, our standard deviations for three wavelengths--521.2,

Table 2

Table of data comparing the log of equilibrium constants and the extinction coefficients of neodymium nitrate in 90% methanol at 25 C.

	Majdan's	± error	ours	± error
log B1	0.565	0.04	1.860	0.07
log B2	0.556	0.00	2.565	0.00
EML1(521.20 nm)	0.000	0.40	2.628	0.17
EML2	3.949	1.62	2.979	0.33
EM	4.727	0.00	4.727	0.00
EML1(521.70 nm)	0.985	0.23	3.473	0.21
EML2	4.369	0.93	2.819	0.40
EM	4.740	0.00	4.740	0.00
EML1(522.20 nm)	1.910	0.26	3.860	0.18
EML2	3.928	1.06	3.011	0.37
EM	4.720	0.00	4.720	0.00
EML1(574.80 nm)	7.696	0.54	7.110	0.19
EML2	11.019	2.13	9.526	0.47
EM	7.720	0.00	7.720	0.00
EML1(575.30 nm)	9.041	0.47	7.664	0.20
EML2	10.566	1.87	9.768	0.45
EM	7.660	0.00	7.660	0.00
EML1(575.80 nm)	10.581	0.42	8.284	0.23
EML2	10.442	1.67	10.261	0.49
EM	7.660	0.00	7.660	0.00
Square of residuals	0.032		0.029	
Standard deviation	0.018		0.018	

Table 3

Table of the standard deviation data for the differences between the measured and the calculated absorbances

Wavelengths (nm)	Stand. dev (ours)	Stand. dev. (Majdan's)
521.20	0.0074	0.0094
521.70	0.0092	0.0057
522.20	0.0097	0.0074
574.80	0.0151	0.0184
575.30	0.0150	0.0155
575.80	0.0128	0.0123

574.80, and 575.30 nm--are lower than theirs.

As mentioned earlier, each of the two complexes was independently measured at 15, 20, 25, 37 °C for each solvent composition. It was thus possible to calculate the ΔH^0 and ΔS^0 of the complexation reactions using a plot of $\ln K$ vs. $1/T$, as seen in Fig. 15. The enthalpy and the entropy of the successive complexation reactions are summarized in Table 4. The enthalpy for the mono-complex is displayed graphically in Fig. 16 and the entropy in Fig. 17. Fig. 18 and Fig. 19 show the combined data of the enthalpy and entropy for the mono-complexes of Er(III), Eu(III) and Nd(III) nitrate in aqueous methanol. The data for the bis-complexes are shown in Figs. 20-23.

Since the enthalpy and entropy have been determined at constant ionic strength of 3.0, the data are concentration based and are not absolute thermodynamic data. According to Choppin²⁵, the ΔH^0 accompanying complexation of a lanthanide ion in aqueous solution is a measure of the difference in energy between the ligand-cation bond and the coordinated water molecule-cation bond. In other words, the enthalpy change actually expresses a difference in energy between the ligand cation bond and the hydration sphere bond. Choppin concluded that for non-chelated species, negative values for both the ΔH^0 and ΔS^0 indicate that the resulting species is an outer sphere complex in which the primary hydration sphere is retained. If the opposite is true, both the ΔH^0 and ΔS^0 are positive, the hydration sphere is ruptured and the complex is an inner sphere complex. Choppin uses the model of ionic solutions proposed by Frank and

Figure 15. $\ln K1$ vs. $1/T$ for $X = 0.90$ at 15°C

Table 4

The thermodynamics values for the mono and bis-complexes as a function of water mole fraction.

	mono-complex	bis-complexes
X = 0.90		
Enthalpy (kJ/mol)	33.0 ± 8	
Entropy (J/mol. K)	137.0 ± 26	
X = 0.77		
Enthalpy (kJ/mol)	36.0 ± 2	
Entropy (J/mol. K)	149.0 ± 6	
X = 0.60		
Enthalpy (kJ/mol)	47.0 ± 3	
Entropy (J/mol. K)	188.0 ± 21	
X = 0.36		
Enthalpy (kJ/mol)	63.0 ± 6	-44.0 ± 8
Entropy (J/mol. K)	249.0 ± 10	-137.0 ± 26
X = 0.20		
Enthalpy (kJ/mol)	63.0 ± 10	-39.0 ± 6
Entropy (J/mol. K)	246.0 ± 11	-119.0 ± 19
X = 0.04		
Enthalpy (kJ/mol)	63.0 ± 11	-28.0 ± 5
Entropy (J/mol. K)	249.0 ± 37	-80.0 ± 15

Figure 16. The enthalpy of the mono-complex for neodymium nitrate as a function of X.

Figure 17. The entropy of the mono-complex for neodymium nitrate as a function of X.

Figure 18. The enthalpy of mono-complexes at 25 ° C for lanthanide nitrates

Figure 19. The entropy for the mono-complex at 25 ° C for the lanthanide nitrates.

Figure 20. Enthalpy of the bis-complex for neodymium nitrate vs. X at 25 °C

Figure 21. Entropy of the bis-complex for neodymium nitrate vs. X at 25 °C

Figure 22. The enthalpy of the bis-complexes as a function of X for lanthanide nitrates at 25 °C

Figure 23. The entropy of the bis-complex as a function of X for lanthanide nitrates at 25 ° C

Evans²⁶ to explain his arguments. According to this model, an ion in solution is surrounded by three concentric zones of water. The inner first zone has one or more layers of water molecules oriented by ionic attraction and the outer-most zone has the hydrogen-bonded structure of normal water. The middle zone is a "thawed" region of less order than the bulk solution phase. The enthalpy change is positive for the disruption of hydration structure and negative for the ionic combination. In the outer sphere complexes the hydration sphere is only partially disrupted and the net enthalpy is negative. Meanwhile, the entropy change is also negative due to the ordering of ionic charges. In the inner sphere complexes the hydration sphere is highly disrupted and this results in a positive enthalpy change. The entropy change is also positive since the elimination of water molecules from the inner hydration zone to the thawed middle zone gives a net positive entropy effect.²⁵

From Table 4, it is clear that both the enthalpy and entropy are positive for the formation of the mono-complex. If Choppin's conclusions are applied here, then the mono-complex is an inner sphere complex. For the bis-complex, both thermodynamic parameters are negative; therefore the complex is an outer sphere complex. Thus, from this equilibrium study, we can conclude that both the inner sphere and the outer sphere complexes are formed for $\text{Nd}(\text{NO}_3)_3$ in aqueous methanol. Since the mono-complex is the predominant species in aqueous methanol, it is reasonable to state that the species formed in this system are inner sphere complexes. This agrees with the ultrasonic study done by Silber et al. in 50%

methanol. His study revealed that these complexes are predominantly inner sphere complexes with some outer sphere complexes.

4. CONCLUSIONS

Both the mono and the bis-complexes are formed from the complexation reactions between neodymium (III) and nitrate ions in aqueous methanol. The bis-complexes are found above 80% methanol ($X = 0.36$); below 80% methanol only the mono-complex exists.

Both K_1 and K_2 increase as methanol is added to the system or as we lower X , the water mole fraction. The increase is expected, since methanol lowers the dielectric constant of the medium making it more susceptible to complexation.

The present work also shows that the effects of temperature are different for each complexation step. K_1 for the mono-complex increases with the increase in temperature, whereas K_2 decreases with the increase in temperature. The enthalpy is therefore positive for the mono-complex and negative for the bis-complexes. Since the entropy is also positive for the mono-complex, we conclude that the mono-complex is predominantly inner-sphere. The reverse is true for the bis-complexes; therefore they are predominantly outer-sphere.

We have also observed that the effects of methanol on the complexation of Nd^{3+} with NO_3^- are different from its effects on Er^{3+} and Eu^{3+} with NO_3^- . Neodymium forms only the mono-complex above $X = 0.40$ and bis-complexes below that. Erbium forms both the mono and the bis-complexes at $X = 0.40$ and above. Below that the tris-complexes are stable. Europium, on the other hand forms all

mono, bis and tris-complexes at and below $X = 0.87$. Future study should be carried out on a different lanthanide, Pr(III) for example. In addition, complex formation between $\text{Nd}^{3+}(\text{aq})$ ions and $\text{NO}_3^{-}(\text{aq})$ ions in other mixed solvent systems such as dimethyl sulfoxide, dimethyl formamide, acetonitrile and ethanol should also be investigated.

