aqueous solvents indicates that specific solvent effects are considerably more important in accounting for the deviations from linearity predicted by Scatchard's equation than are salting out effects.

3. The Arrhenius factors B obtained from the corrected rate constants are lower than the values obtained from the rate constants based on volume concentrations, while the energies of activation are essentially the same.

4. The following predictions based on theory have been verified experimentally: (a) $E^0_C > E^0_D$; (b) $E^0_C > E_C$ ($\sqrt{\mu} = 0.194$); (c) $B^0_C > B^0_D$.

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The Oxidation Potential of Cerous–Ceric Perchlorates

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Introduction and Plan of Investigation

The oxidation potential of an equimolal mixture of cerous and ceric salts of a given acid in the presence of that acid varies considerably with the nature of the common anion and to some extent with the concentration of the acid. Crude measurements of Bauer and Glaessner[1] showed this potential to be 1.84 volts in nitric acid solution and 1.70 volts in sulfuric acid solution. Later Kunz[2] made a thorough and accurate study of the oxidation potential of cerous–ceric sulfates in solutions of sulfuric acid. He concluded from his results that the oxidation potential, referred to the molal hydrogen electrode as zero, is 1.4435 volts in 1.0 molal, and 1.4442 volts in 0.5 molal acid solution. This seems to show that there is little change in the potential between the two concentrations of sulfuric acid.

The lack of dependence of the oxidation potential on the acid concentration over a relatively short range of acid concentration was also noted by Noyes and Garner[3] in their measurements with cerous and ceric nitrates in nitric acid solution. Thus, in solutions 2.0, 1.0 and 0.5 weight formal in nitric acid the oxidation potential was found to be 1.6104, 1.6096 and 1.6085 volts, respectively. The authors concluded from this constancy of the potential that neither complex formation nor partial hydrolysis of the cerium ions occurred over this range of acid concentration.

Smith and Getz[4] determined the oxidation potential not only with mixtures of the nitrates and sulfates, but also with those of the perchlorates, and extended the measurements to acid concentrations as high as 8 normal. With the nitrate and sulfate mixtures the potentials in the solutions of lower acid concentrations exhibited the constancy noted by the previous investigators, but at the higher concentrations decreased perceptibly. These authors attributed this decrease to the formation of complexes between the ceric ions and the acid anions. The results of their measurements with the perchlorate mixtures, however, showed a reverse effect. Thus, the potential increased steadily from 1.70 volts in 1.00 *N* perchloric acid solution to 1.87 volts in 8 *N* perchloric acid solution. Smith and Getz were of the opinion that complexes were present to a large extent even in perchloric acid solutions, although this would seem to be inconsistent with the observed increase in the oxidation potential with increasing acid concentration.

In this investigation a thorough study of the oxidation potential of mixtures of ceric and cerous perchlorates in the presence of excess perchlorate anion was made in order to ascertain what effect, if any, the acid concentration and the perchlorate ion concentration has on this potential. To this end three series of measurements consisting of several runs each were made in the following type of cell, the concentrations being expressed as weight formalities (w. f.)

$$\text{Pt} + H_2(1\ \text{atm.}),\ HClO_4(c_1\ \text{w. f.}) + NaClO_4(c_5\ \text{w. f.}),\ HClO_4(c_2\ \text{w. f.}) + NaClO_4(c_6\ \text{w. f.}) + Ce(ClO_4)_3(c_3\ \text{w. f.}) + Ce(ClO_4)_4(c_4\ \text{w. f.}),\ \text{Pt}$$

In all cases the concentration differences, $c_2 - c_1$ and $c_6 - c_5$, were kept small in order to reduce the liquid potential in the cell occasioned by these differences. It should be noted that the presence of the cerium salts in one-half the cell is partly responsible for this liquid potential. This effect

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[1] Bauer and Glaessner, *Z. Elektrochem.*, **9**, 534 (1903).

[2] Kunz, THIS JOURNAL, **53**, 98 (1931).

[3] Noyes and Garner, *ibid.*, **58**, 1265 (1936).

[4] Smith and Getz, *Ind. Eng. Chem., Anal. Ed.*, **10**, 191 (1938).

was reduced, however, by keeping the total cerium salt concentration, $c_3 + c_4$, small in relation to the sum, c_2+c_6, of the concentrations of the hydrogen and sodium perchlorates. Elimination of the small liquid potential in the cell is discussed under the treatment of results.

The first series of measurements was made to determine the effect of the perchloric acid concentration on the potential. In all the runs of this series no sodium perchlorate was present, the total concentration of the cerium salts was kept constant at 0.01 w. f., while in the separate runs the perchloric acid concentration was varied progressively from 0.2 to 2.4 w. f. In each run measurements were made at different ratios of ceric to cerous salt concentrations.

The second series of measurements was made to determine the effect of the total cerium salt concentration on the potential. There was no sodium perchlorate present, but in this case the acid concentration was kept approximately constant at about 0.5 w. f. in all runs, while in the separate runs the total cerium salt concentration was varied progressively from 0.01 to 0.07 w. f., and, as before, measurements were made at different ratios of ceric to cerous salt concentrations.

The third series of measurements was made to determine what effect the substitution of sodium perchlorate for some of the perchloric acid would have on the potential. In all the runs of this series the total cerium concentration was kept at 0.01 w. f., and the sum of the sodium perchlorate and perchloric acid concentrations, $c_1 + c_6$ and $c_2 + c_6$, was kept approximately constant at 1.3 w. f. but in the separate runs the concentration of sodium perchlorate was varied progressively from 0 to 0.9 w. f., and measurements were made with different ratios of ceric to cerous salt concentrations.

Materials and Apparatus

Preparation of Solutions.—All cerium salt solutions were prepared from ammonium hexanitrato cerate, which was kindly supplied by the G. F. Smith Chemical Company in a state of 95% purity. It was carefully purified by dissolving in a boiling solution of 60% nitric acid containing an excess of ammonium nitrate equivalent to ten per cent. of the dissolved hexanitrato cerate, and recrystallizing at ice temperature.[5] The authors take this opportunity to thank Professor Smith personally for his helpful interest in this investigation.

