[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY, AND CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY]

Kinetics of the Exchange of Nickel Ethylenediaminetetraacetate Ion with Nickelous Ion[1]

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The rate of exchange of hydrated nickelous ion with the nickel of nickel ethylenediaminetetraacetate ion has been studied by use of radioactive nickel. Studies have been made at 25° over a *p*H range of from 1 to 5.3 and at three values of the ionic strength. Interpretation is complicated by the fact that $HNiY^-$ is a weak acid with $K_c = 1.2 \times 10^{-3}$ at an ionic strength of 1.3. However all the data are satisfactorily fitted by the rate law $R = k_1(Ni^{++})(NiY^=) + k_2(H^+)(Ni^{++})(NiY^=) + k_3(H^+)(NiY^=) + k_4(H^+)^2(NiY^=) + k_5(H^+)^3(NiY^=)$ where $(NiY^=)$ refers to the concentration of free $NiY^=$ Values of the rate constants vary moderately with ionic strength. Possible mechanisms for the exchange are discussed.

The exchange behavior of the nickel ethylenediaminetetraacetate ion, $NiY^=$, is of interest because of the stability of this complex and because in it the nickel atom is surrounded by a single complexing Y group. Preliminary experiments have indicated that in solutions of $NiY^=$ the exchange between complexed and aquo-nickelous ion proceeds at a measurable rate.[3] Studies of the rate law governing the metal ion–metal complex type of exchange already have been made[4,5] for FeY^- and $CoY^=$, and it was desired to compare the rate laws governing these exchanges with that of the Ni^{++}–$NiY^=$ exchange.

The nickel ethylenediaminetetraacetate complex ion forms immediately upon mixing a solution containing nickelous ion with one of a sodium salt of the H_4Y acid. The complex is unaffected by ammonium sulfide or sodium hydroxide in ordinary concentrations; it yields a trace of red precipitate with excess dimethylglyoxime and appears to be completely decomposed in cyanide solutions. Since H_4Y is a weak acid the $NiY^=$ ion is largely dissociated in solutions having *p*H less than one. A radioactive indicator method of measuring the extent of this induced dissociation at known acidities led to a value of the dissociation constant, $(Ni^{++})(Y^{\equiv})/(NiY^=)$, of 1×10^{-19} in 0.1 *M* potassium chloride at 20°.[6] Schwarzenbach and Freitag report a value of $10^{-18.45}$ for this same constant.[7]

The solid complex acid, H_2NiY, has a magnetic susceptibility close to that of uncomplexed nickelous salts, which indicates the presence of two unpaired electrons.[8] This implies that $NiY^=$ is not a square four-covalent complex but is most probably octahedral with predominantly ionic bonding.

Experimental

Nickel metal powder containing Ni^{63} (half-life, 85 years; maximum β energy, 63 kev.) was obtained from the Oak Ridge National Laboratory. The nickel was freed from active cobalt and iron contaminants by repeated addition of inactive cobalt and iron and precipitation of nickel dimethylglyoxime. Radioactive $NiY^=$ was prepared by dissolving a slight excess of active $Ni(OH)_2$ in H_4Y, adding sodium hydroxide until the solution had *p*H 10, and filtering several times. This solution was standardized by decomposition of portions and determination of their nickel content.

The exchange reactions were initiated by addition of a known portion of a solution of nickelous chloride or perchlorate to a solution containing Na_2Ni^*Y and a buffer or strong acid in known concentrations. During the course of the reaction aliquots were removed from the solution, and the nickelous ion in each was separated from the complex ion by addition of sodium hydroxide and filtration of the nickelous hydroxide precipitate. After separation the nickelous hydroxide precipitate was washed, dissolved in acid and plated as the metal on copper disks. The filtrate was discarded.

This separation procedure was found to produce a consistent induced exchange of about 2.5% although there was no evidence of an exchange reaction between $NiY^=$ and solid $Ni(OH)_2$. Higher amounts of induced exchange were observed where the reaction solutions were strongly acid; however, this latter induced exchange was the result of acid dissociation of the complex ion[6] and was independent of the separation procedure.

