The present experiments show that each catalytically active site, to which the Michaelis–Menten mechanism applies, is inhibited by combining with one silver ion. These sites must have identical affinity for silver and be mutually independent, to within the imperfect accuracy of the present measurements. The number of such sites cannot be larger than the number of silver ions required for total inhibition, *i.e.*, not larger than three or four; it may be smaller because some of the silver ions may react with some functional groups which are not a part of the catalytically active sites, but have identical affinity for silver. In fact the work of Sumner and Myrback has definitely shown that urease after total inhibition can react with considerable additional quantities of silver. However the affinity of this secondary reaction is relatively low; it should not have manifested itself in the present experiments. In all probability one deals here with electrostatic binding of silver ions to the protein, whereas the specific inhibition reaction is accompanied by such a large chemical potential change ($\Delta\mu^\circ \cong -15{,}000$ cal.) that a formation of covalent linkages is indicated. Cysteine has been observed[14] to form complexes with silver ions in acid *p*H which have an even higher stability. Also in basic solutions a rather stable cysteine–silver complex of the formula RSAg has been observed[15] and silver has been shown to combine with other proteins through the sulfhydryl groups.[16] Although all this evidence points to the inhibition of urease by silver through the reaction with sulfhydryl groups, it does not prove the occurrence of this reaction and the question of the exact nature of the chemical binding of silver must remain unanswered for the time being.

The observation that inactive protein present in recrystallized urease preparations has the same affinity and the same specific binding capacity for silver is of considerable interest. It explains, at least partly, the enhanced stability of impure enzyme preparations to heavy metal poisoning. It also suggests that within a catalytically active site there is present a functional group with a high affinity for silver ions; its reaction with silver causes the loss of catalytic activity by the site, but the inactivation of the site, in the course of crystallization operations, does not block the group from reacting with silver. Such behavior is readily understood if the catalytic activity of a site is due to a particular spatial configuration of several functional groups that may comprise it and the deactivation is due to the loss of this configuration rather than to direct chemical changes in the functional groups. Until the competitive or non-competitive character of the inhibition by silver has been established it is impossible to decide whether the group reacting with silver is involved in the primary reaction of the enzyme with the substrate or whether this group is essential to the second step of the Michaelis–Menten mechanism, the hydrolysis of urea.

CAMBRIDGE, MASS. RECEIVED SEPTEMBER 18, 1950

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[14] S. Valladas-Dubois, *Compt. rend.*, **231**, 53 (1950).

[15] I. M. Kolthoff and W. Stricks, THIS JOURNAL, **72**, 1952 (1950).

[16] R. Benesch and R. E. Benesch, *Arch. Biochem.*, **19**, 35 (1948).

[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS]

Specific Heat of Beryllium between 0° and 900°[1]

BY D. C. GINNINGS, T. B. DOUGLAS AND ANNE F. BALL

Using an ice calorimeter and furnace of improved design, the specific heat of two samples of beryllium was determined by measuring the changes of enthalpy between 0° and 900°. Both samples were more than 99% pure, and additive corrections were applied for the impurities present. Although one sample contained 0.4% magnesium and the other almost none, the specific heat values found for the two samples differed by less than 1% at every temperature investigated, a result in sharp contrast to the large variations found by other workers for various samples of beryllium of purities comparable to those of this investigation. Sources of error in the values obtained are examined. The values of C_v calculated from the data are found to fit the Debye function up to 500°, but near this temperature an abrupt change in slope occurs.

Introduction

The specific heat of beryllium has been determined by a number of observers, with reported values differing by as much as 30%. One observer claimed that the specific heat of beryllium depended on its heat treatment. Another claimed differences of 30% in heat capacity, due to only 1% impurity. The present investigation was undertaken in an effort to clear up some of these discrepancies and, if possible, to obtain accurate values for the specific heat of beryllium.