A stock solution of cerous perchlorate was prepared as follows.[4] Pure ammonium hexanitrato cerate was placed in a casserole and treated with successive portions of concentrated hydrochloric acid, each portion being evaporated to fuming, until further addition gave no evidence of nitric acid remaining in the solution, as shown by the red fumes of nitrogen dioxide. This treatment served to reduce the cerium to the cerous state of oxidation, and to decompose the ammonium and nitrate radicals, thereby leaving a solution of pure cerous chloride in hydrochloric acid. This solution was then treated with portions of C. P. 72% perchloric acid. each portion being evaporated to fuming over a burner. The very volatile hydrogen chloride was thus driven off leaving a solution of cerous perchlorate in perchloric acid which gave no test for chloride, nitrate, or ammonium ions. It was diluted with water and perchloric acid added to make it about 0.5 w. f. in cerous perchlorate and about 2.5 w. f. in perchloric acid.

A stock solution of ceric perchlorate was prepared by the electrolytic oxidation of the cerous perchlorate solution with a diaphragm type of cell.[6] Platinum foil electrodes of a size 5 × 6.5 cm. were used, and a current of 4.5 amperes was passed through the cell for six hours, during which time the cerium solution was stirred by a small stream of air. Analysis showed the cerium to be about 95% oxidized to the ceric state.

The cell solutions for the first series of measurements were made up as follows. The 72% perchloric acid was diluted with water to give a solution of the acid concentration desired for the particular run under investigation. To some of this solution enough of the stock solution of ceric perchlorate was added to make the resulting solution about 0.01 w. f. in total cerium salt content. Since there was an excess of acid in the stock solution, the concentration of the pure perchloric acid which was used in the hydrogen half cell had to be adjusted to a value approximately equal to the acid concentration in the cerium cell solution.

In the second series of measurements the first solution was prepared 0.07 w. f. in total cerium salt concentration and about 0.5 w. f. in perchloric acid. The other solutions were made from it by dilution with 0.5386 w. f. perchloric acid in suitable amounts to give the solutions of lower total cerium salt content.

For the third series of measurements in which sodium perchlorate replaced some of the perchloric acid solution. solutions of acid and ceric perchlorate were made up and analyzed. In order to replace the acid by the salt, weighed amounts of C. P. sodium carbonate were added to weighed portions of both the acid and cerium solutions to make them the same in their concentrations of sodium perchlorate. The slight amount of water in the practically anhydrous sodium carbonate had been determined by titration of a weighed sample with standard acid. With this knowledge, the concentrations of all the components after the addition of the carbonate could be calculated.

Attention should be called to the observation that dilution of the stock ceric perchlorate solution with the acid solution caused appreciable spontaneous reduction of the ceric salt. This was particularly noticeable in the solu-

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(5) Smith. Sullivan and Frank. *Ind. Eng. Chem., Anal. Ed.*, **8**, 449 (1936).

(6) For electrolytic oxidation without use of a diaphragm cell see Smith. Frank and Knott. *Ind. Eng. Chem., Anal. Ed.*, **12**, 268 (1940).

tions of higher acid concentration where, even after the dilution, reduction proceeded at a moderate rate. In more dilute acid, however, there was not nearly so much initial reduction, and the ceric salt concentration remained reasonably constant thereafter. This phenomenon is explained by the fact that solutions of ceric perchlorate are thermodynamically unstable with reference to liberation of oxygen from water. The higher oxidation potential in the more concentrated acid solutions may account for the more rapid reduction in these solutions.

Methods of Analysis.—A weight buret was used in the analysis of all of the cell solutions, and, correspondingly, the concentrations of the components in the solution were expressed as weight formalities, that is, formula weights per kilogram of water. All weights were corrected to vacuum.

The cell solutions were analyzed for perchloric acid by titration with a standard solution of sodium hydroxide with phenolphthalein as indicator. Direct titration in the presence of ceric salts is attended by precipitation of ceric hydroxide which obscures the end-point and gives a false value for the acid content. For this reason the following procedure was used. The cerium in the weighed sample was reduced completely to the cerous state by the addition of a few drops of 3% hydrogen peroxide. Saturated sodium oxalate solution was then added to precipitate the insoluble cerous oxalate. The precipitate was filtered and washed with ten portions of water of 10 ml. each. The filtrate was then titrated with standard sodium hydroxide solution. The acid concentration thus determined was corrected for the acid produced by the reduction of the ceric salt. Tests showed that the presence of excess sodium oxalate had no effect on the titration of the acid. Analyses checked to 0.1%.

The concentration of ceric perchlorate in the cell solution was determined by titration with a standard solution of ferrous sulfate using ferroin as indicator.[7,8]

The standard solution of ferrous sulfate was prepared by dissolving C. P. $FeSO_4 \cdot 7H_2O$ in 0.5 M sulfuric acid to yield a concentration suitable for titration of the cell solutions. It was stored in an air-tight vessel into which hydrogen was led from a Kipp generator containing zinc and sulfuric acid in order to minimize oxidation of the ferrous salt. This solution was standardized against a standard solution of ceric sulfate, which, in turn had been standardized against Bureau of Standards sodium oxalate. The normality of the ferrous sulfate solution over a period of one month changed from 0.005006 to 0.004983, even when protected by the hydrogen atmosphere. Consequently the solution was restandardized before use against the stable ceric sulfate solution.

In the standardization of the ferrous sulfate solution, a weighed sample of the ceric sulfate solution was placed in 50 ml. of 1 M sulfuric acid and titrated with ferrous sulfate until nearly all the yellow ceric color had disappeared. A measured drop of the ferroin indicator was then added and the titration continued until the red color of the indicator appeared. A small correction was applied for the ferrous sulfate in the indicator.

In the analyses of the cell solutions for ceric perchlorate, weighed samples were titrated with the standard ferrous sulfate solution following a slightly modified procedure. It was found that a sharp end-point could not be reached in solutions below 0.2 w. f. in perchloric acid which were 0.01 w. f. in total cerium content. The red color of the indicator would appear and fade out within half a minute to reappear again with addition of another drop of ferrous sulfate. Boiling the solution before the titration, however, gave a sharp permanent end-point and this end-point checked the final end-point of the unboiled solution when the titration was continued till no fading took place.

A probable explanation of this observed effect is that hydrolysis of the ceric salt takes place in solutions of low acid concentration with production of colloidal ceric hydroxide to an appreciable extent. The slow solution of this colloidal material in the cold sulfuric acid solution, followed by its rapid reduction would account for the fading end-point. The sharpness of end-point after boiling is thus ascribed to the rapid and complete solution of this colloidal material in the hot solution.

