PROTON SPIN RELAXATION IN THE $CR(OH_2)_6^{+++}$ - $CrOH(OH_2)_5^{++}$ - H_2O SYSTEM

BY

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Thesis Approved:

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For an education and a free hand in the laboratory credit is due Dr. V. L. Pollak. His forebearance permitted an investiation which started out to be something else and his resistance to a poorly formed idea provided the impetus for a great deal of work. I would also like to express my appreciation for financial support from the Army Research Office, Durham, the Petroleum Research Fund, and the Physics Department, Oklahoma State University.

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1. INTRODUCTION

Although the basic mechanism for proton spin relaxation in aqueous chromium (III) solutions is well understood,[1] relaxation times reported by different observers for apparently identical systems do not agree.[2,3,4] The disagreements appear to be a result of the unusual features of chromium (III) chemistry. Cr (III) forms stable coordination compounds with a large number of ligands, including water, and in aqueous solution long

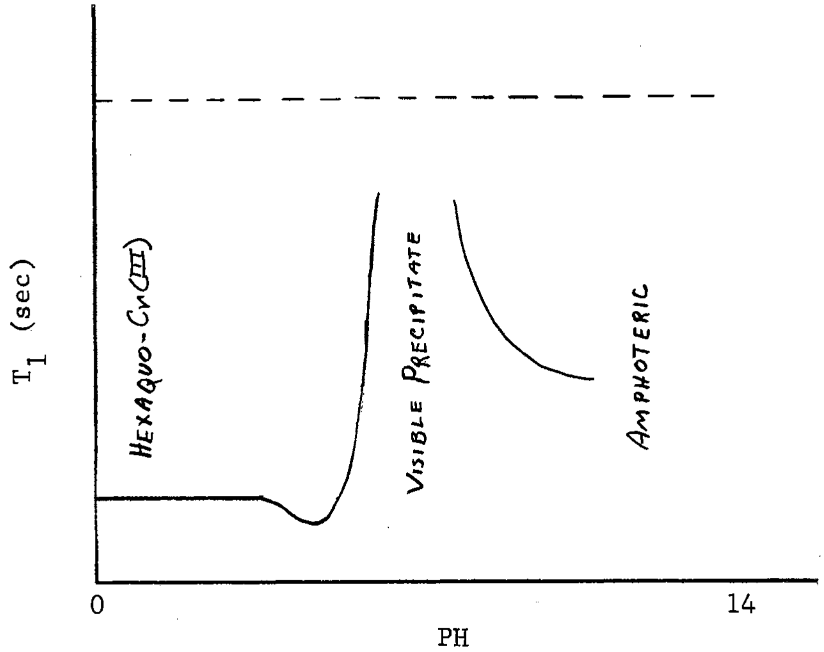

Figure 1. Typical Variation in T_1 for Aqueous Cr(III)

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[1] N. Bloembergen and L. O. Morgan, J. Chem. Phys., 34, 842 (1961).

[2] L. O. Morgan and A. W. Nolle, J. Chem. Phys., 31, 365 (1959).

[3] R. Hausser and G. Laukien, Z. Physik, 153, 394 (1959).

[4] R. Hausser and F. Noack, Z. Physik, 182, 93 (1964).

lasting polymer products are easily formed.[5] These features are mirrored in the nature of some of the observed anomalities for relaxation times of Cr (III) solutions. Thermal hysteresis,[6] solution aging,[7] and specific anion[4] effects have all been noted. The experiment reported upon here adds yet another effect, PH dependence.

In the present work, we have found that the proton spin relaxation time of aqueous Cr (III) is PH dependent. A typical variation is shown in Figure 1. The region to the right of the range in which a visible precipitate is formed reflects the redissolving of the precipitate and the formation of an amphoteric. We believe that the region around the local minima to the left of the visible precipitate range represents an entirely different process, chemical hydrolysis. To support this thesis a model based on PH induced changes in porton chemical exchange times will be developed, and a comparison will be made with quantitative experimental data.

To develop the model, a review of the theory associated with proton spin relaxation times will be presented and this will be followed by a summary of chemical hydrolysis. After development of the model, model and experimental data will be compared and the validity of the comparison will be discussed. Since some extraneous but useful data on Cr (III) compounds was obtained during the problem exploratory phase, the section on results will also contain data not directly associated with the PH

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[5] Marvin J. Udy, Chemistry of Chromium and Its Compounds, Ruhold Publishing Corp., New York, N.Y., 1956, p. 188.

[6] J. Brown, R. Bernheim, and H. Gutowsky, J. Chem. Phys., 33, 1593 (1960).

[7] G. Laukien and J. Schluter, Z. Physik, 146, 113 (1956).

2. PROTON SPIN RELAXATION

When placed in an external magnetic field, proton spins in the 1st coordinator sphere of a paramagnetic ion polarize exponentially with a characteristic time T_{1B} given by[8,9]

$$\frac{1}{T_{1B}} = \frac{4}{30} \frac{S(S+1)\, g^2 \beta^2 \gamma_I^2}{r^6} \left(3\tau_c + \frac{7\tau_c}{1+\omega_2^2\tau_c^2}\right) + \frac{2}{3} S(S+1) \frac{A^2}{\hbar^2} \left(\frac{\tau_e}{1+\omega_s^2\tau_e^2}\right) \qquad (1)$$

The τ's, correlation times, in this equation are functions of temperature and represent processes causing time varying magnetic fields at the proton. In aqueous solution protons may be either in the 1st coordination sphere or in what is essentially bulk water, which has its own characteristic relaxation time T_{1W}.

In dilute solutions of paramagnetic ions the magnetization of the protons associated with the ion is not detectable, the magnetization of the bulk water is. In order for the presence of the ions to be noted there must be a rapid exchange of coordinated protons and bulk water protons. For sufficiently rapid exchange the measured relaxation time of the solution is given by weighting the two relaxation times[1]

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[8] I. Solomon, Phys. Rev., <u>99</u>, 559 (1955).

[9] N. Bloembergen, J. Chem. Phys., <u>27</u>, 572, 595 (1957).

$$\frac{1}{T_1} = \frac{N_W'}{N_W' + N_B'}\left(\frac{1}{T_{1W}}\right) + \frac{N_B'}{N_W' + N_B'}\left(\frac{1}{T_{1B}}\right)$$

with $N_W' \equiv$ number of protons in bulk water

$N_B' \equiv$ number of protons in the 1st coordination sphere of the ion.

If $N_B' \ll N_W'$ this reduces to

$$\frac{1}{T_1} = \frac{1}{T_{1W}} + \frac{N_B'}{N_W'}\,\frac{1}{T_{1B}}$$

While this equation describes the behavior of most of the iron transition metals it does not describe the observed relaxation time of chromium (III). Cr (III) is unique in that the exchange time of coordinated water molecules is or the order of 40 hrs. and the exchange time of protons associated with coordinated water molecules is or the order of T_{1B}.[10,11] Therefore the limit of very rapid exchange is not quite reached. The corrected expression is[1]

$$\frac{1}{T_1} = \frac{1}{T_{1W}} + \frac{N_B'}{N_W'}\,\frac{1}{\tau_h + T_{1B}} \qquad (2)$$

with $\tau h \equiv$ lifetime of one proton in the hydration sphere.

The relaxation properties and τ's of Cr (III) have been reported by two observers and their results are summarized in Table I.

---

[10] R. Plane and H. Taube, J. Phy. Chem., 56, 33 (1952).

[11] R. Pearson, J. Palmer, M. Anderson, and A. Allred, Z. Electrochemie, 64, 110 (1960).

TABLE I

CORRELATION AND RELAXATION TIMES FOR Cr (III) AT DIFFERENT TEMPERATURES[1,4]

	θ(°C)	τ_c(SEC)x10^{11}	τ_e(SEC)x10^{10}	T_{1B}(SEC)x10^6	τ_h(SEC)x10^6
Hausser & Noack	0	7.0	3.1	3.6	3.0
	20	4.8	4.2	4.9	2.0
	25	4.5*	4.5*	5.1*	1.8*
	40	3.4	5.4	6.5	1.4
	65	2.3*	7.3*	9.4*	0.91*
Bloembergen and Morgan	0	14	3.1	3.8	19
	20	9.0	4.2	5.2	5.3
	25	8.0*	4.5*	5.6*	4.0*
	40	5.3	5.4	7.6	1.8

*Reported values. Other values were computed by assuming the validity of the Arrhenius Eq. for τ_H, τ_s, and τ_h.

With the exception of τ_e, a time which for Cr (III) is equal to the electron spin relaxation time τ_s (a measure of the time the electron spends in a particular orientation), discrepancies exist between the correlation times reported. The only reported difference in the experimental conditions is that measurements made by Bloembergen were for acidified solutions[1,2] and measurements made by Hausser were for non-acidified solutions.[4] The significance of the difference will be brought out later.

It will be convenient in the presentation which follows to use the term relaxation rate instead of relaxation time and to let this term refer to the effect of the paramagnetic ion, i.e.,

$$\text{Relaxation Rate} = \frac{1}{T_1} - \frac{1}{T_{1W}}$$

Table II lists the values $\frac{1}{T_{1W}}$ for the temperatures of interest. These were determined using the same distilled water supply which was used to prepare samples.

TABLE II

RELAXATION RATE OF DISTILLED H_2O

Rate (sec^{-1})

θ (°C)	H_2O	H_2O with 0.1M $NaClO_4$
0	0.72	0.68
20	0.42	0.42
40	0.29	0.29

3. HYDROLYSIS AND POLYMERIZATION

In aqueous solution the ion is part of a reaction with water which results in the loss of a proton from the coordination sphere of the ion. This hydrolysis leaves a hydroxide ion in place of a coordinated water molecule and acidifies the solvent. Successive hydrolysis results in the formation of neutral, insoluble hydroxides and in some cases, when the hydroxide ion is capable of forming bridges, polymers are formed.

The 1st hydrolysis of chromium (III) may be represented by the following reaction:

$$Cr(OH_2)_6^{+++} + H_2O \rightleftharpoons CrOH(OH_2)_5^{++} + H_3O^+$$

Since at equilibrium

$$\frac{d\left[Cr(OH_2)_6^{+++}\right]}{dt} = -k_1\left[Cr(OH_2)_6^{+++}\right] + k_2\left[CrOH(OH_2)_5^{++}\right]\left[H_3O^+\right] = 0$$

The relative concentrations may be expressed by a constant X_{11}'[12].

$$X_{11}' = \frac{k_1}{k_2} = \frac{\left[CrOH(OH_2)_5^{++}\right]\left[H_3O^+\right]}{\left[Cr(OH_2)_6^{+++}\right]}$$

---

[12] B. Hedström, Arkiv Kemi, 6, (1952). Notation is due to Hedström. First subscript refers to the number of metal ions and second refers to the protons lost.

For this equation to be rigorously correct it is necessary to include the activities of the reacting ions so that

$$X_{11}' = \frac{[CrOH(OH_2)_5^{++}][H_3O^+]\gamma_{Cr^{++}}\gamma_{H^+}}{[Cr(OH_2)_6^{+++}]\gamma_{Cr^{+++}}}$$

The activities are functions of the number and type of ions present is solution and changes in ion activity caused by variations in the concentration of one of the reactants can be a problem. If however, a large excess of some non-participating ion is added to the system, small changes in the concentration of the reactants will produce small changes in the activity coefficients.[13,14] And

$$\frac{X_{11}'\gamma_{Cr^{+++}}}{\gamma_{Cr^{++}}\gamma_{H^+}} = X_{11},$$ with X_{11}

a constant.

It is to be noted that although this expression presents the concentrations of the products in terms of the reactant, it does not describe a mechanism. An identical reaction could be obtained by assuming that an OH^- reacts with $Cr(OH_2)_6^{+++}$.

---

[13] J. N. Butler, Ionic Equilibrium a Mathematical Approach, Addison-Wesley Publishing Company, Inc., New York, N.Y., 1964, p. 439.

[14] Ibid, p. 369.

TABLE III

REPORTED AND COMPUTED VALUES FOR THE 1st HYDROLYSIS CONSTANT

θ (°C)	X_{11}	X_{11}	X_{11}	X_{11}
0	$2.0\text{x}10^{-5}$[15]	---	$2.9\text{x}10^{-5}$	---
15	$5.4\text{x}10^{-5}$	$7.6\text{x}10^{-4}$[17]	$7.4\text{x}10^{-5}$[18]	---
20	$6.8\text{x}10^{-5}$	---	$9.4\text{x}10^{-5}$	---
25	$9.0\text{x}10^{-5}$[15,20]	$1.58\text{x}10^{-4}$[16]	$1.23\text{x}10^{-4}$[18]	$2.2\text{x}10^{-4}$[19]
40	$2.0\text{x}10^{-4}$	---	$2.6\text{x}10^{-4}$	---

The hydrolysis of chromium has been studied extensively and values of X_{11} reported by different observers are shown in Table III.

The second hydrolysis of Cr (III), X_{12}, is developed in a similar manner so that

---

[15] N. Bjerrum, Z. Physik. Chem., 54 339 (1907). Information on ionic strength not available.

[16] A. Lamb and G. Fonda, J. Am. Chem. Soc. 43, 1155 (1921). A value reported to be independent of ionic strength. Ionic strength =

= concentration of ion; Z = charge of ion.

[17] J. Bronsted and C. King, Z. Physik. Chem., 130 699 (1927). Ionic strength = 0.068.

[18] C. Postmus and E. King, J. Phys. Chem., 59, 1208 (1955). This article includes ΔS for several ionic strengths and ΔH. These values were computed for an ionic strength of 0.232.

[19] W. Hartford, Ind. and Eng. Chem., 34, 920 (1942). Ionic Strength = 0.003.

[20] K. Emerson and W. Graven, J. Inorg. Nuc. Chem., 11, 309 (1959).

$$X_{12} = \frac{[Cr(OH)_2(OH_2)_4{}^{+}]\,[H_3O^{+}]^2}{[Cr(OH_2)_6{}^{+++}]}$$

The sequence continues in this way for chromium (III) and most other trivalent ions into the amphoteric range in which the metal ion has up to six OH^- ions attached to it.[21] The amphoterics are all soluble.

Knowing the hydrolysis constants it is possible to determine the concentrations of various products. For example, if only the concentrations of $Cr(OH_2)_6^{+++}$, $CrOH(OH_2)_5^{++}$, and H_3^+O are considered significant (possible since X_{12} and X_{13} are smaller than X_{11})[13,15]

$$[Cr(III)] = [Cr(OH_2)_6{}^{+++}] + X_{11}\frac{[Cr(OH_2)_6{}^{+++}]}{[H_3O^{+}]}$$

$$[H_3O^{+}] = \frac{10^{-14}}{[H_3O^{+}]} + H + X_{11}\frac{[Cr(OH_2)_6{}^{+++}]}{[H_3O^{+}]}$$

with $H \equiv$ hydrogen ions added to solution, $[Cr(III)] \equiv$ total chromium concentration. In most cases the ionization of water is negligible and this set of equations may be solved exactly so that

$$[CrOH(OH_2)_5] =$$

$$\frac{-(X_{11}+H)+\sqrt{(X_{11}+H)^2+4X_{11}[Cr(III)]}}{2} \qquad (3a)$$

---

[21] J. N. Mulay, Advances in the Chemistry of Coordination Compounds, The Macmillan Co., New York, N.Y., 1961, p. 532.

and

$$[Cr(OH_2)_6^{+++}] = [Cr(III)] - [CrOH(OH_2)_5^{++}] \quad (3b)$$

In Figures 2a, 2b, and 2c are shown the concentrations of $Cr(OH_2)_6^{+++}$ and $CrOH(OH_2)^{++}$ as H is varied for a $[Cr(III)] = 3.00 \times 10^{-4}$ molar. Values reported by Postmus[18] for X_{11} are used. In Figure 3 the effect of changing $[Cr(III)]$ is illustrated. An increase in total chromium (III) concentration results in a smaller percentage concentration of $CrOH(OH_2)_5^{++}$. The reverse is also true. Increasing the Cr(III) concentration increases the hydrogen ion concentration and pushes the reaction towards $Cr(OH_2)_6^{+++}$. The solutions for systems with more components are set up in the same manner. Exact solutions may not be realized.