Samples.—Two samples of beryllium were used. Most of the experiments were made with Sample I, which was of the purest beryllium metal available (1947) from the Chemistry Division of the National Bureau of Standards. This sample, designated by them as BL, was in the form of pieces about 0.1 cubic millimeter in size. The analysis reported from this stock sample showed 99.5% total beryllium, 0.3% oxygen, 0.1% water and 0.3% total of numerous other metallic elements. The sample was used without further treatment except that some of its moisture may have been removed in the process of pumping preliminary to enclosing it. Further check experiments were made with a second sample of beryllium (Sample II, "Brush QT powder," in pieces about 100 cubic millimeters in size) having a somewhat similar analysis except that it contained more magnesium (0.4%), the other metals totaling 0.1%. There was essentially no magnesium in Sample I.

Method and Apparatus.—The method of meas-

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[1] Presented before the American Chemical Society, Division of Physical and Inorganic Chemistry, April 20, 1950, in Detroit, Michigan.

urement and apparatus have been described previously.[2,3,4] In brief, the method consisted in heating the sample in a furnace to a known temperature and dropping it into an ice calorimeter to measure the heat evolved in cooling the sample to 0°. The sample was sealed in a Nichrome-V capsule having a screw cap with gold gasket. The heat capacity of the empty capsule and the heat lost by the container during the drop were accounted for by "blank" experiments made with the empty capsule at the same temperatures as with the filled capsule.

The calorimeter and furnace, shown in Fig. 1, differ in several features from those described in earlier reports.[2,3] A system of tinned copper vanes (F) is used inside the calorimeter to decrease the time for the heat to melt the ice. The mercury-water interface is now located in the bottom part of the calorimeter vessel. Also, during the experiments, dry helium instead of carbon dioxide (as indicated in Fig. 1), is passed up the central calorimeter well (A), to produce more rapid attainment of thermal equilibrium between the sample and the calorimeter. The calibration factor of the ice calorimeter was determined to be 270.47 ± 0.03 absolute joules per gram of mercury, which differs from the mean value determined on the earlier calorimeter (270.41 ± 0.06) within the uncertainty assigned to the latter figure.

The furnace has been improved to reduce temperature gradients in its center and to facilitate more accurate temperature measurement. Its length has been increased to reduce end effects, and temperature gradients in the central portion have been made negligible by the use of three silver cylinders (J,K,L) having 0.5 inch wall thickness. The temperatures of the two end silver cylinders J and L were kept close to that of the middle cylinder K. Thermocouples were inserted in Inconel tubes (N) in the silver for the purpose of temperature measurements. Thin platinum shields (S), suspended on the wire above the capsule (D), served to eliminate errors due to heat loss from the calorimeter after the drop into the calorimeter, as has been shown previously.[3] To compare calorimeters, the enthalpy of pure aluminum oxide (corundum) was measured at 700° and the results were found to agree with those of Ginnings and Corruccini[3] within their estimated accuracy of 0.2%.