The cerous perchlorate content of the cell solutions was obtained as the difference between the total cerium and ceric contents. The total cerium content was determined by titration after complete oxidation of the cerous salt with ammonium persulfate, using silver nitrate as a catalyst.[9] The titration with ferrous sulfate was made under the same conditions as those described in its standardization against ceric sulfate.

The Voltaic Cell.—The cell was of the rocking type which has proved most satisfactory in potential measurements in this Laboratory.[10,11] It was placed in a water thermostat whose temperature was controlled to 25 ± 0.01°. Each half cell was provided with two electrodes. This afforded a check on the equilibrium attained in the cell, for a total of four different pairs could be used in taking readings, and agreement between these four readings should indicate equilibrium. All electrodes were made of platinum foil (1 × 1.5 cm.) welded to platinum wire, to which a length of copper wire had been silver soldered. A soft glass tube was slipped over the wire and sealed to the platinum wire.

The electrodes for the hydrogen half cell were cleaned in aqua regia and platinized in a 2% chloroplatinic acid solution. They were replatinized whenever the difference between the two electrodes exceeded 0.01 millivolt.

The electrodes for the cerium half cell were made of bright platinum. They were prepared by cleaning in hot aqua regia, then in boiling water, and finally placing them in a solution of the ceric perchlorate for about a week. After this treatment they were in equilibrium with the solution in which they had been in contact, and came to equilibrium quickly with all other solutions in which they were placed thereafter. The difference between them was always less than 0.2 millivolt.

Method of Making Measurements.—For measurement of the electromotive force, a Leeds and Northrup Type K potentiometer was used in connection with a Leeds and Northrup high sensitivity galvanometer. An Eppley

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(7) Walden, Hammett and Chapman, THIS JOURNAL, **55**, 2649 (1933).

(8) G. F. Smith, G. F. Smith Chem. Co. Publication, 1938, p. 6.

(9) Willard and Young, THIS JOURNAL, **50**, 1322, 1379 (1928).

(10) Sherrill and Haas, *ibid.*, **58**, 952 (1936).

(11) Schumb, Sherrill and Sweetser, *ibid.*, **59**, 2360 (1937).

standard cell was used as the potential standard. It was placed inside a metal container in the thermostat, and was standardized against the laboratory standard cell.

The potentials to be measured were usually above the range of the potentiometer (0 to 1.6 v.). Therefore, a second standard cell of the Weston type was prepared and introduced into the circuit in opposition to the cell whose electromotive force was to be measured. This reduced the total potential to a value well within the range of the potentiometer. The Weston cell was so connected that its electromotive force could be determined separately from that of the combination. Thus, the electromotive force of the cell under measurement was obtained by adding the electromotive force of the "bucking" cell to that of the combination. In all determinations the sensitivity was 0.01 millivolt, the smallest division which could be read on the potentiometer.

Before making a run the cell was washed and dried thoroughly. The acid solution was placed in the trap and saturator of the cell, and enough of it was placed in the main body of the cell to cover about two-thirds of the hydrogen electrodes and to make contact with the cerium half-cell. The hydrogen electrodes and the dry cerium half-cell, with its stopper firmly in place, were introduced, and the whole assembly was placed in the rocking arm in the thermostat. The rocking was started after connecting the cell with the hydrogen generator.

The cell solutions containing the cerium salts were prepared as follows. About 45 ml. of the previously analyzed ceric perchlorate cell solution was weighed out into a glass-stoppered flask. When it was desired to change the ratio of ceric to cerous salt concentration, from 1 to 6 drops of a hydrogen peroxide solution of a suitable concentration were added to the flask and it was weighed again. Thus the changes in concentration due to dilution could easily be calculated. The flask containing the cerium salt solution was then placed in the thermostat to come to the temperature of the bath. After standing for half an hour in the thermostat, the solution was pipetted into the cerium half-cell. The electrodes were washed with some of the cell solution, placed in the cell, and measurements of the potential were made at about half-hour intervals until the end of the run.

The measured potential rose to a maximum value within half an hour, and thereafter dropped gradually at the rate of about 0.1 millivolt an hour on the average. Readings were continued every half hour for a period of one-half to three hours. Immediately after the final reading the atmospheric pressure was recorded and the cerium cell solution was analyzed for its ceric perchlorate content. Two determinations were made except when its concentration was so small that the total amount of solution was required to obtain an accurate determination.

The initial rise in potential was due to the gradual attainment of equilibrium in the cell. The subsequent fall in potential was attributed to the spontaneous reduction of the ceric perchlorate previously mentioned. A gold electrode was tried with a similar decrease in the potential.

If, as seems to be the case, the irreversible reaction, $4Ce(ClO_4)_4 + 2H_2O = 4Ce(ClO_4)_3 + HClO_4 + O_2$, is accelerated in the presence of the platinum electrodes, then the concentration of ceric salt is smaller, and that of the cerous salt greater, in the diffusion layer at the electrode than in the body of the solution. With the rocking type of cell employed, such concentration differences are probably small, and were assumed to be negligible in the steady state attained after the potential had reached its final value.

Results of Measurements

The results of the different series of measurements are recorded in Table I, in which all but two of the columns are self-explanatory. The values of the electromotive force recorded under the heading E correspond to a hydrogen pressure of 1 atm. at the electrodes. They were calculated from the observed values by adding the correction term $0.05915 \log 1/p^{1/2}$, in which the partial pressure p of the hydrogen was obtained by subtracting from the observed atmospheric pressure the vapor pressure of water in the perchloric acid solutions as determined by Pearce and Nelson.[12] The values of E^0_f recorded in the last column require a more detailed explanation.

It will be noted that the concentration of perchloric acid in the hydrogen half cell c_1 is not always exactly the same as the concentration of perchloric acid in the cerium half cell c_2. The same applies to the concentrations of sodium perchlorate in the third series of measurements. Therefore, it will be more convenient to treat the potential of the actual cell as the sum of the potentials of the two hypothetical cells given below

$$\text{Pt} + H_2(1\text{ atm.}).\ HClO_4(c_1\text{ w. f.}) + NaClO_4(c_5\text{ w. f.}),\ NaClO_4(c_6\text{ w. f.}) + HClO_4(c_2\text{ w. f.}).\ H_2(1\text{ atm.}) + \text{Pt}$$

and

$$\text{Pt} + H_2(1\text{ atm.}),\ HClO_4(c_2\text{ w. f.}) + NaClO_4(c_6\text{ w. f.}).\ HClO_4(c_2\text{ w. f.}) + NaClO_4(c_6\text{ w. f.}) + Ce(ClO_4)_3(c_3\text{ w. f.}) + Ce(ClO_4)_4(c_4\text{ w. f.}),\ \text{Pt.}$$

The concentrations of the components perchloric acid and sodium perchlorate in the second cell are constant throughout, and therefore the liquid potential approaches zero as the total cerium concentration $(c_3 + c_4)$ approaches zero. It is the electromotive force of this second cell which is later considered from a theoretical point of view in the interpretation of the results.

