Discussion

The exchange between hydrogen chloride and solid stannic chloride is much faster than the corresponding exchange with aluminum chloride.[3] This may be related to the existence of $SnCl_4 \cdot 2HCl$ as a stable crystalline solid[7] in contrast to the situation with $AlCl_3$ and HCl.[8]

The exchange between HCl and $SnCl_4$ in the vapor phase affords an interesting comparison to the exchange between HCl and Cl_2.[9] Both are rapid surface catalyzed exchange reactions over Pyrex or silica surfaces. Chlorine is a strong inhibitor of the HCl–$SnCl_4$ exchange; exposure to chlorine gas at low pressures (20 mm.) for an hour is sufficient to produce the effects reported here, and the rate of exchange rises only slowly over a period of several days with long periods of evacuation between runs. Conversely, we have found that complete exchange between HCl and Cl_2 is not attained in several hours in Pyrex reaction vessels which have been exposed to stannic chloride. This may be due completely to the dehydrating action of $SnCl_4$, as a similar effect is reported by Johnston and Walton[9] using B_2H_6. The most logical explanation of the effect of chlorine on vessels used for the HCl–$SnCl_4$ reaction requires extremely strong adsorption of Cl_2 on the Pyrex surfaces at the sites responsible for the HCl–$SnCl_4$ exchange.

The lack of exchange between $SnCl_4$ and most organic chlorides in the vapor phase is not surprising in view of the failure of exchange between CCl_4 and $AlCl_3$ vapor at 140°.[1] The occurrence of exchange with *t*-butyl chloride may be related to the ease of "carbonium ion" formation postulated from its reactivity especially in water solutions, but the relationship is not simple. The exchange does not proceed by recombination of HCl and isobutene, nor through a similar activated complex, since the activation energy for exchange is much lower than that for decomposition. No attempt was made to measure the amount of decomposition accurately, but there was a decrease in the rate of decomposition by a factor of at least five on decreasing the temperature from 190 to 110°.

MADISON, WISCONSIN

---

[7] A. Chretien and G. Varga, *Compt. rend.*, **201**, 1491 (1935).

[8] H. C. Brown and H. Pearsall, THIS JOURNAL, **73**, 4681 (1951); R. L. Richardson and S. W. Benson, *ibid.*, **73**, 5096 (1951).

[9] W. H. Johnston and W. F. Libby, *ibid.*, **73**, 854 (1951); W. H. Johnston and J. R. Walton, unpublished.

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Optical Studies of Cerous Solutions[1]

BY LAWRENCE J. HEIDT AND JANE BERESTECKI

RECEIVED NOVEMBER 22, 1954

A study of the near ultraviolet absorption spectra of aqueous solutions of cerous perchlorate together with perchloric acid and sodium perchlorate has revealed evidence for the existence of a $CeClO_4^{+2}$ complex, for two new absorbance peaks located at about 2010 and 2110 Å. and for an isosbestic point located at about 2790 Å. The difference between the extinction coefficients of the two cerous species is greatest percentagewise at the peak located at 2960 Å. where the complex appears to absorb about one third as much light as the uncomplexed cerous ion. The values of the thermodynamic constants of the reaction $Ce^{+3} + ClO_4^- = CeClO_4^{+2}$ at 25° are $\Delta F^0 = -2.6$ kcal., $\Delta H^0 = -11.8$ kcal., and $\Delta S^0 = -31$ e.u. The absorpton spectra, of the solutions consist of three groups of peaks whose strongest peaks are separated by 5700 cm.$^{-1}$ and are located at 2215, 2530 and 2960 Å. The peaks in each group are separated by about 2300 cm.$^{-1}$; the two new peaks are satellites of the peak at 2215 Å. The highest peak is at 2530 Å. and has one satellite which is located at 2390 Å. and is the next highest peak. The 2960 Å. peak is the lowest of all and has no satellite. Evidence also has been obtained for the existence of a cerous sulfamate complex, $CeSO_3NH_2^{+2}$, whose formation constant is about one-fifth of the value of the perchlorate complex.

Cerous perchlorate in water forms colorless solutions whose absorption spectra have been known for some time[2] to consist of a number of peaks that are located between 2215 and 2960 Å. The cerous species in these solutions have been assumed to exist only as completely hydrated cerous cations whose extinction coefficients depend only upon the wave length of the absorbed light. The present study was made to determine more about the nature of the cerous species, their extinction coefficients and the equilibrium constants of any reactions involving them.

Materials.—The solutions were made up from conductivity water and were free of impurities in excess of more than a few tenths of 1%. Especial care was taken to avoid traces of iron, ammonium salts, nitrates, chlorides and suspended material. None of the solutions exhibited the Tyndall effect. Acidities and ionic strengths were adjusted with stock solutions of J. T. Baker analyzed reagent grade perchloric acid and sodium perchlorate.

The cerous perchlorate was prepared from G. F. Smith reference purity ceric ammonium nitrate. This was done in the following way.