The polymerization of Cr(III), in which the first step is the formation of a dimer, is well documented.[15,21,22,23,24] Hydroxide ions are capable of forming bridges between chromium ions with the same oxygen atom occupying coordination sites on two metal ions. The exact structure of the dimer is unknown; more than one structure is probably present in aqueous solution at the proper PH[5,21,25] and quantitative information concerning their formation is nonexistent. Dimer formation constants

---

[22] J. Laswick and R. Plane, J. Am. Chem. Soc., 81, 3564 (1959).

[23] H. Koleschutter, An. Chemie 49, 865 (1936).

[24] H. Hall and H. Eyring, J. Am. Chem. Soc., 72, 782 (1950).

[25] K. Sancier and J. Mills, J. Phys. Chem., 67, 1438 (1963).

```
CR(NO3)3 0.1 NACLO4                                                            007
 X11= 2.90E-05       X22=  .00E-99                                             008
                                                                               009
 0                    CONC (MOLES)                               3.00E-04      010
 H=  .00E-99                                                                   011
5                   4                                   3                    2
5       4                                                           3        2
5   4                                                                   3    2
5  4                                                                     3   2
5 4                                                                       3  2
5 4                                                                       3  2
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5                                                                           32
 H= 8.00E-03                                                                   012
```

Figure 2a. Concentration of $Cr(OH_2)_6^{+++}$, (3), and $CrOH(OH_2)_5$, (4), vs. Hydrogen Ion Concentration Added (H) at 0°C. [Cr(III)] = 3.00 x 10^{-4} Molar

```
CR(NO3)3 0.1 NACLO4                                                          001
 X11= 9.40E-05      X22=  .00E-99                                            002
                                                                             003
 0                   CONC (MOLES)                              3.00E-04      004
 H=  .00E-99                                                                 005
5                              4           3                               2
5                  4                                   3                   2
5           4                                                 3            2
5        4                                                       3         2
5      4                                                           3       2
5     4                                                             3      2
5    4                                                               3     2
5   4                                                                 3    2
5   4                                                                 3    2
5  4                                                                   3   2
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5                                                                         32
 H= 8.00E-03                                                                 006
```

Figure 2b. Concentration of $Cr(OH_2)^{+++}$, (3), and $CrOH(OH_2)_5$, (4), vs. Hydrogen Ion Concentration Added (H) at 20°C. $[Cr(III)] = 3.00 \times 10^{-4}$ Molar

```
 CR(NO3)3 0.1 NACLO4                                                          013
  X11= 2.60E-04      X22=  .00E-99                                            014
                                                                              015
  0                   CONC (MOLES)                              3.00E-04      016
  H=  .00E-99                                                                 017
 5                             3             4                              2
 5                               4         3                                2
 5                        4                       3                         2
 5                   4                                 3                    2
 5                4                                       3                 2
 5             4                                             3              2
 5           4                                                 3            2
 5          4                                                   3           2
 5         4                                                     3          2
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  H= 8.00E-03                                                                 018
```

Figure 2c. Concentration of $Cr(OH_2)_6$, (3), and $CrOH(OH_2)_5$, (4), vs. Hydrogen Ion Concentration Added (H) at 40°C. [Cr(III)] = 3.00×10^{-4} Molar could be of the form

$$X_{21} = \frac{[Cr_2OH(OH_2)_{10}^{5+}]^2[H_3O^+]}{[Cr(OH_2)_6^{+++}]}$$

$$X_{22} = \frac{[Cr_2(OH)_2(OH_2)_8^{4+}]^2[H_3O^+]^2}{[Cr(OH_2)_6]^{+++}}$$

$$X_{23} = \frac{[Cr_2(OH)_3(OH_2)_6^{3+}]^2[H_3O^+]^3}{[Cr(OH_2)_6^{+++}]}$$

In Figures 4a and 4b are illustrated the effect of an assumed X_{22} on the system. The number and type of ion in solution depends upon the PH. In the range PH < 4 it is possible to restrict the possibilities to the first hydrolysis product and a dimer. As the PH increases the exact nature of a chromium (III) solution becomes more complex.

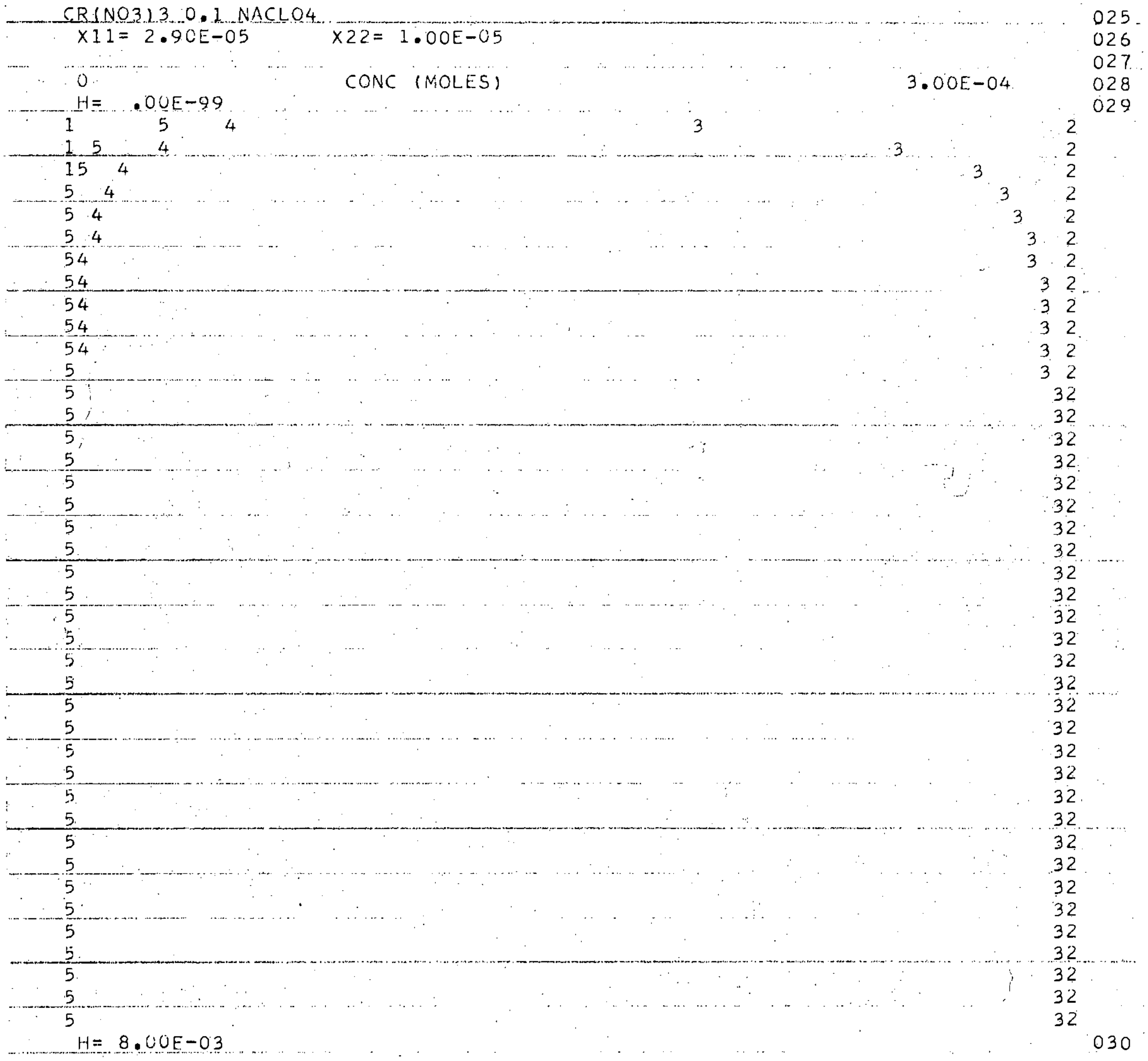

Figure 3a. Concentration of $Cr(OH_2)_6^{+++}$, (3), $CrOH(OH_2)_5$, (4), and $Cr_2(OH)_2(OH_2)_8^{4+}$, (5), vs. Hydrogen Ion Concentration Added (H) at 0°C for an Assumed Value of X_{22}. $[Cr(III)] = 3.00 \times 10^{-4}$ Molar

```
CR(NO3)3 0.1 NACLO4                                                             031
 X11= 2.90E-05       X22= 1.00E-05                                              032
                                                                                033
 5                    CONC (MOLES)                                1.00E-03      034
 H=  .00E-99                                                                    035
1     5                                                   3                   2
1  54                                                            3            2
1 54                                                                 3        2
154                                                                     3     2
5 4                                                                      3    2
54                                                                        3   2
54                                                                         3  2
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5                                                                            32
 H= 8.00E-03                                                                    036
```

Figure 3b. Concentration of $Cr(OH_2)_6^{+++}$, (3), $CrOH(OH_2)_5$, (4), and $Cr_2(OH)_2(OH_2)_8^{4+}$, (5), vs. Hydrogen Ion Concentration Added (H) at 0°C for an Assumed Value of X_{22}. [Cr(III)] = 1.00 x 10^{-3} Molar

4. THEORETICAL RELAXATION RATE

In this section a quantitative model will be developed for aqueous chromium (III) solution which accounts for the variation in relaxation rate with changing PH. This will be done in two steps. First, the increase in rate which accompanies an increase in PH will be associated with the appearance of a particular chemical species. And second, a specific mechanism will be proposed and this mechanism will be expanded into a rate equation. In both steps, alternatives will be examined and the test applied will be the usual. A proposed scheme must be the simplest possible which is consistent with the known data.

The most obvious reaction which occurs in chromium solutions, as the hydrogen ion concentration is lowered, is hydrolysis. As concentrated solutions are diluted the color changes from blue to green. This color change is unmistakable for concentrations to millimole strength. Addition of acid causes an immediate change in color back to blue, a color associated with $Cr(OH_2)_6$.[5,20,22] The absorption spectra of both $CrOH(OH_2)_5^{++}$ and $Cr(OH)_2(OH_2)_4^{+}$ are such that the solutions appear to be a pale green in color.[20,26]

Further insight is obtained by comparing Figures 2 and 5 at values of $H \geqslant 0$. An increase in relaxation rate is matched by an increase in the concentration of $CrOH(OH_2)_5^{++}$. Since the ratio[15,20]

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[26] Charles D. Hodgeman, Handbook of Chemistry and Physics, The Chemical Rubber Publishing Company, Cleveland, Ohio, 1961, p. 2951.

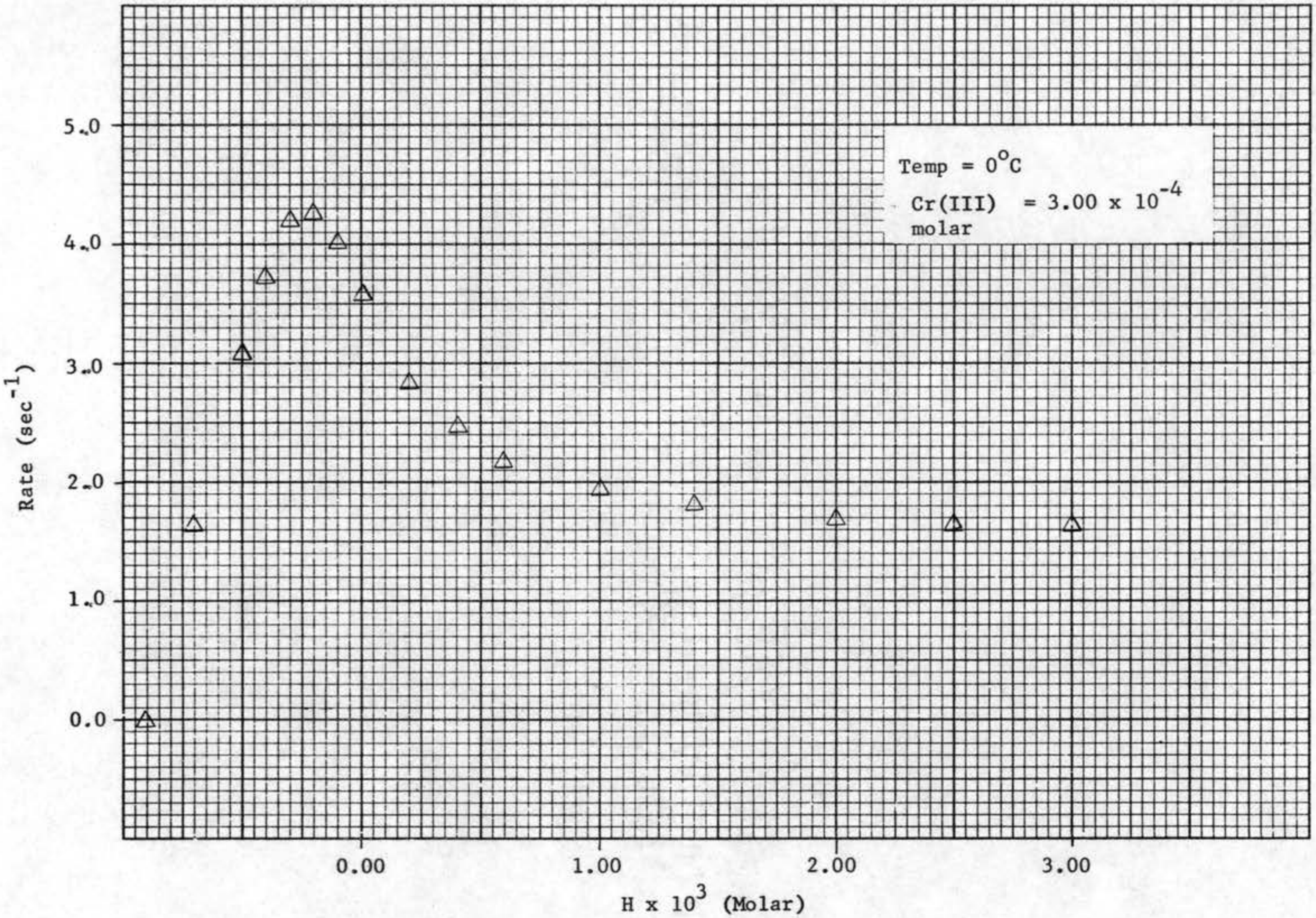

Figure 4. Experimental Relaxation Rate vs. Hydrogen Ion Concentration Added for H > 0 and vs. Hydroxide Ion Concentration Added for H < 0 at $0^{o}C$. For H < 0, H = -OH Added.

$$\frac{[Cr\,OH\,(OH_2)_5^{++}]}{[Cr\,(OH)_2\,(OH_2)_4^{+}]} = \frac{X_{11}}{X_{12}}\,h \approx 100$$

for $h = 10^{-4}$ and $X_{12} = 1.2 \times 10^{-10}$ and since the activation energies are approximately the same[15,18,20], significant concentrations of $Cr(OH)_2(OH_2)_4^{+}$ will not occur in the temperature range 0°C - 40°C unless OH^- ions are added to the solutions. (Measured PH of a 3.0×10^{-4} molar Cr (III) solution is about 4).