The potential for the first cell is given by the equation

$$E_1 = 0.05915 \log c_2/c_1 + E_L \qquad (1)$$

in which E_L, the liquid potential between the two hydrogen half cells, is given by Henderson's formula

$$E_L = 0.05915 \frac{\Sigma_i(c_{iA} - c_{iB})\Lambda_{jo}}{\Sigma_i(c_{iA} - c_{iB})z_i\Lambda_{io}} \log \frac{\Sigma_i c_{iA} z_i \Lambda_{io}}{\Sigma_i c_{iB} z_i \Lambda_{io}} \qquad (2)$$

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(12) Pearce and Nelson, THIS JOURNAL, **55**, 3075 (1933).

TABLE I

Run	c_1	c_2	c_5	c_6	$c_3 + c_4$	Ratio c_4/c_3	E	E_f^0
				Series 1, Temp. 25°				
Ia	2.4427	2.3855	0.0000	0.0000	0.010137	1.8541	1.71754	1.72433
Ib	2.4427	2.3828	.0000	.0000	.010118	0.88593	1.70089	1.72651
IIa	1.6353	1.6310	.0000	.0000	.009733	.95403	1.69983	1.71362
IIb	1.6353	1.6297	.0000	.0000	.009727	.48981	1.68416	1.71506
IIIa	0.8071	0.8024	.0000	.0000	.009983	5.4531	1.73219	1.68301
IIIb	.8071	.8036	.0000	.0000	.009975	1.9312	1.70970	1.68718
IIIc	.8071	.8038	.0000	.0000	.009966	1.3351	1.70110	1.68810
IIId	.8071	.8048	.0000	.0000	.009957	0.66255	1.68456	1.68957
IVa	.4800	.4765	.0000	.0000	.010234	5.4243	1.72872	1.66630
IVb	.4800	.4773	.0000	.0000	.010224	2.5549	1.71137	1.66832
IVc	.4800	.4784	.0000	.0000	.010214	1.3304	1.69618	1.66994
IVd	.4800	.4793	.0000	.0000	.010207	0.83480	1.68530	1.67106
IVe	.4800	.4818	.0000	.0000	.010187	.11054	1.63674	1.67453
Va	.19841	.19460	.0000	.0000	.010073	12.612	1.73307	1.62606
Vb	.19841	.19542	.0000	.0000	.010065	4.8654	1.71412	1.63157
Vc	.19841	.19649	.0000	.0000	.010056	2.4088	1.69824	1.63394
Vd	.19841	.19731	.0000	.0000	.010048	1.5620	1.68792	1.63483
Ve	.19841	.19855	.0000	.0000	.010035	0.85455	1.67367	1.63617
Vf	.19841	.20159	.0000	.0000	.010011	.12143	1.62629	1.63917
				Series 2, Temp. 25°				
VIa	.5384	.4856	.0000	.0000	.07045	2.9915	1.70286	1.65702
VIb	.5384	.4961	.0000	.0000	.07040	1.4632	1.68752	1.66042
VIc	.5384	.5091	.0000	.0000	.07037	0.68799	1.67207	1.66482
VId	.5384	.5218	.0000	.0000	.07032	.28376	1.65402	1.66994
VIIa	.5384	.5170	.0000	.0000	.03471	1.6116	1.69402	1.66516
VIIb	.5384	.5234	.0000	.0000	.03468	0.72685	1.67691	1.66872
VIIc	.5384	.5310	.0000	.0000	.03469	.26145	1.65498	1.67330
VIId	.5384	.5339	.0000	.0000	.03463	.10242	1.63410	1.67660
VIIIa	.5384	.5330	.0000	.0000	.009890	1.2407	1.69353	1.67192
VIIIb	.5384	.5342	.0000	.0000	.009882	0.62134	1.67807	1.67425
VIIIc	.5384	.5352	.0000	.0000	.009873	.30268	1.66143	1.67613
VIIId	.5384	.5362	.0000	.0000	.009865	.09587	1.63352	1.67767
				Series 3, Temp. 25°				
IXa	1.2969	1.2966	.0000	.0000	.009616	.87155	1.69498	1.70519
IXb	1.2969	1.2980	.0000	.0000	.009610	.31284	1.67129	1.70783
IXc	1.2969	1.2985	.0000	.0000	.009597	.11373	1.64693	1.70948
Xa	0.8021	0.8037	.4881	.4881	.009578	.68686	1.68732	1.69144
Xb	.8021	.8047	.4881	.4877	.009567	.37024	1.67302	1.69250
Xc	.8021	.8055	.4881	.4873	.009562	.13079	1.64790	1.69455
XIa	.3134	.3147	.9709	.9709	.009531	.92282	1.68674	1.65903
XIb	.3134	.3155	.9709	.9700	.009523	.44527	1.67040	1.66143
XIc	.3134	.3168	.9709	.9690	.009512	.16640	1.64752	1.66388

where c_i is the concentration of the i'th ionic species, z_i is its charge, and Λ_{io} is its limiting conductance which is reckoned negative for an anion. The subscripts A and B refer to the left and right hand sides of the cell, respectively. Activity coefficients have been neglected in the derivation and use of this equation, it being assumed that the differences in concentration of the species were so slight that the activity coefficients were constant in the two half cells.

