A STUDY OF COMPLEX FORMATION IN SOLUTIONS OF NICKEL AND NITRITE IONS AND NICKEL IONS AND HYDRAZINE

by

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A STUDY OF COMPLEX FORMATION IN SOLUTIONS OF NICKEL AND NITRITE IONS AND NICKEL IONS AND HYDRAZINE

CHAPTER I

INTRODUCTION

One of the major fields of research in inorganic chemistry during the last fifty years has been the large class of complex compounds which are characterized by the presence of a central metallic atom surrounded by one or more atoms or groups of atoms which are bound by covalent forces; the central atom and the coordinated groups form an ion or molecule that is more or less stable. The added groups may be simple ions, such as halogens, ionic radicals, such as cyanide and nitrate, or neutral molecules, such as water and ammonia.

Early investigations of these complex compounds were limited to the preparation and study of the crystalline salts. Later, with the development of experimental techniques, studies have been made of the equilibria existing in solutions of these complexes. Various physico-chemical methods have been used to study these equilibria, including cryoscopy (3, 4, 7), polarography (25), potentiometry (18, 19, 22), the migration of the ions in a potential gradient (10, 11), viscometry (7), conductance (7), and spectrophotometry (1, 8, 16, 17, 18, 20, 22, 27).

These studies have had two objectives: the determination of the formulas of the complexes existing in the solution and then the stability of these complexes. Job (17, 18) has developed a general method for determining both of these, provided that not more than one complex exists in the solution. If more than one complex exists, the formula for each complex may be determined, if some property differing sufficiently for the two complexes may be measured. Vosburgh and co-workers have developed and applied this method (8, 16, 27).

Job's method, which is known as the method of continuous variation, is applied to the formation of complex ions represented by the general equation

$$mM_a + nX_b \rightleftharpoons qM_sX_t \tag{1}$$
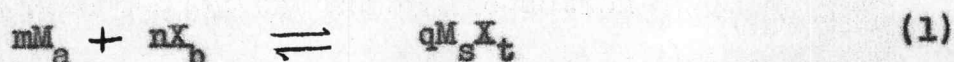
A solution of concentration c in M (not in the associated M_a) and one of concentration pc in X are prepared; a fraction x of a liter of the second is mixed with (1-x) liters of the first, making the total volume one liter, if it is assumed that the change in volume upon mixing is negligible, and the concentration of the complex is determined by some suitable means. To determine the composition of the complex, it is necessary to determine the value of x for which the concentration Z of the complex M_sX_t is a maximum.

By applying the law of mass action to reaction (1), an expression for the dissociation constant of the complex is secured,

$$c_{M_a}^m \times c_{X_b}^n = KZ^q, \tag{2}$$

in which C denotes molecular concentration, and Z is defined above.

From equation (1) two more relations are evident:

$$c(1-x) = ac_{M_a} + sZ \tag{3}$$

$$pcx = bc_{X_b} + tZ \tag{4}$$

The concentration Z of the complex varies only with the composition x, provided p and c are constant. Therefore, to obtain the maximum composition, it is only necessary to take the derivatives of Z in respect to x in equations (2, 3, 4) and set Z' equal to zero. Upon combining the three resulting equations, equation (5) is secured.

$$-\frac{mc}{a}c_{X_b} + \frac{npc}{b}c_{M_a} = 0 \tag{5}$$

Elimination of c_{M_a}, c_{X_b}, and Z from equations (2, 3, 4, 5) gives the desired relation (18, p. 116):

$$\frac{c^{m+n-q} p^{n-q} m^m n^n}{a^m b^n (nps-mt)^{m+n-q}} \left[(t+sp)x - t \right]^{m+n} = K\left[n - (m+n)x \right]^q \quad (6)$$

If M and X are simple molecules in solution, then $a = b=1$ and equation (6) reduces to

$$\frac{c^{m+n-1} p^{n-1}}{m^{n-1} n^{m-1} (p-1)^{m+n-1}} \left[(pm+n)x - n \right]^{m+n} = K\left[n-(m+n)x \right] \quad (7)$$

Equation (6) (or equation (7)) determines the composition of the solution at which the concentration Z of the complex is a maximum, as a function of the concentrations of the two solutions and the equilibrium constant K. In general the maximum depends on the concentration chosen for the solution of M. It is independent, though, if

$$(t+ps)x - t = n - (m+n)x = 0$$

from which

$$x = n/(m+n) = t/(t+p)$$

and

$$n/(m+n) = qt/(qt + qsp) = nb/(nb+pma);$$
$$(m+n)b = nb + mpx$$
$$b = pa \quad \text{or} \quad p = b/a$$

Thus, if the concentrations of the two solutions are in the ratio of b/a, the maximum is independent of the initial concentration, and the value x at which the maximum occurs is the ratio $m/(m+n)$ in which two constituents combine to form the complex.

After the formula of the complex has been determined, K may be evaluated by measurements made with solutions that are not in the ratio b/a, by use of equation (7).

To apply the method it is only necessary to measure the value of some property which is dependent upon the concentration of the complex, such as the refractive index or the absorption of light. The absorption of monochromatic light is especially useful, because complex ions are often differently colored from their components and the absorption is usually directly proportional to the concentration of the absorbing species present.

Job has applied this method to several complex ions with satisfactory results, but upon attempting to apply it to solutions containing cupric and bromide ions in one case and nickel ions and ammonia in another, obtained discordant results, which he explained as due to the formation of more than one complex (18). More recently Vosburgh and others (8, 16, 27) have extended the method to the determination of the formulas for more than one complex in the same solution with good results provided that certain conditions were fulfilled. If two complexes are formed, the stabilities must be such that when the concentration of the first is a maximum, that of the second is small, and conversely. In addition, the two

complexes must have characteristic absorptions of light at different wave lengths, so that the maximum in each may be determined independently.

COMPLEX FORMATION BETWEEN NICKEL AND NITRITE
IONS IN SOLUTION

When a solution containing nitrite ions is added to a nickel solution, the characteristic green nickel color becomes more intense. This deepening is not observed upon the addition of nitrate, sulfate, or chloride ions. Since a number of crystalline triple salts containing nickel, nitrite and some other metal ion have been prepared, all of which seem to contain the hexanitronickelate ion $(Ni(NO_2)_6^{-4})$* (3, 4, 14, 15, 21), it would be of interest to see if the deepening of color were due to the formation of such a complex ion in the solution. All the hexanitronickelates which have been prepared are characterized as easily hydrolyzed; some cannot be prepared in aqueous solutions because of the great extent of hydrolysis (15). Cuttica (3) studied the degree of dissociation of thallium hexanitronickelate by measuring the depression of the freezing point and found that, in the extremely dilute solutions used, there were between nine and ten times as many particles present as would be expected if the simple $Tl_4(Ni(NO_2)_6$ molecules existed in solution, but less than the maximum number of particles

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*In the older literature this ion is called variously nickelhexanitrite or hexanitritonickelate; the name used is that preferred by Chemical Abstracts.