Other possible hydrolysis products which might cause an increase in rate are $Cr(OH)_3(OH_2)_3$ and the first polymer products, dimeric chromium. Chromium Hydroxide, $Cr(OH)_3(OH_2)_3$ is easily eliminated because of its insolubility.[27] When one equivalent NaOH is added to a Cr (III) solution, a visible precipitate is formed and the resultant relaxation rate is equivalent to that of distilled water (Figure 5). The possible presence of polymeric Cr(III) is somewhat more difficult to eliminate from consideration. Quantitative information on formation constants is non-existent and published reports on the magnetic properties of dimeric chromium are contradictory.[25,28] If dimeric chromium (III) is paramagnetic its T_{1B} could be either longer or shorter. A slower tumbling rate for the complex would result in a larger relaxation rate and a possible decrease in τ_e would result in smaller relaxation rate. A change in τ_h is also possible. Data obtained in this investigation,

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[27] Gmelins, *Chrom*, Teil B, Lieferung 2, Verlag Chemie GMBH, Weinheim, Bundesrepublik, 1962, p. 261.

[28] A. Earnshaw and J. Lewis, J. Chem. Soc., 1961, 396 (1961).

Table VIII, indicate that dimeric Cr (III) is paramagnetic and possesses a relaxation rate smaller than that of $Cr(OH_2)_6^{+++}$.

Dimers of chromium (III) do have one differentiating feature. Their formation requires time and temperature. Once formed months are required at room temperature for the polymers to disappear, even in acid solution.[15,20,22,29,30] With the exception of data taken at 40°C, relaxation rates did not change with time. Data points were taken 10 days apart at 0°C and 20 days apart at 20°C on acidified and nonacidified samples. Acidified solutions held at 40°C for 14 hours and then remeasured at 0°C did not drift. This was not true for nonacidified solutions. A small drift was observed. For room temperature and below it appears that any possible concentration of dimers is negligible; at 40°C the concentration of dimers is probably small.

It appears therefore, that the only significant chemical species in the solutions to be considered are $Cr(OH_2)_6^{+++}$ and $CrOH(OH_2)_5^{++}$. It is now necessary to consider the specific way in which the appearance of $CrOH(OH_2)_5^{++}$ modifies the relaxation rate of the system.

In view of the difference in τ_h reported for acidified and nonacidified solution[1,4], Table I, the large magnitude of the observed change in relaxation rate, Figure 5, and the small modification in T_{1B} which would be caused by the loss of a proton,[1,4,31], it appears that the increase in rate associated with the appearance of $CrOH(OH_2)_5$ is a result of a shorter

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[29] Collequim 691, 505 (1927).

[30] A Lottermoesser, R. Smied, and Peh-Chuan Chü, Kolloid-Zeitschrift, 92, 9 (1940).

[31] B. McGarvey, J. Phys. Chem., 61, 1232 (1951)

τ_h. This shorter exchange correlation time could occur in either or both of the complex ions. However, a modification of τ_h in $Cr(OH_2)_6$ seems unlikely. For example, consider the proton exchange reaction

$$Cr\,OHH^*(OH_2)_5^{+++} + H_2O \xrightarrow{k_1} Cr(OH_2)_6^{+++} + H^*HO$$

and

$$\frac{d\left[Cr\,OHH^*(OH_2)_5^{+++}\right]}{dt} = -k_1\left[Cr\,OHH^*(OH_2)_5\right]$$

Since τ_h represents the mean lifetime of a proton in the 1st coordination sphere and since there are 12 protons sites per chromium ion,

$$k_1 = \frac{12}{\tau_h}$$ and at 0°C

$$k_1 \approx 2 \times 10^5 \text{ sec}^{-1}$$

An OH^- activated exchange involves a 2nd order reaction,

$$Cr(OH_2)_6^{+++} + OH^- \xrightarrow{k_2} Cr\,OH\,(OH_2)_5 + H_2O$$

and

$$\frac{d\left[Cr(OH_2)_6^{+++}\right]}{dt} = -k_2\left[Cr(OH_2)_6^{+++}\right]\left[OH^-\right]$$

The quantity $k_2\left[OH^-\right]$ represents the rate per chromium ion for proton removal. At PH 4 and in terms of molar units a

$$k_2 \approx 10^{15}\ \text{sec}^{-1}\text{mole}^{-1}$$

would be necessary in order to compete with k_1. The recombination rate of H^+ with OH^- in water has a $k_2 \approx 10^{11}$ $\text{sec}^{-1}\text{mole}^{-1}$.[32] A reaction ten thousand times faster than this is very unlikely. A reaction involving

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[32] A. Loewenstein and A. Gzöke, J. Chem. Phys., <u>84</u>, 1151 (1962).

OH^- ions is therefore excluded either as a primary or competing reaction.

The only other mechanism to be considered which might modify τ_h is a collision activated exchange between $CrOH(OH_2)_5^{++}$ and $Cr(OH_2)_6^{+++}$. The reaction

$$Cr^*(OH_2)_6^{+++} + CrOH(OH_2)_5^{++} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Cr^*OH(OH_2)_5^{++} + Cr(OH_2)_6^{+++}$$

is one in which an interaction between the two ions results in the exchange of a proton; a water bridge might or might not be involved.

Here

$$\frac{d\left[Cr^*(OH_2)_6^{+++}\right]}{dt} = -k_1\left[CrOH(OH_2)_5^{++}\right]\left[Cr^*(OH_2)^{+++}\right)$$

This is a complicated reaction and in addition to the information already available a prediction of relaxation rates would require the following:

1. T_{1I} for $CrOH(OH_2)_5^{++}$
2. τ_h for $CrOH(OH_2)_5^{++}$
3. k_1
4. information concerning a water bridge.

In addition, since $\left[CrOH(OH_2)_5^{++}\right]$ increases with $\left[Cr(III)\right]$, Equation 3a, collision activated exchange would eventually dominate the proton exchange and would result in an increasing relaxation rate per molar concentration of chromium (III) as the concentration of chromium (III) is increased. Such behavior was not observed in any of the solutions studied here.

Elimination of any mechanism which might modify τ_h leaves only the assumption that τ_h for $CrOH(OH_2)_5^{++}$ is inherently shorter than τ_h for $Cr(OH_2)_6^{+++}$. It is difficult to say whether this shortening of the proton exchange correlation time is due to a new proton exchange rate or an exchange of whole water molecules. Although the exchange time of water molecules in $Cr(OH_2)_6^{+++}$ is on the order of days. The loss of a proton from the 1st coordination sphere introduces a strong perturbation in the complex. The $CrOH(OH_2)_5^{++}$ complex is asymetric and the shift in the absorption spectra to longer wavelengths indicates a weaker bond between the water molecules and the chromium (III) ion.[22,26,33]

To recapitulate, it is now assumed that the following conditions apply:

1. The system of interest for PH values of about 4 or less consists of H_2O, $Cr(OH_2)_6^{+++}$, and $CrOH(OH_2)_5^{++}$.

2. T_{1B} and τ_h for $Cr(OH_2)_6^{+++}$ remain constant regardless of PH change.

3. T_{1B} and τ_h associated with each of the ions are not necessarily the same.

Final development of a model is now only dependent on a mechanism for proton exchange in $Cr(OH_2)_6^{+++}$. The ion may either "lose a proton with a subsequent replacement", a SN_1 reaction, or "gain a proton followed by an immediate loss", a SN_2 reaction.[34] The first of these possibilities is identical with the reaction which produces $CrOH(OH_2)_5^{++}$. The second

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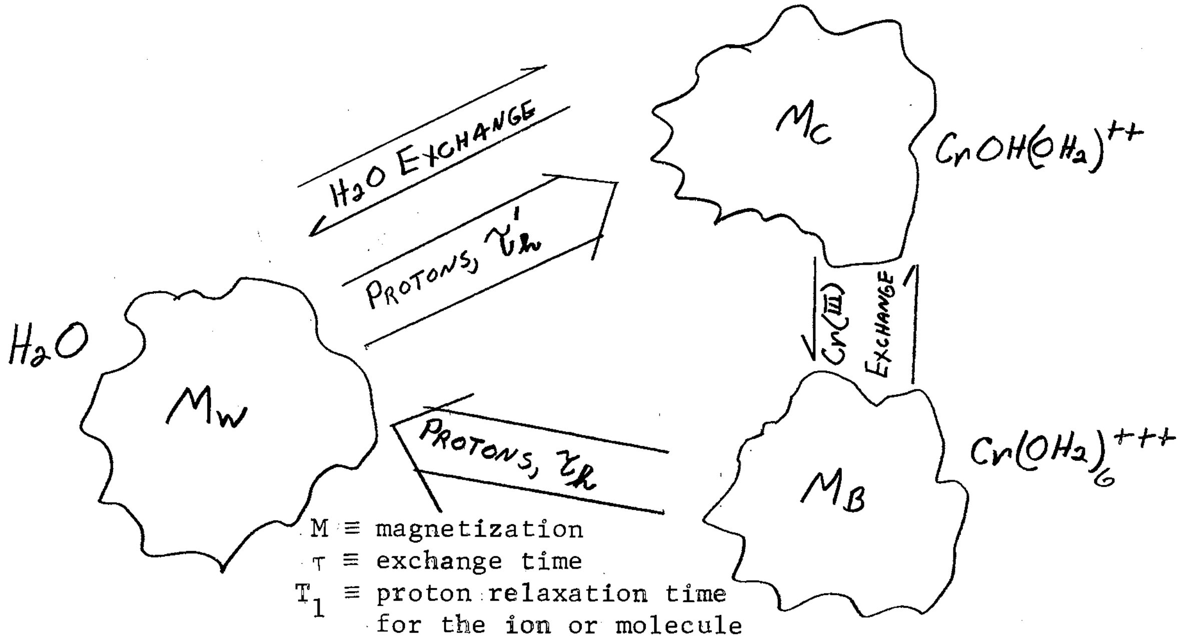
[33] Carl J. Ballhausen, Introduction to Ligand Field Theory, McGraw-Hill Book Company, Inc., New York, N.Y., 1962, p. 235.

[34] Bailar, Chemistry of the Coordination Compounds, Reinhold Publishing Corp., New York, N.Y., 1956, p. 218.

implies a location in the 1st coordination shphere in which an extra proton could be placed and, an increasing relaxation rate as the hydrogen ion conentration is increased. The reaction seems improbable and the associated effect was not observed.



M ≡ magnetization
τ ≡ exchange time
T_1 ≡ proton relaxation time for the ion or molecule

Figure .. Proton Exchange in the System $Cr(OH_2)_6^{+++}$ - $CrOH(OH_2)_5$ - H_2O

Proton exchange in the assumed system is shown in Figure 2. The specific exchanges which occur are as follows:

1. When $Cr(OH_2)_6^{+++}$ looses a proton, one proton is carried into the H_2O sub-system and 11 proton are carried into the $CrOH(OH_2)_5^{++}$ subsystem.

2. When $CrOH(OH_2)_5^{++}$ gains a proton 12 protons are carried into the $Cr(OH_2)_6^{+++}$ sub-system, 11 from $CrOH(OH_2)_5^{++}$ and one from H_2O.

3. During the time which $CrOH(OH_2)_5^{++}$ exists, it exchanges water molecules with the H_2O sub-system or it exchanges protons in such a way as to preclude the appearance of significant quantities of any

other chemical species.

Using a modification of the phenomenological Bloch Equations suggested by McConnell,[35] the rate at which the magnetization of the system approaches its equilibrium value is given by the following set of equations:

$$\dot{M}_W = \frac{M_{0W} - M_W}{T_{1W}} - \frac{M_W}{\tau_h'} - \frac{M_W}{\tau_c'} + \frac{M_B}{\tau_h} + \frac{M_C}{\tau_c}$$

$$\dot{M}_B = \frac{M_{0B} - M_B}{T_{1B}} + \frac{M_W}{\tau_h'} - 12\frac{M_B}{\tau_h} + \frac{M_C}{\tau_h''}$$

$$\dot{M}_C = \frac{M_{0C} - M_C}{T_{1C}} + \frac{M_W}{\tau_c'} + 11\frac{M_B}{\tau_h} - \frac{M_C}{\tau_h''} - \frac{M_C}{\tau_h}$$

with $\frac{M}{\tau}$ ≡ rate at which magnetization is transferred because of proton chemical exchange

$\frac{M_0 - M}{T_1}$ ≡ rate at which magnetization changes because of proton spin relaxation.

As used here, the τ's do not represent mean lifetimes, they stand for chemical exchange times, a quantity more useful in describing a chemical system. The chemical exchange time has a probabalistic meaning. A water proton associated with a $Cr(OH_2)_6^{+++}$ complex ion has a specific probabliity per unit time (for a given temperature and ionic environment) of breaking loose and

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[35] H. McConnell, J. Chem. Phys., 28, 430 (1958).

forming a hydronium ion. Since each of the 12 protons has the same proba-

$$P = e^{-12\frac{t}{\tau_h}}$$

where P ≡ probability that the complex ion will survive time to without the loss of a proton

$\frac{1}{\tau_h}$ ≡ probability/time that a given proton will leave the complex.

Therefore the number of complex ions N_B which survive time t is given by

$$N_B = N_{OB}\, e^{-12\frac{t}{\tau_h}}$$

and

$$\frac{dN_B}{dt} = -N_{OB}\,\frac{12}{\tau_h}\, e^{-12\frac{t}{\tau_h}}$$

The quantity $N_{OB}\,\frac{12}{\tau_h}$ ≡ rate at which $Cr(OH)_6^{+++}$ is converted to $CrOH(OH_2)_5^{++}$. $(12N_{OB})\,\frac{12}{\tau_h}$ ≡ rate at which protons are removed from the B system. In this way the rate at which magnetization is transferred out of B is seen to be

$$12\,\frac{M_B}{\tau_h}$$

and

$\frac{M_B}{\tau_h}$ ≡ rate at which B's magnetization appears in A.

$11\frac{M_B}{\tau_h}$ ≡ rate at which B's matnetization appears in C.

By defining τ_h in this way a quantity is developed which is not a function of the concentrations of $Cr(OH_2)_6^{+++}$ and $CrOH(OH_2)_5^{++}$, and which as will be shown later; is equal to the mean proton lifetime for an acidified system.

τ'_h and τ''_h may now be developed from τ_h by considering the rate of transfer between sub-systems when the species concentrations are not function of time, that is, in equilibrium.

Letting $N_W = H_2O$

$N_B = Cr(OH_2)_6^{+++}$

$N_C = CrOH(OH_2)_5^{++}$

The rate of transfer of protons from A to B is

$$\frac{2N_W}{\tau_h'} \text{ and since}$$

$$2N_W = 12\frac{N_B}{\tau_h} ,$$

$$\frac{1}{\tau_h'} = \frac{12N_B}{2N_W}\frac{1}{\tau_h}$$

In a similar fashion τ'' may be expressed in terms of τ_h. Since

$\frac{11 N_C}{\tau_h''} \equiv$ rate at which protons are transferred from C to B

and $\frac{N_C}{\tau_h''} \equiv$ rate at which $CrOH(OH_2)_6^{++}$ becomes $Cr(OH_2)_6^{+++}$, by considering the equilibrium condition

$$\frac{N_C}{\tau_h''} = \frac{12}{\tau_h}N_B$$

then

$$\frac{1}{\tau_h''} = \frac{12}{\tau_h} \frac{N_B}{N_C}$$

Since τ_C and τ'_C represent a completely different exchange mechanism one of these quantities must be independent. Defining $\frac{1}{\tau_C}$ as the probability per unit time that a water proton associated with CrOH $(OH_2)_5$ will exchange with the bulk water without producing a new species (equivalent to saying that if a new species is formed it exists for a time which is short when compared with τ_C or τ_h)

$$\frac{2N_W}{\tau_c'} = \frac{nN_C}{\tau_C} \quad \text{AND,} \quad \frac{1}{\tau_c'} = \frac{nN_C}{2N_W} \frac{1}{\tau_C}$$

with n ≡ number of exchanging protons in the complex.