The limiting values used for the ion conductances were those tabulated in Landolt–Börnstein:[13]

$$\Lambda_{\mathrm{Na}0} = 50.10 \quad \Lambda_{\mathrm{H}0} = 349.7 \quad \Lambda_{\mathrm{ClO_4}0} = -68$$

The potential of the second cell is given by the equation

$$E_2 = E^0 + 0.05915 \log c_4/c_3c_2 + 0.05915 \log \gamma_4/\gamma_3\gamma_2 + E_L \tag{3}$$

It should be pointed out here that the activity coefficients γ_3, γ_4 and γ_2 are the stoichiometric

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[13] Landolt–Börnstein, "Tabellen," Part 3, p. 2144 (1936 ed.).

activity coefficients of the components $Ce(ClO_4)_4$, $Ce(ClO_4)_3$, and $HClO_4$ which are involved in the reaction of the second cell, and are not to be confused with the activity coefficients of any particular ionic species such as Ce^{++++}, Ce^{+++}, and H^+. Accordingly, E^0 is the molal potential of the cell reaction referred to the components rather than to any particular ionic species. The liquid potential E_L' arises from the presence of the cerium salts in the cerium half cell.

Since neither the activity coefficients nor the liquid potential appearing in Equation 3 are known, it is convenient to introduce a new quantity E_f^0 as defined by the equation

$$E_f^0 = E^0 + 0.05915 \log \gamma_4/\gamma_3\gamma_2 + E_L' \qquad (4)$$

Then, by combining Equations 3 and 4, there results

$$E_2 = E_f^0 + 0.05915 \log c_4/c_3c_2 \qquad (5)$$

The quantity E_f^0 will be called the formal potential since it is calculated from the formalities of the components rather than their activities. From the relation $E = E_1 + E_2$, it follows that

$$E_f^0 = E - 0.05915 \log \frac{c_4}{c_3c_1} - E_L \qquad (6)$$

Values of the formal potential calculated from Equations 2 and 6 for each of the three series of measurements are recorded in Table I. Such values for any one of the separate runs vary appreciably with the ratio c_4/c_3 of the ceric to cerous salt concentrations. This variation was unexpected, and cannot be accounted for by any obvious chemical effects, such as hydrolysis or the formation of complex anions. The results were interpreted on the basis of the following considerations.

In the second series of measurements the three runs were made at as nearly the same acid concentration as possible, but at different total cerium concentrations in order to determine by extrapolation the value of the formal potential corresponding to cerium salt concentration of zero.

The results of this series are shown in Fig. 1 by three curves, one for each run. In each case values of the formal potential are plotted against the fraction of the total cerium present in the ceric state of oxidation. It will be seen from this figure that the change in the formal potential E_f^0 with the fraction of cerium in the ceric state becomes much less marked as the total cerium salt content decreases. Furthermore the curves for the separate runs made at different total cerium salt concentrations all seem to meet at a single point, where the fraction of cerium in the ceric state is zero.

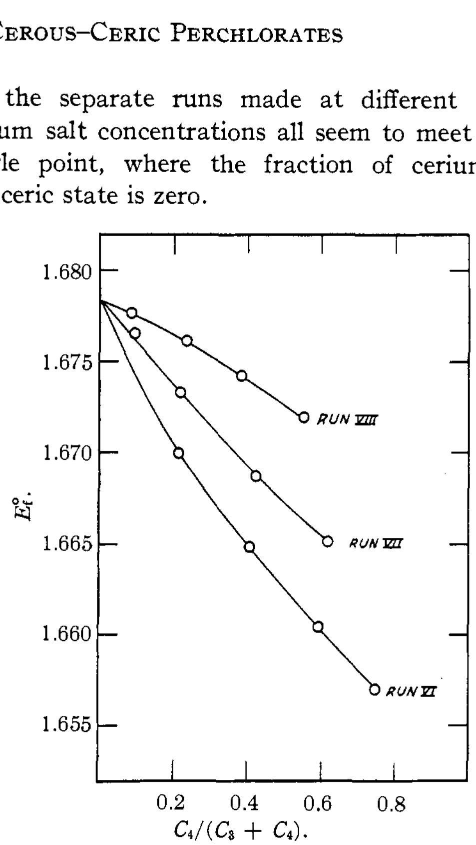

Fig. 1.

In considering any one of the three curves, it should be noted that neither the total cerium salt concentration nor the acid concentration is held exactly constant. This is due to the fact that the added hydrogen peroxide not only dilutes the solution but also reduces the ceric perchlorate with the formation of an equivalent quantity of perchloric acid. The dilution effect is, however, so small that the total cerium salt concentration remains almost constant throughout any one of the three runs. The perchloric acid concentration c_2 varies appreciably, and for each run approaches a definite value as the fraction of the cerium in the ceric state of oxidation approaches zero. This limiting value of c_2 was found for each run by plotting values of c_2 in the solution against the fraction of cerium in the ceric state and extrapolating the corresponding curve to a point where that fraction is zero.

The experiments were so planned that the limiting values of the acid concentration c_2 for the three runs of this series are all equal. The corresponding limiting values of the formal potential E_f^0 are shown in the figure to be equal, and therefore independent of the total cerium salt concentration. Since the liquid potential E_L' in the cell, H_2 (1 atm.), $HClO_4(c_2)$, $HClO_4(c_2)$ +

$Ce(ClO_4)_3(c_3) + Ce(ClO_4)_4(c_4)$, Pt, approaches zero as the total cerium salt concentration is progressively reduced, this extrapolated value of E_f^0 may be assumed to be equal to the formal potential of the cell reaction, $1/2H_2(g) + Ce(ClO_4)_4 = Ce(ClO_4)_3 + HClO_4$ in a perchloric acid solution of concentration c_2 containing cerous and ceric perchlorate at such low concentrations that the ionic strength of the solution may be considered to be determined by the acid alone.

In order to confirm this assumption plots were made of values of E_f^0 interpolated from the graphs in Fig. 1, against the square root of the total cerium salt content of the solution for several fixed values of the fraction of cerium in the ceric state. As shown in Fig. 2 lines drawn through the separate values converge and, without undue prejudice, can be made to meet at a point where the total cerium content is zero and where the potential has the same value as the intersection of the previous curves.

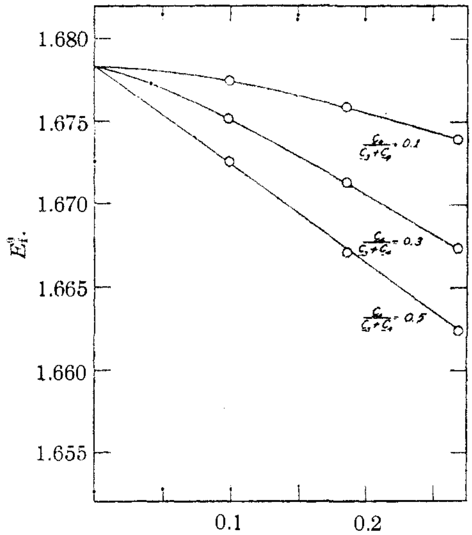

Fig. 2.