into which the complex compound could theoretically dissociate, eleven. From this he concluded that the complex thallium hexanitronickelate dissociated first into thallium ions, nitrite ions, and nickel nitrite, with the latter further dissociating, although incompletely, into nickel ions and more nitrite ions. Ferrari and Curti (15), however, assume that there is complete dissociation into the metal and hexanitronickelate ions, with the latter dissociating further into nickel and nitrite ions. It seems probable that in either mechanism there is a stepwise dissociation, with perhaps the intermediate formation of a tetranitronickelate ion, which further dissociates to nickel nitrite. This is confirmed by some work of Cuttica and Paoletti on the more stable hexanitrocobaltate (II) ion, which dissociates to give appreciable amounts of the tetranitro complex (5). The stepwise addition of the nitrite ion is further confirmed by the work of Vosburgh and Cooper (27) with nickel sulfate and both o-phenanthroline and ethylenediamine. In each case, the coordinating group entered stepwise, bonding with two of the coordinating valences of the nickel atom. DeWijs (9) also found that there were three nickel ammonia complexes formed, with two, four, and six molecules of ammonia per nickel ion. The present work confirms this tendency of nickel to form complexes in which

pairs of coordinating valences are satisfied by the same group, since evidence was secured for the existance of the $Ni(NO_2)_2$ and $Ni(NO_2)_4^{-2}$ complexes in solution. Since the nickel ion in aqueous solution coordinates six water molecules, unless there is some other more readily coordinated group, it is probable that the nitrite ions each remove a molecule of water, attaching themselves in their places. Since the non-hydrated nickel ion does not appear to exist in water solutions, the equilibria should be written to show the coordinated water molecules, which would saturate the six coordinate valences of the nickel, such as $Ni(NO_2)_2(H_2O)_4$, but for simplicity the water has been omitted.

CHAPTER III

EXPERIMENTAL

In order to determine the formulas for any complexes present in solutions of nickel and nitrite ions, measurements were made of the conductance of solutions of nickel and nitrate and sodium nitrite of various composition, and the conductance was plotted against concentration. If complexes with different ionic charges existed in the solutions, the slope of the curve should change with the concentration due to the formation of the complexes whose conductances will be different from that of the simple nickel ion. The points at which this change of slope takes place indicate the composition of the complex.

The measurements were made in a thermostat at 25.0 ± 0.5°C, using a Leeds and Northrup Kohlrausch type Wheatstone bridge and a modified Jones and Bollinger conductance cell (18a). The solutions were made with redistilled water and Baker's CP nickel nitrate and sodium nitrite. A series of trials gave inconclusive results, and in order to check the apparatus, it was decided to attempt to repeat the work of Cuttica and Paciello (4a), who used this method to determine the existance of two nitrocuprates, $Cu(NO_2)^+$ and $Cu(NO_2)_2$, in solutions of

cupric chloride and barium nitrite. The results were
again inconclusive, and were also quite erratic. In
addition, the odor of nitric oxide could be detected over
the solutions, and after these had stood for a short
time, a white precipitate formed, which was identified as
cuprous chloride.

A time study of the conductance of a solution of
cupric chloride and sodium nitrite showed a large change
in conductance with time; a precipitate formed in the cell
during the run. This reduction of the cupric copper by
the nitrite, with simultaneous oxidation to the nitrate,
casts considerable doubt upon the results of Cuttica and
Paciello. They mention that their solutions had a
slight odor of nitric oxide, but appear to have attached
no importance to this. Their results were confirmed by
Kossiakoff and Sickman, who used an optical method (20),
but they give insufficient experimental details and there-
fore it is impossible to make a positive decision. From
the data given, it appears that they have made a funda-
mental error in the derivation of one of their equations
(their equation (5)); at least, it has been impossible
to repeat their derivation. If this equation is in error,
the interpretation given of their experimental data is
subject to serious doubt.

Because of the insensitivity of the conductance

apparatus available, which gave data from which no decision could be made as to the existence of any complex, conductivity measurements with nickel solutions were discontinued, and the data discarded as unreliable.

To determine if Job's method of continuous variation could be applied, to determine convenient wave lengths at which to work, and to see if there was any evidence for the existence of more than one complex, a series of measurements was made with solutions 0.1M in nickel nitrate and with various ratios of added nitrite ion, in the form of sodium nitrite, to nickel. Baker's CP nickel nitrate, low in cobalt, was used without further purification, as were Baker's CP sodium nitrate and sodium nitrite. All solutions were kept at a constant ionic strength of 1.20M by the addition of sodium nitrate; the absorption of the nitrate ion is negligible in the region studied, and it does not appreciably form any colored complexes (22). The absorption of monochromatic light in bands of 100Å width was measured at intervals of 200Å over the spectral range $4000 - 7200$ Å using a Cenco-Sheard spectrophotelometer with 1 cm absorption cells of fused Corex. The results are summarized in Table I and Figure I. The optical density, $\log I_0/I$, where I_0 is the intensity of the light transmitted by a reference solution of sodium nitrate of the same ionic strength as that used

TABLE I

OPTICAL DENSITY OF SOLUTIONS OF NICKEL AND NITRITE IONS

Ratio NO_2^-/Ni^{++}	Pure $Ni(NO_3)_2$ Solution		1:1		2:1	
Wave Length $\overset{o}{A}$	Absorption I_o/I	Optical Density $\log I_o/I$	Absorption I_o/I	Optical Density $\log I_o/I$	Absorption I_o/I	Optical Density $\log I_o/I$
4000	2.26	.354	2.61	.416	2.83	.452
4200	1.41	.149	1.47	.168	1.53	.184
4400	1.085	.036	1.17	.070	1.20	.079
4600	1.06	.025	1.08	.034	1.11	.047
4800	1.01	.004	1.03	.012	1.035	.014
5000	1.005	.003	1.01	.004	1.015	.006
5200	1.015	.006	1.01	.004	1.02	.008
5400	1.025	.010	1.015	.006	1.035	.014
5600	1.035	.014	1.05	.022	1.07	.030
5800	1.09	.038	1.10	.042	1.125	.052
6000	1.185	.074	1.21	.083	1.24	.094
6200	1.32	.122	1.375	.138	1.41	.149
6400	1.45	.160	1.49	.178	1.565	.194
6600	1.48	.169	1.51	.180	1.58	.200
6800	1.50	.176	1.58	.200	1.59	.202
7000	1.57	.196	1.65	.218	1.575	.198
7200	1.535	.186	1.615	.208	1.575	.198