About 25 g. of ceric ammonium nitrate was dissolved in 20 ml. of water in a 210-cc. porcelain casserole; the mixture was heated to complete solution and filtered if not clear. About 50 ml. of concd. (12 *N*) HCl was added to the clear solution. The resulting solution was boiled to dryness and the residue was heated strongly until the evolution of red fumes ceased. The solid obtained in this way was crushed into a fine yellow powder while it was still hot and it was then reheated strongly until fuming ceased.

The powder was allowed to cool and then 50 ml. of concd. HCl was added to it whereupon the mixture was stirred to produce a fine suspension to which was added enough (about 35 ml.) 30% H_2O_2 without preservative, to produce a clear colorless solution of cerous chloride. Care was taken to add the hydrogen peroxide in small enough portions to prevent frothing over. The resulting colorless solution was carefully boiled down to fine dry white crystals.

---

[1] Appreciation is expressed to the Charles F. Kettering Foundation and to the Godfrey L. Cabot Fund of M. I. T. for financial support. This is publication No. 56 of the M. I. T. Solar Energy Conversion Project.

[2] (a) D. C. Stewart A.E.C.D.-2389; (b) D. M. Bose and P. C. Mukherji, *Phil. Mag.*, **26**, 768 (1938); (c) D. M. Yost, H. Russell, Jr., and C. S. Garner, "Rare-Earth Elements and their Compounds," John Wiley and Sons, Inc., New York, N. Y.

The white solid was allowed to cool, then 40 ml. of 72% perchloric acid was added and if all the white solid did not dissolve, the mixture was heated gently and if necessary H_2O_2 was added to complete solution. The clear solution was boiled down to a dry yellow residue nearly free from acid. The residue was ground to a fine powder and heated strongly but cautiously to drive off any remaining HCl, HNO_3 and excess $HClO_4$. At this stage the fine dry powder first appeared to glow while being strongly heated. When this glowing stopped the heat treatment was terminated and the procedure thus far described in this paragraph was repeated until one obtained a dry yellow residue free of nitrate, chloride and ammonium compounds.

The yellow residue was treated with 20 ml. of 1 *N* $HClO_4$ and if solution was not complete a few drops of H_2O_2 were added to produce a clear colorless solution. The solution was then boiled down to not less than 17 ml. to decompose any H_2O_2. The resulting solution was about 2.5 *M* in $Ce(ClO_4)_3$ and 1 *M* in $HClO_4$.

Concentrations of the components of the stock solutions were determined in terms of moles per liter of solution at room temperature by analytical methods previously described.[3] Solutions were made up volumetrically from the stock solutions with measured volumes of not less than 5 ml. The formal concentrations of the components of all the solutions were known within a few per cent.

Volume concentrations of the solutions employed for absorbance measurements were taken to be the same at 15° to 60° since the error introduced by this simplification was comparatively negligible. The grams of water per liter of solution equal

$$1000 \times \text{sp. gr.} - M_1[Ce(ClO_4)_3]_f - M_2[HClO_4]_f - M_3[NaClO_4]_f = B \quad (1)$$

where M_1, M_2 and M_3 represent the formula weights of the respective substances. Specific gravities were measured at 25 ± 2°. The compositions of the cerous perchlorate solutions whose optical densities were measured and the values of *B* are given in Table I.

TABLE I

THE COMPOSITION OF THE CEROUS PERCHLORATE SOLUTIONS AT 25° IN TERMS OF FORMAL CONCENTRATIONS EXPRESSED IN MOLES PER LITER

$\mu_f = 6[Ce(ClO_4)_3]_f + [HClO_4]_f + [NaClO_4]_f$. *B* equals the grams of water per liter of solution.

Soln.	$10^2[Ce(ClO_4)_3]$	$10^2[HClO_4]$	$[NaClO_4]$	μ_f	*B*
1	0.068	0.057	0.000	0.0047	1000
2	.68	0.57	.000	.047	996
3	.68	0.57	.42	.47	914
4	.68	4.3	.37	.50	..
5	.68	42.0	.025	.50	..
6	6.8	5.7	.000	.47	965
7	6.8	5.7	4.19	4.7	803
8	68	57	0.000	4.7	906

Optical density measurements were made with a Cary Recording spectrophotometer Model 11 Ms, No. 69. The optical density and wave length scales had been calibrated as described elsewhere.[4] The pair of fused quartz windows of every absorption cell was selected so that the transmission of visible and ultraviolet light down to 1950 Å. of the two windows agreed within 0.01 optical density unit. The lengths of the light paths in the solutions held by the cells were 10.0, 1.00, 0.098 and 0.0176 cm.

The cells and contents were kept within ±0.05° of the recorded temperature by means of the thermostated cell compartment furnished with the instrument. The compartment was thermally insolated from the rest of the instrument by several layers of asbestos sheet. The air in the compartment was circulated by a small fan built into the light tight cover of the compartment. The inside walls of the compartment were kept at constant temperature by forced circulation of thermostated water.