The nickel samples were counted in the form of a shiny plated metal surface containing about four mg./cm.^{2} of nickel. For purposes of radioactivity measurement these samples were effectively "infinitely thick,"[9] and, since a constant sample area was exposed to the counter, the counting rate was directly proportional to the specific radioactivity of the nickel. All counting was done inside flow-type windowless counters which were monitored daily with a standard sample.

For all of the exchange experiments the acidity was maintained constant and its value determined with a *p*H meter. Strong acids were used to adjust the *p*H of the more acid solutions; for *p*H values above three, acetic acid–acetate buffers were used. The temperature for all experiments was 25°.

The majority of the exchange studies were made at three values of the ionic strength: 0.028, 0.10 and 1.25 (moles per liter concentration units). For the first two of these the nickelous ion was added as nickelous chloride; the added strong acid was hydrochloric and potassium chloride was used to adjust the ionic strength. For experiments at ionic strength 1.25 it was desired to avoid chloride ion; hence nickelous perchlorate, perchloric acid and sodium perchlorate were employed. No evidence was obtained for specific effects attributable to either chloride or perchlorate ion.

Since any shifts in hydrogen or complex ion concentrations caused by the addition of nickelous ion to an $NiY^=$ solution are both small and rapid, the concentrations of reacting ions become constant immediately after the initiation of exchange. It can similarly be assumed that the acid–base equilibria between the various complex ion species, *e.g.*, between $NiY^=$, $HNiY^-$ and H_2NiY, are established rapidly compared to the rate of exchange of these complexes with the aquo-nickel ion. Hence the rate of the latter exchange will be given by the usual equation

$$R = -2.3 \frac{ab}{a + b} \frac{d}{dt} \log (1 - F)$$

where *F* is the fractional exchange at time *t* and *a* and *b* are the concentrations of free and of complexed nickel ions.

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[4] S. Jones and F. A. Long, *J. Phys. Chem.*, **56**, 25 (1952).

[5] F. A. Long, M. Burke and J. Backus, unpublished work.

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[7] G. Schwarzenbach and E. Freitag, *Helv. Chim. Acta*, **34**, 1503 (1951).

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Accordingly a plot of log $(1 - F)$ *vs.* t is expected to be a straight line of slope $- R(a + b)/2.3\,ab$ independent of the presence of induced exchange. Straight lines were observed in all cases.

In considering the mechanism of the exchange reaction it was important to know the strength of the complex acid, H_2NiY. To measure this, a 0.01 M solution of H_2NiY was titrated with carbonate-free sodium hydroxide solution and the variation of pH with equivalents of added base was followed with a Beckman pH meter. The titration curve of H_2NiY corresponded to that of a dibasic acid which is completely strong in one proton but moderately weak in the second. At 25° the dissociation constant for the second proton was found to be $K_{A_2} = 1 \times 10^{-3}$ in 0.1 M potassium chloride and $K_{A_2} = 1.2 \times 10^{-3}$ in 1.25 M sodium perchlorate. Similar titrations of 0.02 M hydrochloric acid were carried out at the same ionic strengths and temperature to serve as a standard.

Discussion

The rate of exchange was studied as a function of the concentrations of nickelous ion and hydrogen ion and of the gross concentration of complex ion. This latter quantity, written $(NiY^=)_t$, is taken to be the sum of the concentrations of the ions $NiY^=$ and $HNiY^-$. The rate was found to depend upon (H^+), (Ni^{++}) and $(NiY^=)_t$ (the parentheses refer to molar concentrations) and was complex in that its dependence could not be expressed by a single combination of these concentrations. Figure 1, in which rate of exchange is plotted against log(H^+) for two series of runs at constant (Ni^{++}) and $(NiY^=)_t$ illustrates the complexity of the dependence on acidity. The upper curve of this figure is a plot of rates determined at ionic strength 0.028 and clearly shows contributions to the total rate from a term which is independent of acidity and from a term which is first order in (H^+). The rates plotted in the lower curve are for solutions of ionic strength 1.25 where salt effects cause the term that is zero order in (H^+) to be negligible. At high acidities this curve shows a contribution from a term in $(H^+)^2$ in addition to one from a term in (H^+).