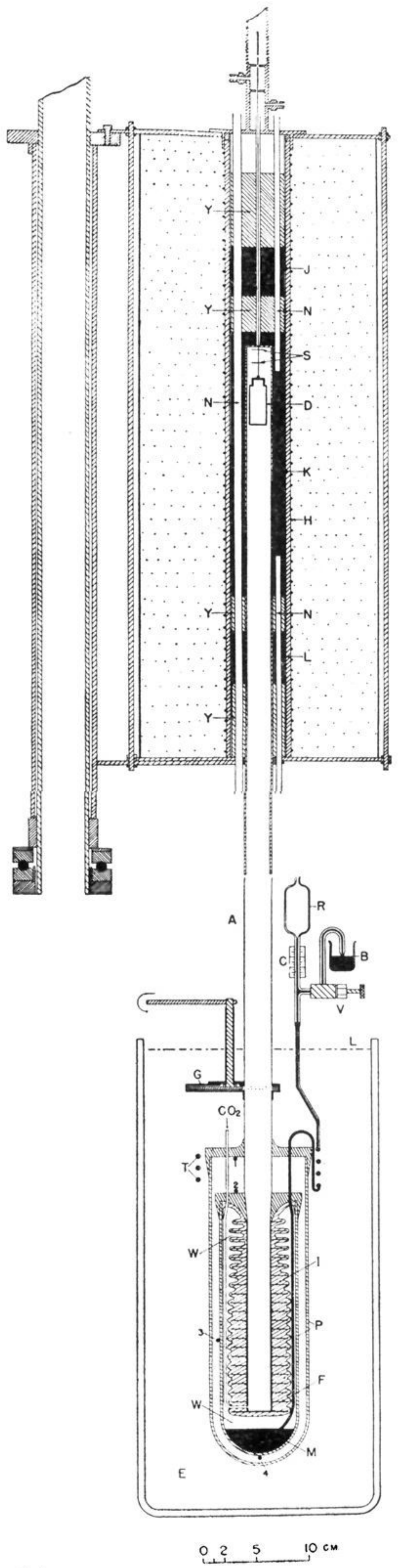

Fig. 1.—**Schematic diagram of furnace and ice calorimeter: A, calorimeter well; B, beaker of mercury; C, glass capillary; D, sample container; E, ice-bath; F, copper vanes; G, gate; H, platinum heater; I, ice mantle; J, K, L, silver cylinders; M, mercury; N, Inconel tubes; P, Pyrex containers; R, mercury reservoir; S, platinum shields; T, mercury "tempering" coil; V, needle valve; W, water; Y, porcelain spacers; 1, 2, 3, 4, thermocouple junctions.**

Results

A total of 90 experiments were made on Sample I, 39 with the empty capsule and 51 with the capsule containing 3.6 g. of the sample. The heat capacity of the sample was about twice as large as that of the capsule. The average deviation from the mean value of enthalpy at any one temperature was about 0.06% in the experiments with the empty capsule and about 0.04% with the experiments with the sample. Of the corrections applied to the experimental results, those for the impurities in the sample were by far the largest, amounting to about 0.5%. These corrections

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(2) D. C. Ginnings and R. J. Corruccini, *J. Research Natl. Bur. Standards*, **38**, 583 (1947).

(3) D. C. Ginnings and R. J. Corruccini, *ibid.*, **38**, 593 (1947).

(4) D. C. Ginnings, T. B. Douglas and A. F. Ball, *ibid.*, **45**, 23 (1950).

were made assuming that the effects of the impurities were simply additive.

In addition, 32 more experiments were made on Sample II, 17 with the empty capsule and 15 with the capsule containing 3.1 g. of sample. These experiments were intended to check the experiments on Sample I and were made at only five of the nine temperatures used on that sample.

Because one group of previous workers had claimed[5] that certain samples of beryllium metal showed small increases in specific heat following recent previous heating to high temperatures (400 to 600°), the measurements on Sample I were repeated at 100°, 300° (twice), 500°, 600° and 700°, and at various times after the original measurements from 100 to 700°. Contrary to these claims, the repeated values of enthapy were all found to be lower than the original values, by a small but fairly constant amount of about one calorie. This change might plausibly be explained quantitatively by assuming that the small amount of water originally present in the sample had reacted chemically at the high temperatures and hence was not present during the later measurements to contribute its heat of vaporization. On the other hand, the discrepancy found could be explained as logically by attributing it to the small changes that were observed in the calibration (before and after the measurements) of the thermocouple used to measure the furnace temperatures. However, the specific heats calculated by either assumption do not differ by more than 0.2% from the values given in Table II for the same temperatures.

The corrected mean values (not smoothed) of $(H_t - H_0)$, the enthalpy at temperature t referred to 0°, obtained for the pure beryllium present in the samples, are shown in Table I.