Absorbance values of the solute species are defined as

$$A = \log_{10}(I_0/I) - \log_{10}(I_0/I') = \log_{10}(I'/I) \quad (2)$$

The optical density equals

$$D = \log_{10}(I_0/I) \quad (3)$$

The term I'/I_0 is the fractional decrease in the intensity of the light that is not attributable to absorption by the solute species. These definitions extend the notation proposed by Brode[5] since optical density is defined in terms of the fractional decrease in light intensity due to the sample ensemble including the cell and contents, and absorbance is defined in terms of the fractional decrease I/I', attributable only to the light absorbing solute species. The value of the optical density read off the scale of the spectrophotometer, therefore, equals the absorbance of the solute species under investigation if the optical density scale of the spectrophotometer is set at zero when the absorption cell containing the solution without the solute species is in the light path and an identical cell is employed for the solution containing the solute species.

Molar extinction coefficients or simply extinction coefficients are defined as

$$\epsilon_i = A_i/c_i d \quad (4)$$

where d is the length in cm. of the light path through the solution, c_i is the concentration of the light absorbing species in moles per liter of solution at the prevailing temperature and

$$\Sigma A_i = d\Sigma\epsilon_i c_i = A \quad (5)$$

Values of ϵ_i, therefore, have the dimensions of liter mole^{-1} cm.$^{-1}$ since A is dimensionless.

Equilibrium constants as employed by us are of three different kinds: a concentration constant, K_c, in terms of concentrations expressed in moles per liter of solution at the prevailing temperature since absorbance depends directly upon the number of potential absorbing units per unit volume; a concentration constant, K_m, in terms of concentrations expressed in moles per 1000 g. of water; a thermodynamic constant, K_0, obtained by extrapolation of log K_m to zero ionic strength by means of the equation of Debye and Hückel.

The employment of concentrations and ionic strengths expressed in moles per 1000 g. solvent in the D-H equation conforms to the assumption that the dielectric constant is proportional to the volume concentration of the solvent or that the solute ions behave like holes with zero dielectric constant. This assumption is believed to be much nearer actuality especially when the dielectric constant of the solvent is as high as that of water.[6]

Results and Discussion

The average value of the extinction coefficient of all the cerous species in our solutions was set equal in every case to

$$\bar{\epsilon} = A/c_f d \quad (6)$$

where A and d have already been defined and c_f is the formal concentration of the cerous perchlorate in moles per liter of solution. Typical absorption curves based on these values of $\bar{\epsilon}$ are presented in Fig. 1. The existence of the isosbestic point at 2970 Å. suggests that there are only two light absorbing cerous species in these solutions.

The values of $\bar{\epsilon}$ at the 2960 Å. peak change the most percentagewise; they range from 10.5 to 25.6; they approach the higher limit when the temperature is raised and when the concentration of the cerous perchlorate is decreased but the reverse is the case at the 2530 and 2390 Å. peaks and the change in $\bar{\epsilon}$ is negligible at wave lengths shorter than 2300 Å.

The negligible influence of the acidity upon the value of $\bar{\epsilon}$ is shown by the results presented in Table II. The concentration of the perchloric

---

[3] M. S. Sherrill, C. B. King and R. C. Spooner, THIS JOURNAL, **65**, 170 (1943).

[4] L. J. Heidt and D. E. Bosley, *J. Opt. Soc. Am.*, **43**, 760 (1953).

[5] W. R. Brode, *Proc. Am. Soc. Testing Materials*, **50**, 513 (1950).

[6] G. Scatchard, *Chem. Revs.*, **19**, 309 (1936).