Substituting and rearranging the rate equations become

$$\dot{M}_W + M_W\left(\frac{1}{T_{1W}} + \frac{N_B'}{N_W'}\frac{1}{\tau_h} + \frac{N_C'}{N_W'}\frac{1}{\tau_C}\right) - \frac{M_B}{\tau_h} + \frac{M_C}{\tau_C} = M_{0W}$$

$$-\frac{N_B'}{N_W'}\left(\frac{M_W}{\tau_h}\right) + \dot{M}_B + M_B\left(\frac{1}{T_{1B}} + \frac{12}{\tau_h}\right) - 12\frac{N_B}{N_C}\left(\frac{M_C}{\tau_h}\right) = M_{0B}$$

$$-\frac{N_C'}{N_W'}\frac{M_W}{\tau_C} - 11\frac{M_B}{\tau_h} + \dot{M}_C + M_C\left(\frac{1}{T_{1C}} + 12\frac{N_B}{N_C}\frac{1}{\tau_h} + \frac{1}{\tau_C}\right) = M_{0C}$$

N' ≡ total number of protons in the system.

By assuming that

$$M_W = C_W e^{\lambda t} + C_{0W}$$

$$M_B = C_B e^{\lambda t} + C_{0B}$$

$$M_C = C_C e^{\lambda t} + C_{0C}$$

The rate equations may be expressed in the following form:

$$M\begin{pmatrix} C_W e^{\lambda t} \\ C_B e^{\lambda t} \\ C_C e^{\lambda t} \end{pmatrix} + (M - \lambda I)\begin{pmatrix} C_{0W} \\ C_{0B} \\ C_{0C} \end{pmatrix} = \begin{pmatrix} \frac{M_{0W}}{T_{1W}} \\ \frac{M_{0B}}{T_{1B}} \\ \frac{M_{0C}}{T_{1C}} \end{pmatrix}$$

with

$$\mathcal{M} = \begin{pmatrix} \lambda + \frac{1}{\tau_{1W}} & -\frac{1}{\tau_{\ell}} & -\frac{1}{\tau_C} \\ -\frac{1}{\tau_{\ell}}\frac{N_B'}{N_W} & \lambda + \frac{1}{\tau_{1B}} & -\frac{12}{\tau_{\ell}}\frac{N_B}{N_C} \\ -\frac{1}{\tau_C}\frac{N_C'}{N_W'} & -\frac{11}{\tau_{\ell}} & \lambda + \frac{1}{\tau_{1C}} \end{pmatrix}$$

and will always have a solution if

$$|\mathcal{M} - \lambda I| \neq 0$$

and there exists a λ such that $|\mathcal{M}| = 0$

A simplification can be realized if it is assumed that for one of the three possible values of λ

$$\lambda \ll \frac{1}{\tau_{1B}} \quad \text{and} \quad \frac{1}{\tau_{1C}}$$

This is a reasonable assumption since each value of λ corresponds to a characteristic time associated with each of the three sub-systems. Two of these sub-systems will approach equilibrium very quickly. The equation which must now be solved is 1st order in λ and after rearranging is given by

$$\begin{vmatrix} \lambda + \frac{1}{T_{1W}} & \frac{1}{T_{1B}} & \frac{1}{T_{1C}} \\ -\frac{1}{\tau_h}\frac{N_B'}{N_W'} & \frac{1}{\tau_{1B}} & -\frac{12}{\tau_h}\frac{N_B}{N_C} \\ -\frac{1}{\tau_c}\frac{N_c'}{N_W'} & -\frac{11}{\tau_h} & \frac{1}{\tau_{1C}} \end{vmatrix} = 0$$

Expanding this,

$$\lambda = -\frac{1}{T_{1W}} - \frac{\frac{N_B'}{N_W'}\frac{1}{\tau_h}\begin{vmatrix} \frac{1}{T_{1B}} & \frac{1}{T_{1C}} \\ -\frac{11}{\tau_h} & \frac{1}{\tau_{1C}} \end{vmatrix}}{D} - \frac{\frac{N_C'}{N_W'}\frac{1}{\tau_c}\begin{vmatrix} \frac{1}{T_{1C}} & \frac{1}{T_{1B}} \\ \frac{12}{\tau_h}\frac{N_B}{N_C} & \frac{1}{\tau_{1B}} \end{vmatrix}}{D} ;$$

$$D = \begin{vmatrix} \frac{1}{\tau_{1B}} & -\frac{12N_B}{\tau_h N_C} \\ -\frac{11}{\tau_h} & \frac{1}{\tau_{1C}} \end{vmatrix}$$

Finally

$$\lambda = -\frac{1}{T_{1W}} - \frac{N_B'}{N_W'}\,\frac{\tau_h(T_{1C}+\tau_h)+\tau_c\left(11\,T_{1B}+12\,\frac{N_B}{N_C}\,T_{1C}\right)}{D}$$

$$-\frac{N_C'}{N_W'}\,\frac{\tau_h\left(12\,T_{1B}+\tau_h+12\,\frac{N_B}{N_C}\,T_{1C}\right)}{D} \qquad (5)$$

with $D = \tau_h(\tau_h + 12T_{1B})(\tau_c + T_{1C}) + 12\frac{N_B}{N_C}T_{1C}\,\tau_c(\tau_h + T_{1B})$

It is of interest to note that in addition to predicting correctly the limits[1]

$$\lim_{N_C \to 0}\left(\lambda + \frac{1}{T_{1W}}\right) = -\frac{N_B'}{N_W'}\,\frac{1}{T_{1B}+\tau_h}$$

$$\lim_{N_B \to 0}\left(\lambda + \frac{1}{T_{1W}}\right) = -\frac{N_C'}{N_W'}\,\frac{1}{T_{1C}+\tau_h}$$

$$\lim_{\substack{\tau_h \to 0\\ \tau_c \to 0}}\left(\lambda + \frac{1}{T_{1W}}\right) = -\frac{N_C'}{N_W'}\,\frac{1}{T_{1C}} - \frac{N_B'}{N_W'}\,\frac{1}{T_{1B}}$$

The possibility of a relative maximum is suggested. For example,

$$\lim_{\tau_c \ll 12\frac{N_B}{N_C}T_{1C}}\left(\lambda + \frac{1}{T_{1W}}\right) = -\frac{N_B'}{N_W}\,\frac{1}{\tau_h+12T_{1B}} - \frac{N_C'}{N_W'}\,\frac{12T_{1B}+\tau_h+12\frac{N_B}{N_C}T_{1C}}{T_{1C}(\tau_h+12T_{1B})}$$

$$= -\frac{N_B'}{N_W'}\,\frac{1}{\tau_h+12T_{1B}} - \frac{N_C'}{N_W'}\left(\frac{1}{T_{1C}} - \frac{12\frac{N_B}{N_C}}{\tau_h+12T_{1B}}\right)$$

$$= -\frac{N_B'}{N_W'}\left(\frac{1+n}{\tau_h + 12T_{1B}}\right) - \frac{N_C'}{N_W'}\frac{1}{T_{1C}}$$

if 11 protons are exchanging in $CrOH(OH_2)_5^{++}$

$$= -\frac{N_B'}{N_W'}\frac{1}{\tau_h/12 + T_{1B}} - \frac{N_C'}{N_W'}\frac{1}{T_{1C}}$$

This is a rate, which for some values of N_B, is greater than either

$$\frac{N_B'}{N_W'}\frac{1}{\tau_h + T_{1B}}, \quad N_C = 0$$

or

$$\frac{N_C'}{N_W'}\frac{1}{T_{1C}}, \quad N_B = 0$$

When τ_C is small $CrOH(OH_2)_5^{++}$ acts as a bridge for M_B into the H_2O subsystem. This produces an effective reduction in τ_h.

Therefore, it is possible that as the hydrogen ion concentration of the system is varied, the relaxation rate will pass through a maximum. Actual existence of the maximum depends on the exchange rates and the validity of assuming that no other hydrolysis products are present.

Using Equations 3a, 3b, and 5, and published values for T_{1B} and X_{11} relaxation rates may be predicted for solutions of different hydrogen ion concentration. Values of T_{1C} and τ_C will have to be assumed. The degree of agreement between computed and experimental data points will validate the assumed values and the proposed model.

5. EXPERIMENTAL

Relaxation times (T_1) were determined using earth's field free precession and a magnetic flux density of 3.8 x 10^{-2} weber/meter.^{2} Where appropriate, data were corrected for the rise time of the coil (about 10 milliseconds).

Sample temperatures were obtained in the following way. An ice bath was used for 0°C and a commercial regulated temperature bath was used for the 20°C and 40°C measurements. At the time data was taken the samples were removed from the constant temperature bath. This technique lead to some temperature drift during the time required to measure T_1 (about 90 seconds). Temperature drift for samples at 0°C was $+ 1.5^\circ$C. For the samples at 20°C and 40°C the temperature drift was less than 0.5°C. To insure thermal equilibrium, measurement on samples at 0°C and 20°C were made four hours after the samples were placed in the temperature bath. In an attempt to obtain some degree of chemical equilibrium, measurement made at 40°C were made after 14 hrs. at that temperature.

The chemicals used in preparing the samples were all Baker Analyzed Reagent Grade. As an additional check, Perchloric Acid, Sodium Hydroxide, and Sodium Perchlorate were tested for paramagnetic impurities by comparing the relaxation rate of a 2.0 molar solution with that of distilled water. No impurity effects were found.

Concentration of Cr(III) was determined primarily by weighing. In order to insure absolute comparability between measurements made at different times, a 0.05 molar "master" solution was prepared and sample concentrations were determined by diluting the "master" solution volumetricaly. This standard solution was allowed to age one month before data was taken. Relaxation rate per mole of samples prepared this way were within 3% of the published value of 1.00 x 10^4 sec^{-1}/mole.[2]

Hydrogen ions were added to the solution in the form of Perchloric Acid. One molar concentrations were prepared by weighing 61.2% solutions; sample concentrations were established by pipetting the requisite quantity of this one molar solution. H represents the hydrogen ion concentration of the sample due only to the addition of Perchloric Acid. H does not represent hydrogen ion concentration due to hydrolysis, water ionization, or acid impurities in the chromium (III).

Sample volumes were 500 cm^3 and distilled water was used in all preparations. Unless othewise stated all samples contained 0.1M $NaClO_4$.

6. RESULTS

$Cr(OH_2)_6^{+++}$ - $CrOH(OH_2)_5^{++}$ - H_2O System

Relaxation rate vs H, was determined for three temperatures, 0°C, 20°C, and 40°C. The results are shown in Figure 5 for the range H = 0.00 to 8.00 x 10^{-3} molar. The important qualitative feature of these curves are as follows. At 0°C a very fast decrease in rate occurs as H increases. At H = 2.00 x 10^{-3} molar the decrease is essentially complete. At 20°C the decrease is much smaller and it is interesting to note that the relaxation rate appears to be constant in the vicinity of H = 0.00 molar. The actual existence of this absolute maximum is confirmed in Figure 8, the same experiment with an expanded abciss . At 40°C, instead of decreasing, the rate first increases rapidly and then decreases slowly. In addition to providing quantitative information on the chromium (III) ion, the unique features of the curves provide a reasonably restrictive check on the model developed in the preceeding section.

The data confirms the existence of a minimum in the T_1 vs. temperature curve as reported by Hausser and Laukien.[3] However, the minimum will occur at 25°C only for a nonacidified system. For an acidified system it appears that a minimum will occur at a temperature greater than 40°C. The position of the minimum is a function of H.

In order to compare the relaxation rates predicted by the model, Equation (5), with the experimental relaxation rates, a computer program

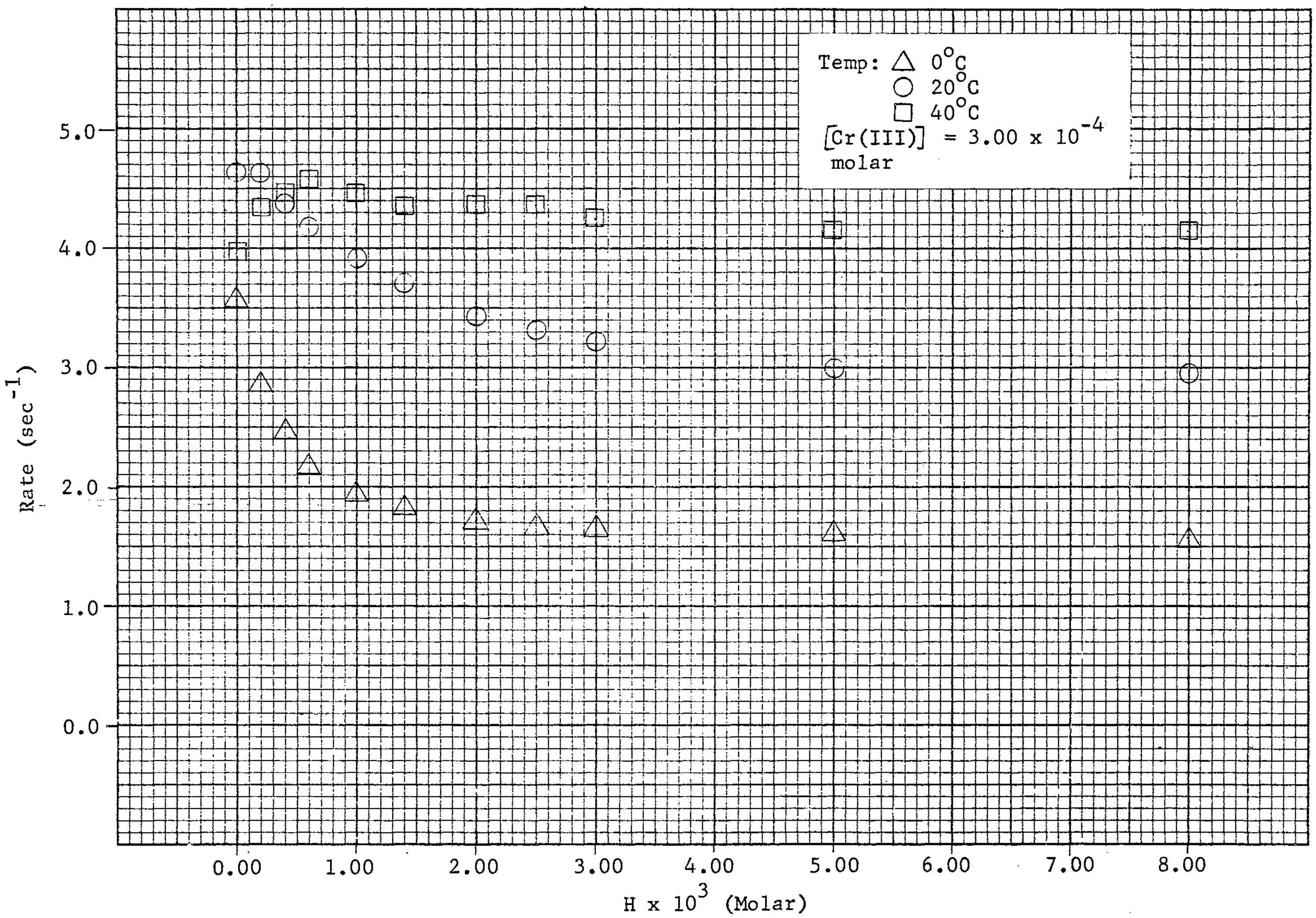


Figure 6. Experimental Relaxation Rate vs. H for $Cr(NO_3)_3$ at 0°C, 20°C, and 40°C $[Cr(III)] = 3.00 \times 10^{-4}$ molar.

was written which would plot experimental and computed data points on the same graph, using H as the independent variable. The input for the program consisted of the following:

1. experimental relaxation rates, uncorrected
2. relaxation rate of H_2O
3. experimental concentration of Cr(III)
4. concentration of Cr(III) to be used in the computations
5. X_{11}
6. X_{22} (taken to be zero)
7. T_{1B}
8. T_{1C}
9. τ_C

Program output consisted of the simultaneous plot of experimental and computed data points, and τ_h. Values used for X_{11} were those reported by Postmus and King[18] and values used for T_{1B} were essentially those computed from the data of Hausser and Noack, Table I. Small changes were made in T_{1B} to get slightly better data. τ_h was obtained by assuming the validity of Equation (2) for an acidified solution, Table V. Therefore, a fit of computed curve to experimental curve was primarily obtained by "guessing" at T_{1C} and τ_C.