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APPENDIX A

Figure 24. The mole ratio plot for $X = 0.90$ at 15°C

Figure 25. The mole ratio plot for $X = 0.90$ at $20^\circ C$

Figure 26. The mole ratio plot for $X = 0.90$ at 25°C

Figure 27. The mole ratio plot for $X = 0.90$ at 37°C

Figure 28. The mole ratio plot for $X = 0.77$ at 15°C

Figure 29. The mole ratio plot for $X = 0.77$ at 20°C

Figure 30. The mole ratio plot for $X = 0.77$ at $25^\circ C$

Figure 31. The mole ratio plot for $X = 0.77$ at 37°C

Figure 33. The mole ratio plot for $X = 0.60$ at 20°C

Figure 32. The mole ratio plot for $X = 0.60$ at $15^\circ C$

Figure 34. The mole ratio plot for $X = 0.60$ at 25°C

Figure 35. The mole ratio plot for $X = 0.60$ at $37^\circ C$

Figure 36. The mole ratio plot for $X = 0.36$ at $15^\circ C$

Figure 37. The mole ratio plot for $X = 0.36$ at $20^\circ C$

Figure 38. The mole ratio plot for $X = 0.36$ at 25°C

Figure 39. The mole ratio plot for $X = 0.36$ at $37^\circ C$

Figure 40. The mole ratio plot for X= 0:20 at 15 ° C

Figure 41. The mole ratio plot for $X = 0.20$ at 20°C

Figure 42. The mole ratio plot for $X = 0.20$ at $25^\circ C$

Figure 43. The mole ratio plot for $X = 0.20$ at $37^\circ C$

Figure 44. The mole ratio plot for $X = 0.04$ at 15°C

Figure 45. The mole ratio plot for $X = 0.04$ at 20°C Celcius

Figure 46. The mole ratio plot for $X = 0.04$ at $25^\circ C$

Figure 47. The mole ratio plot for $X = 0.04$ at 37°C

APPENDIX B

Table 5.

The absorbance data for $X = 0.90$ at 15°C $l = 3$ (sodium perchlorate) $X = 0.899$

Wavelengths (nm)	521.20	521.70	522.20	574.80	575.30	575.80
Absorbance Data						
[Nitrate], M						
0.010	0.1970	0.2167	0.1940	0.2736	0.2818	0.2915
0.014	0.2032	0.2151	0.1773	0.2746	0.2829	0.2934
0.019	0.1991	0.2072	0.1679	0.2719	0.2791	0.3000
0.029	0.1941	0.2048	0.1610	0.2848	0.2938	0.2972
0.038	0.1937	0.1979	0.1552	0.2693	0.2776	0.2973
0.048	0.1858	0.1952	0.1570	0.2895	0.2971	0.3034
0.060	0.1869	0.1923	0.1522	0.2933	0.3023	0.3129
0.072	0.1862	0.1913	0.1450	0.2932	0.3013	0.3142
0.096	0.1803	0.1909	0.1528	0.2893	0.2982	0.3266
0.120	0.1864	0.1901	0.1454	0.2934	0.3029	0.2811
0.144	0.1807	0.1874	0.1458	0.2981	0.3074	0.2791
0.192	0.1772	0.1856	0.1540	0.2949	0.3036	0.2745
0.240	0.1696	0.1787	0.1426	0.2991	0.3077	0.2906
0.268	0.1635	0.1783	0.1528	0.3015	0.3099	0.2727
0.336	0.1654	0.1740	0.1450	0.3108	0.3200	0.2890
0.384	0.1549	0.1714	0.1481	0.3107	0.3207	0.2946
0.432	0.1614	0.1686	0.1430	0.3245	0.3331	0.2921

Table 6

The absorbance data for $X = 0.90$ at 20°C

$l = 3.0$ (sodium perchlorate)

$X = 0.899$

Wavelengths (nm)	521.20	521.70	522.20	574.80	575.30	575.80
Absorbance Data						
[Nitrate], M						
0.010	0.2111	0.2151	0.1714	0.2697	0.2711	0.2660
0.014	0.2012	0.2108	0.1832	0.2697	0.2776	0.2754
0.019	0.1951	0.2026	0.1634	0.2643	0.2852	0.2618
0.029	0.1939	0.2008	0.1610	0.2795	0.2880	0.2858
0.038	0.1912	0.1947	0.1517	0.2627	0.2897	0.2660
0.048	0.1817	0.1898	0.1528	0.2828	0.2913	0.2846
0.060	0.1809	0.1883	0.1482	0.2865	0.2957	0.2903
0.072	0.1831	0.1890	0.1500	0.2841	0.2925	0.2871
0.096	0.1809	0.1883	0.1482	0.2546	0.2952	0.2854
0.120	0.1777	0.1865	0.1495	0.2884	0.2962	0.2848
0.144	0.1777	0.1828	0.1427	0.2875	0.2968	0.2861
0.192	0.1721	0.1815	0.1487	0.2887	0.2971	0.2914
0.240	0.1655	0.1737	0.1388	0.2922	0.3006	0.2935
0.288	0.1643	0.1731	0.1477	0.3062	0.3131	0.3036
0.336	0.1643	0.1720	0.1404	0.3036	0.3129	0.3061
0.384	0.1586	0.1678	0.1429	0.3181	0.3263	0.3219
0.432	0.1581	0.1668	0.1388	0.3143	0.3224	0.3107

Table 7

The absorbance data for $X = 0.90$ at 25°C

$l = 3.0$ (sodium perchlorate)

$X = 0.899$

Wavelengths (nm)	521.20	521.70	522.20	574.80	575.30	575.80

Absorbance data

[Nitrate], M

0.010	0.2105	0.2141	0.1760	0.2622	0.2708	0.2720
0.014	0.1976	0.2067	0.1798	0.2620	0.2703	0.2679
0.019	0.1953	0.2024	0.1683	0.2663	0.2735	0.2718
0.029	0.1923	0.1993	0.1637	0.2624	0.2703	0.2679
0.038	0.1875	0.1907	0.1528	0.2575	0.2765	0.2614
0.048	0.1762	0.1851	0.1488	0.2760	0.2836	0.2815
0.060	0.1755	0.1841	0.1493	0.2775	0.2846	0.2780
0.072	0.1799	0.1840	0.1483	0.2814	0.2904	0.2840
0.096	0.1792	0.1826	0.1455	0.2828	0.2910	0.2848
0.120	0.1742	0.1800	0.1424	0.2871	0.2949	0.2893
0.144	0.1691	0.1762	0.1465	0.2819	0.2881	0.2798
0.192	0.1623	0.1704	0.1465	0.2820	0.2892	0.2803
0.240	0.1618	0.1689	0.1354	0.2869	0.2948	0.2882
0.288	0.1606	0.1682	0.1407	0.2996	0.3080	0.3025
0.336	0.1564	0.1651	0.1407	0.2999	0.3065	0.2982
0.384	0.1563	0.1648	0.1398	0.3126	0.3195	0.3168
0.432	0.1538	0.1623	0.1399	0.3126	0.3205	0.3105

Table 8

The absorbance data for $X = 0.77$ at 37°C

$l = 3.0$ (sodium perchlorate)