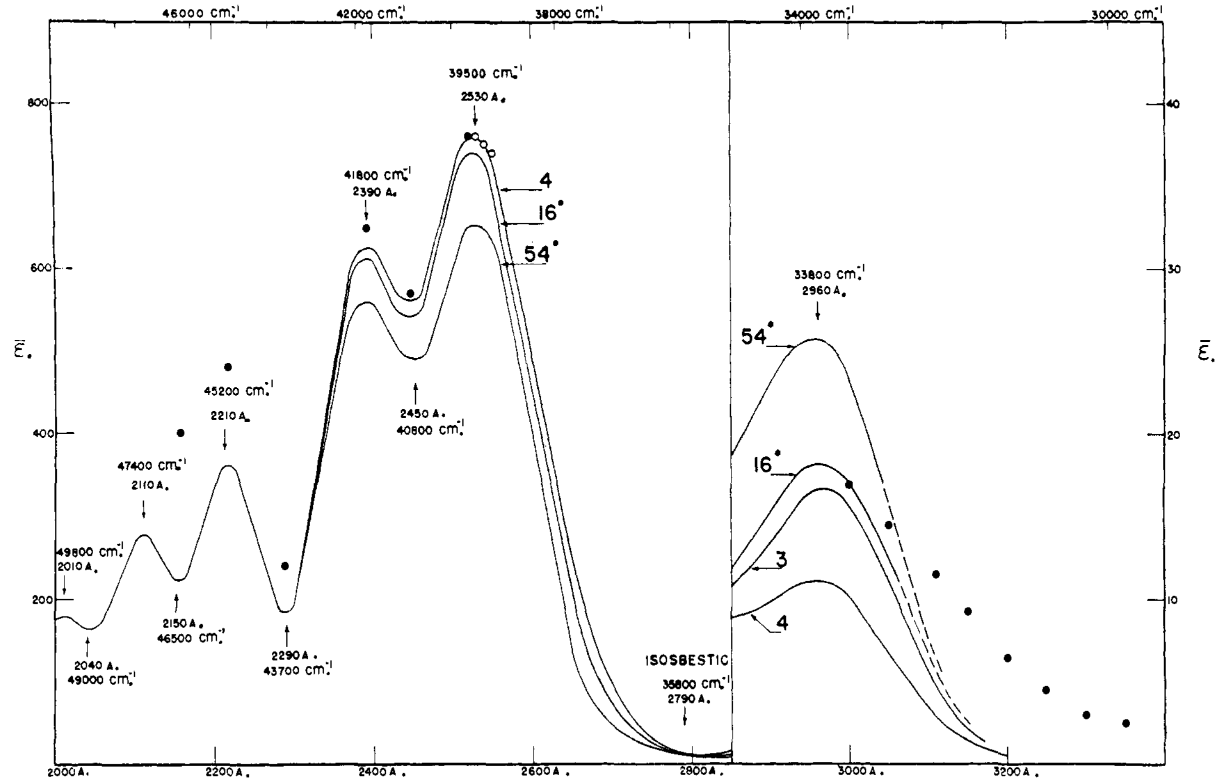

Fig. 1.—The near ultraviolet absorption spectrum of cerous perchlorate in water solution at *p*H values less than three. The solutions do not absorb a significant amount of visible light. The peaks fall into three groups whose principal peaks are at 2210, 2530 and 2960 Å. and are separated by 5700 cm.$^{-1}$. The peaks in each group are separated by 2300 cm.$^{-1}$. The peaks at 2010 and 2110 Å. have not been previously reported. Solutions of sodium perchlorate and of perchloric acid absorb little of this light. The values of $\bar{\epsilon}$ are the extinction coefficients per gram mole of cerous perchlorate per liter per cm. depth of solution; the scale of the right-hand ordinate applys only to wave lengths longer than 2850 Å. as indicated by the break in the absorption curves at this wave length. Variations in temperature and concentration of the cerous perchlorate change the values of $\bar{\epsilon}$ but do not significantly change the wave lengths of the absorption maxima and minima. Lines marked 16 and 54° show the effect of temperature upon $\bar{\epsilon}$ in the case of solution 1 whose composition is given in Table I. Line 3 is for solution 3 at 25°. Line 4 is for solution 7 at 16°; the difference between line 4 and the one marked 16° represents the effect upon $\bar{\epsilon}$ of increasing the concentration of the cerous perchlorate. An isosbestic is at 2790 Å. Filled circles represent the results at 25° reported by Stewart.[8] His data at 2130 to 2800 Å. are for a solution 0.00147 *M* in $Ce(ClO_4)_3$ and 0.94 *M* in $HClO_4$ compared to 0.94 *M* $HClO_4$ and his data at 2800 to 11000 Å. are for a solution 0.0147 *M* in $Ce(ClO_4)_3$ and 0.90 *M* in $HClO_4$ compared to 0.88 *M* $HClO_4$. The part of his results between 2500 and 2800 Å. coincide with line 4 and the part between 2500 and 3000 Å. coincide with the line marked 16°. His data would agree with our results if they fell below line 3 at wave lengths longer than 2800 Å. and lay between lines 4 and 16° at shorter wave lengths. Open circles represent results previously obtained in this Laboratory[7] at 23 ± 3° with a precision of ±10% in $\bar{\epsilon}$ at 2530, 2540 and 2550 Å. for solutions 0.00007 to 0.03 *M* in $Ce(ClO_4)_3$, 1 *M* in $HClO_4$ and containing about three times more $NaClO_4$ than $Ce(ClO_4)_3$ on a mole basis.

acid was varied nearly one hundred-fold under conditions where $\bar{\epsilon}$ is most sensitive to changes in the relative concentrations of the light absorbing cerous species. Since $\bar{\epsilon}$ remained unchanged it seems reasonable to conclude that neither of the cerous species is a product of the hydrolysis of cerous ions.

The influence of the temperature and the ionic strength upon the value of $\bar{\epsilon}$ is shown by the results presented in Table III. The variations in $\bar{\epsilon}$ produced by variation of these variables can be attributed to the reaction

$$Ce^{+3} + ClO_4^- = CeClO_4^{+2} \qquad (7)$$

if one assigns the values of the lower and upper limits of $\bar{\epsilon}$ at 2960 Å. to the extinction coefficients at this wave length of the complex and of the free cerous ions, respectively. When this is done

$$A/d = \epsilon_2(CeClO_4^{+2}) + \epsilon_3(Ce^{+3}) \qquad (8)$$

where $\epsilon_2 = 10.5$ and $\epsilon_3 = 25.6$ at 2960 Å. and

$$K_c = (CeClO_4^{+2})/(Ce^{+3})(ClO_4^-) \qquad (9)$$

The best values of K_c are obtained when the concentrations of the light absorbing species are nearly equal, the observed value of A is in the range of 0.2 to 2.8 for reasons stated elsewhere[4] and the concentration of the perchlorate ion is relatively high.