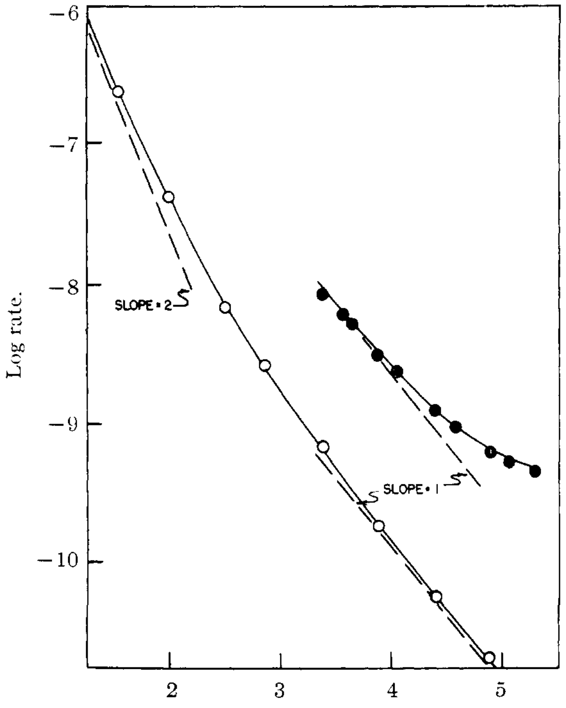

Fig. 1.—Exchange rate as a function of acidity. For solid circles $(Ni^{++}) = 3.6 \times 10^{-3}$ M, $(NiY^=) = 1.8 \times 10^{-3}$ M and $\mu = 0.028$; for open circles $(Ni^{++}) = 1.8 \times 10^{-3}$ M, $(NiY^=)_t = 0.9 \times 10^{-3}$ M and $\mu = 1.25$.

The rate of exchange is proportional to $(NiY^=)_t$ over the entire pH range. However, the dependence of rate upon (Ni^{++}) varies from first order at low acidity to zero order at high acidities. Table I gives selected values of the data at three ionic strengths and also lists calculated values of the rates. Columns two to four give values of (Ni^{++}), $(NiY^=)_t$ and (H^+) and column five gives the observed rate of exchange at 25°.

The procedure for obtaining the rate terms and rate constants was to focus first on regions of either quite high or quite low acidity where it could be assumed that the complex ion was present almost entirely as either $(HNiY^-)$ or $(NiY^=)$, respectively. With this assumption approximate values of the rate constants could be obtained. Then for intermediate acidities the actual values of $(HNiY^-)$ and $(NiY^=)$ were calculated, using the known values of the acid ionization constant of $HNiY^-$, and with these a further analysis of the rate data was made. Finally for each value of the ionic strength the approximate values of the rate coefficients were adjusted to give the best over-all fit to the data. Two examples of this procedure follow.

The data at ionic strength 0.10 and high acidities (where the complex is present almost entirely as $HNiY^-$) show clearly that the rate is essentially independent of concentration of nickelous ion and contains terms in $(H^+)^2$ and (H^+). Writing the rate as

$$R = k_5(H^+)^2(HNiY^-) + k_4(H^+)(HNiY^-)$$

it follows that a plot of $R/(H^+)(NiY^=)_t$ *versus* (H^+) should give a straight line with a slope of k_5 and an intercept of k_4. Figure 2 is such a plot for runs 15