$X = 0.899$

Wavelengths (nm)	521.20	521.70	522.20	574.80	575.30	575.80
Absorbance Data						
[Nitrate], M						
0.010	0.2047	0.2076	0.1721	0.2567	0.2649	0.2643
0.014	0.1970	0.2016	0.1699	0.2564	0.2642	0.2618
0.019	0.1893	0.1941	0.1698	0.2445	0.2689	0.2471
0.029	0.1859	0.1892	0.1578	0.2630	0.2710	0.2707
0.038	0.1757	0.1775	0.1411	0.2569	0.2754	0.2595
0.048	0.1698	0.1749	0.1414	0.2671	0.2743	0.2694
0.060	0.1698	0.1736	0.1416	0.2716	0.2776	0.2717
0.072	0.1676	0.1725	0.1374	0.2740	0.2769	0.2757
0.096	0.1683	0.1723	0.1390	0.2670	0.2739	0.2690
0.120	0.1712	0.1720	0.1390	0.2674	0.2736	0.2665
0.144	0.1677	0.1699	0.1361	0.2690	0.2766	0.2719
0.192	0.1585	0.1652	0.1387	0.2693	0.2748	0.2687
0.240	0.1531	0.1606	0.1368	0.2719	0.2784	0.2712
0.288	0.1552	0.1600	0.1394	0.2885	0.2950	0.2890
0.336	0.1545	0.1573	0.1259	0.3022	0.3056	0.2986
0.384	0.1517	0.1565	0.1356	0.2969	0.3024	0.2960
0.432	0.1448	0.1538	0.1348	0.3014	0.3088	0.3022

Table 9

The absorbance data for $X = 0.90$ at 15°C
 $l = 3.0$ (sodium perchlorate)
 $X_w = 0.77$

Wavelengths (nm)	521.20	521.70	522.20	574.80	575.30	575.80
Absorbance Data						
[Nitrate], M						
0.010	0.2093	0.2100	0.1621	0.2754	0.2740	0.2570
0.014	0.2048	0.2073	0.1790	0.2800	0.2750	0.2680
0.019	0.2075	0.2072	0.1594	0.2852	0.2798	0.2680
0.029	0.1974	0.2043	0.1681	0.2757	0.2850	0.2858
0.038	0.2083	0.1926	0.1447	0.2884	0.2953	0.2920
0.048	0.1902	0.1821	0.1433	0.2809	0.2908	0.2926
0.060	0.1876	0.1832	0.1490	0.2908	0.3004	0.3004
0.072	0.1887	0.1802	0.1380	0.2827	0.3064	0.2828
0.096	0.1670	0.1760	0.1587	0.2777	0.3035	0.2887
0.120	0.1750	0.1737	0.1394	0.2991	0.3071	0.2954
0.144	0.1754	0.1730	0.1495	0.2933	0.3017	0.2967
0.192	0.1626	0.1720	0.1514	0.2997	0.3074	0.2984
0.240	0.1748	0.1725	0.1474	0.3236	0.3275	0.3083
0.288	0.1624	0.1706	0.1485	0.3072	0.3135	0.3017
0.336	0.1559	0.1710	0.1387	0.3230	0.3249	0.3002
0.384	0.1540	0.1700	0.1356	0.3209	0.3307	0.3299
0.432	0.1520	0.1705	0.1344	0.3317	0.3308	0.3291

Table 10

The absorbance data for $X = 0.77$ at 20°C
 $l = 3.0$ (sodium perchlorate)
 $X = 0.77$

Wavelengths (nm)	521.20	521.70	522.20	574.80	575.30	575.80
Absorbance Data						
[Nitrate], M						
0.010	0.2053	0.1987	0.1488	0.2768	0.2829	0.2779
0.014	0.2068	0.1974	0.1500	0.2716	0.2800	0.2820
0.019	0.2060	0.1969	0.1503	0.2781	0.2875	0.2904
0.029	0.1925	0.1933	0.1630	0.2727	0.2813	0.2846
0.038	0.1922	0.1900	0.1626	0.2770	0.2885	0.2984
0.048	0.1861	0.1832	0.1450	0.2882	0.2966	0.2950
0.060	0.1870	0.1843	0.1548	0.2920	0.2991	0.2929
0.072	0.1850	0.1820	0.1498	0.2932	0.3009	0.2903
0.096	0.1761	0.1808	0.1498	0.2920	0.3008	0.2929
0.120	0.1845	0.1769	0.1370	0.2940	0.3042	0.2978
0.144	0.1761	0.1762	0.1469	0.3025	0.3083	0.3001
0.192	0.1734	0.1749	0.1465	0.3001	0.3027	0.2896
0.240	0.1715	0.1749	0.1444	0.3071	0.3162	0.3153
0.288	0.1653	0.1719	0.1538	0.3046	0.3130	0.3106
0.336	0.1618	0.1688	0.1476	0.3168	0.3184	0.2970
0.384	0.1595	0.1666	0.1444	0.3187	0.3250	0.3070
0.432	0.1712	0.1672	0.1343	0.3238	0.3210	0.2947

Table 11

The absorbance data for $X = 0.77$ at 25°C

$I = 3.0$ (sodium perchlorate)

$X = 0.77$

Wavelengths (nm)	521.20	521.70	522.20	574.80	575.30	575.80
Absorbance data						
[Nitrate], M						
0.010	0.1947	0.1919	0.1736	0.2694	0.2762	0.2673
0.014	0.1889	0.1908	0.1627	0.2740	0.2824	0.2862
0.019	0.1987	0.1903	0.1441	0.2670	0.2848	0.2790
0.029	0.2011	0.1903	0.1458	0.2836	0.2921	0.2896
0.038	0.1864	0.1870	0.1606	0.2861	0.2933	0.2843
0.048	0.1965	0.1844	0.1508	0.2885	0.2927	0.2847
0.060	0.1858	0.1830	0.1394	0.2995	0.2963	0.2898
0.072	0.1829	0.1795	0.1444	0.2969	0.2974	0.2924
0.096	0.1796	0.1779	0.1414	0.2918	0.2957	0.2848
0.120	0.1912	0.1758	0.1363	0.2950	0.3035	0.2969
0.144	0.1921	0.1757	0.1345	0.3002	0.3061	0.2924
0.192	0.1711	0.1754	0.1452	0.3071	0.3099	0.2905
0.240	0.1793	0.1732	0.1342	0.3009	0.3102	0.3101
0.288	0.1694	0.1715	0.1433	0.3120	0.3156	0.2986
0.336	0.1615	0.1656	0.1486	0.3153	0.3107	0.2867
0.384	0.1595	0.1650	0.1457	0.2955	0.3081	0.3072
0.432	0.1674	0.1629	0.1247	0.2978	0.3095	0.3086

Table 12

The absorbance data for $X = 0.77$ at 37°C

$l = 3.0$ (sodium perchlorate)

$X = 0.77$

Wavelengths (nm)	521.20	521.70	522.20	574.80	575.30	575.80
Absorbance Data						
[Nitrate], M						
0.010	0.1909	0.1848	0.1490	0.2577	0.2634	0.2602
0.014	0.1836	0.1847	0.1484	0.2535	0.2626	0.2660
0.019	0.1785	0.1807	0.1584	0.2661	0.2729	0.2746
0.029	0.1801	0.1804	0.1436	0.2547	0.2634	0.2688
0.038	0.1909	0.1798	0.1406	0.2641	0.2730	0.2781
0.048	0.1656	0.1694	0.1367	0.2705	0.2777	0.2716
0.060	0.1755	0.1696	0.1393	0.2729	0.2814	0.2807
0.072	0.1681	0.1649	0.1336	0.2806	0.2776	0.2731
0.096	0.1686	0.1648	0.1374	0.2677	0.2784	0.2717
0.120	0.1798	0.1627	0.1273	0.2735	0.2795	0.2749
0.144	0.1618	0.1641	0.1401	0.2838	0.2904	0.2861
0.192	0.1670	0.1616	0.1276	0.2634	0.2855	0.2605
0.240	0.1520	0.1586	0.1426	0.2942	0.2942	0.2781
0.288	0.1497	0.1555	0.1409	0.2775	0.2817	0.2685
0.336	0.1590	0.1537	0.1339	0.2909	0.2994	0.3008
0.384	0.1457	0.1523	0.1358	0.2854	0.2924	0.2840
0.432	0.1565	0.1504	0.1237	0.2975	0.3017	0.2908

Table 13

The absorbance data for $X = 0.60$ at 15°C

$l = 3.0$ (sodium perchlorate)