Ionic strengths have been evaluated in terms of the concentrations of the species based on reaction (7).

$$\mu_c = [HClO_4] + [NaClO_4] + 6[Ce(ClO_4)_3] + 3[CeClO_4(ClO_4)_2] = \mu_m B/1000 \qquad (10)$$

$$K_c = K_m B/1000 \qquad (11)$$

(7) L. J. Heidt and M. E. Smith, THIS JOURNAL, **70**, 2476 (1948).

TABLE II

Absorbance values at the 2960 Å. peak of ten cm. depths of solutions of the same concentrations of cerous perchlorate, namely, 0.0068 *M* but of different acidities when the ionic strength is held constant at $\mu_f = 0.5$ by replacing perchloric acid with sodium perchlorate. The absorbance values of these solutions at about the same temperature agree within the limits of error and this was also the case at all other wave lengths. It will be noted that this agreement exists even in the center of the range of $\bar{\epsilon}$ where $\bar{\epsilon}$ is most sensitive to changes in the ratio of the concentrations of the absorbing species.

Soln.	($HClO_4$)	Temp., °C.	*A*	
3	0.0057	25.3	1.13	16.6
4	.043	23.2	1.11	16.4
		30.7	1.25	18.4
		40.7	1.37	20.2
5	.42	23.2	1.13	16.5
		30.7	1.26	18.5
		40.7	1.38	20.4

TABLE III

ABSORBANCE VALUES, *A*, AT THE 2960 Å. ABSORPTION MAXIMUM OF SOLUTIONS OF CEROUS PERCHLORATE

The values of the ionic strength, μ_c, are based on the composition of the solution as obtained from the values of K_c. The values of μ_c approach the values of μ_f, given in Table I, as an upper limit. The values of $\bar{K}_c$, $\bar{\mu}_c$ and $\bar{A}$ are smoothed values that were obtained as explained in the text. The differences between the raw and smoothed values of *A* are tabulated under ΔA.

Soln.	Temp., °C.	*A*	*d*	$\bar{\epsilon}$	K_c	μ_c	$\bar{\mu}_c$	$\bar{K}_c$	$\bar{A}$	ΔA
1	15.9	0.122	10.0	18.0	....	0.00357	0.00422	101	0.153	−0.03
	25.1	0.132	10.0	19.4	....	.00377	.00441	52.7	0.162	− .03
	54.0	0.170	10.0	25.0	....	.00457	.00460	8.72	0.171	− .00
2	15.8	1.11	10.0	16.3	72.1	.0340	.0346	53.7	1.14	− .03
	25.2	1.25	10.0	18.4	39.7	.0368	.0386	26.4	1.34	− .09
	42.4	1.48	10.0	21.8	13.8	.0413	.0429	8.24	1.56	− .08
	54.0	1.70	10.0	25.0	....	.0457	.0445	3.96	1.65	+ .05
3	16.7	1.02	10.0	15.0	5.31	.452	.452	10.05	0.90	+ .12
	25.3	1.13	10.0	16.6	3.30	.454	.454	5.19	1.02	+ .11
	35.4	1.24	10.0	18.3	2.14	.456	.456	2.84	1.17	+ .07
6	15.4	1.03	1.00	15.2	10.8	.323	.324	14.3	0.970	+ .06
	25.2	1.18	1.00	17.4	5.41	.353	.356	6.85	1.12	+ .06
	42.5	1.45	1.00	21.4	1.58	.408	.416	1.90	1.42	+ .03
	54.3	0.170	0.098	25.6	....	.464	.446	0.856	0.154	+ .02
7	15.2	0.752	1.00	11.1	....	4.46	4.46	1.74	0.832	− .08
	25.2	0.916	1.00	13.5	0.922	4.50	4.50	0.860	0.927	− .01
	42.4	1.17	1.00	17.2	0.281	4.55	4.55	0.253	1.19	− .02
	54.3	1.38	1.00	20.3	0.124	4.59	4.59	0.113	1.40	− .02
8	15.1	0.809	0.098	12.2	4.05	2.83	3.22	2.71	0.853	− .04
	25.2	0.990	.098	14.9	1.14	3.20	3.49	1.29	0.968	+ .02
	42.4	1.22	.098	18.3	0.415	3.65	4.13	0.343	1.25	− .03
	54.3	1.49	.098	22.4	0.112	4.20	4.53	0.148	1.44	+ .05

$$K_0 = K_m\Gamma \qquad (12)$$

$$\log \Gamma = -a\sqrt{\bar{\mu}_m}(\Sigma Z_i^2)/(1 + b\sqrt{\bar{\mu}_m}) \qquad (13)$$