While this method is not the most elegant and eventually required a great deal of trial and error time on an IBM 1620, it had the advantage of putting the experimenter in the computation cycle. This provided some degree of insight into the relative importance of the input parameters in causing relaxation.

At $0^{\circ}C$ the results were very sensitive to changes (1%) in τ_C and almost impervious to changes in T_{1B} and T_{1C}. At $20^{\circ}C$ T_{1C} became important for values of H around 0.00 and at $40^{\circ}C$ T_{1B} became important. At $40^{\circ}C$ large changes (20%) in τ_C caused little change in the curve fit. As might be expected a relative maximum in the relaxation rate requires a $T_{1C} > T_{1B}$.

Most of the data was obtained for solutions with a $[Cr(III)] = 3.00 \times 10^{-4}$ molar. However as an additional check some data was taken for $[Cr(III)] = 1.00 \times 10^{-4}$, 6.00×10^{-4}, and 1.00×10^{-3} molar. So that all data could be displayed on the same scale, computed relaxation rates for concentrations other than 3.00×10^{-4} molar were divided by the ratio of the concentrations before plotting. For example, a computed relaxation rate of 6.40 sec^{-1} for a $[Cr(III)] = 6.00 \times 10^{-4}$ molar would be plotted as 3.20 sec^{-1} on the graph. Computer plotted experimental data points for $[Cr(III)]$ other than 3.00×10^{-4} molar are those for $[Cr(III)] = 3.00 \times 10^{-4}$ molar. This procedure leads to some confusion but makes obvious the non-linear variation in relaxation rate with respect to changes in Cr(III) concentration. This additional data on concentration dependence is presented in Table IV.

The values obtained for τ_h, T_{1C}, and τ_C along with the values used for T_{1B} are summarized in Table VI. The graphs which resulted in these quantities are shown in Figures 7a, 7b, 7c, 7d, 9a, 9b, 9c, 10a, 10b, and 10c.

The computer program was written so that 10 or 11 protons would exchange in $CrOH(OH_2)_5^{++}$. Better results were obtained with 10. It appears that an even better fit could have been obtained if it had been

```
CR(NO3)3 0.1 NACLO4
 TEMP= 273.0
 RELAX RATE WATER= 6.80E-01
 RELAX RATE FREE ION= 5.06E+03
 METAL CONC,REF= 3.00E-04
 METAL CONC= 3.00E-04

 T1B= 3.00E-06      TAUH= 1.85E-05
 T1C= 3.20E-06      TAUC= 1.05E-06
 X11= 2.90E-05
 X22=  .00E-99       R22=  .00E-99
```

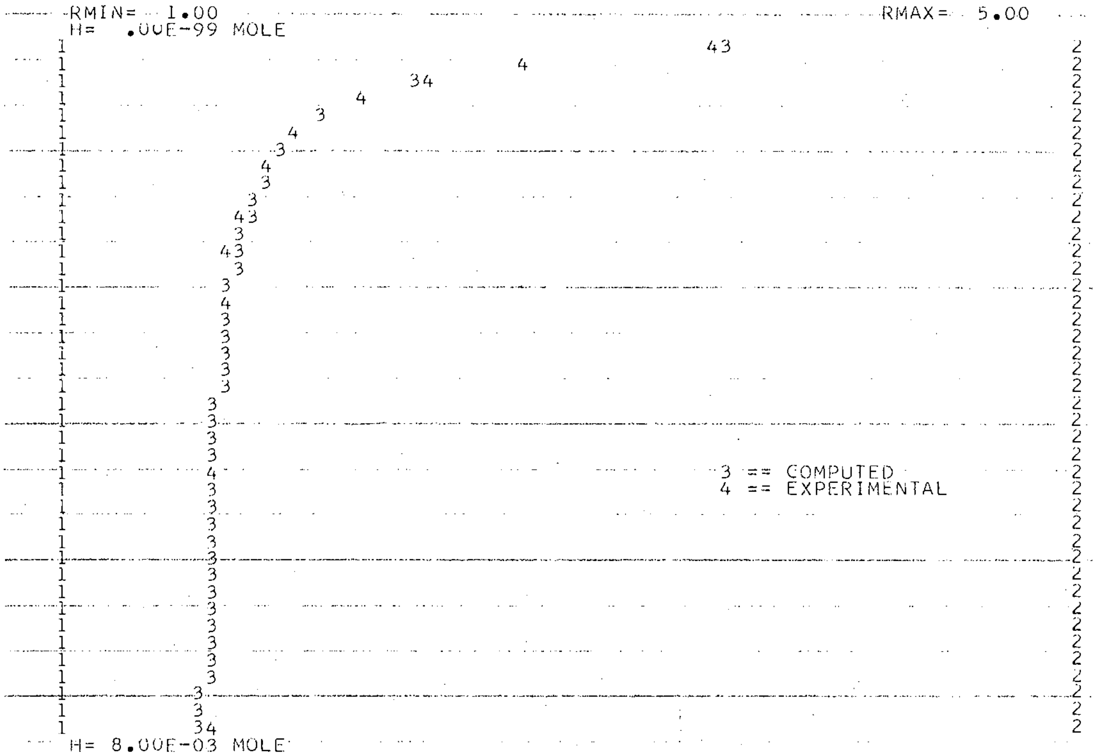


Figure 7a. Experimental and Computed Relaxation Rates vs. H at 0°C. [Cr(III)] = 3.00 x 10^{-4} Molar

```
CR(NO3)3 0.1 NACLO4
 TEMP= 273.0
 RELAX RATE WATER= 6.80E-01
 RELAX RATE FREE ION= 5.06E+03
 METAL CONC,REF= 3.00E-04
 METAL CONC= 1.00E-04

 T1B= 3.00E-06       TAUH= 1.85E-05
 T1C= 3.20E-06       TAUC= 1.05E-06
 X11= 2.90E-05
 X22=  .00E-99        R22=  .00E-99


 RMIN=  1.00                                              RMAX=  5.00
 H=  .00E-99 MOLE
```

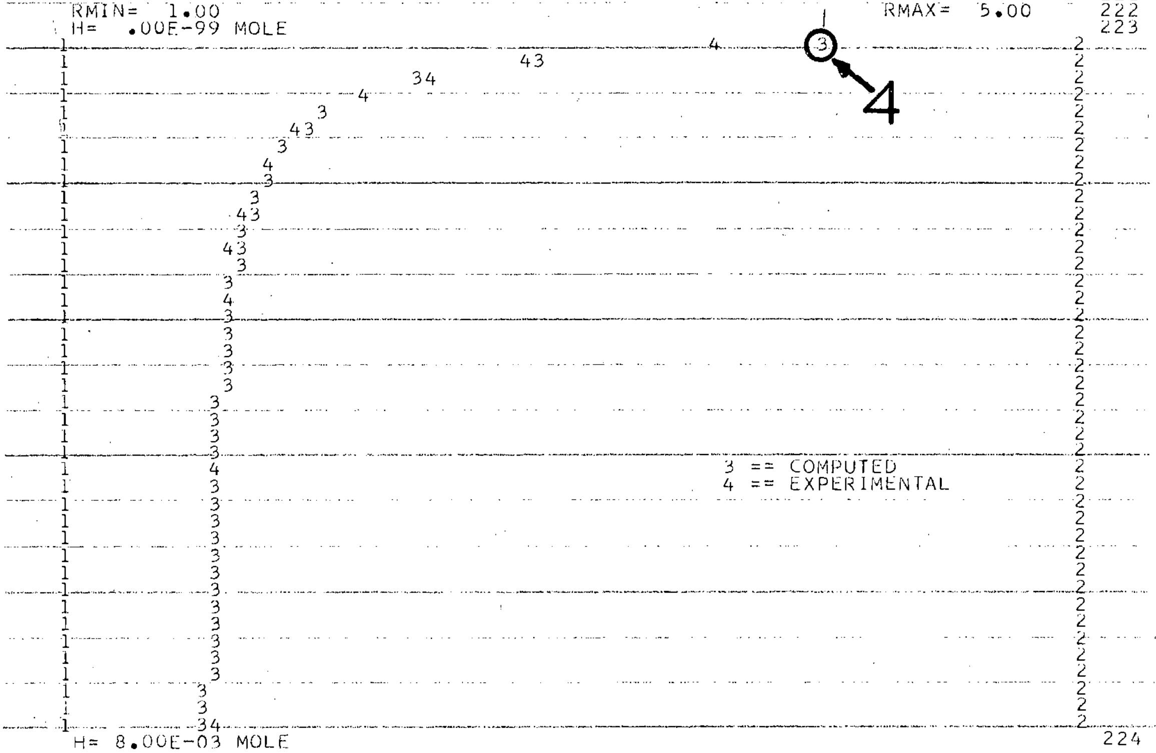


Figure 7c. Normalized Experimental Relaxation Rate (○← 4) and Computed Relaxation Rates vs. H at 0°C. [Cr(III)] = 6.00 x 10^{-4} Molar

```
CR(NO3)3 0.1 NACLO4
 TEMP= 273.0
 RELAX RATE WATER= 6.80E-01
 RELAX RATE FREE ION= 5.06E+03
 METAL CONC,REF= 3.00E-04
 METAL CONC= 6.00E-04

 T1B= 3.00E-06      TAUH= 1.85E-05
 T1C= 3.20E-06      TAUC= 1.05E-06
 X11= 2.90E-05
 X22=  .00E-99       R22=  .00E-99
```

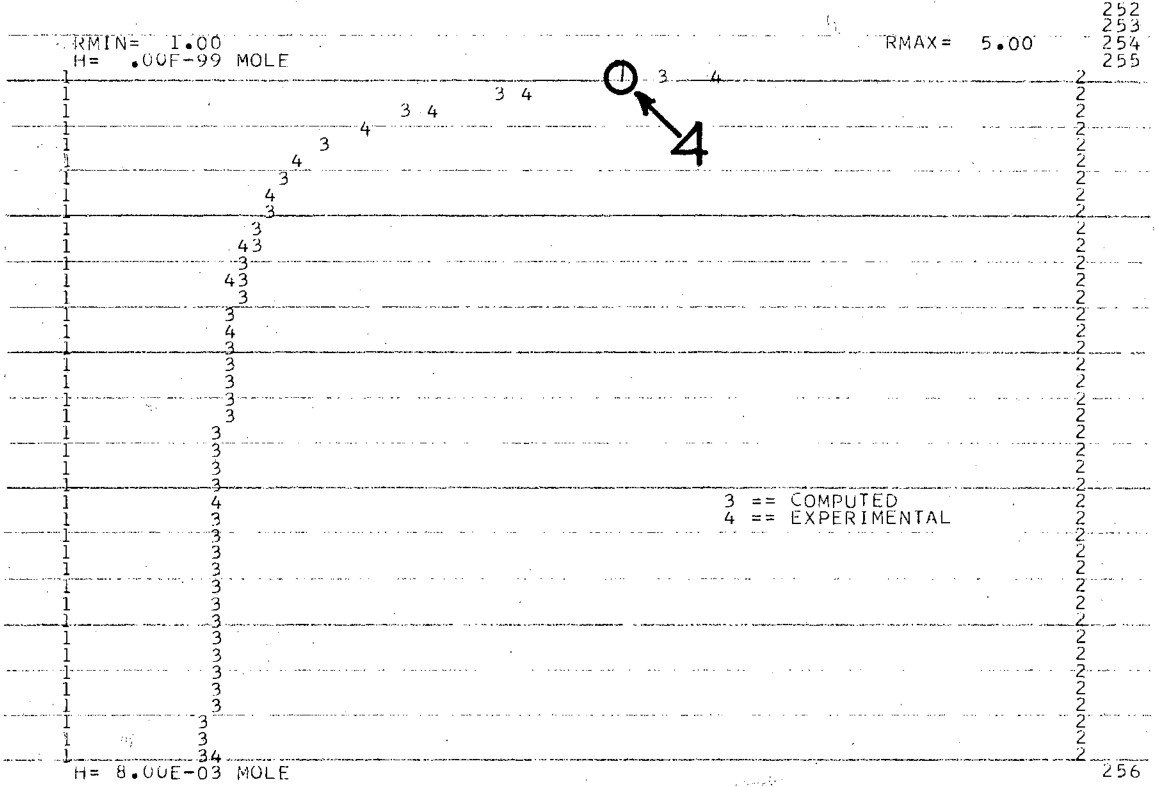


Figure 7b. Normalized Experimental Relaxation Rate (○⟵ 4) and Computed Relaxation Rates vs. H at $0^{o}C$. [Cr(III)] = 1.00 x 10^{-4} Molar

```
CR(NO3)3 0.1 NACLO4
 TEMP= 273.0
 RELAX RATE WATER= 6.80E-01
 RELAX RATE FREE ION= 5.06E+03
 METAL CONC,REF= 3.00E-04
 METAL CONC= 1.00E-03

 T1B= 3.00E-06       TAUH= 1.85E-05
 T1C= 3.20E-06       TAUC= 1.05E-06
 X11= 2.90E-05
 X22=  .00E-99        R22=  .00E-99
```