TABLE I

ENTHALPY OF BERYLLIUM

Temp. [t], °C.	Enthalpy [$H_t - H_0$] cal.[a]/gram Sample I	Sample II	Difference [Sample I − Sample II], cal./gram
94.0	42.67	42.65	+0.02
195.8	97.68	....	
298.3	158.32	157.86	0.46
394.6	218.94	....	
497.8	286.38	285.36	1.02
597.6	354.04	....	
699.7	426.06	424.03	2.03
796.9	496.98	....	
896.4	572.22	569.95	2.27

[a] 1 cal. = 4.1840 absolute joules.

The values of specific heat listed in Table II were derived from the values of enthalpy by the equation

$$C_p = \frac{H_t - H_0}{t} + t\,\frac{d(H_t - H_0)/t}{dt}$$

The slopes indicated by the derivative in the last term of the equation were determined graphically.

TABLE II

SPECIFIC HEAT OF BERYLLIUM

Temp. [t], °C.	Specific heat [C_p] cal./g.-deg. Sample I	Sample II
100	0.5096	0.5090
200	.5714	.5687
300	.6133	.6092
400	.6434	.6388
500	.6678	.6622
600	.6936	.6880
700	.7188	.7145
800	.7433	.7429
900	.7721	.7724

Estimated Uncertainty of Results and Comparison with Results of Other Workers.—A number of previous workers[6–12] have determined the specific heat of beryllium in the range above 0°, and some of these results, as well as those (on Sample I only) of the present investigation, are shown in the accompanying graph, Fig. 2. Some of these workers claimed an accuracy of a few tenths of 1%, which is far smaller than the 30% spread of specific-heat values shown in this graph.

Jaeger and Rosenbohm[5] claimed a small increase in the specific heat of the same sample of beryllium and several other hard metals after recent heating to higher temperatures. However, the change they claim is barely outside their precision. In the present investigation no such increase was detected with Sample I.

Far more striking is the variation from one sample to another. In fact, it will be noted that the curve of Magnus and Holtzmann[6] lies very close to one of Jaeger and Rosenbohm,[5] who claimed that these two curves were obtained using beryllium of the same source. In particular, Losana[7] obtained values of specific heat some 30% higher for a sample claimed to be 99.96% pure than for a sample only 99% pure.

The curve of the values for specific heat obtained in the present investigation shows a slight indication of a point of inflection in the neighborhood of 500°, a temperature at which several other workers[5–8] found similar rather abrupt changes in the specific heat, temperature coefficient of electrical resistivity, and coefficient of thermal expansion. There is thus some evidence that some sort of transition may occur in beryllium or its impurities in this temperature region.

A comparison of the specific heats of Samples I and II shows a maximum difference of less than 1%. The presence of 0.4% of magnesium thus apparently does not affect the specific heat of beryllium very much.

If the procedure of applying additive corrections for the impurities is valid, the present values of enthalpy as given in Table I are estimated to be probably within 0.5% of the true enthalpies of the pure beryllium in the sample used. However, there still remains the possibility that other im-

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(5) F. M. Jaeger and E. Rosenbohm, *Rec. trav. chim.*, **53**, 451 (1934).

(6) A. Magnus and H. Holtzmann, *Ann. Physik*, **3**, 585 (1929).

(7) L. Losana, *Alluminio*, **8**, 67 (1939).

(8) E. J. Lewis, *Phys. Rev.*, **34**, 1577 (1929).

(9) F. Simon and M. Ruhemann, *Z. physik. Chem.*, **129**, 321 (1927).

(10) T. S. Humpidge, *Proc. Roy. Soc.* (*London*), **35**, 137, 358 (1883).

(11) Nilson and Pettersson, *Ber.*, **13**, 1451 (1881).

(12) P. Vernotte and A. Jeufroy, *Compt. rend.* (*Paris*), **192**, 612 (1931).