On the basis of these findings, although measurements at different total cerium salt concentrations were not carried out in the other series of measurements, it was assumed that the value approached by the formal potential as the fraction of the total cerium present as ceric salt approaches zero is the limiting value corresponding to a total cerium salt concentration of zero and to concentrations of perchloric acid and sodium perchlorate obtained by the method of extrapolation previously described. Such extrapolated values of the formal potential E_f^0 (extr.) and of the corresponding concentrations of perchloric acid and sodium perchlorate are recorded in Table II for the separate runs of all three series of measurements.

TABLE II

Basis for Calculation of E_1^0:
$K = (Ce(OH^{++})_2)(H^+)/(CeOH^{+++}) = 0.6$

Run	c_2 (extr.)	c_6 (extr.)	E_f^0 (extr.)	$E_1^{0'}$	$E_2^{0'}$	E_1^0
V	0.2025	0.00	1.6400	1.6810	1.7220	1.7164
IV	.4826	.00	1.6755	1.6942	1.7129	1.7150
VI–VIII	.5368	.00	1.6783	1.6943	1.7103	1.7136
III	.8075	.00	1.6930	1.6985	1.7040	1.7128
IX	1.299	.00	1.7107	1.7040	1.6973	1.7138
II	1.627	.00	1.7180	1.7055	1.6930	1.7136
I	2.385	.00	1.7309	1.7086	1.6863	1.7144
XI	0.3180	.9681	1.6659	1.6953	1.7247	(1.7225)
X	0.8060	.4869	1.6958	1.7013	1.7069	(1.7156)

A plot of these extrapolated values of the formal potential against the perchloric acid concentration is shown in Fig. 3. It will be noted that there is a considerable change in the potential with the acid concentration, indicating that the third term in Equation 4, the one containing the activity coefficients, is greatly affected by the concentration of the acid.

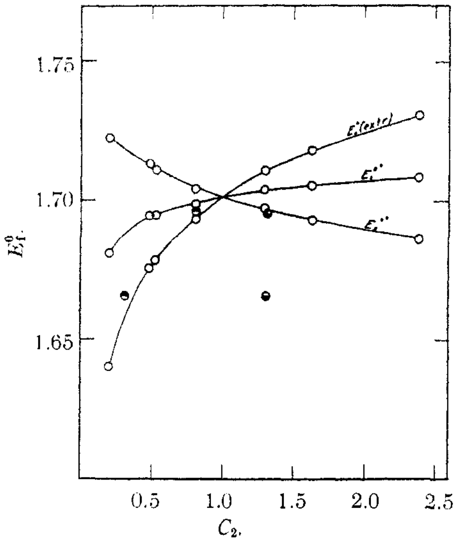

Fig. 3.—○, Series 1 and 2; ◓, Series 3, E_f^0 (extr.) *vs.* C_2; ◒, Series 3, E_f^0 (extr.) *vs.* $C_2 + C_6$.

Interpretation of Results

It has just been pointed out that the observed change in the formal potential of the cell reaction with the concentration of the perchloric acid is caused by the effect of this acid on the stoichiometric activity coefficients. These activity coefficients of the components of the cell solutions are largely dependent on the equilibrium concentrations of the ionic species in which the oxidized and reduced forms of cerium exist. Hydrolysis and the formation of complex anions are the main factors to be considered in determining what these ionic species are.

Hydrolysis of the trivalent cerous ions in the presence of the perchloric acid at relatively high concentrations in the cell solutions is probably negligible. The extent to which cerous ions react with perchlorate ions to form complex anions is also probably small, even under the favorable conditions of relatively high concentrations of the perchlorate ion. The tendency for hydrolysis of the tetravalent ceric ions is, on the other hand, so great that stepwise hydrolysis with formation of $CeOH^{+++}$, $Ce(OH)_2^{++}$, . . . is probably appreciable. Similarly, the tendency of the ceric ions, and the hydrolyzed ions to react with the perchlorate ions at relatively high concentration may be large enough to form complex anions of the types

$$Ce(ClO_4)^{x-}_{4+x},\ CeOH(ClO_4)^{x-}_{3+x},\ \ldots$$

in appreciable amount.

The ionic species of cerium in the cell solutions predicted by these *a priori* considerations are accordingly, —Ce^{+++}, Ce^{++++}, $CeOH^{+++}$, $Ce(OH)_2^{++}$, . . ., $Ce(ClO_4)^{x-}_{4+x}$, $CeOH(ClO_4)^{x-}_{3+x}$, . . . In the interpretation of the results which follows, the attempt is made to determine which of these ionic species are present in predominating amounts.

A comparison is made in Fig. 3 of the results of the first two series with those of the third in order to judge of the extent to which complex formation takes place. In this figure values of the formal potential E^0_f (extr.) are plotted against the acid concentration c_2 for the first two series (Runs I–IX), and a smoothed curve is drawn through the points, indicated by circles. For the third series (Runs X–XI), in which the solutions contained added sodium perchlorate at concentration c_6, the values of the potential were plotted not only against the concentration c_2 of the hydrogen ion, but also against that, $c_2 + c_6$, of the perchlorate ion. These two pairs of points are represented on the figure by half-shaded circles. The first pair deviate only slightly from the smoothed curve, whereas the second pair show large deviations. The results therefore show that the formal potential is a function of the concentration of the hydrogen ion, and that it is practically independent of that of the perchlorate ion. This is strong evidence that the extent to which complex anions are formed is small enough to be considered negligible.

The results might also be explained by the assumption that both cerous and ceric ions form complex ions with the same ratio of perchlorate to cerium. This possibility seems remote.

The treatment of the effect of hydrolysis on the electromotive force of the cell is simplified by the conclusion just reached that the tetravalent cerium in the cell solution exists only as the ionic species Ce^{++++}, $CeOH^{+++}$, $Ce(OH)_2^{++}$, . . . in proportions determined by the equilibrium conditions of the reactions written for the various stages of the hydrolysis.