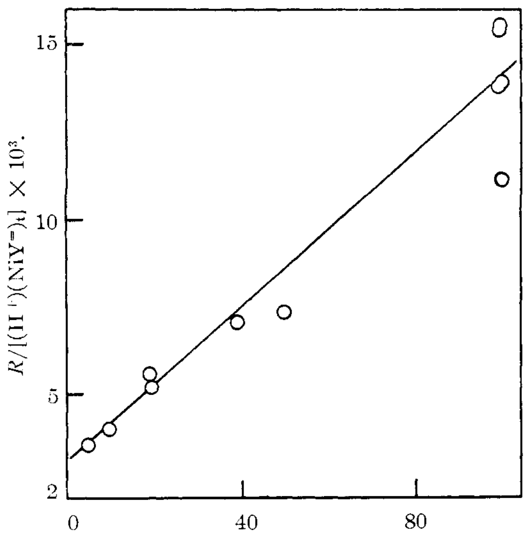

Fig. 2.—Plot of $R/[(H^+)(NiY^=)_t]$ *vs.* (H^+) for data at $\mu = 0.10$.

TABLE I

OBSERVED AND CALCULATED RATES FOR Ni^{++}–$NiY^{=}$ EXCHANGE, 25°

Run	$10^3(Ni^{++})$	$10^3(NiY^{-})_t$	$10^3(H^+)$	Obsd. R, $\times 10^9$	Calcd. contributions, $\times 10^9$ R_1	R_2	R_3	R_4	R_5	Calcd. R $\times 10^9$
A. Ionic strength = 0.028										
1	3.60	1.85	0.0051	0.45	0.34	0.10	0.02	.....	.....	0.46
3	3.60	1.85	.0132	.64	.34	.26	.05	.....	.....	.65
7	3.60	1.85	.135	3.1	.30	2.4	.4	0.1	.....	3.2
10	3.60	1.85	.427	8.4	.23	5.4	1.15	.83	.....	7.6
11	1.80	0.93	.407	2.4	.06	1.4	0.58	.4	.....	2.5
12	0.90	0.46	.389	0.86	.015	0.35	.28	.18	.....	0.83
B. Ionic strength = 0.10										
15	0.51	0.16	99.7	220	...	0.2	0.2	49	168	217
18	.44	.23	19.7	23.3	...	.2	.3	13.6	9.2	23.3
20	.44	.23	4.8	3.9	...	.1	.3	2.9	0.48	3.8
21	.96	.36	99.1	565	...	.7	.5	113	384	498
22	1.89	.72	98.7	992	...	2.3	.9	224	757	984
26	1.71	.89	7.2	26	...	2.2	1.0	18	4.4	25.6
27	1.73	.89	0.49	1.7	...	0.83	0.39	0.45	0.01	1.7
29	0.45	.093	0.45	0.10	...	0.022	0.039	0.041	0.001	0.10
C. Ionic strength = 1.25										
31	1.80	0.924	29.2	235	...	1	1	52	176	230
33	1.80	.924	3.15	6.8	...	0.6	0.6	4.1	1.5	6.7
36	1.80	.924	0.131	0.18	0.002	.08	.09	0.02	.....	0.19
41	4.5	2.31	.379	2.13	...	1.07	.53	.42	0.02	2.04
42	9.0	2.31	.128	0.90	...	0.92	.21	.06	.....	1.2
43	9.0	4.62	.388	6.2	.03	4.70	1.08	.88	.....	6.7
46	18.0	9.24	.338	21.0	.2	16.8	2.0	1.3	.....	20.3

to 25. The data are adequately fitted by a straight line and the resulting values of the rate constants are $k_4 = 0.0032$ liter/mole/sec. and $k_5 = 0.11$ liter²/mole²/sec. At the lower acidities small contributions to the rate are made by the terms $k_2(H^+)\cdot(Ni^{++})(NiY^{=})$ and $k_3(H^+)(NiY^{=})$. From experiments at low acidity and high concentrations of (Ni^{++}) and $(NiY^{=})_t$ the values of k_2 and k_3 were found to be 1.7 l.²/mole²/sec. and 0.0013 l./mole/sec., respectively. Columns 6 to 10 of Table I give calculated values for the various rate terms using the above rate constants and column 11 gives the calculated value of the rate of exchange, *i.e.*, the sums of R_2 to R_5. The agreement between observed and calculated rates is quite satisfactory.