$X = 0.60$

Wavelengths (nm)	521.20	521.70	522.20	574.80	575.30	575.80
Absorbance Data						
[Nitrate], M						
0.010	0.2593	0.2498	0.2159	0.2989	0.3142	0.3094
0.015	0.2533	0.2437	0.2168	0.2999	0.3110	0.3251
0.020	0.2308	0.2259	0.1876	0.3085	0.3125	0.3363
0.025	0.2214	0.2180	0.2007	0.2934	0.3117	0.3049
0.033	0.2215	0.2172	0.1789	0.3071	0.3134	0.3125
0.040	0.2245	0.2125	0.1770	0.3131	0.3167	0.3103
0.045	0.2302	0.2024	0.1692	0.3249	0.3233	0.3144
0.050	0.2027	0.1970	0.1624	0.3161	0.3238	0.3245
0.075	0.2175	0.1904	0.1587	0.3296	0.3352	0.3238
0.100	0.1932	0.1873	0.1651	0.3163	0.3221	0.3111
0.125	0.2178	0.1861	0.1514	0.3410	0.3469	0.3347
0.150	0.2000	0.1838	0.1623	0.3401	0.3465	0.3363
0.200	0.1889	0.1812	0.1602	0.3293	0.3381	0.3306
0.250	0.1750	0.1706	0.1577	0.3408	0.3497	0.3542
0.300	0.1550	0.1705	0.1709	0.3415	0.3496	0.3394
0.350	0.1562	0.1707	0.1676	0.3704	0.3765	0.3730
0.400	0.1558	0.1690	0.1600	0.3703	0.3765	0.3678

Table 14

The absorbance data for $X = 0.60$ at 20°C
 $l = 3.0$ (sodium perchlorate)
 $X = 0.60$

Wavelengths (nm)	521.20	521.70	522.20	574.80	575.30	575.80
Absorbance Data						
[Nitrate], M						
0.010	0.2488	0.2381	0.2072	0.2721	0.2839	0.2983
0.015	0.2351	0.2308	0.2049	0.2789	0.2896	0.3030
0.020	0.2277	0.2192	0.1827	0.2923	0.2974	0.2979
0.025	0.2166	0.2119	0.1763	0.3102	0.2987	0.3422
0.033	0.2178	0.2117	0.1761	0.2917	0.2991	0.3021
0.040	0.2093	0.2066	0.1719	0.2645	0.3078	0.2521
0.045	0.2049	0.2014	0.1837	0.2746	0.3154	0.2665
0.050	0.2100	0.1986	0.1667	0.3100	0.3193	0.3201
0.075	0.1893	0.1869	0.1597	0.3066	0.3110	0.3006
0.100	0.1944	0.1865	0.1549	0.3013	0.3076	0.3044
0.125	0.1891	0.1865	0.1650	0.3231	0.3291	0.3211
0.150	0.1820	0.1797	0.1494	0.3242	0.3328	0.3374
0.200	0.1719	0.1704	0.1404	0.3147	0.3212	0.3114
0.250	0.1721	0.1689	0.1511	0.3241	0.3314	0.3231
0.300	0.1511	0.1680	0.1697	0.3228	0.3310	0.3207
0.350	0.1723	0.1679	0.1475	0.3350	0.3424	0.3329
0.400	0.1353	0.1498	0.1473	0.3518	0.3584	0.3573
0.450	0.1256	0.1400	0.1388	0.3560	0.3612	0.3543

Table 15

The absorbance data for $X = 0.60$ at 25°C
 $l = 3.0$ (sodium perchlorate)
 $X = 0.60$

Wavelengths (nm)	521.20	521.70	522.20	574.80	575.30	575.80
Absorbance Data						
[Nitrate], M						
0.010	0.2360	0.2293	0.1985	0.2708	0.2832	0.2979
0.015	0.2253	0.2217	0.1972	0.2764	0.2879	0.3013
0.020	0.2178	0.2117	0.1761	0.3090	0.2912	0.3401
0.025	0.2093	0.2066	0.1719	0.2878	0.2947	0.2998
0.033	0.2138	0.2047	0.1707	0.2645	0.2965	0.2521
0.040	0.1955	0.1959	0.1791	0.2970	0.2999	0.2948
0.045	0.2015	0.1931	0.1615	0.2970	0.3006	0.2911
0.050	0.1947	0.1837	0.1464	0.3012	0.3084	0.3020
0.075	0.1835	0.1825	0.1618	0.3050	0.3127	0.3149
0.100	0.1912	0.1811	0.1490	0.3001	0.3042	0.2927
0.125	0.1835	0.1807	0.1500	0.3135	0.3199	0.3133
0.150	0.1833	0.1793	0.1547	0.3157	0.3241	0.3288
0.200	0.1719	0.1704	0.1414	0.3223	0.3288	0.3229
0.250	0.1682	0.1675	0.1510	0.3147	0.3212	0.3114
0.300	0.1458	0.1642	0.1675	0.3241	0.3314	0.3233
0.350	0.1293	0.1463	0.1462	0.3427	0.3491	0.3475
0.400	0.1221	0.1388	0.1397	0.3446	0.3498	0.3417

Table 16

The absorbance data for $X = 0.60$ at 37°C

$l = 3.0$ (sodium perchlorate)

$X = 0.60$

Wavelengths (nm)	521.20	521.70	522.20	574.80	575.30	575.80
Absorbance Data						
[Nitrate], M						
0.010	0.2150	0.2084	0.1817	0.2636	0.2755	0.2900
0.015	0.2064	0.2017	0.1814	0.2716	0.2829	0.2961
0.020	0.2036	0.1955	0.1631	0.2706	0.2767	0.2880
0.025	0.2054	0.1948	0.1651	0.2444	0.2763	0.2361
0.033	0.1945	0.1898	0.1587	0.3007	0.2854	0.3312
0.040	0.1795	0.1797	0.1652	0.2778	0.2857	0.2907
0.045	0.1860	0.1781	0.1508	0.2772	0.2809	0.2715
0.050	0.1853	0.1746	0.1463	0.2788	0.2828	0.2797
0.075	0.1714	0.1692	0.1528	0.2782	0.2818	0.2758
0.100	0.1698	0.1653	0.1385	0.2893	0.2975	0.3007
0.125	0.1696	0.1650	0.1445	0.2928	0.2992	0.2932
0.150	0.1748	0.1636	0.1312	0.2946	0.3003	0.2964
0.200	0.1593	0.1596	0.1446	0.2992	0.3069	0.3131
0.250	0.1477	0.1590	0.1574	0.2951	0.3005	0.2932
0.300	0.1587	0.1555	0.1290	0.3115	0.3171	0.3109
0.350	0.1530	0.1515	0.1351	0.3044	0.3104	0.3026
0.400	0.1347	0.1434	0.1387	0.3211	0.3277	0.3274
0.450	0.1230	0.1332	0.1298	0.3203	0.3247	0.3205

Table 17

The absorbance data for $X = 0.36$ at 15°C

$l = 3.0$ (lithium perchlorate)

$X = 0.36$

Wavelengths (nm)	521.20	521.70	522.20	574.80	575.30	575.80
Absorbance Data						
[Nitrate], M						
0.010	0.2966	0.3073	0.2889	0.3197	0.3080	0.3281
0.015	0.2706	0.2771	0.2562	0.3254	0.3130	0.3448
0.020	0.2586	0.2754	0.2543	0.3220	0.3290	0.3283
0.025	0.2595	0.2700	0.2443	0.3263	0.3350	0.3386
0.033	0.2582	0.2675	0.2343	0.3301	0.3320	0.3390
0.040	0.2546	0.2664	0.2503	0.3372	0.3350	0.3524
0.045	0.2258	0.2379	0.2132	0.3452	0.3390	0.3502
0.050	0.2216	0.2327	0.2046	0.3550	0.3470	0.3467
0.075	0.2230	0.2262	0.1703	0.3454	0.3546	0.3506
0.100	0.2243	0.2178	0.2220	0.3557	0.3647	0.3654
0.125	0.2089	0.2153	0.1982	0.3872	0.3961	0.4005
0.150	0.2069	0.2148	0.1848	0.3774	0.3858	0.3786
0.200	0.1990	0.2132	0.1962	0.3880	0.3973	0.3967
0.250	0.2004	0.2100	0.1770	0.3865	0.3945	0.3972
0.300	0.1890	0.2051	0.1967	0.4024	0.4099	0.4142
0.350	0.1890	0.2043	0.1751	0.4285	0.4377	0.4424