| Ratio NO_2^-/Ni^{++}	3:1		4:1		9:1	
4000	2.92	.466	4.3	.636	4.83	.684
4200	1.565	.195	1.70	.230	1.905	.280
4400	1.235	.092	1.31	.118	1.43	.156
4600	1.13	.054	1.17	.070	1.245	.096
4800	1.045	.020	1.06	.025	1.10	.042
5000	1.015	.006	1.03	.012	1.045	.020
5200	1.02	.008	1.035	.014	1.03	.012
5400	1.035	.014	1.05	.022	1.04	.018
5600	1.08	.034	1.09	.038	1.09	.038
5800	1.145	.059	1.175	.071	1.180	.073
6000	1.26	.100	1.31	.118	1.335	.126
6200	1.44	.158	1.505	.177	1.55	.191
6400	1.58	.200	1.68	.225	1.705	.232
6600	1.60	.204	1.70	.230	1.73	.239
6800	1.61	.206	1.655	.219	1.69	.227
7000	1.67	.222	1.60	.204	1.70	.230
7200	1.57	.196	1.63	.213	1.63	.213
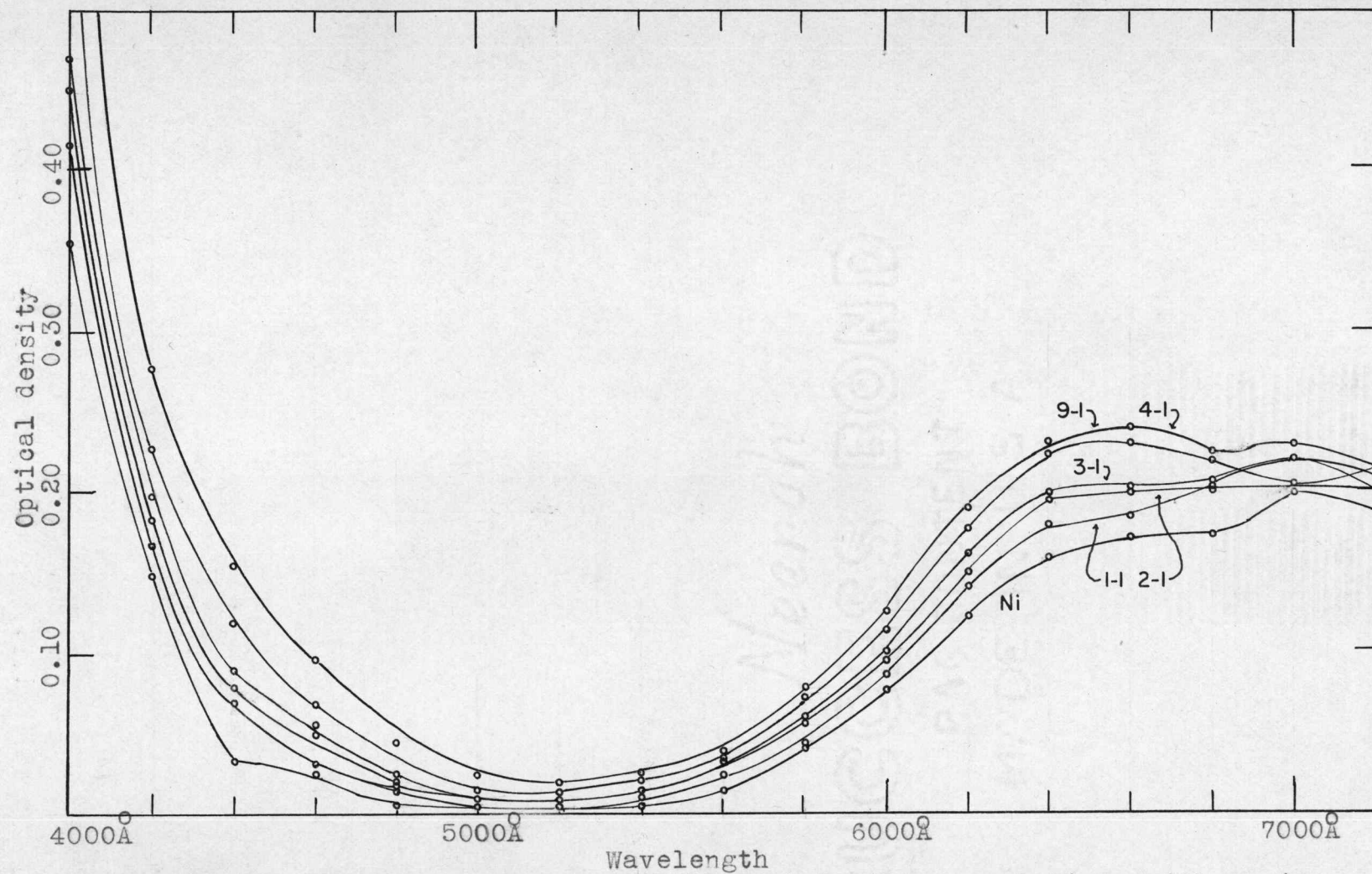
Figure I. Absorption spectra of 0.1M nickel nitrate solutions with various ratios of added sodium nitrite

in the nickel solutions and I is the intensity when the
nickel solution is used, is plotted in Figure I against
the wave length.