From the data at ionic strength 0.03 and low acidity, where the complex ion is present almost entirely as $NiY^{=}$, it appears that three terms contribute to the rate[10]

$$R = k_1(Ni^{++})(NiY^{=}) + k_2(H^+)(Ni^{++})(NiY^{=}) + k_3(H^+)(NiY^{=})$$

Thus at constant (Ni^{++}) a plot of $R/(Ni^{++})\cdot(NiY^{=})$ *versus* (H^+) should give a straight line with intercept k_1 and slope $k_2 + k_3/(Ni^{++})$. A plot of the data for runs 1 to 6 is shown in Fig. 3. From the resulting straight line the values obtained are $k_1 = 5.2 \times 10^{-5}$ l./mole/sec. and $[k_2 + k_3/(Ni^{++})] = 3.6$ l.²/mole²/sec. Further analysis of the data of runs 1 to 14 give as separate values, $k_2 = 3.0$ l.²/mole²/sec. and $k_3 = 0.0022$ l./mole/sec. Finally there is a small contribution from a term $k_4(H^+)\cdot(HNiY^-)$ with $k_4 = 0.0035$ l./mole/sec. Table I again compares observed and calculated values.

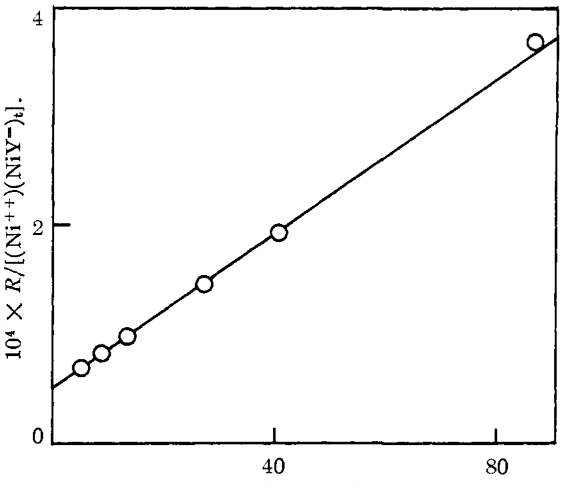

Fig. 3.—$R/[(Ni^{++})(NiY^{=})_t]$ *vs.* (H^+) at $\mu = 0.028$.

As Table I shows the experiments at ionic strength 1.25 cover a broad range of acidities and hence show a wide variation in the observed rate of exchange. Proceeding as in the above cases leads to the rate law

$$\begin{aligned} R &= R_1 + R_2 + R_3 + R_4 + R_5 \\ &= 8 \times 10^{-7}\,(Ni^{++})(NiY^{-}) + 0.38(H^+)(Ni^{++})(NiY^{=}) \\ &\quad + 0.0008(H^+)(NiY^{=}) + 0.0020(H^+)(HNiY^-) \\ &\quad + 0.22(H^+)^2(HNiY^-) \end{aligned} \tag{1}$$

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[10] The data of Table I do not show clearly that the rate at low acidities and ionic strengths varies with (Ni^{++}) as well as with $(NiY^{=})$. This is, however, shown by the tabulated data, which are for $(H^+) = 1.3 \times 10^{-5}\ M$ and $\mu = 0.020$.

$10^3 \times (Ni^{++})$	$10^3 \times (NiY^-)_t$	Obsd. R, $\times 10^9$
1.8	0.9	0.16
1.8	1.8	.32
3.6	1.8	.63

The lowest acidity for this series of experiments was *p*H 4.9 (run 38) and even here the contribution of R_1 is small. Hence the value $k_1 = 8 \times 10^{-7}$ l./mole/sec. is very approximate. However, for each of the other four rate terms there is a region where its contribution to the total rate is dominant. Thus the above decidedly complex rate law appears necessary to explain the data.