Table 18

The absorbance data for $X = 0.36$ at 20°C

$l = 3.0$ (lithium perchlorate)

$X = 0.36$

Wavelengths (nm)	521.20	521.70	522.20	574.80	575.30	575.80
	Absorbance Data					
[Nitrate], M						
0.010	0.2657	0.2766	0.2606	0.3170	0.3273	0.3397
0.015	0.2599	0.2661	0.2380	0.3210	0.3284	0.3324
0.020	0.2540	0.2633	0.2288	0.3182	0.3267	0.3262
0.025	0.2469	0.2621	0.2409	0.3137	0.3220	0.3202
0.033	0.2280	0.2383	0.2162	0.3198	0.3287	0.3285
0.040	0.2143	0.2350	0.2410	0.3240	0.3334	0.3402
0.045	0.2232	0.2323	0.2042	0.3208	0.3287	0.3325
0.050	0.2240	0.2261	0.2098	0.3439	0.3530	0.3578
0.075	0.2147	0.2259	0.2078	0.3455	0.3540	0.3618
0.100	0.2137	0.2145	0.2090	0.3578	0.3599	0.3409
0.125	0.1934	0.2078	0.1929	0.3427	0.3515	0.3492
0.150	0.1919	0.2057	0.1917	0.3523	0.3598	0.3598
0.200	0.1989	0.2055	0.1783	0.3555	0.3640	0.3651
0.250	0.1956	0.2024	0.1725	0.3689	0.3780	0.3807
0.300	0.1956	0.2031	0.1738	0.3719	0.3815	0.3817
0.350	0.1771	0.1936	0.1778	0.3809	0.3890	0.3899
0.400	0.1603	0.1806	0.1794	0.3948	0.4031	0.4082

Table 19

The absorbance data for $X = 0.36$ at 25°C $l = 3.0$ (lithium perchlorate) $X = 0.36$

Wavelengths (nm)	521.20	521.70	522.20	574.80	575.30	575.80
Absorbance data						
[Nitrate], M						
0.010	0.2482	0.2601	0.2459	0.3015	0.3115	0.3233
0.015	0.2505	0.2570	0.2327	0.3215	0.3321	0.3457
0.020	0.2446	0.2519	0.2190	0.3128	0.3174	0.3274
0.025	0.2361	0.2486	0.2293	0.3160	0.3249	0.3315
0.033	0.2189	0.2322	0.2122	0.3167	0.3262	0.3364
0.040	0.2189	0.2266	0.1999	0.3234	0.3322	0.3362
0.045	0.2324	0.2199	0.1682	0.3079	0.3116	0.3125
0.050	0.2091	0.2197	0.2065	0.3098	0.3186	0.3201
0.075	0.1934	0.2025	0.1868	0.3128	0.3220	0.3410
0.100	0.1898	0.2002	0.1855	0.3129	0.3205	0.3246
0.125	0.1893	0.2000	0.1724	0.3207	0.3289	0.3354
0.150	0.1900	0.1994	0.1737	0.3373	0.3465	0.3532
0.200	0.1925	0.1992	0.1686	0.3478	0.3507	0.3334
0.250	0.1826	0.1977	0.1837	0.3356	0.3441	0.3410
0.300	0.1825	0.1975	0.1909	0.3475	0.3552	0.3562
0.350	0.1837	0.1958	0.1788	0.3556	0.3634	0.3640
0.400	0.1738	0.1939	0.1999	0.3556	0.3637	0.3572
0.450	0.1667	0.1881	0.1867	0.3686	0.3769	0.3784
0.500	0.1466	0.1685	0.1656	0.3768	0.3846	0.3908

Table 20

The absorbance data for $x = 0.36$ at 37°C

$l = 3.0$ (lithium perchlorate)

$x = 0.36$

Wavelengths (nm)	521.20	521.70	522.20	574.80	575.30	575.8
Absorbance Data						
[Nitrate], M						
0.010	0.2327	0.2521	0.2579	0.2991	0.2963	0.3160
0.015	0.2255	0.2309	0.2053	0.3018	0.3036	0.3214
0.020	0.2177	0.2293	0.2166	0.2888	0.3300	0.2955
0.025	0.2211	0.2265	0.1986	0.2946	0.3045	0.3084
0.033	0.2092	0.2203	0.2053	0.3225	0.3278	0.3330
0.040	0.2011	0.2141	0.1981	0.2953	0.3325	0.3063
0.045	0.2034	0.2088	0.1844	0.3172	0.3224	0.3421
0.050	0.1968	0.2057	0.1936	0.3112	0.2963	0.3442
0.075	0.2167	0.2048	0.1575	0.3161	0.3301	0.3290
0.100	0.1790	0.1928	0.1809	0.2889	0.3232	0.2955
0.125	0.1711	0.1912	0.1982	0.3208	0.3343	0.3382
0.150	0.1682	0.1875	0.1859	0.3149	0.3000	0.3225
0.200	0.1813	0.1872	0.1629	0.3218	0.3343	0.3310
0.250	0.1767	0.1866	0.1651	0.3225	0.3310	0.3340
0.300	0.1716	0.1851	0.1739	0.3268	0.3348	0.3315
0.350	0.1790	0.1841	0.1588	0.3442	0.3529	0.3598
0.400	0.1697	0.1839	0.1789	0.3235	0.3350	0.3330
0.450	0.1708	0.1830	0.1699	0.3620	0.3759	0.3952

Table 21

The absorbance data for $X = 0.20$ at 15°C

$l = 3.0$ (lithium perchlorate)

$X = 0.20$

Wavelengths (nm)	521.20	521.70	522.20	574.80	575.30	575.80
Absorbance Data						
[Nitrate], M						
0.010	0.2491	0.2689	0.2847	0.3368	0.3435	0.3538
0.015	0.2165	0.2462	0.2489	0.3552	0.3614	0.3704
0.020	0.2275	0.2456	0.2432	0.3539	0.3685	0.3864
0.025	0.2025	0.2440	0.2520	0.3581	0.3702	0.3860
0.033	0.1977	0.2396	0.2498	0.3714	0.3760	0.3849
0.040	0.1988	0.2370	0.2444	0.3715	0.3765	0.3859
0.045	0.1838	0.2184	0.2300	0.3807	0.3906	0.4037
0.050	0.1809	0.2089	0.2240	0.3858	0.3911	0.3989
0.075	0.1694	0.2023	0.2152	0.3879	0.3932	0.4045
0.100	0.1468	0.1812	0.1912	0.3935	0.3990	0.4091
0.125	0.1565	0.1775	0.1933	0.3909	0.3991	0.4112
0.150	0.1482	0.1733	0.1909	0.3807	0.4009	0.4263
0.200	0.1379	0.1694	0.1843	0.3890	0.4060	0.4273
0.250	0.1435	0.1684	0.1835	0.3869	0.4106	0.4418
0.300	0.1344	0.1528	0.1662	0.4039	0.4316	0.4700
0.350	0.1256	0.1466	0.1633	0.4154	0.4318	0.4530
0.400	0.1298	0.1463	0.1601	0.4164	0.4450	0.4823

Table 22

The absorbance data for $X = 0.20$ at 20°C $l = 3.0$ (lithium perchlorate) $X = 0.20$

Wavelengths (nm)	521.20	521.70	522.20	574.80	575.30	575.80
Absorbance Data						
[Nitrate], M						
0.010	0.2361	0.2555	0.2705	0.3320	0.3401	0.3495
0.015	0.2022	0.2401	0.2474	0.3347	0.3420	0.3529
0.020	0.2100	0.2378	0.2415	0.3486	0.3622	0.3796
0.025	0.2002	0.2343	0.2472	0.3637	0.3692	0.3788
0.033	0.1994	0.2205	0.2404	0.3666	0.3717	0.3820
0.040	0.2032	0.2093	0.2204	0.3652	0.3719	0.3800
0.045	0.1770	0.2047	0.2201	0.3627	0.3746	0.3898
0.050	0.1730	0.1847	0.2149	0.3772	0.3866	0.4003
0.075	0.1570	0.1823	0.2020	0.3824	0.3873	0.3969
0.100	0.1489	0.1778	0.1929	0.3805	0.3892	0.4013
0.125	0.1580	0.1755	0.1939	0.3805	0.3892	0.4013
0.150	0.1460	0.1755	0.1907	0.3790	0.3974	0.4216
0.200	0.1451	0.1697	0.1867	0.3837	0.3998	0.4211
0.250	0.1408	0.1649	0.1813	0.3958	0.4111	0.4321
0.300	0.1443	0.1614	0.1766	0.3906	0.4140	0.4432
0.350	0.1394	0.1553	0.1693	0.4140	0.4423	0.4809
0.400	0.1299	0.1501	0.1657	0.4235	0.4511	0.4881
0.450	0.1287	0.1495	0.1667	0.4240	0.4545	0.4912
0.500	0.1277	0.1487	0.1654	0.4254	0.4596	0.4936