These curves show that there is an increase in ab-
sorption in the two regions from 4000 to 4800Å and from
6200 to 7200Å. The lower region was discarded because
nitrite ion was found to have an appreciable absorption
at the shorter wave lengths; in addition, the curves are
changing rapidly, so that a small error in wave length
setting would make a large error in the absorption read-
ing. Because of the low intensity of the light available
there was a greater relative error in the readings above
6600Å and this region was not used for quantitative
measurements. For this reason, also, the small variations
in the curves around 7000Å were discarded as unreliable;
they may or may not be significant, but the apparatus
available did not permit any decision. It was therefore
decided that the most satisfactory wave lengths for further
work were 6400 and 6600Å. A Beckman spectrophotometer
ordered for this work, and of considerably more preci-
sion and greater spectral range than the spectrophotel-
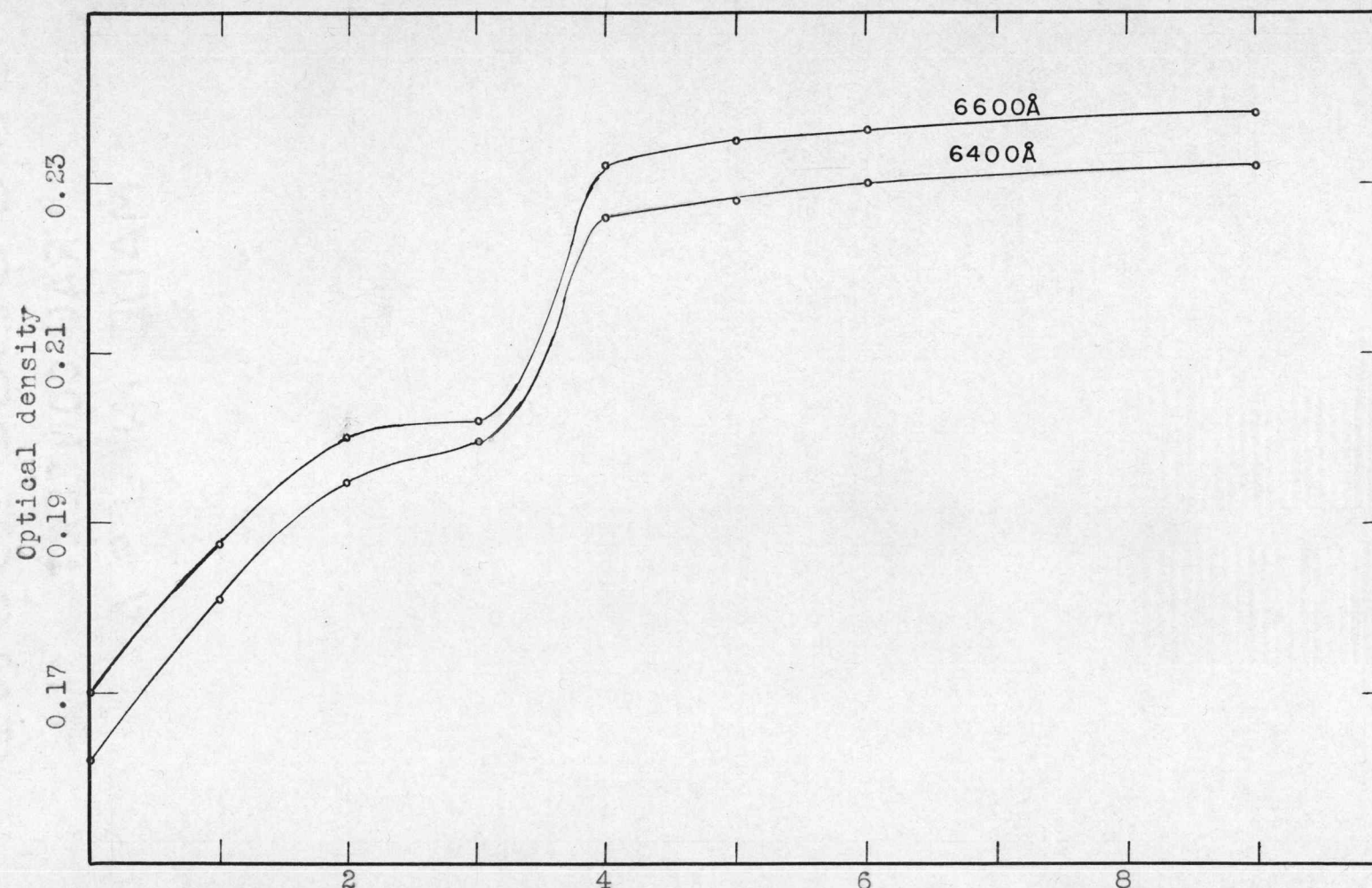ometer used, was still unavailable when this thesis was
completed.

A preliminary study using nickel solutions of vary-
ing concentrations gave inconclusive results with the

method of continuous variation, and it was decided there-
fore that there must be at least two complexes present
that differed in the characteristic wave length of light
absorbed to such a small degree that their effects could
not be separated. The next best method appeared to be
one similar to that used by Kossiakoff and Sickman (20)
in studying the nitrocuprates (II), in which formulas
for the complexes are assumed and the equilibrium con-
stants calculated from measurements of the amounts present
in different solutions. Therefore, a series of measure-
ments was made keeping the total concentration of nickel
0.1 M and varying that of the nitrite, using the two
wave lengths selected. From these data (Table II) Figure
II was constructed. The shape of the curves indicates

TABLE II

OPTICAL DENSITY OF SOLUTIONS OF NICKEL AND NITRITE IONS AT $6400\overset{\circ}{A}$ and $6600\overset{\circ}{A}$

| Ratio NO_2^-/Ni^{++} | $6400\overset{\circ}{A}$ | | $6600\overset{\circ}{A}$ | |
	Absorption I_o/I	Optical Density Log I_o/I	Absorption I_o/I	Optical Density log I_o/I
0:1	1.452	.162	1.480	.170
1:1	1.483	.174	1.518	.181
2:1	1.567	.195	1.584	.200
3:1	1.584	.200	1.591	.202
4:1	1.682	.226	1.706	.232
5:1	1.693	.229	1.718	.235
6:1	1.698	.230	1.722	.236
9:1	1.706	.232	1.730	.238

All solutions are 0.1M in Nickel Nitrate.

Figure II.   Absorption of 0.1M nickel nitrate solutions containing sodium nitrite.

the existence of two complexes, one with two nitrite groups coordinated and the second with four. It also appears that the addition of each pair of nitrite groups increases the extinction coefficient by about the same amount. Since the curves seem to approach a limit as the amount of nitrite ion is increased, it is assumed that the extinction coefficient of the tetranitro complex is that of the solution at the highest ratio of nitrite to nickel. This introduces some error, but probably not more than 5%. On the basis of these three assumptions the stability constants for the two complexes are calculated.

The equilibria assumed to be present in the solution may be represented by the following equations and stability constants:

$$Ni(NO_2)_2 \rightleftharpoons Ni^{++} + 2NO_2^- \; ; \; K' = \frac{[Ni^{++}] \times [NO_2^-]^2}{[Ni(NO_2)_2]} \quad (9)$$

$$Ni(NO_2)_4^{--} \rightleftharpoons Ni(NO_2)_2 + 2NO_2^- \; ;$$

$$K'' = \frac{[Ni(NO_2)_2] \times [NO_2^-]^2}{[Ni(NO_2)_4^{--}]} \quad (10)$$
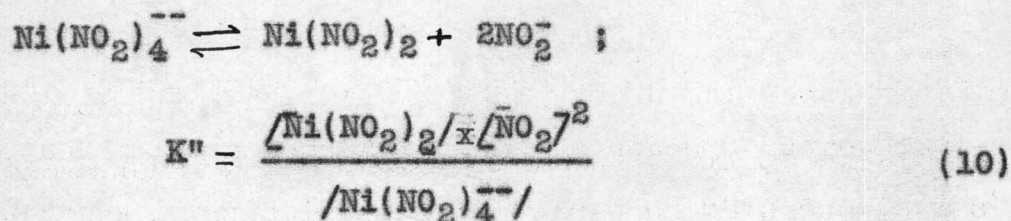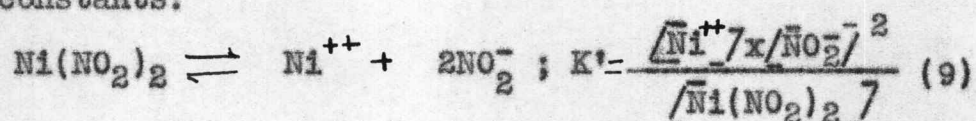
In general, the optical density of the solution may be represented by

$$d = (\epsilon_1 C_1 + \epsilon_2 C_2 + \epsilon_3 C_3)L = \log I_0/I$$

where ϵ_1 is the extinction coefficient of the component whose concentration is C_1 and L is the length of the absorption cell; in this work cells with a length of $1 \pm .005$ cm were used. Since the nitrite and nitrate ions have no appreciable absorption in the region chosen (20,22), the optical density of a solution containing nickel nitrite ions and the two complexes assumed present is given by

$$d = \epsilon_{Ni}C_{Ni} + \epsilon_A C_A + \epsilon_B C_B \qquad (11)$$

where A and B represent the two complexes $Ni(NO_2)_2$ and $Ni(NO_2)_4^{--}$. The extinction coefficient of nickel, found from measurements on 0.1M solutions of nickel nitrate of the same ionic strength as that used for all the other measurements, is 1.62 at 6400Å and 1.70 at 6600Å.