It may be recalled that the electromotive force of the cell investigated was considered to be equal to the sum of the electromotive force of two cells. The limiting value E_2 of the electromotive force of the second cell, corresponding to a reduction of the cerium salt concentrations in the cell to zero, is very simply related to the molal potential of any one of the three cell reactions

$$^1/_2H_2(g) + Ce^{++++} = Ce^{+++} + H^+$$
$$^1/_2H_2(g) + CeOH^{+++} = Ce^{+++} + H_2O$$
$$^1/_2H_2(g) + Ce(OH)_2^{++} + H^+ = Ce^{+++} + 2H_2O$$

The quantitative relations are expressed by the following equations, in which the molal potentials of the three cell reactions are designated E^0, E^0_1, and E^0_2, respectively.

$$E_2 = E^0 - 0.05915 \log \frac{(Ce^{+++})(H^+)}{(Ce^{++++})} \times \frac{\gamma_{Ce^{+++}}\gamma_{H^+}}{\gamma_{Ce^{++++}}}$$
$$E_2 = E^0_1 - 0.05915 \log \frac{(Ce^{+++})}{(CeOH)^{+++}} \times \frac{\gamma_{Ce^{+++}}}{\gamma_{CeOH^{+++}}}$$
$$E_2 = E^0_2 - 0.05915 \log \frac{(Ce^{+++})}{(Ce(OH)_2^{++})(H^+)} \times \frac{\gamma_{Ce^{+++}}}{\gamma_{Ce(OH)_2^{++}}\gamma_{H^+}}$$

In order to judge of the extent of the hydrolysis, values of these three constants characteristic of the cell reactions were calculated from the formal potential E^0_f (extr.) on the basis of three limiting assumptions—first, no hydrolysis of the ceric ions, second, complete hydrolysis with formation of $CeOH^{+++}$ and, third, complete hydrolysis with formation of $Ce(OH)_2^{++}$. These constants, now designated $E^{0\prime}$, $E^{0\prime}_1$, and $E^{0\prime}_2$ as a means of indicating the limiting assumptions, are related to the formal electrode potential by the following equations

$$E^{0\prime} = E^0_f(\text{extr.}) + 0.05915 \log \frac{\gamma_{Ce^{+++}}\gamma_{H^+}}{\gamma_{Ce^{++++}}}$$

$$E_1^{0\prime} = E^0\,(\text{extr.}) - 0.05915 \log c_2 + 0.05915 \log \frac{\gamma_{\text{Ce}^{+++}}}{\gamma_{\text{CeOH}^{+++}}}$$

$$E_2^{0\prime} = E^0\,(\text{extr.}) - 0.05915 \log c_2^2 + 0.05915 \log \frac{\gamma_{\text{Ce}^{+++}}}{\gamma_{\text{Ce(OH)}_2^{++}}\gamma_{\text{H}^+}}$$

The values of $E_1^{0\prime}$ and $E_2^{0\prime}$ recorded in the fifth and sixth columns of Table II, and plotted in Fig. 3, were calculated from the formal potential E_f^0 (extr.) at different concentrations c_2 (extr.) of perchloric acid assuming the activity coefficients of the individual ions to be unity. Values of the molal potential $E^{0\prime}$ calculated on this same basis are identical with the formal potential E_f^0 (extr.).[14] As shown in Fig. 3, the values of $E_1^{0\prime}$, like those of $E^{0\prime}$, increase with the acid concentration c_2, but at a less rapid rate. The values of $E_2^{0\prime}$ decrease as the acid concentration is increased.

These effects are most simply explained by assuming complete hydrolysis of the ceric ions to form two ions CeOH^{+++} and Ce(OH)_2^{++} in proportions determined by the equilibrium conditions of the reaction $\text{CeOH}^{+++} + \text{H}_2\text{O} = \text{Ce(OH)}_2^{++} + \text{H}^+$. It follows from these assumptions that the sum, $(\text{CeOH})^{+++} + (\text{Ce(OH)}_2^{++})$, of the concentrations of these two ions is equal to c_4 the total ceric salt concentration, and that the concentration ratio $(\text{Ce(OH)}_2^{++})/(\text{CeOH})^{+++}$ is given in terms of the equilibrium constant K by the mass-action expression

$$\frac{(\text{Ce(OH)}_2^{+++})}{(\text{CeOH}^{+++})} = \frac{K}{(\text{H}^+)} \times \frac{\gamma_{\text{CeOH}^{+++}}}{\gamma_{\text{Ce(OH)}_2^{++}}\gamma_{\text{H}^+}}$$

If for practical purposes all activity coefficients are considered to be unity, the following expressions for the molal potentials E_1^0 and E_2^0 in terms of the equilibrium constant K and the calculated values of $E_1^{0\prime}$ readily can be derived.

$$E_1^0 = E_1^{0\prime} + 0.05915 \log (1 + K/c_2)$$
$$E_2^0 = E_1^0 - 0.05915 \log K$$

It was found possible to deduce fairly constant values of the molal potential E_1^0 by a suitable choice of the equilibrium constant K. Thus, the values of E_1^0 recorded in the last column of Table II were based on the assumption that $K = 0.6$. In choosing this value for the equilibrium constant, runs X and XI, which contained added perchlorate, were disregarded. The recorded values for the other runs are very nearly constant for the range of acid concentration c_2 from 0.54 to 1.6 w. f., but show a trend both at the lower and the higher concentrations of acid. The trend at the lower acid concentrations may be attributed to the incipient influence of the reaction, $\text{Ce(OH)}_2^{++} + \text{H}_2\text{O} = \text{Ce(OH)}_3^{+} + \text{H}^+$, corresponding to the third stage of the hydrolysis, and that at the higher concentrations to the repression to a slight extent of the first stage of the hydrolysis of the ceric ions. Accordingly, the average of the four values for this middle range of acid concentration, $E_1^0 = 1.7134$ volts, may be regarded as the molal potential of the ionic reaction $1/2\text{H}_2(\text{g}) + \text{CeOH}^{+++} = \text{Ce}^{+++} + \text{H}_2\text{O}$. The corresponding molal potential of the ionic reaction $1/2\text{H}_2(\text{g}) + \text{Ce(OH)}_2^{++} + \text{H}^+ = \text{Ce}^{+++} + 2\text{H}_2\text{O}$ is $E_2^0 = 1.7265$ volts. These potentials are evidently equal to the molal oxidation potentials of the electrode reactions, $\text{CeOH}^{+++} + \text{H}^+ + E^- = \text{Ce}^{+++} + \text{H}_2\text{O}$ and $\text{Ce(OH)}_2^{++} + 2\text{H}^+ + E^- = \text{Ce}^{+++} + 2\text{H}_2\text{O}$, referred to the molal hydrogen electrode potential as zero.