Table 23

The absorbance data for $X = 0.20$ at 25°C
 $l = 3.0$ (lithium perchlorate)
 $X = 0.20$

Wavelengths (nm)	521.20	521.70	522.20	574.80	575.30	575.80
Absorbance data						
[Nitrate], M						
0.100	0.2284	0.2472	0.2611	0.3215	0.3300	0.3403
0.015	0.1983	0.2343	0.2408	0.3462	0.3539	0.3663
0.020	0.2030	0.2317	0.2361	0.3482	0.3556	0.3676
0.025	0.1952	0.2316	0.2396	0.3567	0.3621	0.3736
0.033	0.1965	0.2289	0.2344	0.3601	0.3657	0.3768
0.040	0.1955	0.2230	0.2290	0.3754	0.3812	0.3911
0.045	0.1953	0.2223	0.2298	0.3764	0.3824	0.3955
0.050	0.1931	0.2116	0.2118	0.3869	0.3959	0.4102
0.075	0.1722	0.1989	0.2043	0.3808	0.3968	0.4166
0.100	0.1478	0.1765	0.1913	0.3890	0.3984	0.4129
0.125	0.1557	0.1756	0.1909	0.3803	0.3994	0.4227
0.150	0.1458	0.1706	0.1870	0.3935	0.4059	0.4216
0.200	0.1418	0.1692	0.1865	0.3938	0.4075	0.4249
0.250	0.1386	0.1627	0.1793	0.3894	0.4120	0.4394
0.300	0.1445	0.1608	0.1760	0.4021	0.4188	0.4397
0.350	0.1399	0.1544	0.1685	0.4107	0.4374	0.4739
0.400	0.1341	0.1534	0.1683	0.4202	0.4469	0.4829

Table 24

The absorbance data for $X = 0.20$ at 37°C

$l = 3.0$ (lithium perchlorate)

$X = 0.20$

Wavelengths (nm)	521.20	521.70	522.20	574.80	575.30	575.80
Absorbance data						
[Nitrate], M						
0.010	0.1969	0.2151	0.2285	0.3055	0.3142	0.3263
0.015	0.1906	0.2157	0.2201	0.3271	0.3385	0.3491
0.020	0.1845	0.2115	0.2224	0.3365	0.3442	0.3565
0.025	0.1751	0.2002	0.2113	0.3331	0.3474	0.3640
0.033	0.1799	0.1966	0.1984	0.3406	0.3480	0.3599
0.040	0.1583	0.1860	0.1954	0.3497	0.3562	0.3689
0.045	0.1578	0.1840	0.2020	0.3538	0.3649	0.3801
0.050	0.1492	0.1709	0.1881	0.3609	0.3681	0.3792
0.075	0.1421	0.1697	0.1845	0.3617	0.3691	0.3832
0.100	0.1401	0.1645	0.1801	0.3731	0.3831	0.3951
0.125	0.1425	0.1614	0.1757	0.3736	0.3895	0.4091
0.150	0.1396	0.1553	0.1686	0.3865	0.3906	0.4109
0.200	0.1321	0.1549	0.1721	0.3851	0.4068	0.4345
0.250	0.1384	0.1529	0.1659	0.4002	0.4166	0.4371
0.300	0.1234	0.1500	0.1670	0.3978	0.4241	0.4565
0.350	0.1304	0.1496	0.1512	0.4124	0.4379	0.4701

Table 25

The absorbance data for $X = 0.04$ at 15°C

$l = 3.0$ (lithium perchlorate)

$X = 0.044$

Wavelengths (nm)	521.20	521.70	522.20	574.80	575.30	575.80
Absorbance data						
[Nitrate], M						
0.013	0.2708	0.2809	0.2579	0.3500	0.3524	0.3348
0.025	0.3365	0.2581	0.2672	0.3670	0.3747	0.3753
0.038	0.2466	0.2565	0.2427	0.3764	0.3855	0.3971
0.050	0.2430	0.2543	0.2324	0.3799	0.3908	0.4058
0.063	0.2331	0.2471	0.2440	0.3911	0.3995	0.4010
0.075	0.2213	0.2401	0.2451	0.3916	0.4046	0.4242
0.100	0.2180	0.2329	0.2319	0.4007	0.4063	0.4076
0.125	0.2228	0.2323	0.2246	0.4123	0.4278	0.4491
0.150	0.2151	0.2284	0.2057	0.4136	0.4298	0.4699
0.200	0.2016	0.2226	0.2189	0.4186	0.4448	0.4829
0.250	0.2150	0.2183	0.2154	0.4256	0.4534	0.4848
0.300	0.1799	0.2002	0.2106	0.4342	0.4644	0.5006
0.350	0.1742	0.1934	0.2030	0.4348	0.4654	0.5063
0.400	0.1694	0.1894	0.1994	0.4411	0.4713	0.5094

Table 26

The absorbance data for $X = 0.04$ at 20°C

$l = 3.0$ (lithium perchlorate)

$X = 0.044$

Wavelengths (nm)	521.20	521.70	522.20	574.80	575.30	575.80
Absorbance Data						
[Nitrate], M						
0.013	0.2544	0.2595	0.2374	0.3418	0.3418	0.3263
0.025	0.2308	0.2513	0.2604	0.3609	0.3688	0.3783
0.038	0.2399	0.2467	0.2303	0.3734	0.3848	0.3989
0.050	0.2298	0.2420	0.2391	0.3828	0.3909	0.3933
0.063	0.2275	0.2372	0.2249	0.3864	0.3989	0.4183
0.075	0.2133	0.2311	0.2367	0.3929	0.4029	0.4124
0.100	0.2186	0.2267	0.2181	0.4127	0.4208	0.4233
0.125	0.2122	0.2265	0.2259	0.4077	0.4217	0.4435
0.150	0.2140	0.2209	0.2112	0.4127	0.4314	0.4563
0.200	0.1991	0.2166	0.2048	0.4308	0.4518	0.4779
0.250	0.1802	0.2095	0.1968	0.4310	0.4586	0.4938
0.300	0.1716	0.1909	0.1962	0.4318	0.4603	0.4955
0.350	0.1693	0.1881	0.1974	0.4553	0.4842	0.5201
0.400	0.1623	0.1825	0.1941	0.4757	0.4992	0.5285

Table 27

The absorbance data for $X = 0.04$ at 25°C

$l = 3.0$ (lithium perchlorate)

$X = 0.044$

Wavelengths (nm)	521.20	521.70	522.20	574.80	575.30	575.80
Absorbance data						
[Nitrate], M						
0.013	0.2579	0.2618	0.2413	0.3312	0.3335	0.3208
0.025	0.2258	0.2457	0.2555	0.3535	0.3618	0.3648
0.038	0.2335	0.2426	0.2298	0.3694	0.3802	0.3790
0.050	0.2320	0.2404	0.2209	0.3709	0.3805	0.3820
0.063	0.2259	0.2386	0.2356	0.3739	0.3820	0.3859
0.075	0.2141	0.2261	0.2222	0.3904	0.3962	0.3994
0.100	0.2121	0.2225	0.2153	0.3865	0.3963	0.4180
0.125	0.2013	0.2187	0.2247	0.4020	0.4172	0.4379
0.150	0.2080	0.2171	0.1974	0.4048	0.4242	0.4494
0.200	0.1939	0.2140	0.2224	0.4281	0.4333	0.4690
0.250	0.1819	0.2037	0.1710	0.4340	0.4577	0.4881
0.300	0.1692	0.1915	0.1997	0.4576	0.4584	0.4926
0.350	0.1685	0.1874	0.1963	0.4685	0.4845	0.5120
0.400	0.1663	0.1849	0.1943	0.4754	0.4992	0.5315