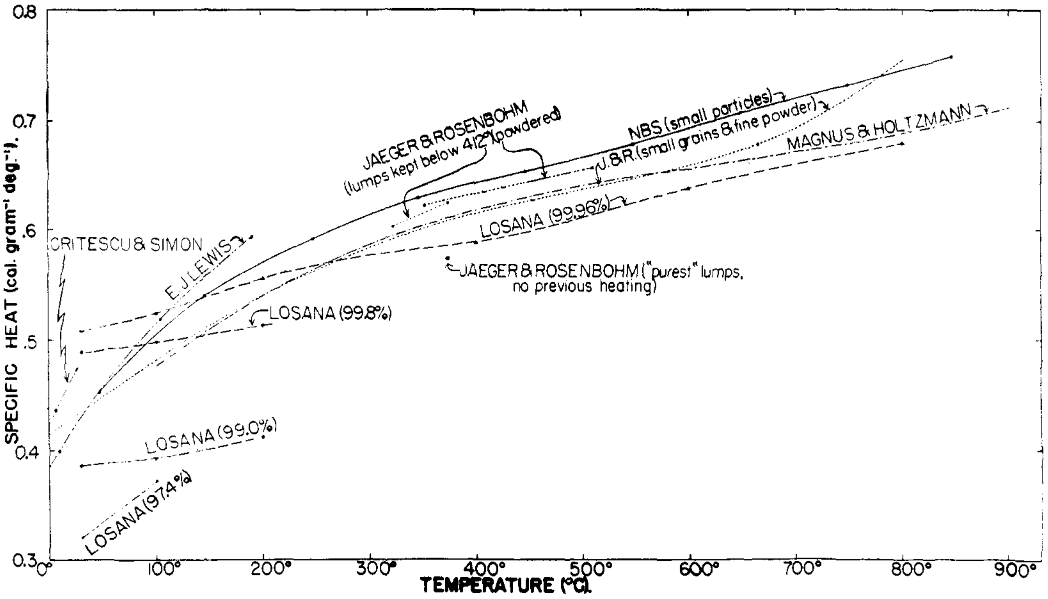

Fig. 2.—Specific heat of beryllium ("NBS" indicates values obtained by the National Bureau of Standards, 1948).

purities may cause larger deviations from simple additivity than that found for magnesium. The values for specific heat derived from these enthalpies may be considered to have an additional uncertainty of a few tenths of 1%. In addition, some small uncertainty may arise, as already discussed, due to some small dependence of the specific heat on the mechanical state of the sample.

Calculation of C_v and the Debye Temperature.—The measurement of the specific heat of beryllium has added interest since beryllium has one of the highest Debye temperatures of all the elements. The values of C_v shown in Fig. 3 were calculated from the experimental values of C_p reported in this paper by use of the Nernst–Grüneisen approximation

$$C_p - C_v = aC_p^2T$$

where T is in °K. The value of the constant a was obtained by substituting the value of C_v calculated at 47° from the equation

$$C_p - C_v = \alpha^2VT/\beta$$

where α is the coefficient of thermal expansion, β the compressibility, and V the gram-atomic volume. The value of α at 47° was taken as 3.7×10^{-5} per °K.,[13] whereas the corresponding value of β was taken as 8.55×10^{-7} per kg./cm.^{2}.[14] The volume V was taken to be 4.97 cm.^{3}/g.-atom. Using these constants gives 1.11×10^{-5} g.-atom/cal. for the value of the constant a in the above equation.