$$\Sigma Z_i^2 = 2^2 - (3^2 + 1^2) = -6 \qquad (14)$$

$$\log K_m = \log K_0 - 6a\sqrt{\bar{u}_m}/(1 + b\sqrt{\mu_m}) \qquad (15)$$

The values of the constants *a* and *b* in the Debye–Hückel equation can be calculated conveniently at temperatures between 0 and 100° by means of equations given elsewhere.[8] The value of *a* increases about 7.5% between 15 and 55°; the increase in *b*, exclusive of the average ionic radius, is only about 1% over this range of temperatures and has been ignored. The values of the constant *a* at ten degree intervals at 5 to 95° are 0.4921, 0.5001, 0.5085, 0.5174, 0.5269, 0.5371, 0.5480, 0.5597, 0.5723 and 0.5858, respectively. The difference between one liter and 1000 g. of water at 15 to 55° is about 1.5% and this also has been ignored.

The best value of the constant *b* was obtained by constructing curves of $a\sqrt{\bar{\mu}_m}/(1 + b\sqrt{\bar{\mu}_m})$ *vs.* $\sqrt{\bar{\mu}_m}$ for values of *b* equal to 0, 0.5, 1.0, 1.5, etc., and finding the curve among them that best fit the experimental values of $\log K_m/6$ *vs.* $\sqrt{\bar{\mu}_m}$ when plotted on the same scale.

A plot of this kind is presented in Fig. 2 where the curve for $b = 1.2$ best fits the data. This was found to be the case at all the temperatures employed. The deviations of the values of $\log K_m + 6a\sqrt{\bar{\mu}_m}/(1 + 1.2\sqrt{\bar{\mu}_m}) = \log K_0$ from the average value of this sum at each of the temperatures is given by the plot at the bottom of Fig. 2. The deviations in most cases amount to less than a factor of 1.5 in the value of K_m and this is about the same as its reproducibility in most cases.

It will be noted that the deviations at low values of the ionic strength exhibit a trend suggesting that the data could be fitted better by employing a smaller value of *b* and adding a term $\beta\mu$ where β is a constant. This procedure does indeed reduce most of the deviations to a factor of 1.4 but this is not a significant improvement since the trend still persists. In order to eliminate the trend it is necessary to employ very small values of both *b* and β and then the fit at the high values of μ is very bad. The best fit is obtained when $\Sigma Z^2{}_i = -5$, $b = 0.05$ and $\beta = 0.03$ but even then the deviations are only reduced to a factor of about 1.3 in K_m and the trend still persists.

The significant fact brought out by these calculations is that the dependence of K_m upon the ionic strength is roughly in accord with the equation of Debye and Hückel for the reaction postulated and this lends strong support to the hypothesis that the effect is indeed due to reaction 7.

---

(8) G. Scatchard, THIS JOURNAL, **65**, 1249 (1943).

The average values of log K_0 obtained by setting b equal to 1.2 are plotted against 1000/(273.2 + °C.) at the top of Fig. 2. The equation for the best straight line through these points is

$$\log K_0 = -6.749 + 2583/T \qquad (16)$$

The maximum deviation from this line amounts to a factor of 1.16 in the value of K_0.

The values of the thermodynamic constants based on equation 16 are $\Delta F^0 = -2.61$ kcal., $\Delta H^0 = -11.82$ kcal., and $\Delta S^0 = -31$ e.u. all at 25°. The value of ΔF^0 at 25° is about the same as that for the formation of the bisulfate anion but the value of ΔH^0 in the latter case is +5.2 kcal.

The values given for $\bar{K}_c$ in Table III were obtained from the above equation for log K_0 in terms of $1/T$, the equation for log K_m in terms of log K_0 and μ_m and the equation for K_c in terms of K_m and B. The calculated values of A, namely, $\bar{A}$, appearing in Table III are based on these values of $\bar{K}_c$. It was found that the process of recycling the values of K_m and μ_m produced a difference in the values of $\bar{A}$ of less than 1% even in those solutions whose ionic strengths were not buffered with sodium perchlorate or perchloric acid. The tabulated values of $\bar{K}_c$ and $\bar{\mu}_c$ are those obtained by the second approximation. The differences, ΔA, between the raw and smoothed values of A are within the limits of error.

There have been a number of publications recently[9] dealing with the entropies of ions in water and the change in entropy upon the formation of a complex of these ions. It has been pointed out that the value of ΔS^0 is usually positive for a reaction producing a complex when the ligand replaces, by thrusting out into the solution, one or more molecules of water originally coördinated with the cation. The increase in entropy is about 16.5 e.u. per mole of water freed.[9c]

The large negative value of ΔS^0 for the formation of the cerous perchlorate complex suggests that the complex is an extended one of the outer complex type in which hydrogen bonds are formed between two or more oxygen atoms of the perchlorate ligand and oxygen atoms of the water molecules coördinated with the cerous cation. Two or three of these bonds could be formed depending upon whether an edge or a face, respectively, of the perchlorate tetrahedron entered into the formation of the complex.