Table 28

The absorbance data for $X = 0.04$ at 37°C $l = 3.0$ (lithium perchlorate) $X = 0.044$

Wavelengths (nm)	521.20	521.70	522.20	574.80	575.30	575.80
Absorbance data						
[Nitrate], M						
0.013	0.2306	0.2351	0.2181	0.3113	0.3122	0.3031
0.025	0.2144	0.2333	0.2435	0.3423	0.3494	0.3534
0.038	0.2079	0.2241	0.2238	0.3568	0.3653	0.3691
0.050	0.2170	0.2233	0.2063	0.3555	0.3674	0.3807
0.063	0.2126	0.2219	0.2112	0.3723	0.3822	0.3928
0.075	0.1958	0.2118	0.2130	0.3698	0.3836	0.4031
0.100	0.1982	0.2101	0.2039	0.3826	0.3907	0.3957
0.125	0.1974	0.2047	0.2045	0.3861	0.4006	0.4215
0.150	0.1848	0.2040	0.2058	0.3895	0.4095	0.4336
0.200	0.1830	0.2002	0.2041	0.4196	0.4352	0.4745
0.250	0.1788	0.1878	0.1992	0.4240	0.4487	0.4792
0.300	0.1597	0.1783	0.1876	0.4256	0.4490	0.4778
0.350	0.1587	0.1774	0.1863	0.4434	0.4690	0.5002
0.400	0.1534	0.1724	0.1824	0.4652	0.4896	0.5198

Table 29
The equilibrium constants and the extinction coefficients of
both the metal and the complexes at X = 0.90

Temp.(C)	15	± error	20	± error	25	± error	37	± error
log B1	1.0039	0.0704	1.2103	0.1165	1.3154	0.0621	1.4607	0.0896
EC1 (521.2) EM	3.4786 3.8500	0.1163 0.0000	3.4694 3.8550	0.0857 0.0000	3.3778 3.8550	0.0959 0.0000	3.2376 3.8550	0.0769 0.0000
EC1(521.7) EM	3.7407 3.9500	0.1373 0.0000	3.6686 3.9500	0.1025 0.0000	3.5477 3.9500	0.0954 0.0000	3.3340 3.9500	0.0695 0.0000
EC1(522.2) EM	2.5088 3.9500	0.1120 0.0000	2.6271 3.9500	0.0729 0.0000	2.6359 3.9500	0.0536 0.0000	2.5161 3.9500	0.0657 0.0000
EC1(574.8) EM	5.6675 6.3900	0.0784 0.0000	5.2705 6.4000	0.2511 0.0000	5.4254 6.4000	0.0556 0.0000	4.9060 6.4000	0.2406 0.0000
EC1(575.3) EM	5.9792 6.4000	0.1090 0.0000	5.6152 6.4000	0.2256 0.0000	5.6880 6.4000	0.0702 0.0000	5.4877 6.4000	0.0456 0.0000
EC1(575.8) EM	5.7028 6.4100	0.0813 0.0000	5.5901 6.4150	0.0773 0.0000	5.5275 6.4100	0.0579 0.0000	5.2970 6.4150	0.0557 0.0000
K1	10.0900	1.1760	16.2290	1.3290	20.6730	1.1540	28.8600	1.2290

Table 30

The equilibrium constants and the extinction coefficients of

both the metal and the complexes at $X = 0.77$

Temp.(C)	15	± error	20	± error	25	± error	37	± error
log B 1	1.3481	0.0708	1.4327	0.0711	1.5356	0.0700	1.8000	0.0732
K1	22.2900	1.1800	27.0800	1.1800	34.3240	1.1750	63.0960	1.1840
EC1	3.3856	0.1144	3.5545	0.0816	3.6319	0.0763	3.2975	0.0581
EM	4.0000	0.0000	4.0000	0.0000	4.0030	0.0000	4.0030	0.0000
EC1	3.5296	0.0821	3.5668	0.0450	3.5321	0.0341	3.2228	0.0243
EM	4.0100	0.0000	4.0100	0.0000	4.0100	0.0000	4.0100	0.0000
EC1	2.5869	0.1242	2.6996	0.1206	2.5972	0.0960	2.5463	0.0972
EM	4.0300	0.0000	4.0300	0.0000	4.0300	0.0000	4.0300	0.0000
EC1	5.7004	0.0745	5.7456	0.0471	5.7968	0.0696	5.3606	0.0670
EM	6.6700	0.0000	6.6700	0.0000	6.6700	0.0000	6.6700	0.0000
EC1	5.8259	0.0806	5.9604	0.0499	5.9482	0.0501	5.5435	0.0410
EM	6.7000	0.0000	6.7000	0.0000	6.7000	0.0000	6.4500	0.0000
EC1	5.6038	0.0853	5.8385	0.0735	5.7563	0.0601	5.4330	0.0922
EM	6.7500	0.0000	6.7500	0.0000	6.7500	0.0000	6.7500	0.0000

Table 31

The equilibrium constants and the extinction coefficients of

both the metal and the complexes at $\chi = 0.60$

Temp. (C)	15	$\pm$ error	20	$\pm$ error	25	$\pm$ error	37	$\pm$ error
log B1	1.3650	0.0893	1.4785	0.0674	1.6626	0.1113	1.9550	0.0617
K1	23.1700	1.2300	30.0950	1.1679	45.9830	1.2920	90.1600	1.1530
EC1	3.5101	0.2222	3.1602	0.1650	3.0949	0.1492	3.1120	0.0805
EM	4.3120	0.0000	4.3125	0.0000	4.3120	0.0000	4.3120	0.0000
EC1	3.3792	0.1437	3.1940	0.1102	3.1519	0.0917	3.0296	0.0243
EM	4.3000	0.0000	4.3050	0.0000	4.3120	0.0000	4.3120	0.0000
EC1	2.7550	0.1358	2.5944	0.0960	2.5953	0.1118	2.4756	0.1008
EM	4.3000	0.0000	4.3000	0.0000	4.3000	0.0000	4.3000	0.0000
EC1	5.8587	0.0995	5.4205	0.1026	5.4269	0.0893	5.2103	0.0993
EM	7.0500	0.0000	7.0500	0.0000	7.0500	0.0000	7.0500	0.0000
EC1	6.0989	0.1051	5.8418	0.0655	5.6151	0.0470	5.3653	0.0629
EM	7.0800	0.0000	7.0800	0.0000	7.0800	0.0000	7.0800	0.0000
EC1	6.0658	0.1250	5.8612	0.1720	5.7348	0.1502	5.2994	0.0889
EM	7.0800	0.0000	7.0500	0.0000	7.0800	0.0000	7.0800	0.0000