The experimental values of C_v so calculated should be decreased by the electronic heat capacity before being compared with the values of C_v calculated from Debye's equation. Values of the electronic contribution, assumed proportional to the absolute temperature, were calculated so as to give the best agreement up to 800 °K. between (C_v − $C_{\text{electronic}}$) and the theoretical values (C_v·(Debye)), which are shown for comparison in Fig. 3. Though the free-electron model is of rather doubtful validity in the case of beryllium,[15] it is of interest to equate the temperature coefficient of this empirically derived electronic contribution to the theoretical coefficient given by the Fermi–Dirac statistics

$$C_{\text{electronic}}T = R\pi^2k/2\epsilon_0$$

This gives for the Fermi energy ϵ_0 a value of 4.5 electron-volts, which is about one-third of the value calculated on the assumption of two absolutely free valence electrons per atom of beryllium, and so corresponds to an effective electron mass which is about three times the mass of a free electron. This is roughly in line with the corresponding results claimed for many other metals.

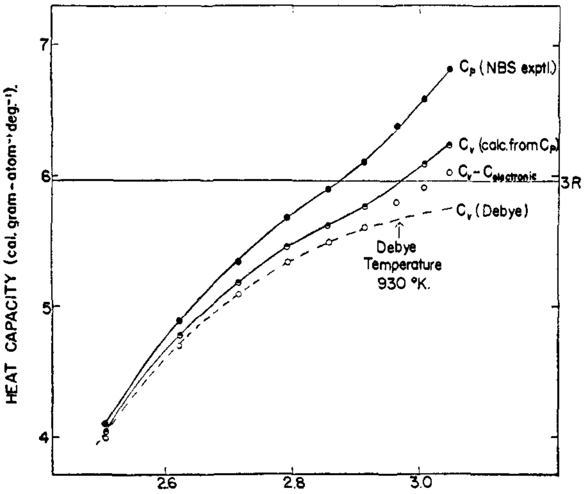

Fig. 3.—Comparison of specific heat values with those calculated from the Debye function.

It may be noted from Fig. 3 that above 800° K. the values of (C_v − $C_{\text{electronic}}$) rise markedly above the Debye curve. This change in the

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(13) P. Hidnert and W. T. Sweeney, *Phys. Rev.*, [2] **29**, 616 (1927).

(14) P. W. Bridgman, *Proc. Am. Acad. Sci.*, **62**, 207 (1927).

(15) F. Seitz, "The Modern Theory of Solids," McGraw-Hill Book Co., Inc., New York, 1940, p. 371.

trend of the values based on experiment does not depend appreciably on the value selected for the temperature coefficient of the electronic contribution, but it does depend on the validity of extrapolating the Nernst–Grüneisen approximation for ($C_p - C_v$) to these higher temperatures. As stated previously, there is evidence both from thermal expansion data and electrical resistivity data that some sort of transition occurs in beryllium or its impurities in this temperature region. Whereas in Fig. 3 the values of C_p give some indication that there is such a change in this region, it is much more obvious from the deviations of the values of ($C_v - C_{\text{electronic}}$) from the Debye curve that the change in the material is real.

It is of interest as to what electronic contribution, if any, is shown by the specific heat of beryllium at very low temperatures. Such measurements of its specific heat have been made in the range from 10 to 300 °K. primarily for the express purpose of answering this question.[16] Disregarding a pronounced irregularity found in the variation with temperature up to approximately 15 °K., these workers deduced some systematic deviation of C_v from the T^3 law. However, they preferred to agree with other authors that this law is very likely to be inaccurate in the case of crystals of the type assumed by beryllium, and hence is incapable of being used for even an estimation of the electronic contribution. In fact, their specific-heat values cannot be assumed to follow the T^3 law and to contain as well more than a small fraction of the electronic contribution predicted from that indicated in Fig. 3. The available low-temperature evidence thus seems inconclusive.

The agreement is good between the values for ($C_v - C_{\text{electronic}}$) and the Debye curve between 300 and 800 °K., as shown in Fig. 3, and leads to a value of θ_D, the Debye temperature, of 930°. This value from the high-temperature measurements reported in this paper may be compared with the value of 1050° given by the low-temperature specific heat values between 20 and 60 °K. referred to above.[16]

WASHINGTON, D. C.