It should be pointed out that all three of the constants, K, E_1^0, and E_2^0, were evaluated in terms of the ion-concentrations, since the activity coefficients of all the ionic species were assumed to be unity. The errors introduced by this assumption are reduced by the fact that the ratios of the activity coefficients of the ionic species which appear in the exact expressions for these constants are more nearly equal to unity than are the individual values themselves. For example, in the exact expression for E_1^0 in terms of ion-activities, the activity coefficients $\gamma_{\text{Ce}^{+++}}$ and $\gamma_{\text{CeOH}^{+++}}$ of the triply charged Ce^{+++} and CeOH^{+++} ions are nearly equal, and therefore, although the individual values of these coefficients differ greatly from unity, the ratio of $\gamma_{\text{Ce}^{+++}}$ to $\gamma_{\text{CeOH}^{+++}}$ does not.

Summary

Measurements were made at 25° of the electromotive force of cells in which the reaction, written in terms of the components of the cell solutions, is $1/2\text{H}_2(\text{g}) + \text{Ce(ClO}_4)_4 = \text{Ce(ClO}_4)_3 + \text{HClO}_4$. By this means the formal oxidation potential of cerous–ceric perchlorates in solutions of perchloric acid, containing also in two cases sodium perchlorate, was determined at a series of acid concentrations ranging from 0.2 to 2.4 weight formal. This potential was found to vary with the concentration of the hydrogen ion from 1.6400 to 1.7310 volts, and to be practically independent of that of the perchlorate ion.

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(14) Similarly the molal potentials $E_1^{0\prime}$ and $E_2^{0\prime}$ calculated in this way may be regarded as formal potentials dependent on the choice of $\text{CeOH(ClO}_4)_3$ or of $\text{Ce(OH)}_2(\text{ClO}_4)_2$ as the component to represent the tetravalent cerium.

The results seem to indicate that neither cerous nor ceric perchlorate reacts with the perchloric acid, that cerous perchlorate is not hydrolyzed in the presence of the perchloric acid, but that ceric perchlorate is hydrolyzed in stages with formation of two ions $CeOH^{+++}$ and $Ce(OH)_2^{++}$ in proportions to satisfy the equilibrium conditions of the reaction, $CeOH^{+++} + H_2O = Ce(OH)_2^{++} + H^+$. The equilibrium constant of this reaction was estimated to be 0.6, and the molal oxidation potentials of the electrode reactions $CeOH^{+++} + H^+ + E^- = Ce^{+++} + H_2O$ and $Ce(OH)_2^{++} + 2H^+ + E^- = Ce^{+++} + 2H_2O$ were found to be 1.7134 and 1.7265 volts, respectively.

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[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY. No. 915]

The Molecular Structure of Ozone

BY W. SHAND, JR., AND R. A. SPURR

Ozone has interested many investigators, but, because of the difficulties of preparation of pure ozone, its great reactivity, and its explosive nature, no complete structure determination has yet been reported. Table I gives a summary of some of the structural parameters and oscillational frequency assignments which have been suggested for ozone. The present work was suggested by the idea that the purity of gas required for an electron diffraction determination is not so great as for spectroscopic work, and it seemed to us that a purity of 95% or better could readily be obtained in a suitable apparatus.

TABLE I

Author	Year	Angle	Distance	Fundamental frequencies[1] ν_1	ν_2	ν_3
G. N. Lewis[2]	1923	Like SO_2				
S. L. Gerhard[3]	1933	*ca.* 60°		528	1033	1355
R. M. Badger and L. Bonner[4]	1933	*ca.* 120°		1050	440	1355
W. S. Benedict[5]	1933	*ca.* 122°	1.29 ± 0.1 Å.	1046	760	1355
Hettner, *et al.*[6]	1935	38°		2105	1037	710
Penney and Sutherland[7]	1936	127 ± 20°	1.23 Å.	1037	710	1740
Smyth and Lewis[8]	1939	140°	1.13 Å.			
Present Work	1942	127 ± 3°	1.26 ± 0.02 Å.			

Experimental.—The ozone was prepared by the method of Karrer and Wulf[9] using a silent electric discharge and an all-Pyrex glass apparatus attached directly to a glass nozzle in the electron diffraction apparatus described by Brockway.[10] A mixture of Apiezon M and graphite, which did not seem to be attacked by ozone, was used as a stopcock lubricant. Tank oxygen was passed through the ozonizer and a light blue mixture of oxygen and ozone was collected in a large trap cooled in liquid air. This mixture was fractionated into a smaller storage trap at hourly intervals until several ml. of blue-black ozone had accumulated for the final purification. This was fractionated into the large trap again and the system was pumped down until the pressure, indicated by a Pirani gage on the electron diffraction apparatus, was negligible. Enough ozone was usually made to fill a 300 ml. storage bulb at 1 atm. pressure.

It is important to establish the purity of the preparation. Oxygen (b. p. −183°), nitric oxide (b. p. −152°), and the other oxides of nitrogen (b. p. above 0°) boil at temperatures sufficiently removed from the boiling point of ozone (−112°) that they should be nearly completely removed by the fractionation and pumping off of the residual gases. After each set of pictures the

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(1) ν_1 is essentially the symmetrical stretching frequency, ν_2 the symmetrical bending frequency, and ν_3 the antisymmetrical stretching frequency.

(2) G. N. Lewis, "Valence and the Structure of Molecules," Chemical Catalog Co., New York, N. Y., 1923, p. 130.

(3) S. L. Gerhard, *Phys. Rev.*, **42**, 622 (1933).

(4) R. M. Badger and L. G. Bonner, *ibid.*, **43**, 305 (1933).

(5) W. S. Benedict, *ibid.*, **43**, 580 (1933).

(6) G. Hettner, R. Pohlman and H. J. Schumacher, *Z. Elektrochem.*, **41**, 524 (1933).

(7) W. G. Penney and G. B. B. M. Sutherland, *Proc. Roy. Soc.* (London), **A156**, 578, 654 (1936).

(8) C. P. Smyth and G. L. Lewis, THIS JOURNAL, **61**, 3063 (1939).

(9) S. Karrer and O. R. Wulf, *ibid.*, **44**, 2391 (1922).

(10) L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).