Table 32
The equilibrium constants and the extinction coefficients of

50th the metal and the complexes at $X = 0.36$

Temp. (C)	15	± error	20	± error	25	± error	37	± error
log B1	1.4068	0.2335	1.5942	0.1947	1.7948	0.1331	2.2221	0.1725
log B2	2.2724	0.3693	2.4060	0.3150	2.4099	0.1880	2.5420	0.2018
EC1	4.7307	0.4383	4.2476	0.2941	3.8489	0.2080	3.6949	0.1201
EC2	3.7569	0.2648	3.7710	0.2094	3.6651	0.2337	3.3264	0.2587
EM	4.7035	0.0000	4.7000	0.0000	4.7030	0.0000	4.7030	0.0000
EC1	4.9844	0.4785	4.5196	0.3069	4.0645	0.2099	3.9493	0.0998
EC2	3.9552	0.2896	3.9473	0.2189	3.9032	0.2447	3.4479	0.2069
EM	4.7250	0.0000	4.7250	0.0000	4.7250	0.0000	4.7250	0.0000
EC1	3.8708	0.4606	3.6127	0.3215	3.3782	0.1723	3.4357	0.1391
EC2	3.7590	0.2833	3.7312	0.2317	3.7743	0.2181	3.4543	0.3289
EM	4.6980	0.0000	4.6980	0.0000	4.6980	0.0000	4.5000	0.0000
EC1	5.5790	0.7137	5.4553	0.5692	5.3190	0.3229	5.4252	0.2021
EC2	7.2011	0.3757	7.0994	0.3516	7.2518	0.3320	7.2634	0.4256
EM	7.6500	0.0000	7.6500	0.0000	7.6500	0.0000	7.6500	0.0000
EC1	6.0337	0.7427	5.8632	0.5753	5.6168	0.3198	5.6832	0.2018
EC2	7.2964	0.3971	7.1510	0.3598	7.1510	0.3307	7.2979	0.4216
EM	7.5700	0.0000	7.5700	0.0000	7.5700	0.0000	7.5700	0.0000
EC1	5.9209	0.7729	5.7919	0.6258	5.7919	0.3117	5.7618	0.2227
EC2	7.4076	0.4271	7.2486	0.4033	7.2486	0.3309	7.4721	0.4897
EM	7.6000	0.0000	7.6000	0.0000	7.6000	0.0000	7.6000	0.0000
K1	25.5270	1.7100	39.2820	1.5670	62.3400	1.3580	166.7300	1.4860
K2	7.3280	1.3680	6.4860	1.3180	4.1220	1.1350	2.0888	1.0698

Table 33
The equilibrium constants and the extinction coefficients of

both the metal and the complexes at X = 0.2021

Temp.(C)	15	± error	20	± error	25	± error	37	± error
log B1	1.4355	0.1864	1.6544	0.1027	1.8599	0.2562	2.2463	0.1635
log B2	2.3125	0.1766	2.5015	0.1233	2.5652	0.2199	2.6400	0.1629
EC1	2.7360	0.3220	2.5868	0.2367	2.8660	0.2150	2.4730	0.1322
EC2	2.7890	0.3220	2.9808	0.2452	2.7690	0.2620	2.7199	0.3090
EM	4.7250	0.0000	4.7260	0.0000	4.7270	0.0000	4.7270	0.0000
EC1	3.8080	0.3250	3.3867	0.2318	3.5540	0.2040	3.0809	0.1212
EC2	2.8570	0.2840	3.1321	0.2620	2.9640	0.2820	2.8185	0.2660
EM	4.7300	0.0000	4.7400	0.0000	4.7400	0.0000	4.7400	0.0000
EC1	4.2560	0.2710	4.0391	0.2239	4.0960	0.1950	3.4447	0.1154
EC2	3.0490	0.2590	3.1955	0.2719	3.0760	0.2860	2.8602	0.2616
EM	4.7000	0.0000	4.7100	0.0000	4.7200	0.0000	4.7200	0.0000
EC1	6.7950	0.2170	6.6706	0.1865	6.8360	0.1680	6.9241	0.1781
EC2	8.8290	0.2410	9.1039	0.2812	9.1640	0.3200	10.1040	0.5854
EM	7.7000	0.0000	7.7100	0.0000	7.7200	0.0000	7.7000	0.0000
EC1	7.3790	0.1180	7.2367	0.1657	7.2570	0.1380	7.2695	0.1766
EC2	9.1080	0.1560	9.3790	0.2411	10.1350	0.3060	10.5885	0.5350
EM	7.6500	0.0000	7.6555	0.0000	7.6600	0.0000	7.6600	0.0000
EC1	7.9020	0.1590	7.8094	0.2296	7.7880	0.4763	7.7779	0.2082
EC2	9.6500	0.1700	9.8950	0.2767	10.1350	0.6043	11.2745	0.5456
EM	7.6500	0.0000	7.6500	0.0000	7.6500	0.0000	7.6500	0.0000
K1	27.2580	1.5360	45.1230	1.2670	72.4300	1.8038	176.3190	1.4570
K2	7.5530	1.0230	7.0323	1.0480	5.0734	1.0872	2.4757	1.4550

Table 34

The equilibrium constants and the extinction coefficients of

both the metal and the complexes at $X = 0.04$

Temp. (C)	15	± error	20	± error	25	± error	37	± error
log B1	1.5013	0.1058	1.7392	0.2988	1.9197	0.1345	2.3241	0.1904
log B2	2.4114	0.1072	2.6392	0.2882	2.6650	0.1441	2.8984	0.1878
EC1	4.4920	0.5160	4.2605	0.2185	3.9770	0.2070	3.1760	0.1471
EC2	3.3080	0.4810	3.2898	0.1944	3.3160	0.2670	2.7200	0.4020
EM	4.7540	0.0000	4.7540	0.0000	4.7540	0.0000	4.7540	0.0000
EC1	4.9550	0.2750	4.7380	0.1517	4.4240	0.1710	4.0430	0.1200
EC2	3.5790	0.2420	3.5795	0.1469	3.4780	0.2200	2.9390	0.3150
EM	4.7350	0.0000	4.7400	0.0000	4.7400	0.0000	4.7400	0.0000
EC1	4.7290	0.1870	4.5938	0.1321	4.2760	0.1700	3.9700	0.1270
EC2	3.6740	0.1860	3.7573	0.1441	3.6200	0.2500	3.2100	0.4190
EM	4.7700	0.0000	4.7700	0.0000	4.7700	0.0000	4.7700	0.0000
EC1	7.5960	0.2900	7.4647	0.1731	7.4970	0.2450	7.3370	0.1980
EC2	9.4680	0.2460	9.7007	0.2118	9.9700	0.3500	10.6140	0.6660
EM	7.7650	0.0000	7.7650	0.0000	7.7650	0.0000	7.7650	0.0000
EC1	8.6880	0.5120	7.9660	0.2422	8.2530	0.3360	7.5420	0.2380
EC2	9.6960	0.4270	10.1229	0.2457	10.6860	0.6040	10.1600	0.7540
EM	7.6750	0.0000	7.7650	0.0000	7.6750	0.0000	7.6750	0.0000
EC1	9.6630	0.5120	8.5888	0.3990	8.9480	0.4760	7.5500	0.2350
EC2	10.0660	0.4270	10.6533	0.3680	10.6860	0.6040	10.8990	0.7540
EM	7.6850	0.0000	7.6850	0.0000	7.7400	0.0000	7.6850	0.0000
K1	31.7200	1.2800	54.8530	1.9897	83.1190	1.3610	210.9100	1.5500
K2	8.1280	1.0020	7.9433	1.0271	5.5630	1.0224	3.7523	1.0050

APPENDIX C


```
10 INPUT "Conc. of  $\text{Nd}(\text{ClO}_4)_3$ "; C
20 INPUT "Conc. of  $\text{NaNO}_3$ "; A
30 INPUT "K1"; K
25     F = A + C + 1/K
26     G = A*C
30     X = (F - ((F^2) - (4*G))^0.5)/2
40     B = 3 + 3*X - 6*C - A
45 LPRINT "Conc. of  $\text{Nd}(\text{ClO}_4)_3$  = ", C
46 LPRINT "Conc. of  $\text{NaClO}_4$  = ", B
50 LPRINT "Conc. of  $\text{NaNO}_3$  = ", A
51 LPRINT "X = ", X
60 GOTO 10
70 END
```

```
10 INPUT "Nd = " ; Z
20 INPUT "LiNO3 = " ; B
25 LET D = B
30 FOR W = 1 TO 5
40 LET K1 = 77
50 LET K2 = 5
60 LET A = Z / (1 + K1*B + K1*K2*B*B)
70 LET X = K1*B*A
80 LET Y = K1*K2*B*B*A
90 LET B = B - X - 2*Y
100 NEXT W
110 LET C = 3 - 6*A + 3*X + 5*Y - B
120 PRINT C
130 LPRINT "ORIGINAL Nd = " Z
135 LPRINT " ORIGINAL LiNO3 = " D
140 LPRINT "X = " X
150 LPRINT "Y = " Y
160 LPRINT " Nd3+ = " Z - X - Y
190 LPRINT " C = " C
200 LPRINT : LPRINT
210 GOTO 20
```