RECEIVED OCTOBER 2, 1950

(16) S. Critescu and F. Simon, *Z. physik. Chem.*, **B25**, 273 (1934).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF UTAH]

Polarographic Study of Chromium(III) Chloride Solutions[1]

BY RANDALL E. HAMM AND CHARLES M. SHULL, JR.

Fresh solutions of chromium(III) chloride were found to be reduced at a half-wave potential of −0.61 v. *vs.* S.C.E., whereas aged solutions of this salt were reduced at a much more negative half-wave potential. This ambiguous new wave was found to decrease in height and disappear as the solution aged. It was assumed that the wave at −0.61 v. was due to reduction of $[CrCl_2(H_2O)_4]^+$, while that from the fully aged solution was due to reduction of hexaquochromium(III) ion. A study of this new wave was made using it as a method of following the first step of the transition of green to violet modification of chromium(III) chloride. The transition was found to be first order with respect to chromium and independent of the chloride concentration. The rate was proportional to the reciprocal of the hydrogen ion concentration. A rate equation was developed which showed this dependence upon hydrogen ion concentration, and was consistent with the equations usually given for the reaction. The temperature dependence of the rate of transition was studied and the activation energy calculated.

A complete investigation of the behavior of chromium(III) chloride when reduced at the dropping mercury electrode has never been reported, although Demassieux and Heyrovsky,[2] Prajzler,[3] and Lingane and Pecsok[4] have reported on the reduction of chromium(III) chloride in aged solutions. None of these investigators have reported on the results with fresh solutions or on any attempt to follow the aging process at the dropping mercury electrode, although Demassieux and Heyrovsky[2] did make the observation that concentrated solutions were more easily reduced and attributed this, correctly, to the presence of $[CrCl_2(H_2O)_4]^+$ in the concentrated solutions.

Many workers[5-9] have made investigations of the chemistry of chromium(III) chloride solutions, but there is still some discussion of the changes taking place in solution. It is the purpose of this paper to present the behavior of fresh chromium(III) chloride solutions at the dropping mercury electrode and to contribute to the studies of the chemistry of trivalent chromium solutions.

The transition from green to violet chromic chloride has been followed by Bjerrum[7a] and Lamb and Fonda,[9] by means of the change of conductance of solutions of green chromic chloride solutions. The data taken in this manner were difficult to interpret because of the simultaneous change of conductance caused by different degrees of hydrolysis of the various ionic species, and because the transition is essentially two consecutive steps. These difficulties did not seriously interfere in the polarographic method since it was found that the original green form was reduced at a potential sufficiently different that the change in concentration of the green form could be followed.

Pfeiffer[10] originally, without experimental data, proposed reactions for the transition according to the usual Werner scheme. The following represent the transitions that occur in a fresh chromium(III) chloride solution. They are consistent with the

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(1) Presented before the Annual Meeting of the Pacific Division of the American Association for the Advancement of Science held in Salt Lake City, Utah, June 19 to 24, 1950.

(2) N. Demassieux and J. Heyrovsky, *J. chim. phys.*, **26**, 219 (1929).

(3) J. Prajzler, *Collection Czechoslov. Chem. Commun.*, **3**, 406 (1931).

(4) J. J. Lingane and R. L. Pecsok, THIS JOURNAL, **71**, 425 (1949).

(5) A. B. Lamb, *ibid.*, **28**, 1710 (1906).

(6) J. Olie, *Z. anorg. Chem.*, **51**, 29 (1907); **53**, 268 (1908).

(7) (a) N. Bjerrum, *Z. physik. Chem.*, **59**, 336, 581 (1907); (b) **73**, 724 (1910).

(8) A. Heydweiller, *Z. anorg. Chem.*, **91**, 66 (1915).

(9) A. B. Lamb and G. R. Fonda, THIS JOURNAL, **43**, 1154 (1921).

(10) P. Pfeiffer, *Ber.*, **34**, 2559 (1901).