If it is assumed that practically all the nickel in the nine nitrite:one nickel solution is in the form of the tetranitro complex, the extinction coefficient ϵ_B of this complex is 2.32 at 6400Å and 2.38 at 6600Å. Because of the shape of the curves in Figure II, the extinction coefficient of the dinitro complex is reasonably assumed to be halfway between that of nickel and the tetranitro complex, or 1.97 at 6400Å and 2.04 at 6600Å.

In order to calculate the stability constant K" it is assumed that the amount of nickel not in a complex

form in a solution of ratio 6:1 is negligible; this enables two simultaneous equations to be written, using the data for 6600$\overset{\text{o}}{\text{A}}$ as an example:

$$.236 = 2.04c_A + 2.38c_B; \quad c_A + c_B = 0.1M$$

Solution of these equations and substitution in equation (10) yields $K'' = 2.7 \times 10^{-3}$, with concentrations expressed in moles per liter.   The data for 6400$\overset{\text{o}}{\text{A}}$ give $K'' = 2.8 \times 10^{-3}$, in satisfactory agreement.

K' may now be found from the optical density of one of the solutions of lower nitrite-nickel ratio, where there are appreciable amounts of Ni^{++} still uncombined. With the values for the extinction coefficients used above, the value for K" found above, and equations (9), (10), and (11), K' is found to be 6.7×10^{-5} and 6.9×10^{-5} at the two wave lengths.

CHAPTER IV
DISCUSSION

The stability constants found indicate that the second complex, $Ni(NO_2)_4^{--}$, is only about one tenth as stable as the first, in qualitative agreement with the results of Cuttica (3, 5). The fact that two nitrite groups coordinate at one time might seem to be surprising, since a stepwise addition was assumed by Kossiakoff and Sickman (20) for nitrite and cupric ions. However, from the data presented in their paper, it is impossible to determine if their assumption is justified. Vosburgh and Cooper (27) found stepwise addition for o-phenanthroline and ethylenediamine to nickel ion, but in this case the groups coordinating have two active points, and one group satisfies two of the coordination valences of the nickel. On the other hand, nickel and ammonia seem to add two molecules at a time (9, 27). A possible explanation may be the formation of an intermediate mononitro complex, which is so unstable that it either adds a second nitrite ion, or dissociates immediately into the nickel and nitrite ions.

No trace was found of the hexanitronickelate ion in the solutions studied. An attempt was made to employ much higher ratios of nitrite to nickel, but the solutions became so absorbing that satisfactory, reproducible

readings could not be secured, if 0.1M nickel solutions saturated or nearly saturated with sodium nitrite were employed. Solutions dilute enough to measure at the higher ratios could not be measured at the lower ratios with enough precision to warrant calculations. The color did increase to some extent in the solutions with a very high ratio of nitrite ion to nickel ion, indicating that there was probably some of the hexanitro complex formed. When the more precise Beckman spectrophotometer becomes available, it should be possible to prove the existence of this complex and measure its stability.

No attempt has been made to estimate thermodynamic activities of the ions and complexes, since the various assumptions made in the calculations introduce approximations greater than the error made by employing concentration units rather than activities. It is estimated that the precision in the determination of the optical density is from 0.3 to 2.0%, depending upon the degree of absorption and the intensity of light available. Since in the calculations, the small difference of two such values are used, the precision in the actual determination of K' and K" is about 5%. In addition, the assumptions (1) that all the nickel is in the form of the tetranitro complex in the solution of highest nitrite-nickel ratio, (2) that the addition of each pair of

nitrite ions increases the extinction coefficient by the
same amount, and (3) that there is no appreciable amount
of nickel ion in the solution with a ratio of 6:1, intro-
duce additional uncertainties, which may make K' and K"
in error by as much as 10-15%. The order of magnitude,
though, would remain that determined.

CHAPTER V

COMPLEX FORMATION BETWEEN NICKEL IONS AND HYDRAZINE IN SOLUTION

When hydrazine is added to a solution of nickel, a
deep blue color is formed, followed shortly by the pre-
cipitation of a red-violet precipitate if the solution
is at all concentrated (12). If nickel sulfate is used,
the precipitation occurs at a very low concentration;
with the chloride and especially the nitrate, a much more
intense color may be secured before precipitation occurs.
This is probably due to both the variation in stability
of any complexes formed because of the change in ionic
strength with change in anion, and the greater solubility
of the complex nitrate. The limited solubility of most
of the complex hydrazine compounds was first used by
Curtius and Schrader (2) shortly after the discovery of
hydrazine to prepare a number of hydrazine complexes in
crystalline form, including $NiSO_4(N_2H_4)_2$. Later workers
(6, 7, 12, 13, 23, 24) have prepared numerous highly
colored complex salts of hydrazine with various nickel
salts, including the sulfate, acetate, benzoate, chloride,
bromide, pyrophosphate, oxalate, and cyanide. Franzen
and von Mayer (12) prepared a complex with nickel nitrate
containing three hydrazine molecules; this was a red
violet color and appears to be the precipitate that forms

when nickel nitrate and hydrazine solutions are mixed
and allowed to stand. In every case there were two or
three hydrazine molecules per nickel atom, which would
indicate the formation of two complexes, $Ni(N_2H_4)_2^{++}$ and
$Ni(N_2H_4)_3^{++}$, corresponding to the tetrammine and hexammine
complexes with ammonia. However, Sommer and Weise report
the preparation of a deep blue hydrated nickel sulfate
containing only one molecule of hydrazine (26). This
indicates that there might be a stepwise addition of the
hydrazine, with the formation of the monohydrazinenickel-
ate as an intermediate step in the formation of the di-
hydrazine or trihydrazine complexes. It would be of
interest to know what complexes exist in solution, and if
the higher complexes are soluble enough to be detected.