Some idea of the relative contributions of the various rate terms at different acidities is given by Fig. 4 which is a plot at ionic strength 1.25 of the logarithms of the rate terms R_1 to R_5 *versus* log (H^+) for the particular case of $(Ni^{++}) = 1.8 \times 10^{-3}$ *M* and $(NiY^{=})_t = 0.924 \times 10^{-3}$ *M*. At these concentrations the contribution of the R_1 term (for *p*H values above 5) is negligible but the other terms are all of consequence in some *p*H region. The decreases in slope as one goes from low to high acid are, of course, the result of a decrease in the ratio $(NiY^{=})/(HNiY^{-})$.

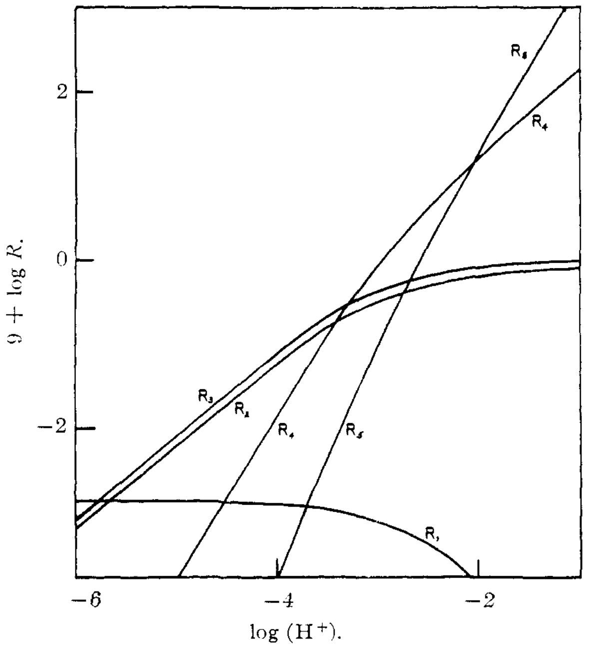

Fig. 4.—Contributions of the separate rate terms for $(Ni^{++}) = 1.8 \times 10^{-3}$ *M*, $(NiY^{=})_t = 0.92 \times 10^{-3}$ *M* and $\mu = 1.25$.

The experimental rate law of eq. 1 fits the data at all three ionic strengths although at $\mu = 0.03$ the data do not permit a determination of k_5 and at $\mu = 0.10$ do not permit a determination of k_1. Table II summarizes the values of the rate constants. Due to the complexity of the rate law, none of the constants is known to better than ±10% and in some cases the precision is much less than this.[11] As can be seen in Table II the values of the rate constants k_1 to k_4 decrease with ionic strength which is the expected direction of change, at least in the Debye–Hückel limiting law region. The value of k_5 increases from ionic strength 0.1 to 1.25, opposite to the limiting law prediction. However for this system even ionic strength 0.1 is "high" so no great significance can be attached to this discrepancy.

TABLE II

RATE CONSTANTS FOR RATE LAW OF EQ. 1

Ionic strength	k_1	k_2	k_3	k_4	k_5
0.028	5.2×10^{-5}	3.0	0.0022	0.0035	Not det.
0.10	Not det.	1.7	.0013	.0032	0.11
1.25	8×10^{-7}	0.38	.0008	.0020	0.21

Although the rate law of eq. 1 is the simplest one to use in treating the experimental data, it is obvious that, since the concentration of $(HNiY^{-})$ and $(NiY^{=})$ are related through the acid ionization constant of the former, one can express the dependence of the rate on complex ion concentration by using only $HNiY^{-}$, only $NiY^{=}$ or a combination of the two as in eq. 1. Using only $NiY^{=}$ the rate equation is

$$\begin{aligned}R = {} & k_1(Ni^{++})(NiY^{=}) + k_2(H^{+})(Ni^{++})(NiY^{=}) \\ & + k_3(H^{+})(NiY^{=}) + k_4'(H^{+})^2(NiY^{=}) \\ & + k_5'(H^{+})^3(NiY^{=})\end{aligned} \tag{2}$$

For the particular case of $\mu = 1.25$ and using $K_A = 1.2 \times 10^{-3}$ for the acid ionization constant of $HNiY^{-}$, the values of k_4' and k_5' are $k_4' = 1.7$ l.²/mole²/sec. and $k_5' = 180$ l.³/mole³/sec.