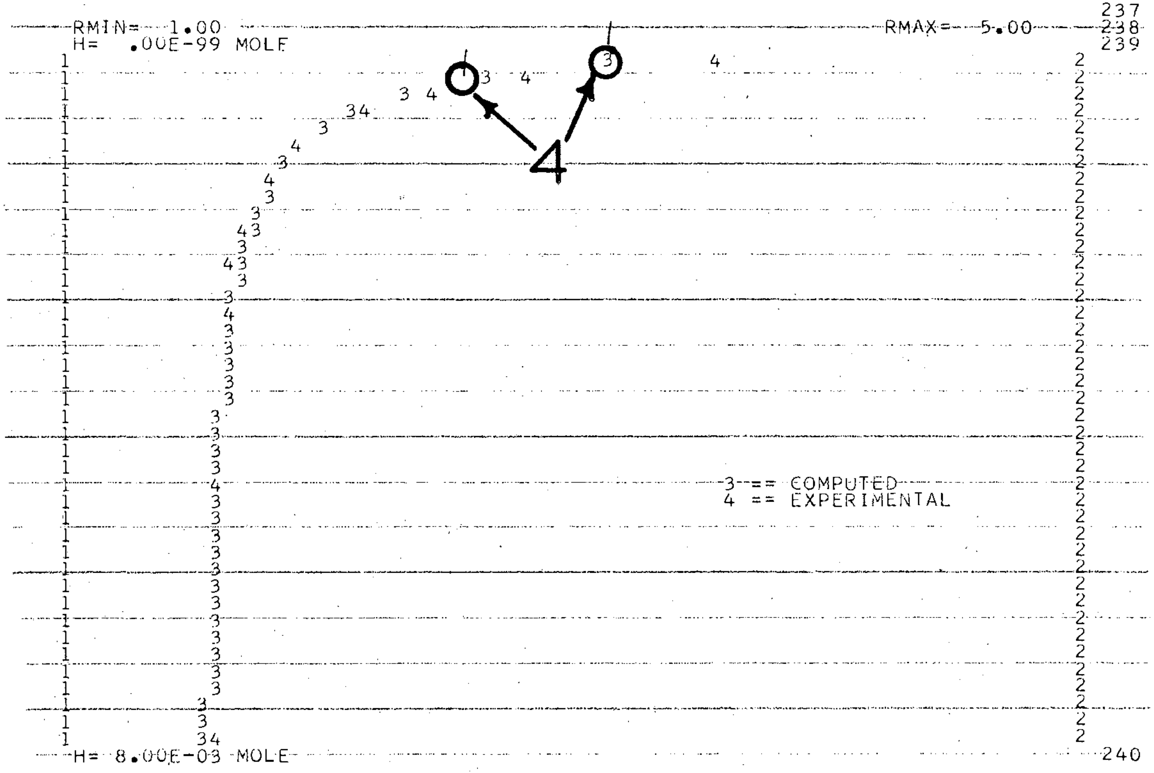


Figure 7d. Normalized Experimental Relaxation Rates (O—4) and Computed Relaxation Rates vs. H at 0°C. [Cr(III)] = 1.00 x 10^{-3} Molar

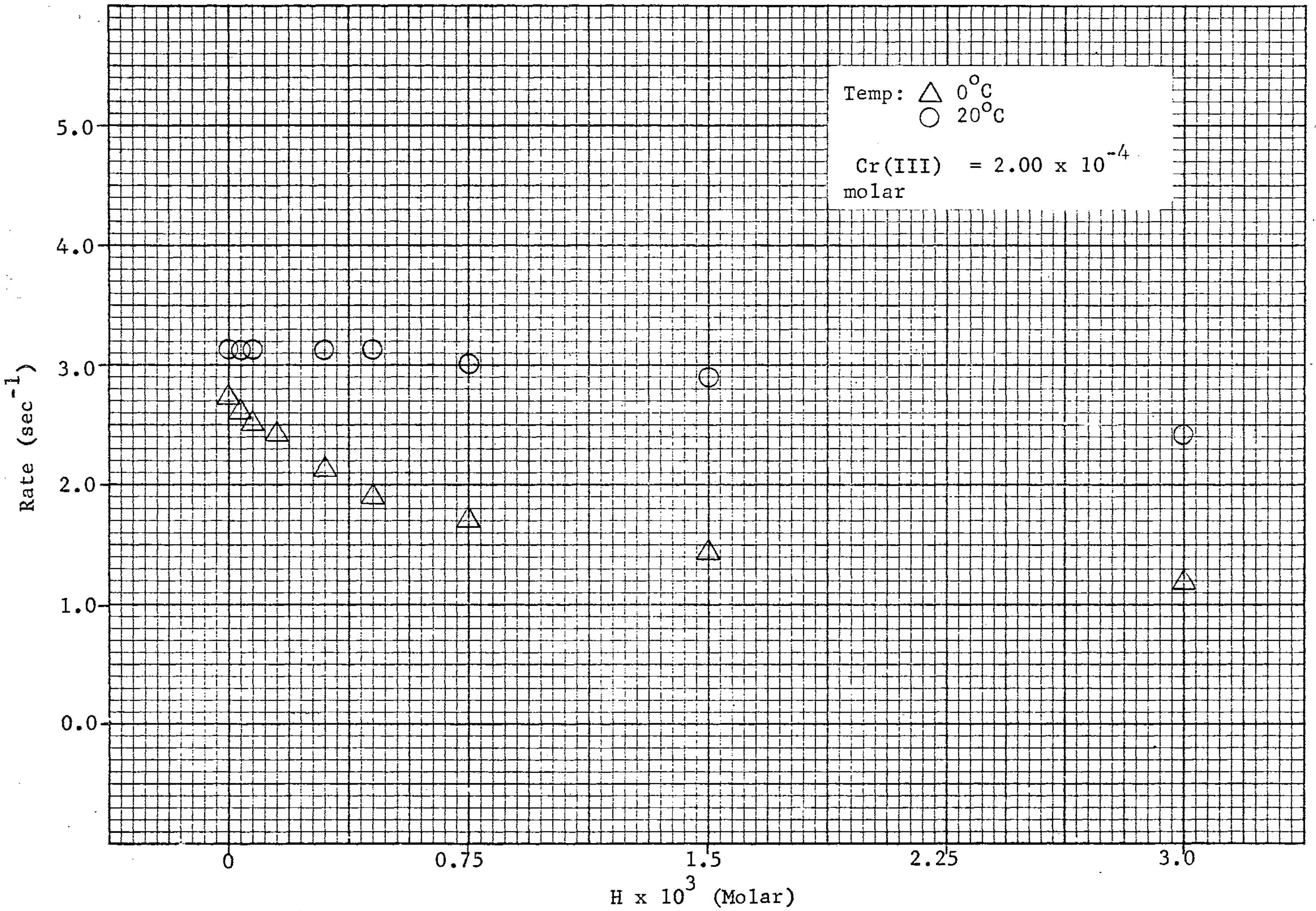


Figure 8. Experimental Relaxation Rate vs. H for $Cr(NO_3)_3$ at 0°C and 20°C. $NaClO_4$ not added. $[Cr(III)] = 2.00 \times 10^{-4}$ molar.

```
CR(NO3)3 0.1 NACLO4
 TEMP= 293.0
 RELAX RATE WATER= 4.20E-01
 RELAX RATE FREE ION= 9.10E+03
 METAL CONC,REF= 3.00E-04
 METAL CONC= 3.00E-04

 T1B= 4.00E-06       TAUH= 7.98E-06
 T1C= 6.00E-06       TAUC= 4.50E-07
 X11= 9.40E-05
 X22=  .00E-99        R22=  .00E-99
```

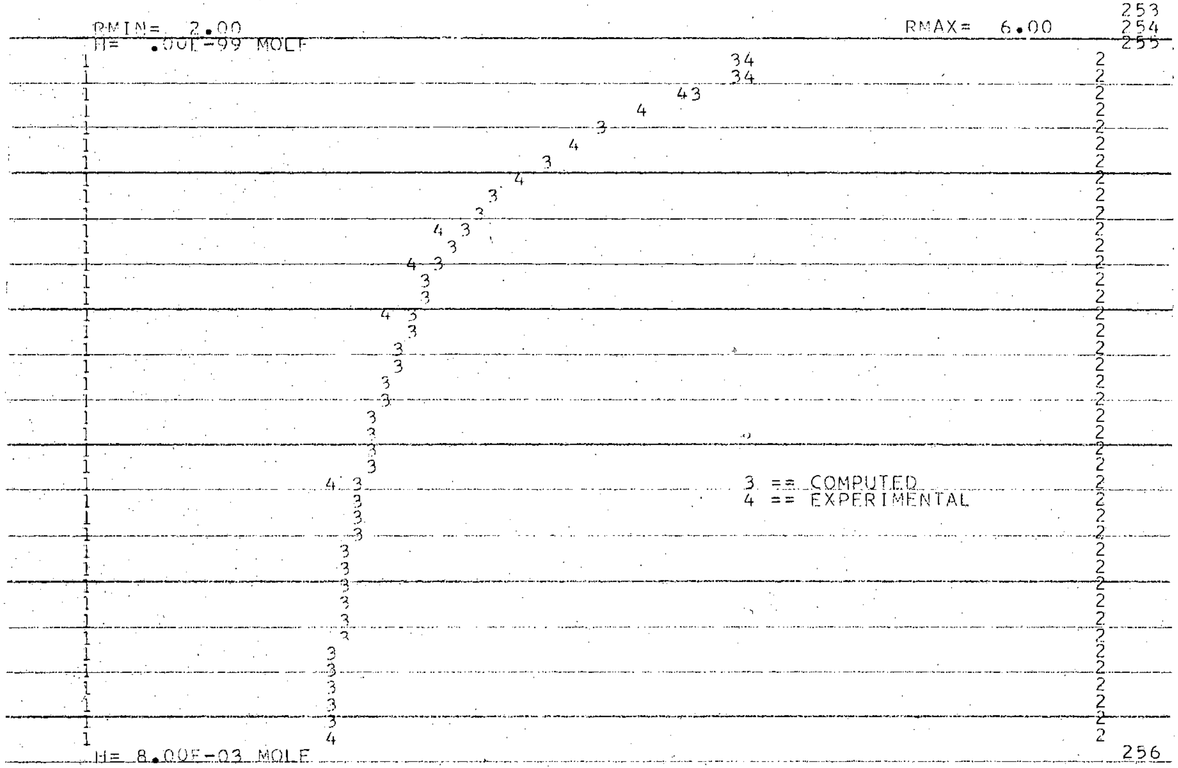


Figure 9a. Experimental and Computed Relaxation Rates vs. H at 20°C. [Cr(III)] = 3.00 x 10^{-4} Molar

```
CR(NO3)3 0.1 NACLO4
 TEMP= 293.0
 RELAX RATE WATER= 4.20E-01
 RELAX RATE FREE ION= 9.10E+03
 METAL CONC,REF= 3.00E-04
 METAL CONC= 6.00E-04

 T1B= 4.00E-06       TAUH= 7.98E-06
 T1C= 6.00E-06       TAUC= 4.50E-07
 X11= 9.40E-05
 X22=  .00E-99        R22=  .00E-99

 RMIN=  2.00                                            RMAX=  6.00
 H=  .00E-99 MOLE
```

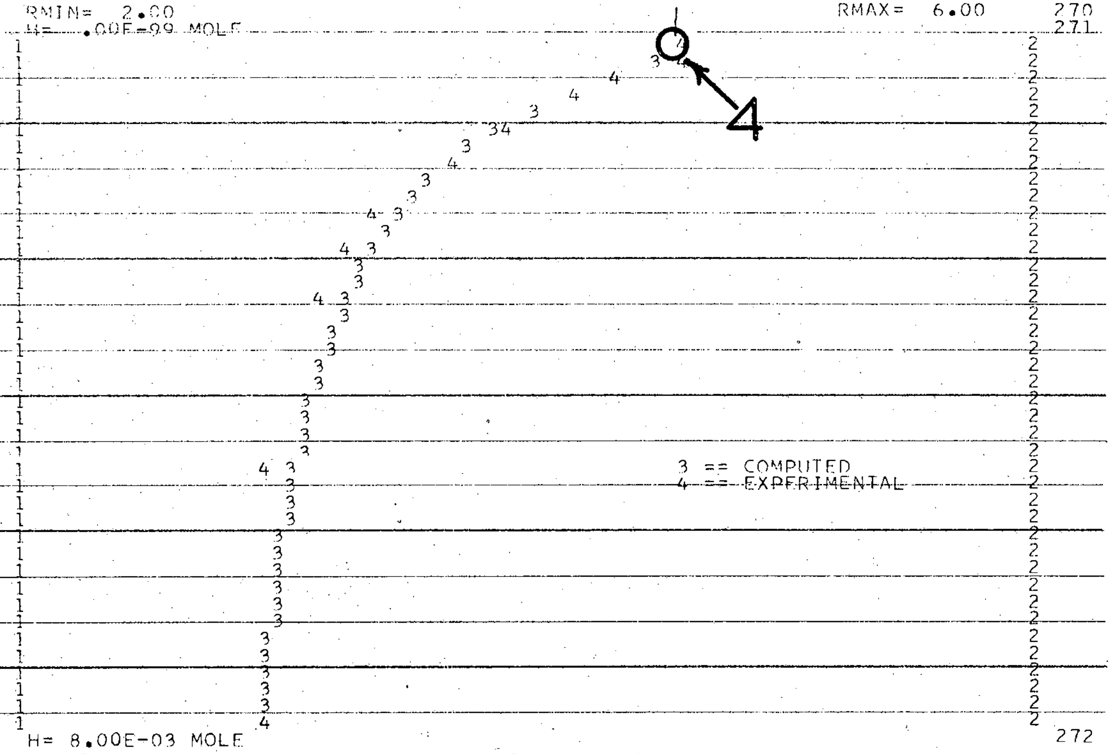
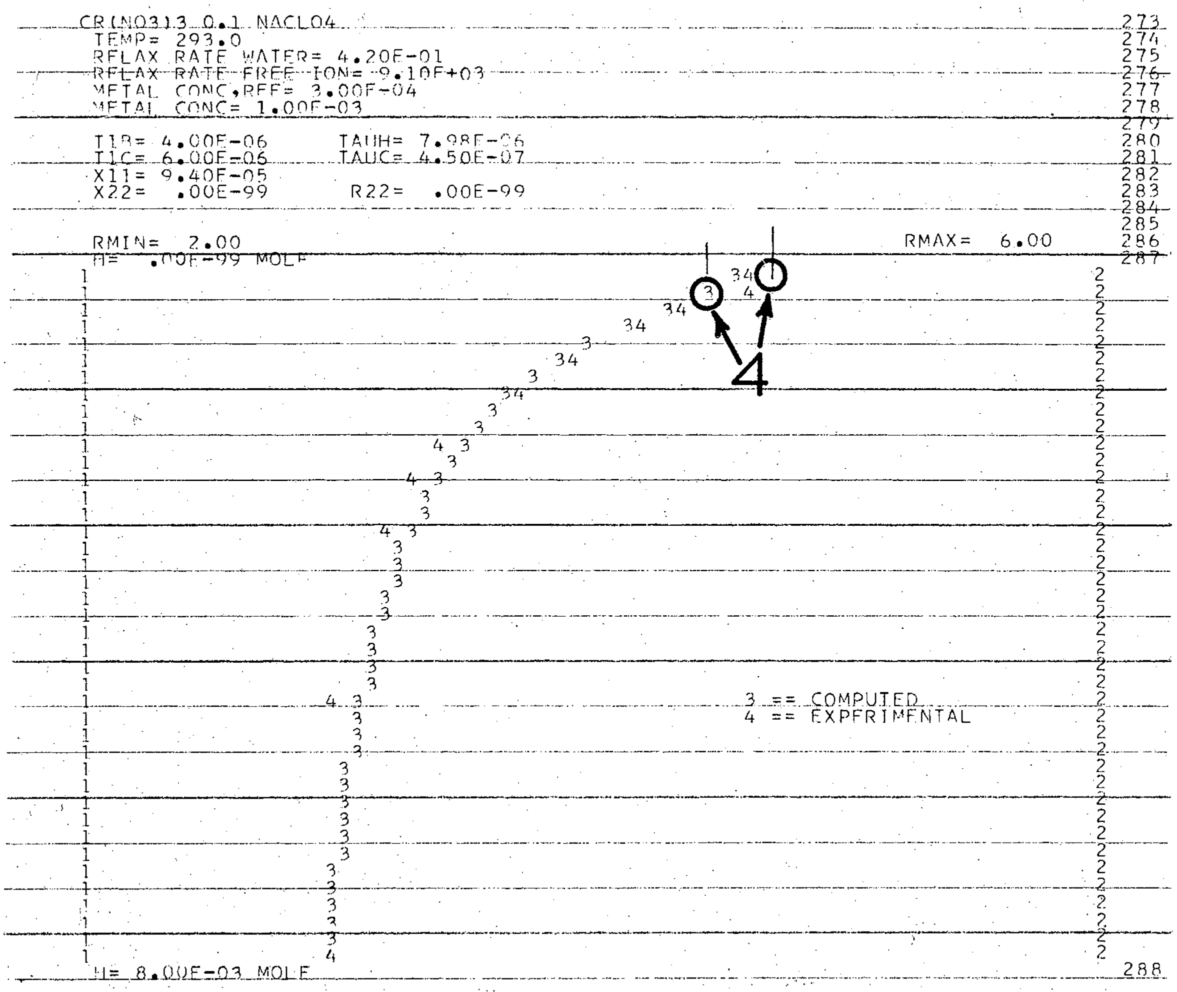