A complex of this type is sketched in Fig. 3. The number and position of the water molecules nearest the cerous cation are not as definite as depicted and there are water molecules not shown that surround the perchlorate anion. The sketch is only meant to depict one of several possible forms of the complex whose formation would not free any molecules of water coördinated with the cation but would quench the free rotation of the parts of the complex. The complex would rotate less freely than its parts because of the much greater size and the complex would produce less disturbance of the water lattice than its separate parts because it would behave somewhat like a polarized particle like water instead of two independent centers of unlike charge.

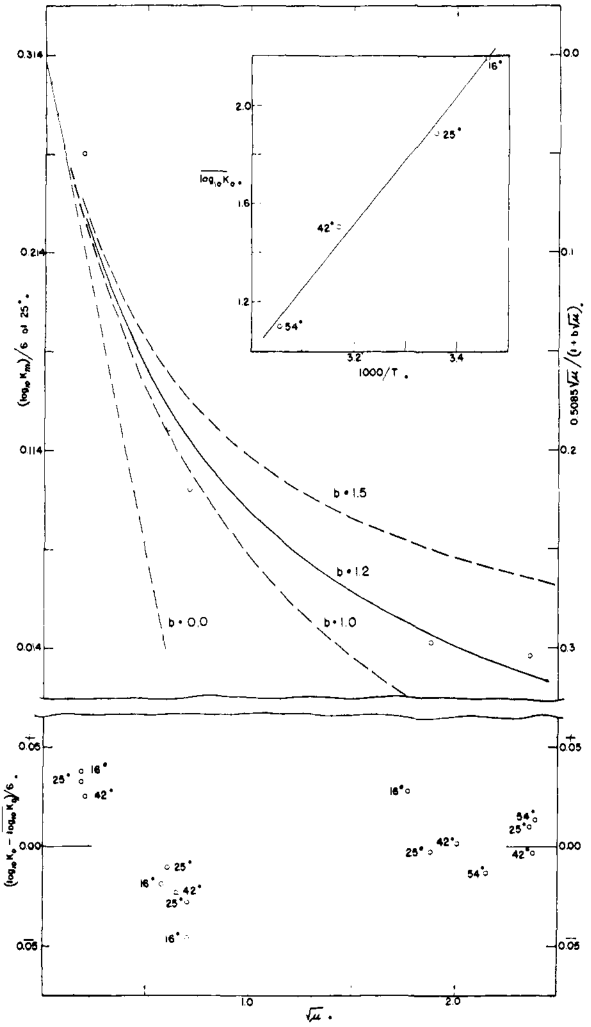

Fig. 2.—Influence of ionic strength and temperature upon the equilibrium quotient, K_m, of the reaction $Ce^{+3} + ClO_4^- = CeClO_4^{+2}$. The curved lines represent the values of the term $0.5085\sqrt{\mu}/(1 + b\sqrt{\mu})$ at 25° as a function of the $\sqrt{\mu}$ for selected values of b. The circles represent the values of log $K_m/6$ at various ionic strengths; they fit best the line for which $b = 1.2$. Near the bottom of the fig. is given a deviation plot showing the fit of the data to the lines for which $b = 1.2$ at all the temperatures employed. Near the top of the fig. is given a plot of the values of log K_0 vs. $1/T$. The points are seen to be represented adequately by the straight line.

The slightly improved fit of the data to the Debye–Hückel equation when the charge on the complex is considered to be slightly more than 2 but less than 3 as well as the negative value of ΔH^0 also conform to the picture that the complex is one of the outer type.

A complex or ion-pair also has been postulated to exist between ferric and perchlorate ions based on a lowering of the absorbance of ferric ions of about 3% at the 2450 Å. peak and on a slight elevation of the long wave length toe of this peak.[10] This effect has been observed in solutions 1 to 7 M in per-

---

[9] (a) R. E. Powell, *J. Phys. Chem.*, **58**, 528 (1954), (b) R. J. P. Williams, *ibid.*, **58**, 121 (1954), (c) J. W. Cobble, *J. Chem. Phys.*, **21**, 1443, 1446 (1953).

[10] J. Sutton, *Nature*, **169**, 71 (1952).