The rate law as expressed in either eq. 1 or 2 indicates that over the *p*H range 1 to 5 there are five different paths for the exchange process. The five different activated complexes indicated are: Ni_2Y, HNi_2Y^{+}, $HNiY^{-}$, H_2NiY and H_3NiY^{+}. In the rate terms of eq. 2 $NiY^{=}$ enters only to the first power, Ni^{++} enters to the 0 or 1 power and H^{+} enters to the 0, 1, 2 or 3 power. With these ranges there are actually eight possible activated complexes, five of which are encountered in the concentration ranges studied here.

The reaction mechanism leading to the above rate law can be visualized as a series of rapidly established preliminary equilibria between protons and $NiY^{=}$ ion followed by a competition between either unimolecular decomposition of the protonated complex ions or bimolecular collision and exchange with nickelous ion.

$Ni^{++} + Ni^{*}Y^{=} = Ni^{*++} + NiY^{=}$ (slow) R_1 (1)
$H^{+} + Ni^{*}Y^{=} = HNi^{*}Y^{-}$ (equil.) (2)
$HNi^{*}Y^{-} = Ni^{*++} + HY^{\equiv}$ (slow) R_3 (3)
$Ni^{++} + HNi^{*}Y^{-} = Ni^{*++} + HNiY^{-}$ (slow) R_2 (4)
$H^{+} + HNi^{*}Y^{-} = H_2Ni^{*}Y$ (equil.) (5)
$H_2Ni^{*}Y = Ni^{*++} + H_2Y^{=}$ (slow) R_4 (6)
$Ni^{++} + H_2Ni^{*}Y = Ni^{*++} + H_2NiY$ (slow) (7)
$H^{+} + H_2Ni^{*}Y = H_3Ni^{*}Y^{+}$ (equil.) (8)
$H_3Ni^{*}Y^{+} = Ni^{*++} + H_3Y^{-}$ (slow) R_5 (9)

Unfortunately in only a few cases can values be calculated for the rate constants of the slow steps postulated in the above mechanism since the dissociation constant is known for only one of the proposed protonated complex species. (Experimentally, H_2NiY behaves like a strong acid and H_3NiY^{+} would be expected to be even stronger.) As a result, the only comparison that can be made of rate coefficients for similar processes is for the slow steps

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(11) The data of Table I also can be fitted by a rate law containing the preceding five terms plus an additional $k_6(H^{+})(Ni^{+})(HNiY^{-})$ term. In this alternative case k_2 and k_4 are about 75% of the values listed in Table II and $k_6 \sim k_2$. The proposed R_6 term is consistent with the reaction mechanism discussed below.

1 and 4 above. At ionic strength 0.028 the rate constant for step 1, the bimolecular reaction between Ni^{++} and $\text{NiY}^{=}$, is 5×10^{-5} l./mole/sec. whereas for step 4, the bimolecular reaction between Ni^{++} and HNiY^{-}, the rate constant is 0.003. The greater reactivity of HNiY^{-} is quite understandable since addition of a proton should decrease the stability of the complex ion. Similarly we would expect the rates for the unimolecular decompositions of HNiY^{-}, H_2NiY and H_3NiY^{+} to be increasingly larger for the more highly protonated species. A comparison for somewhat similar bimolecular steps has been given by Ackermann and Schwarzenbach[12] who report that cupric ion reacts 20-fold more rapidly with HCdY^{-} than with $\text{CdY}^{=}$.