Figure 9b. Normalized Experimental Relaxation Rates (O←4) and Computed Relaxation Rates vs. H at 20°C. [Cr(III)] = 6.00 x 10^{-4} Molar



```
CR(NO3)3 0.1 NACLO4
 TEMP= 293.0
 RELAX RATE WATER= 4.20E-01
 RELAX RATE FREE ION= 9.10E+03
 METAL CONC,REF= 3.00E-04
 METAL CONC= 1.00E-03

 T1B= 4.00E-06        TAUH= 7.98E-06
 T1C= 6.00E-06        TAUC= 4.50E-07
 X11= 9.40E-05
 X22=   .00E-99        R22=   .00E-99

 RMIN=   2.00                                        RMAX=   6.00
 H=   .00E-99 MOLE

                                   3 == COMPUTED
                                   4 == EXPERIMENTAL

 H= 8.00E-03 MOLE
```

Figure 9c. Normalized Experimental Relaxation Rates (○←4) and Computed Relaxation Rates vs. H at 20°C. [Cr(III)] = 1.00 x 10^{-3} Molar

```
CR(NO3)3 0.1 NACLO4
 TEMP= 313.0
 RELAX RATE WATER= 2.90E-01
 RELAX RATE FREE ION= 1.22E+04
 METAL CONC.REF= 3.00E-04
 METAL CONC= 3.00E-04

 T1B= 5.20E-06        TAUB= 2.74E-06
 T1C= 8.00E-06        TAUC= 2.25E-07
 X11= 2.60E-04
 X22=  .00E-99         R22=  .00E-99

 RMIN=  2.00                                          RMAX=  6.00
 H=  .00E-99 MOLE
```

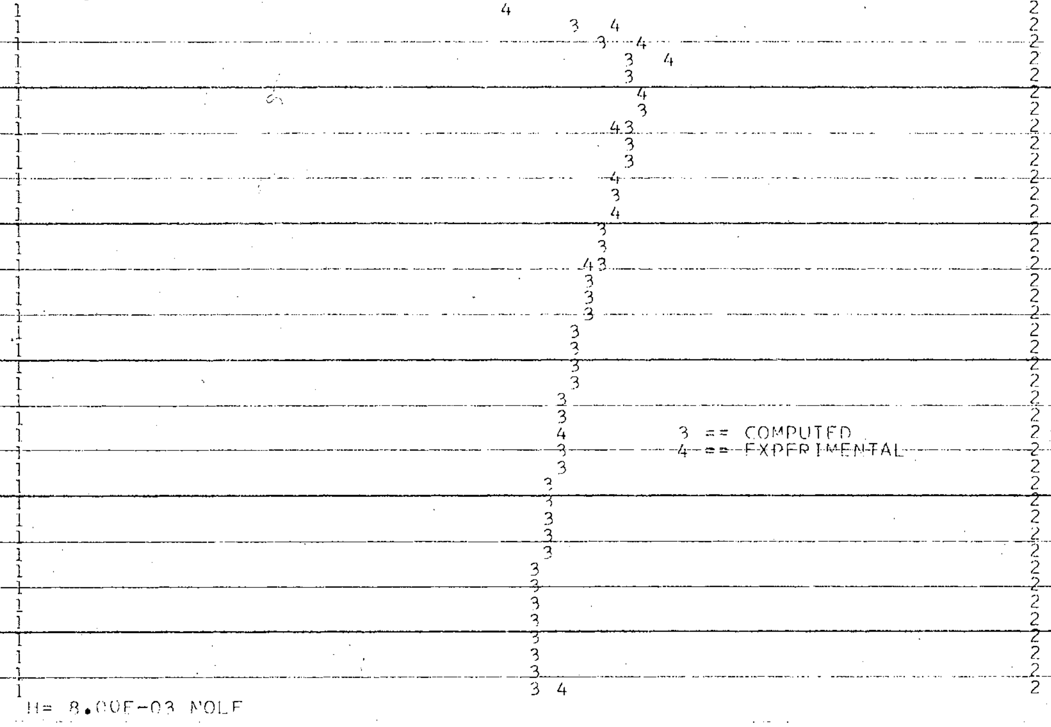


Figure 10a. Experimental and Computed Experimental Relaxation Rates vs. H at 40°C. [Cr(III)] = 3.00 x 10^{-4} Molar

```
 CR(NO3)3 0.1 NACLO4
  TEMP= 313.0
  RELAX RATE WATER= 2.90E-01
  RELAX RATE FREE ION= 1.22E+04
  METAL CONC,REF= 3.00E-04
  METAL CONC= 6.00E-04

  T1B= 5.20E-06       TAUH= 3.74E-06
  T1C= 8.00E-06       TAUC= 2.25E-07
  X11= 2.60E-04
  X22=  .00E-99        R22=  .00E-99

  RMIN=  2.00                                                    RMAX=  6.00
```

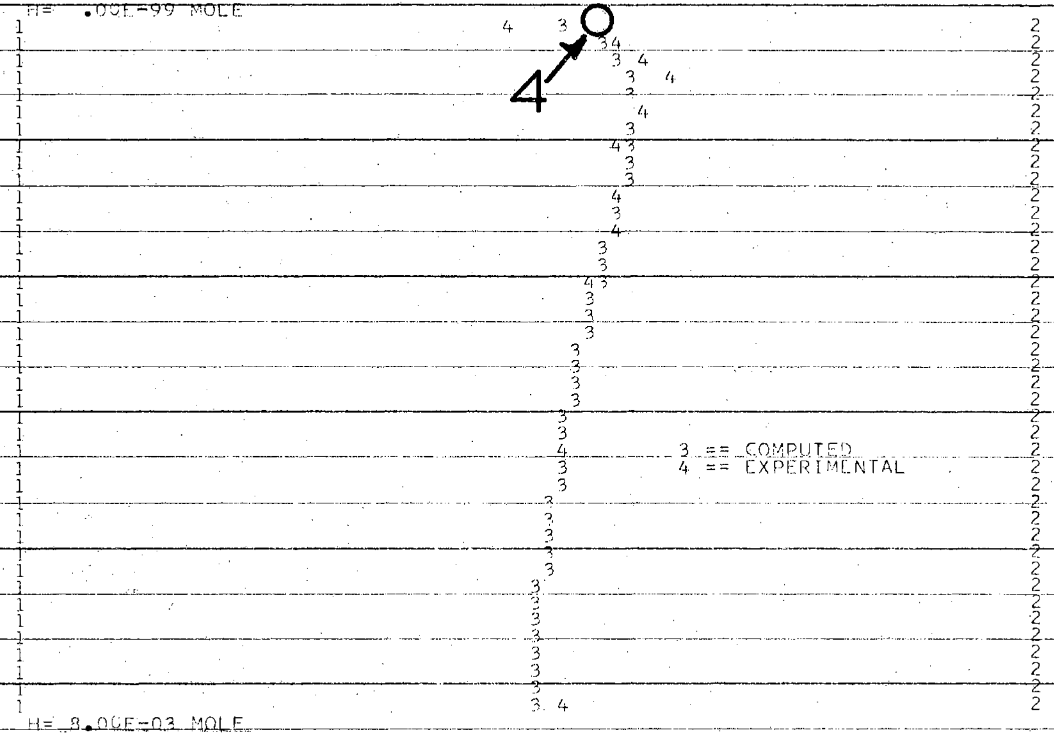
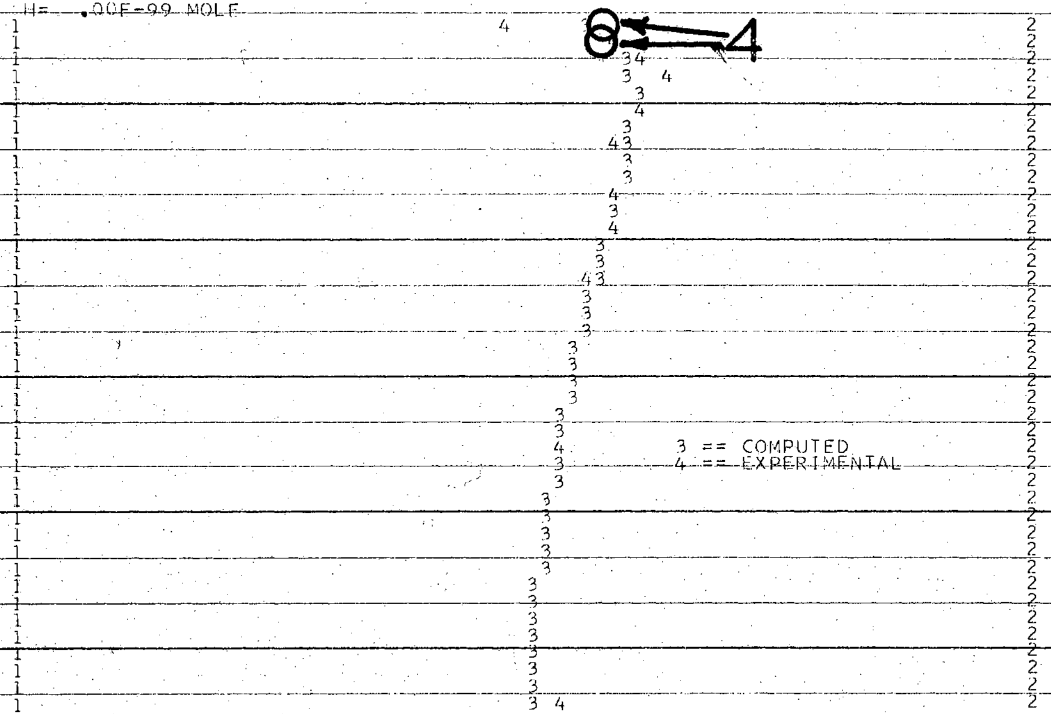


Figure 10b Normalized Experimental Relaxation Rate (○← 4) and Computed Relaxation Rates vs. H at 40°C. [Cr(III)] = 6.00 x 10^{-4} Molar

```
CR(NO3)3 0.1 NACLO4
TEMP= 313.0
RELAX RATE WATER= 2.90E-01
RELAX RATE FREE ION= 1.22E+04
METAL CONC,REF= 3.00E-04
METAL CONC= 1.00E-03

T1B= 5.20E-06      TAUH= 3.74E-06
T1C= 8.00E-06      TAUC= 2.25E-07
X11= 2.60E-04
X22=  .00E-99       R22=  .00E-99

RMIN=  2.00                                          RMAX=  6.00
H=  .00E-99 MOLE
```



```
H= 8.00E-03 MOLE
```

Figure 10c. Normalized Experimental Relaxation Rates (O— 4) and Computed Relaxation Rates vs. H at 40°C. [Cr(III)] = 1.00 x 10^{-3} Molar

TABLE IV

CONCENTRATION AND TEMPERATURE DEPENDENCE OF RELAXATION RATE FOR NONACIDIFIED SOLUTIONS. $[NaClO_4]$ = 0.1 MOLAR

Cr(III)	Rate (sec^{-1})		
	0°C	20°C	40°C
1.00×10^{-4}	4.02	----	---
3.00×10^{-4}	3.58	4.66	4.26
6.00×10^{-4}	3.18	4.68	4.33
1.0×10^{-3}	3.14	4.72	4.21
1.0×10^{-3} with 2.0×10^{-4} molar $HClO_4$	2.60	4.45	4.21

TABLE V

RELAXATION RATE FOR $[Cr(III)] = 3.0 \times 10^{-4}$ MOLAR AND $H^+ = 0.20$ MOLAR

θ(°C)	Rate (sec^{-1})
0°C	1.55
20°C	2.78
25°C	2.94
40°C	3.75

TABLE VI

TEMPERATURE DEPENDENCE OF τ_h, τ_C, T_{1B}, T_{1C} FOR Cr(III) IN 0.1 MOLAR $NaClO_4$ AQUEOUS SOLUTION

$\theta(^{o}C)$	$X_{11} \times 10^5$	$Cr(OH_2)_6$		$CrOH(OH_5)_5$		
		τ_h	T_{1B}	τ_C	T_{1C}	$\times 10^6$ (sec)
0	2.9	19	3.0	1.05	3.2	
20	9.4	8.0	4.0	.45	6.0	
40	26	3.74	5.20	.23	8.0	

assumed that 8 protons were exchanging in the 1st hydrolysis product. This number could be rationalized physically. The loss of a proton from an axial water molecule would cause the resulting OH^- to move in closer to the Cr(III) nucleus. Electrostatic repulsion would cause the four equatorial water molecules to move outward and the other axial water molecule would move inward. Four water molecules would be bound loosely and one water molecule and one OH^- would be bound tightly.

Ionic Strength-Activities

As illustrated in Table VII the relaxation rate of Cr(III) is a function of the ionic environment. The following observations are significant:

1. The relaxation rate for the concentrations observed does not depend on the type of anion present in solution.

2. Changes in relaxation rate produced by adding ions (excluding protons) are small.

Although there is some evidence for a change in water exchange rate in $Cr(OH_2)_6^{+++}$ with respect to a change in anion, Figure 11 does not