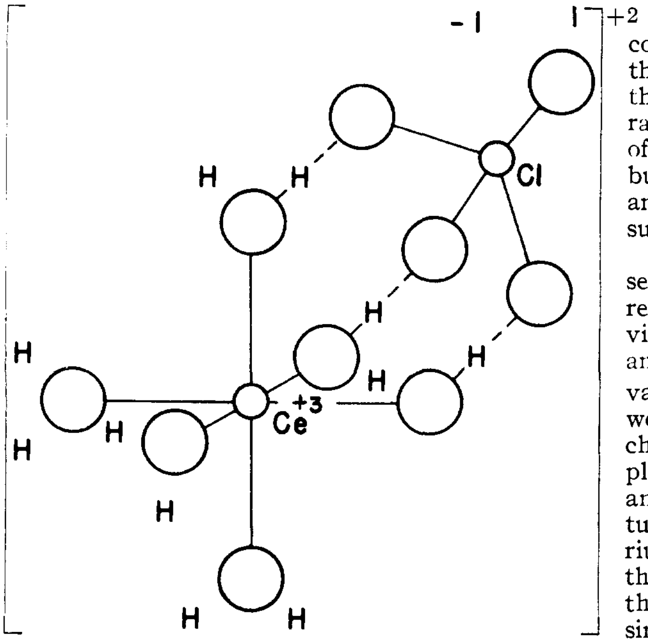

Fig. 3.—One of several possible structures of the cerous perchlorate complex resulting from the union of one hydrated cerous cation and one hydrated perchlorate anion. The drawing illustrates a complex in which there is hydrogen bonding between the three oxygen atoms forming one face of the perchlorate tetrahedron and three of the water molecules surrounding the cerous ion. The relative positions of the water molecules are not as definite as is depicted and there are water molecules not shown that are closely associated with the perchlorate and cerous parts of the complex. The sketch is not drawn to scale.

chloric acid at a concentration of ferric perchlorate of about 10^{-4}. The value reported for the formation constant at zero ionic strength is 0.475 ± 0.075 for concentrations expressed in moles per liter of solution presumably at a room temperature near 25°.

There also has been reported[11] a specific effect of perchlorate ions upon the hydrolysis of ferric perchlorate based on deviations in the optical density of about 0.02 unit at values of the optical density of about 0.5 under conditions where the experimental error was "a few units in the third decimal place of optical density."

The effect observed by us is several orders of magnitude greater than in the above cases and there is little doubt that it is attributable to an interaction between unhydrolyzed cerous cations and perchlorate anions.

The formation of a complex between the perchlorate anion and the cerous cation raises the question of whether there exist anions that have a smaller tendency than perchlorate to enter into complex formation with cerous ions. We have, therefore, explored the effect of sulfamic acid upon the optical density of solutions of cerous perchlorate. The wave lengths of the absorption extremes of the solutions were found to remain unchanged but the value of $\bar{\epsilon}$ at the 2960 Å. peak first increased and then decreased as the concentration of the sulfamic acid was increased.

The results obtained at the 2960 Å. peak are presented in Table IV, and can be explained by the reaction $Ce^{+3} + SO_3NH_2^{-1} = CeSO_3NH_2^{+2}$ provided that $\bar{\epsilon}$ equals 6.5 for the sulfamate complex and its formation constant is about one-fifth of the value of the perchlorate complex. The values of A were calculated on the basis that ϵ remains unchanged at 10.5 and 25.6 for the perchlorate complex and uncomplexed cerous ions, respectively, and that the effects of ionic strength and temperature are the same upon the values of both equilibrium constants. The values of ΔH^0 and ΔS^0, therefore, are about the same for the formation of the complexes and their structures are probably similar.

TABLE IV

ABSORBANCE VALUES AT THE 2960 Å. PEAK OF CEROUS IONS OF MIXTURES IN WATER OF CEROUS PERCHLORATE AND PERCHLORIC AND SULFAMIC ACIDS

In every case $[Ce(ClO_3)_3]_f = 0.0068\ M$, $[HClO_4]_f = 0.0057\ M$, $d = 10.0$ cm., $\epsilon = 6.5$ for $CeSO_3NH_2^{+2}$ and $\bar{K}_o/\bar{K}_s = 4.5$ where $\bar{K}_o$ and $\bar{K}_s$ are the formation constants of the perchlorate and sulfamate complexes, respectively. The other symbols have the same meaning as in Table III.

$[HSO_3NH_2]_f$	°C.	A	$\bar{\epsilon}$	$\bar{K}_o$	$\bar{K}_s$	$\bar{A}$	ΔA
0.00	15.0	1.12	16.4	60.0		1.14	−0.02
	25.0	1.24	18.3	27.0		1.33	−0.09
0.19	15.0	1.14	16.7	20.0	4.4	1.07	+0.07
	25.0	1.35	19.8	9.6	2.2	1.27	+0.08
0.57	15.0	1.12	16.5	9.5	2.1	1.00	+0.12
	25.0	1.28	18.9	4.8	1.1	1.21	+0.07
1.7	15.0	0.87	12.8	4.2	0.95	0.93	−0.06
	25.0	1.06	15.5	2.2	0.50	1.13	−0.07

The sulfamate complex was found to decompose thermally in water into species that more strongly absorb light of 2960 Å. The decomposition was negligible in our solutions in one day at 25° or less but was nearly complete in a few minutes at 100°. The reaction is attributable to the hydrolysis of the sulfamate ion into the ammonium cation and the sulfate anion[12] and the formation of cerous sulfate complexes.[13] The cerous perchlorate complex was found to be thermally stable in water.

CAMBRIDGE, MASS.

---

[11] A. R. Olsen and T. R. Simonson, *J. Chem. Phys.*, **17**, 1322 (1949).

[12] M. E. Cupery, *Ind. Eng. Chem.*, **30**, 627 (1938).

[13] T. W. Newton and G. M. Arcand, THIS JOURNAL, **75**, 2449 (1953).