CHAPTER VI
EXPERIMENTAL

Solutions 0.02M in nickel nitrate and containing Edwal 100% hydrazine hydrate in various ratios were prepared and the absorption spectra determined as before. From the data obtained (Table III, Figure III) it appeared that there was only one complex present. (This was true even for solutions concentrated enough for precipitation to take place. Apparently the higher complexes were so insoluble that they did not affect the absorption spectra, or did not absorb in the region available.) Accordingly, solutions $0.02(1-x)$M in nickel nitrate and $0.02x$M in hydrazine were prepared and the absorption determined at 5800$\overset{o}{A}$, 6000$\overset{o}{A}$, and 6200$\overset{o}{A}$. (Table IV). Upon graphing these data, Figure IV, two maxima were observed, one at $x =$

TABLE IV

OPTICAL DENSITY OF SOLUTIONS 0.02xM IN HYDRAZINE
AND 0.02(1-x)M IN NICKEL ION

Wave length $\overset{o}{A}$	5800		6000		6200	
x	Absorption I_o/I	Optical Density $\log I_o/I$	Absorption I_o/I	Optical Density $\log I_o/I$	Absorption I_o/I	Optical Density $\log I_o/I$
0.0	1.035	.016	1.055	.023	1.070	.030
0.1	1.060	.026	1.060	.026	1.070	.030
0.2	1.095	.040	1.120	.049	1.110	.046
0.3	1.130	.054	1.150	.061	1.140	.057
0.4	1.165	.067	1.190	.076	-----	---
0.5	1.180	.071	1.210	.084	1.205	.081
0.6	1.160	.065	1.190	.076	1.210	.083
0.75	1.120	.049	1.125	.052	1.190	.076

TABLE III

ABSORPTION SPECTRA OF SOLUTIONS OF 0.02M NICKEL NITRATE WITH ADDED HYDRAZINE

| Ratio N_2H_4/Ni^{++}	0:1		1:1	
Wave length $\overset{\circ}{A}$	Absorption I_o/I	Optical Density $\log I_o/I$	Absorption I_o/I	Optical Density $\log I_o/I$
4000	1.140	.057	1.160	.066
4200	1.090	.039	1.105	.043
4400	1.050	.022	1.065	.028
4600	1.040	.018	1.060	.026
4800	1.025	.011	1.050	.022
5000	1.030	.013	1.045	.018
5200	1.020	.010	1.065	.028
5400	1.030	.013	1.100	.041
5600	1.030	.013	1.145	.058
5800	1.035	.016	1.190	.076
6000	1.055	.024	1.210	.084
6200	1.070	.030	1.215	.085
6400	1.110	.044	1.205	.082
6600	1.105	.043	1.165	.067
6800	1.110	.044	1.145	.058
7000	1.100	.042	1.120	.047
	2:1		3:1	
4000	1.170	.068	1.230	.090
4200	1.095	.040	1.145	.058
4400	1.085	.036	1.130	.054
4600	1.085	.036	1.095	.040
4800	1.065	.028	1.070	.030
5000	1.070	.030	1.080	.034
5200	1.090	.039	1.120	.050
5400	1.145	.058	1.170	.068
5600	1.215	.085	1.250	.098
5800	1.280	.107	1.300	.115
6000	1.305	.116	1.320	.121
6200	1.280	.107	1.305	.116
6400	1.245	.096	1.270	.104
6600	1.205	.082	1.230	.092
6800	1.175	.070	1.185	.074
7000	1.135	.056	1.150	.060
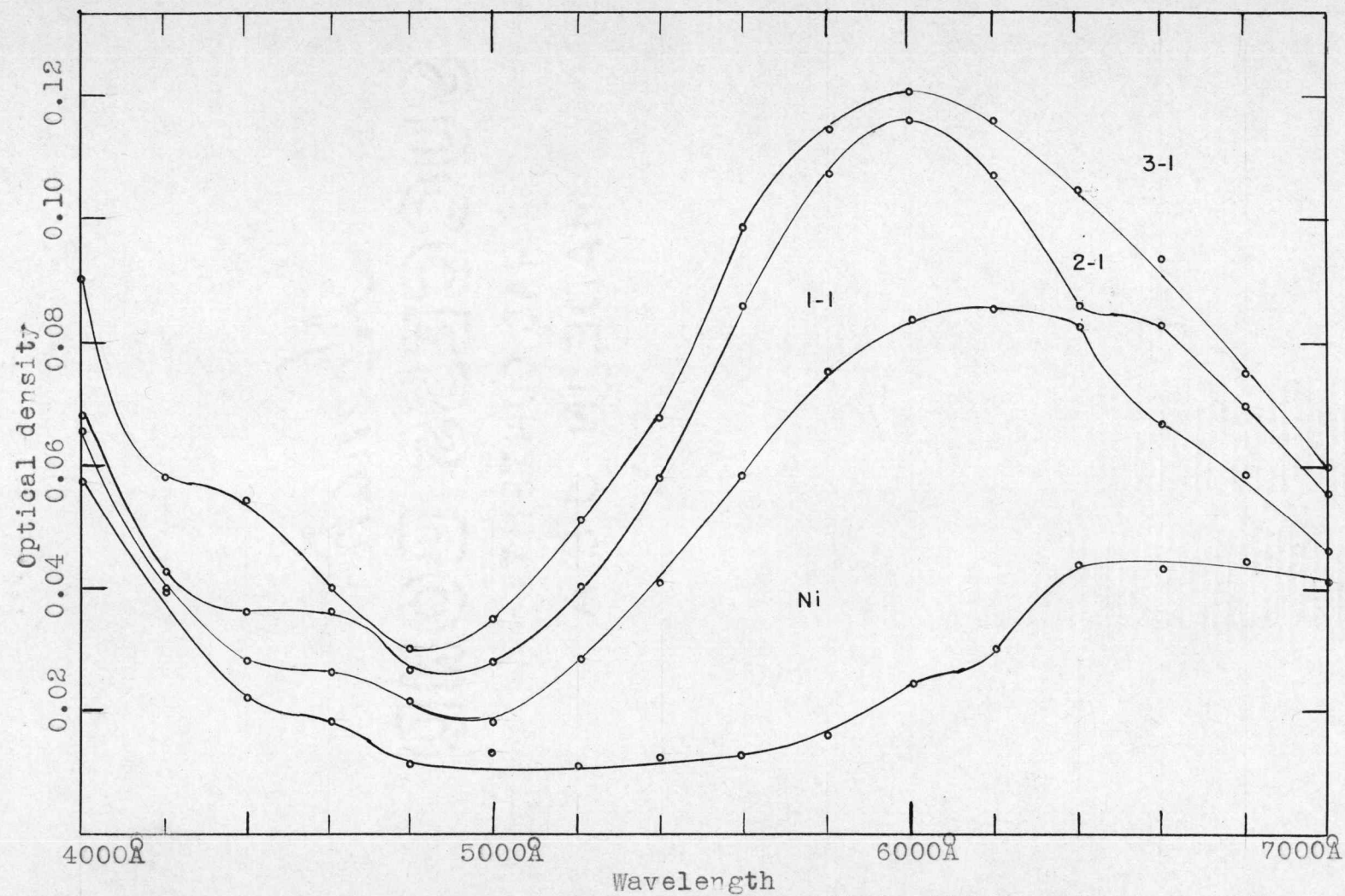
Figure III.   Absorption spectra of 0.02M nickel nitrate solutions with various ratios of added hydrazine.
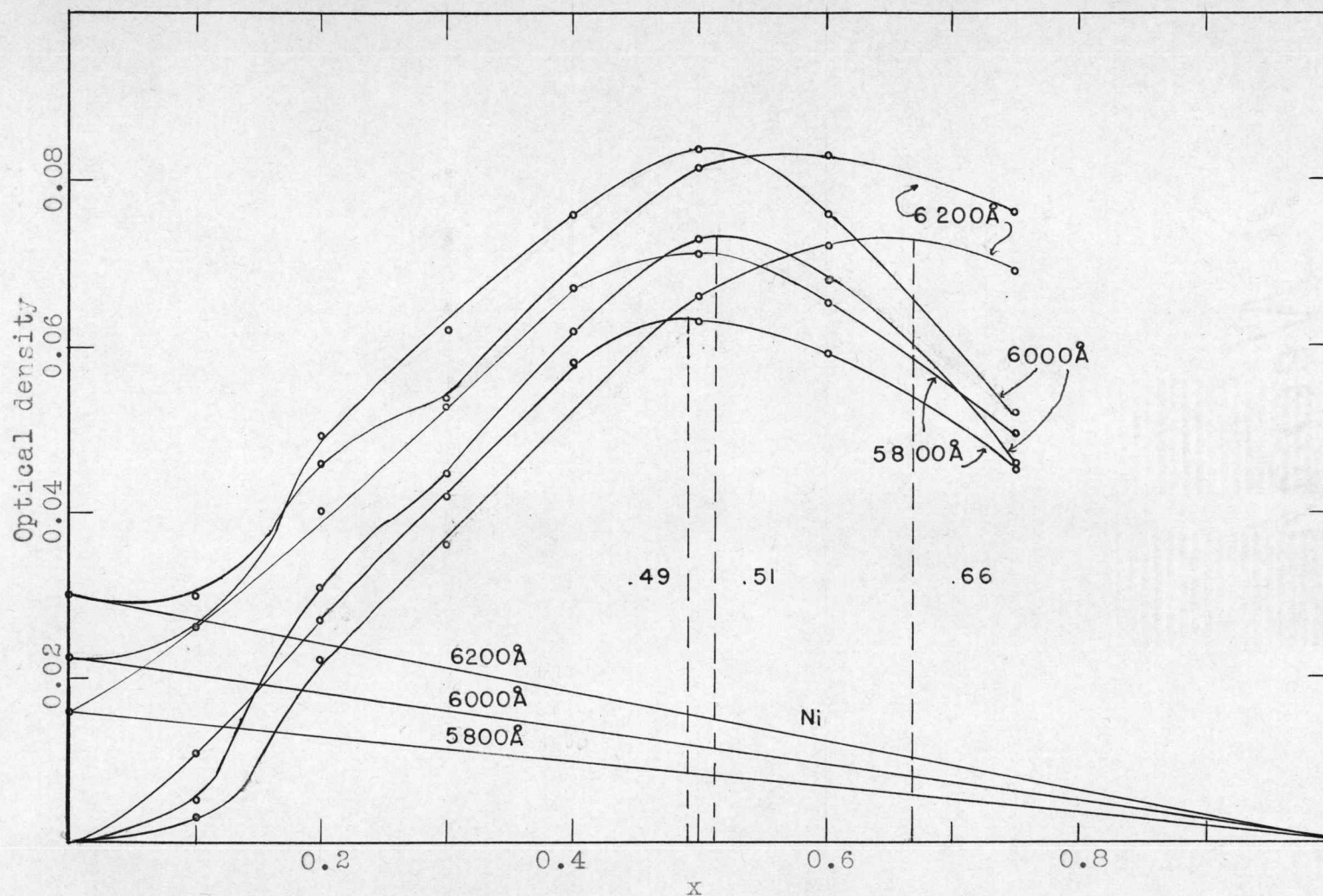
Figure IV.   Absorption of (1-x) liters of 0.02M nickel nitrate and
x liters of 0.02M hydrazine.