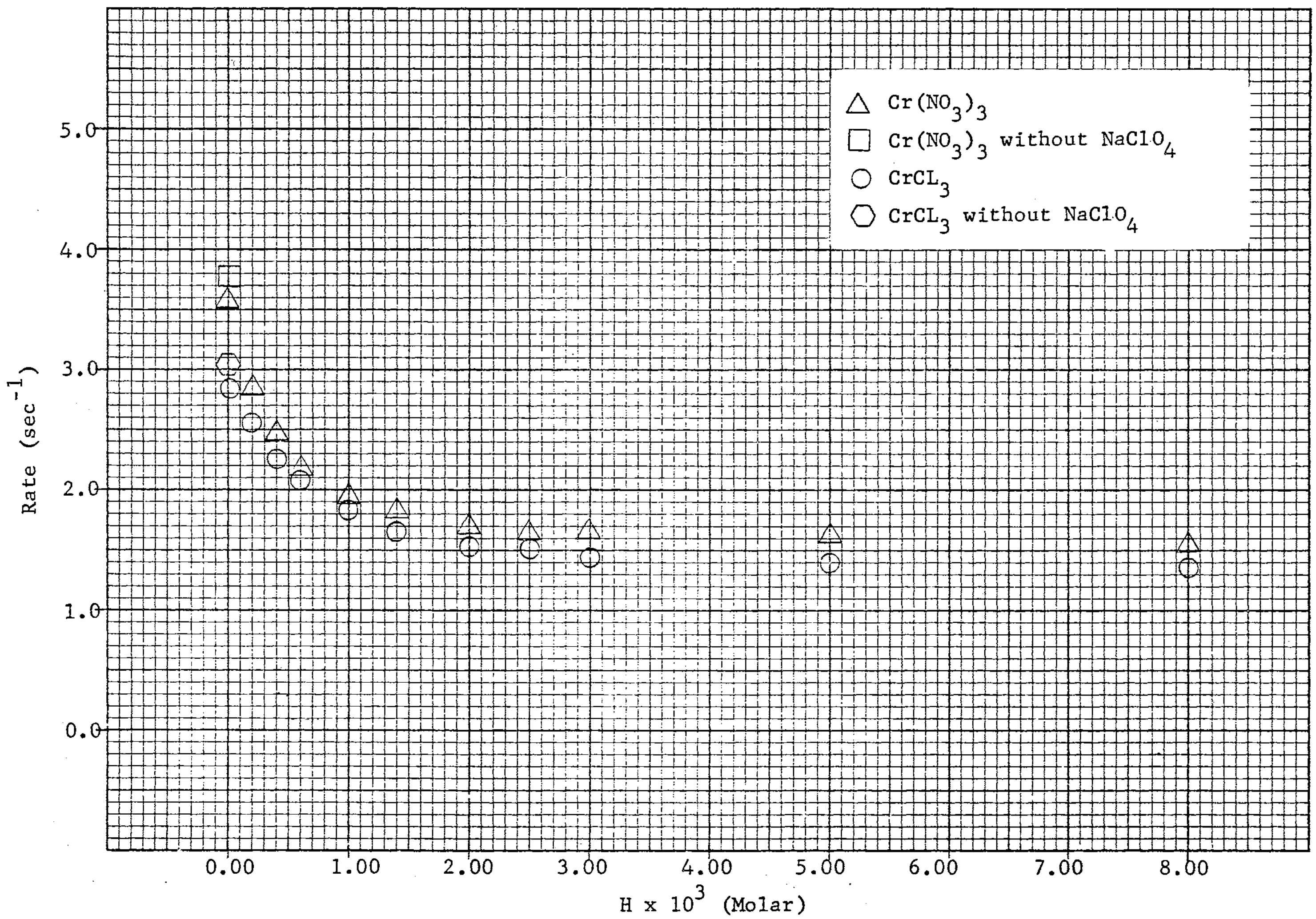


Figure 11. Comparison of Experimental Relaxation Rates vs. H of $CrCl_3$ and $CrNO_3$ at 0°C. $[CrCl_3]$ = 2.6 x 10^{-4} molar. $[Cr(NO_3)_3]$ = 3.00 x 10^{-4} molar.

show any significant difference in relaxation rate between $CrCl_3$ and $Cr(NO_3)_3$ at low acidities.[36]

TABLE VII

RELAXATION RATE OF 3×10^{-4} MOLAR Cr(III) IN VARIOUS IONIC ENVIRONMENTS AT 0°C

Ionic Environment		Rate (sec^{-1})
0		3.78
0.05M	$NaClO_4$	3.78
0.1M	$NaClO_4$	3.58
0.5M	$NaClO_4$	3.49
0.1M	NaCL	3.54
0.001M	HCL	2.22
0.001M	$HClO_4$	2.22
0.001M	HNO_3	2.22
0.1M	HCL	1.55
0.1M	$HClO_4$	1.55
0.1M	HNO_3	1.60
0.1M $HClO_4$ + 0.1M $NaClO_4$		1.55

Dimeric Forms

In an attempt to isolate the relaxation rate properties of possible dimers, two different methods were used to prepare solutions which would reputedly contain only dimeric forms. The first method due to

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[36] John P. Hunt, Metal Ions in Aqueous Solution, W. A. Benjamin Inc., New York, N.Y., 1963, p. 85.

Lottermosser[30] requires the addition of 1/3 equivalent OH^- ions (one OH^- ion per Cr(III) ion) and the use of heat over a period of time (about 120 hours). The second method due to Laswick and Plane[22] depends on the air oxidation of chromous ion, Cr(II). The results were interesting but inconclusive.

In the air oxidation of Cr(II), Cr(II) was prepared by reducing $Cr(OH_2)_6^{+++}$ electrolytically under a nitrogen atmosphere. Pure oxygen was bubbled through this pale blue solution of $Cr(OH_2)_6^{++}$ resulting in a dark green solution. The entire process was performed in acid solution, 0.1M $HClO_4$.

The dark green solution of $Cr_2(OH)_2(OH_2)_8^{++}$ prepared in this manner was extremely long lived.[8] In a experiment to determine the exact concentration[37] of Cr(III) present by giving the dimer time to break up into $Cr(OH_2)_6^{+++}$, a sample was still green after 30 days at room temperature. The sample did not turn blue until after 48 hours at 50°C. The results of the experiments on this sample are summarized in Table VIII.

The data tend to support a prediction by Earnshaw and Lewis[28] that binuclear chromium compounds would be paramagnetic. A scalar exchange interaction between two ions will result in a different susceptability and a different τ_e, electron correlation time. Since the rotational correlation times, τ_r, would be expected to be longer, τ_e could be the dominate correlation time and easily produce a smaller proton relaxation rate.

---

[37] Concentration was determined by measuring the proton spin relaxation rate at 0°C and using Table VII. Significant quantities of chromous oxide were formed at the cathode. This precluded relying on the master solution.

TABLE VIII

RELAXATION RATE vs. FIELD FOR $Cr_2(OH)_2(OH_2)_8$ AT 0°C

Form	Rate (sec^{-1})			
	8.2 gauss	165 gauss	380 gauss	586 gauss
$Cr_2(OH)_2(OH_2)_8{}^{4++}$	3.86	4.27	4.05	3.86
$Cr(OH_2)_6{}^{+++}$	---	---	5.14	---

$[Cr(III)] = 1.0 \times 10^{-3}$ molar

At room temperature the relaxation rate for $Cr_2(OH)_2(OH_2)_8$ was 4.54 sec^{-1}.

The limited data on field and temperature dependence do indicate a small τ_h and a small τ_C ($\tau_C{}^{-1} = \tau_r{}^{-1} + \tau_e{}^{-1}$) for this dimer.

In preparing the dimer according to Lottermoeser an error was made in computing the OH^- needed. Too little was added. A reduction in relaxation rate was noted.

Amphoteric and Hydroxide

At PH7 Cr(III) and Cr_2(III) are precipitated and the addition of excess base causes both to go back into solution. It is interesting to note that if this amphoteric is freshly made, its relaxation rate, for both the monomer and dimer, is almost exactly 2/3 that of the original acidified solution. At 0°C the solutions presist for longer than two weeks and at room temperature reprecipitate in less than 48 hours. An amphoteric solution prepared by rapid addition of base and the reacidified has the same relaxation rate of the original acidified solution. The relaxation rate of an acidified precipitate is smaller than that of the original, even at 0°C and a precipitate lifetime of 5 min.

These experiments were too sketchy to provide much information about the physical properties of amphoterics and hydroxides of Cr(III). They do provide a picture of some chemical changes and the rates at which they occur. It appears that substances characterized by the formulas $Cr(OH)_3$ and $Cr(OH)_4^-$ do exist. Modern texts hedge on this question and express the hydroxide products of Cr(III) as $Cr_2O_3 \cdot XH_2O$.[27]

7. CONCLUSION

Conclusions

Any explanation of a phenomena based upon an assumed rate and mechanism will contain some ambiguities. Only the slow steps can be identified. Short lived intermediates will not be detectable. There are always several possible alternative mechansims. However in keeping with the principle of using the simplest possible mechanism which explains the data, the model proposed in Section 4 is an accurate representation. It certainly seems safe to assume that the PH dependence of the relaxation rate is a result of hydrolysis and that the maximum in the relaxation rate is caused by the appearance of the 1st hydrolysis product. Support for the specific model assumed is not as straightforward. It is worth noting however, that the shape of the curves at $0^{o}C$, $20^{o}C$, and $40^{o}C$ provides a critical test of the assumed mechanism.

The input and output data could easily be refined by doing the experiment in a higher magnetic field. The nature of the relaxation rate vs. magnetic field curve for Cr(III) makes calculations for correlation times and T_{1B} using Equation 1 difficult when field strengths below 500 gauss are used.[2,4] Using the method of Emerson and Graven[20] to prepare $CrOH(OH_2)_5^{++}$ it would even be possible to determine the correlation times and T_{1C} of this ion. This would permit an independent determination of X_{11} and a better determination of τ_C.

Further Investigations

There is a lack of extensive data on metal hydrolysis and the fundamental nature of this process makes it worthy of research effort. There are about 54 transition metals. Many of these could be expected to have hydrolysis products whose magnetic properties are sufficiently different from the parent ion to permit detection. NMR data could be expected to provide information on the mechanism involved in hydrolysis and the magnetic properties of the hydrolysis product.

In a more specific vein, there were several experiments on chromium which were suggested by this investigation. Since this study resulted from an attempt to exhibit enhanced relaxation[38] with some simple inorganic molecules, the information developed here could be used to this end. In a solution of Cr(III) and an organic molecule such as pyridine, hydrogen ions and $Cr(OH_2)_6^{+++}$ compete for the donor pair on nitrogen atom. In acidified solutions the hydrogen ion wins. In the nonacidified solution the base characteristics of the molecules may cause precipitation or the effects of enhanced relaxation may be masked by the effects of $CrOH(OH_2)_5^{++}$. The stability of Cr(III) complexes makes it possible to prepare the complex under conditions favorable to their formation and make NMR measurements at other concentrations. It should be possible to obtain data on complex molecule formation constants and the magnetic properties of complex molecules.

Another investigation of interest would be to study the reaction

$$Cr^{*}(II) + Cr(III) \overset{OH^{-}}{\rightleftharpoons} Cr^{*}(III) + Cr(II)$$

In this reaction an electron is transferred from Cr(III) to Cr(II) via

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[38] J. Eisinger, R. Shulman, and B. Szymanski, J. Chem. Phys., 36, 1721 (1962).

a hydroxide bridge.[39] Since the magnetic properties of Cr(II) and Cr(III) are different this reaction would be easy to detect using proton spin relaxation if a relatively pure sample of Cr(II) is investigated first. The OH^- group is involved in many electronic changes and an interaction with OH^- ion usually precedes isomeric changes[40] in

$$CrCl_2^+ \xrightarrow{OH^-} CrCl^{++}$$

The last investigation to be proposed is a continuation of an experiment started here, an examination of the dimer of Cr(III). In addition to $0^=$ and OH^- bridging groups other anions are also known to produce bridges in Cr(III).[41,42] Little is known of the magnetic properties of bridged complexes.

---

[39] A. Anderson and N. Bonner, J. Amer. Chem. Soc., 76, 3826 (1954).

[40] Bailar, p. 262.

[41] Klixbüll Jorgensen, Inorganic Complexes, Academic Press, New York, N.Y., 1963, p.23.

[42] Hunt, p. 69.

APPENDIX. COMPUTER PROGRAM

```
      DIMENSION H1(20),H2(50),R1(20),R2(50)
      READ 1
    1 FORMAT (20H                    )
   10 READ 11,TEMP,RW,RF,TI
   11 FORMAT (F10.2,F10.2,F10.2,E10.2)
      RF=(RF-RW)/TI
      READ 6,ND
    6 FORMAT (I3)
      DO 8 I=1,ND,1
      READ 9,H1(I),R1(I)
    9 FORMAT (E10.2,F10.2)
    8 R1(I)=R1(I)-RW
    2 READ 13,HM,DEL,NC
   13 FORMAT (E10.2,E10.2,I3)
   14 READ 15,T
   15 FORMAT (E10.2)
      Q=TI/T
   16 READ 19,X11,T1B
   17 READ 19,X22,R22
      READ 19,T1C,TAC
   19 FORMAT (E10.2,E10.2)
      TAH=(12.0/(110.0*RF))-T1B
      H=HM
      X=T/H
      DO 33 I=1,NC,1
   21 F=2.0*X22*X*X*X+(X11+2.0*X22)*X*X+(H+X11)*X-T
      D=6.0*X22*X*X+2.0*(X11+2.0*X22)*X+H+X11
      X=X-(F/D)
      E=ABS (F/D)
      IF (0.0001-(E/X)) 21,21,26
   26 J=NC+1-I
      C22=X22*X*X
      C11=X11*X
      CF=T-C11-2.0*C22
      IF (SENSE SWITCH 1) 25,24
   25 C11=11.0*C11/10.0
   24 DEN=TAH*(TAH+12.0*T1B)*(TAC+T1C)+12.0*T1C*TAC*(TAH+T1B)*CF/C11
      BNU=TAH*(T1C+TAC)+TAC*(11.0*T1B+12.0*T1C*CF/C11)
      CNU=TAH*(12.0*T1B+12.0*T1C*CF/C11)
      R2(J)=(CF*12.0*(BNU/DEN)+C11*10.0*(CNU/DEN))/110.0
      R2(J)=R2(J)*Q
      H2(J)=H
   33 H=H-DEL
      PUNCH 1
      PUNCH 36,TEMP
   36 FORMAT (6H TEMP=,F6.1)
      PUNCH 38,RW
   38 FORMAT (18H RELAX RATE WATER=,E9.2)
      PUNCH 40,RF
   40 FORMAT (21H RELAX RATE FREE ION=,E9.2)
      PUNCH 1042,TI
 1042 FORMAT (16H METAL CONC,REF=,E9.2)
      PUNCH 42,T
   42 FORMAT (12H METAL CONC=,E9.2/)
      PUNCH 30,T1B,TAH
      PUNCH 31,T1C,TAC
   30 FORMAT (5H T1B=,E9.2,5X,5HTAUH=,E9.2)
   31 FORMAT (5H T1C=,E9.2,5X,5HTAUC=,E9.2)
      PUNCH 44,X11
   44 FORMAT (5H X11=,E9.2)
      PUNCH 46,X22,R22
   46 FORMAT (5H X22=,E9.2,5X,5H R22=,E9.2//)
```

```
      READ 6,N
      READ 15,HE
      RMAX=0.0
      RMIN=R1(1)
      DO 76 I=1,ND,1
      X=R1(I)
      IF (X-RMAX) 74,74,73
   73 RMAX=X
   74 IF (X-RMIN) 75,76,76
   75 RMIN=X
   76 CONTINUE
      DO 80 I=1,NC,1
      X=R2(I)
      IF (X-RMAX) 78,78,77
   77 RMAX=X
   78 IF (X-RMIN) 79,80,80
   79 RMIN=X
   80 CONTINUE
      PUNCH 86,RMIN,RMAX
   86 FORMAT (6H RMIN=,F6.2,48X,6H RMAX=,F6.2)
      H=H2(1)
      PUNCH 88,H
   88 FORMAT (3H H=,E9.2)
      D=N-1
      DELTA=(HE-H)/D
      K=1
      L=1
      DO 116 I=1,N,1
      M=H/DELTA
      P1=PLT (1.0)
      P2=PLT (76.0)
   96 IF (NC-L) 105,97,97
   97 J=H2(L)/DELTA
      IF (M-J) 105,99,103
   99 X=75.0*(R2(L)-RMIN)/(RMAX-RMIN)+1.0
      P3=PLT (X)
      L=L+1
      IT=1
      GO TO 106
  103 L=L+1
      GO TO 96
  105 IT=2
  106 IF (ND-K) 115,107,107
  107 J=H1(K)/DELTA
      IF (M-J) 115,100,113
  100 X=75.0*(R1(K)-RMIN)/(RMAX-RMIN)+1.0
      GO TO (110,108),IT
  108 P3=PLT (X)
  110 P4=PLT (X)
      K=K+1
      GO TO 115
  113 K=K+1
      GO TO 106
  115 P=PLT(0.0)
  116 H=H+DELTA
      H=H-DELTA
      PUNCH 88, H
      READ 6,INSTR
      GO TO (16,17,14,10,2),INSTR
      END
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VITA

Claude Edward Manley

Candidate for the Degree of

Master of Science

Thesis: PROTON SPIN RELAXATION INTHE $Cr(OH_2)_6^{+++}$ - $CrOH(OH_2)_5$ - H_2O SYSTEM

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