Complexity of exchange behavior seems to be typical of the MeY complexes studied thus far. In the pH region four to seven the cobaltous complex, $\text{CoY}^{=}$, exchanges with cobaltous ion according to[5]

$$R_t = k_1(\text{Co}^{++})(\text{CoY}^{=})_t + k_2(\text{H}^{+})(\text{CoY}^{=})_t$$

The exchange between ferric ion and FeY^{-} at hydrogen ion concentrations of from 0.003 to 0.3 M has been shown to follow the law

$$R_t = k_1(\text{FeOH}^{++})(\text{FeY}^{-}) + k_2(\text{Fe}^{+++})(\text{FeY}^{-}) + k_3(\text{H}^{+})^3(\text{FeY}^{-})$$

with indications of a possible contribution from a term that is first order in hydrogen ion.[4] The terms in these rate laws, with the exception of the term in (FeOH^{++}), are similar to those for the nickelous–$\text{NiY}^{=}$ exchange. Reactions of the type $\text{A}^{++} + \text{BY}^{-} = \text{AY}^{=} + \text{B}^{++}$ also exhibit rate laws with several terms[12,13] and these have been interpreted by mechanisms which are closely related to the one suggested here.

ITHACA, N. Y.
UPTON, N. Y.

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[CONTRIBUTION FROM THE WATSON LABORATORIES OF INTERNATIONAL BUSINESS MACHINES]

Reactions of the Group VB Pentoxides with Alkali Oxides and Carbonates. VII. Heterogeneous Equilibria in the System Na_2O or Na_2CO_3–Nb_2O_5

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The heterogeneous equilibria in the system Na_2O or Na_2CO_3 with Nb_2O_5 have been investigated using differential thermal analysis, X-ray analysis and density measurements. Four compounds corresponding to the formulas (I) $Na_2O·14Nb_2O_5$, (II) $Na_2O·4Nb_2O_5$, (III) $Na_2O·Nb_2O_5$ and (IV) $3Na_2O·Nb_2O_5$, have been identified. Compounds I and II melt incongruently at 1309 and 1277°, respectively, and compounds III and IV melt congruently at 1422 and 997°, respectively. The polymorphism of compound III has been reinvestigated, and results indicate the existence of four phases with transitions at 640, 562 and 354°. The 562° transition was observable, as a sharp heat effect at this temperature, only after extensive annealing. In a reëxamination of the polymorphic behavior of Na_2CO_3, latent heat anomalies were observed at 485 and 355°. X-Ray powder data have been obtained for compounds I, II, III and IV.

Introduction

Although the preparation and chemistry of the sodium niobates have been the subject of a considerable number of papers, dating back to 1812, the major emphasis has been placed on the study of those salts derived from aqueous media. In 1897, Holmquist[2] reported that the anhydrous compounds $2Na_2O·Nb_2O_5$ and $Na_2O·Nb_2O_5$ resulted from the reaction of stoichiometric quantities of Na_2CO_3 and Nb_2O_5 in the presence of NaF flux. Subsequently, Barth,[3] in determining the lattice constants of $Na_2O·Nb_2O_5$, provided the first X-ray confirmation of any of the sodium niobates. In an investigation of the reactivity of $NaNbO_3$ with molten Na_2CO_3 Lapitskiĭ[4] concluded that the meta salt was unreactive toward the molten alkali and consequently more basic niobates do not exist. The anomalous dielectric behavior of $NaNbO_3$ was discovered in 1949,[5] and since that time the transition temperatures and accompanying structural changes have been studied extensively.[6–11] The only other anhydrous sodium niobate reported is the compound $5Na_2O·Nb_2O_5$.[12]

In this, the seventh paper in a series involving the reactions of alkali oxides and group VB pentoxides, the heterogeneous equilibria in the anhydrous system Na_2O or Na_2CO_3–Nb_2O_5 have been investigated in order to resolve the ambiguities concerning the number of compounds formed and their stoichiometries. Included is a study of the polymorphic behavior of $NaNbO_3$ and Na_2CO_3.

Experimental Procedure

1. **Reagents.**—The Na_2CO_3 used in this study was Mallinckrodt analytical reagent. Prior to use, the carbonate was dried to constant weight at 400° and stored in a desiccator over drierite. The niobium pentoxide was obtained from two sources, the Fansteel Metallurgical Co. and the Var-lac-oid Co. These reagents were of the highest purity available, containing as a maximum contaminant 0.2% Ta.

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