0.5, and the other at 0.66, indicating the formation of two complex ions, $Ni(N_2H_4)^{++}$ and $Ni(N_2H_4)_2^{++}$. (In Figure IV, the upper curves are the observed optical densities, the lower curves, the increase in optical density over that expected if no complex is formed. By use of the latter curves, a sharper maximum is secured.)

To determine the stability constant for the mono-hydrazine nickel complex,

$$K = \frac{[Ni^{++}] \times [N_2H_4]}{[Ni(N_2H_4)^{++}]} \quad ,$$

solutions 0.04(1-x)M in nickel nitrate and 0.08xM in hydrazine were prepared and the absorption measured in the usual manner. From the measured optical density, (Table V), Figure V was constructed, giving an average

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TABLE V

OPTICAL DENSITY OF SOLUTIONS 0.08xM IN HYDRAZINE
AND 0.04(1-x)M IN NICKEL ION

Wave length Å	5800		6000		6200	
	Absorption I_0/I	Optical Density $\log I_0/I$	Absorption I_0/I	Optical Density $\log I_0/I$	Absorption I_0/I	Optical Density $\log I_0/I$
x						
0.0	1.075	.032	1.110	.046	1.150	.061
0.1	1.105	.044	1.140	.057	1.190	.076
0.2	1.170	.068	1.215	.085	1.240	.094
0.3	1.225	.089	1.265	.102	1.280	.108
0.4	1.250	.098	1.290	.111	1.310	.117
0.5	1.245	.096	1.275	.106	1.270	.104
0.6	1.205	.081	1.220	.087	1.210	.083

value for x of 0.443 at the maximum. Substitution of
this value in equation (7), with m and n = 1, p = 2, gives
a stability constant of 0.10, with concentrations express-
ed in moles per liter. The stability constant of the
dihydrazine complex could not be determined because of
the interfering absorption of the first complex in the
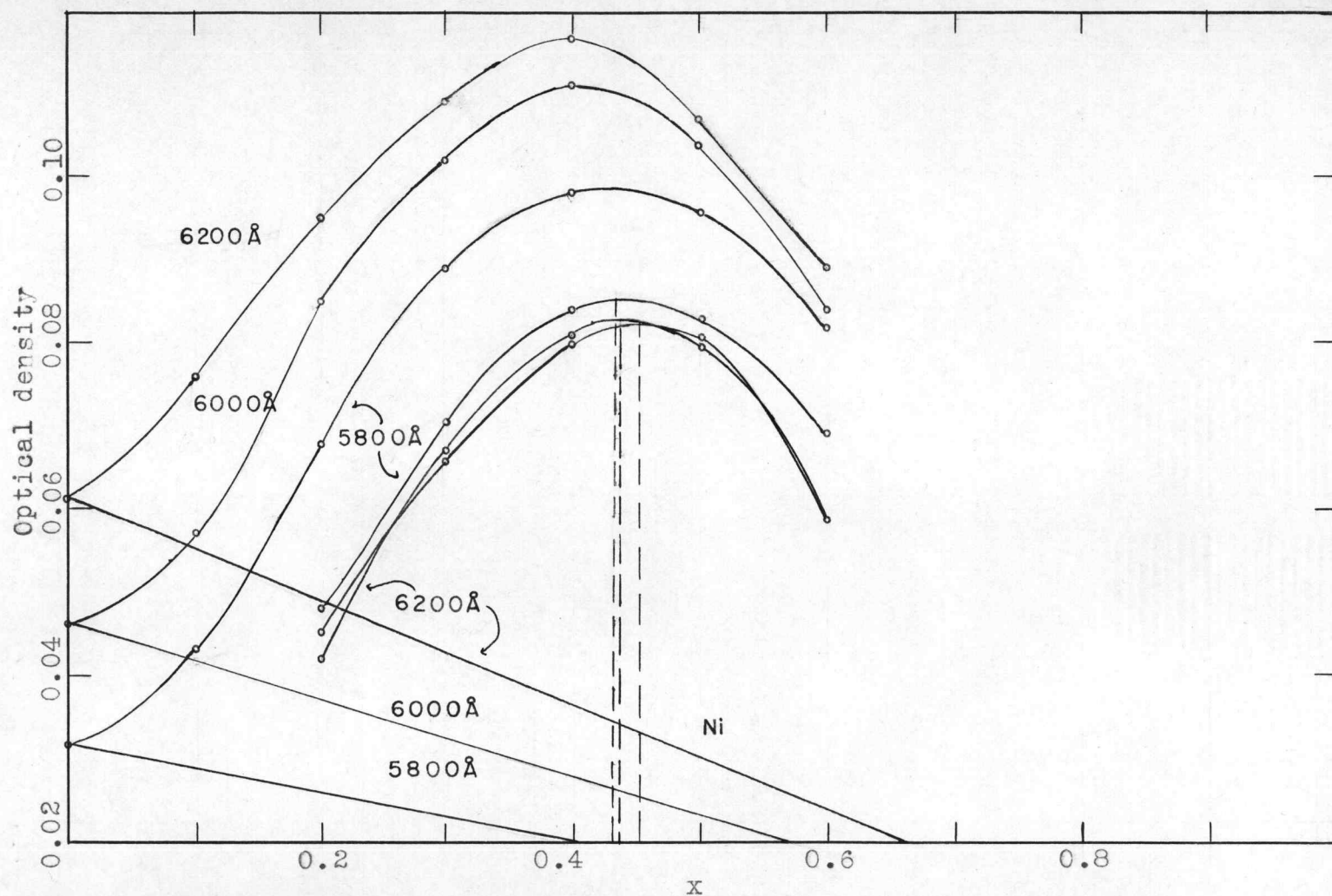same region.

Figure V. Absorption of (1-x) liters of 0.04M nickel nitrate and x liters of 0.08M hydrazine.

CHAPTER VII
DISCUSSION

The stability constant found for the monohydrazine-
nickel ion indicates that most of the nickel present is
in the form of complexes in solutions of this concentra-
tion. It is unfortunate that because of the precipita-
tion of the insoluble trihydrazine complex, solutions of
greater concentration could not be used, and the stability
constant for the dihydrazine complex determined. It
seems reasonable that in more concentrated solutions the
third complex would exist, although in quite small
concentrations because of its insolubility. It might be
possible to investigate this by the use of solvents other
than water, in which the complexes would be more soluble.

It is impossible to apply here the method used for
the determination of the nitronickelate complexes, be-
cause of the insolubility of the trihydrazine nickel
complex. A ratio of hydrazine to nickel high enough to
convert all the nickel into the dihydrazine complex
cannot be secured, since the formation of the insoluble
trihydrazine nickel complex would remove almost all of
the nickel from the solution.

The existence of the mono- and dihydrazine complexes
in solution is in accord with the o-phenanthroline and

ethylenediamine complexes found by Vosburgh and Cooper (27); in their work the higher tricoordinated complexes could also be shown, since precipitation did not occur. Hydrazine, because of its structure of two substituted amine groups, H_2N-NH_2, should coordinate in the place of two molecules of ammonia; this was demonstrated by Franzen and von Mayer (12), who prepared solid complex hydrazine compounds from the corresponding ammonia complexes, and found that two molecules of ammonia were eliminated for each molecule of hydrazine that was coordinated.

It is estimated that the accuracy of the stability constant calculated above is ± 5%, with the greatest uncertainty caused by the errors of graphical analysis and the effect of the dihydrazinenickel ion. It is believed that the formulas for the complexes have been determined definitely.

CHAPTER VIII

SUMMARY

The existence, in solutions of nickel and nitrite ions, of two nitronickelate complexes has been demonstrated and their formulas determined to be $Ni(NO_2)_2$ and $Ni(NO_2)_4^{--}$, probably with the other coordination valences of the nickel atom occupied by water molecules. The stability constants of the complexes are found to be 6.8×10^{-5} for the dinitro complex and 2.79×10^{-3} for the tetranitro complex. The existence of the hexanitronickelate in solution has not been established, because of instrumental difficulties.

The existence, in dilute solutions of hydrazine and nickel ions, of two complex ions, $Ni(N_2H_4)^{++}$ and $Ni(N_2H_4)_2^{++}$, has been proved and the stability constant of the first determined to be 0.10. Higher complexes do not appear to exist in dilute solutions; any trihydrazine complex formed is precipitated because of the limited solubility of the complex salt.

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ADDENDA

Shortly after this thesis was completed the
Beckman spectrophotometer ordered for the work arrived.
Since there was still some question as to the existence
of the hexanitro complex in solution it was decided to
run a series of solutions of high nitrite-nickel ratio
using this instrument, with which the absorption of the
concentrated solutions could be measured more accurately.
These solutions could not be measured with the Cenco-
Sheard spectrophotelometer by changing the cell width,
since the instrument is designed for cells of only
one width, 1 cm., and could not be changed without
extensive remodeling, which would have made the
regular cells unusable. A series of solutions 0.1M
in nickel nitrate and containing sodium nitrite up to
1.6M were prepared and the absorption measured at 6400$\overset{\circ}{A}$.
The results indicate that the curve in Figure II has
almost reached the maximum, since the optical density
of the solution containing a ratio of nitrite to nickel
of 16 to 1 was 0.234, in substantial agreement with that
observed with a ratio of 9 to 1 (Table II), 0.232. The
other solutions with lower ratios had optical densities

from 0.234 to 0.230 for a solution with a ratio of
6 to 1.

These results confirm the assumption that the
complexes existing in solution are the dinitro and
tetranitro, with the hexanitronickelate practically
absent. The only other explanation for the observed
curve would be that the tetranitro and hexanitro complexes
had the same absorption. This would invalidate the
stability complexes calculated, since the concentration
of neither of the complexes could be found. This
possibility seems rather remote, though, since in
every other series of complexes for which data have
been noted the absorption is different for the
various complexes.