THE PARAMETERS a AND b FOR THE FORMULA $\Theta/T_B = a + bt_B$ FOR TEN COX CHART FAMILIES

Family	a	b
Phenols	0.03733	0.00296
Anilines	−.1447	.00309
Aliphatic-aromatic ketones	.4630	.000432
Aliphatic hydrocarbons (satd.)	.3262	.000795
Aliphatic hydrocarbons (unsatd.)	.3437	.000736
Aliphatic ketones	.3180	.000144
Aliphatic esters	.3547	.000936
Aliphatic acids[a]	.0943	.000281
Aliphatic alcohols	.1164	−.00353
Cyclopentanes	.3100	.0000700

[a] Not including formic acid.

The Ramsay–Young rule (equation (7)) was used in the estimation of the accuracy of the determined data in reference.[7]

Conclusions.—The Ramsay–Young rule is shown to be as accurate as the data used, and can be used for chemically unrelated compounds as well as for chemically related compounds. Dühring's rule is excellent for chemically related compounds, but for chemically unrelated compounds the error varies from 0.6–1.0°. The Θ value of the theoretical Antoine equation is shown to be either a constant for Θ/T_B, or a linear function of the normal boiling point for Θ/T_B.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Observations on the Rare Earths. LX.[1] The Ultraviolet Absorption Spectrum of the Gadolinium Ion in Aqueous Solutions

BY THERALD MOELLER AND FRANK A. J. MOSS

The ultraviolet absorption spectrum of the gadolinium ion has been reinvestigated for both aqueous chloride and perchlorate solutions under conditions of high resolution. The spectrum is characterized by eighteen absorption peaks and two definite inflections in the wave length region 2400-3150 Å. The major and most complex absorption bands lie in the range 2720-2765 A., where greater resolution than previously reported has been obtained. Absorption is essentially the same for both chloride and perchlorate solutions. For both, absorptions at 2729, 2741-2 and 2756 Å. are in accord with Beer's law to concentrations above 0.25 *M*.

Introduction

The gadolinium ion is colorless, but it is characterized by a complex absorption spectrum in the ultraviolet region, presumably because of transitions involving the 4*f* orbitals. The spectra of aqueous chloride solutions were investigated comprehensively by Prandtl and Scheiner,[2] but the photographic technique employed and the method used for expressing the results render the data obtained of little value beyond accurate positioning of the absorption maxima. More recent spectrophotometric investigations, although recording the major absorption bands and characterizing their intensities relative to each other, fail to detect certain of the more minor bands and are not in complete agreement with each other. Thus, although Prandtl and Scheiner[2] recorded wave lengths for ten bands and suggested the existence of two others, Moeller and Brantley[3,4] could find only ten for chloride solutions, and these not all at the same wave lengths given by Prandtl and Scheiner. Stewart,[5] using perchlorate solutions, reported eight bands and gave evidences for a ninth but failed to find certain ones reported by other investigators.

Lack of complete agreement between data obtained by photographic and spectrophotometric techniques is apparently due to difficulties in the resolution of closely spaced absorption bands as imposed by the Beckman instruments used in the latter studies. The major absorption bands of the gadolinium ion all lie in the relatively narrow wave length interval 2720–2765 Å. and are extremely sharp. They are difficult, therefore, to pick up and to reproduce by anything but the most exacting manual adjustment of the measuring instrument. The ±10% deviations from Beer's law noted in the vicinity of 2730 Å. have been ascribed to this difficulty.[4] Inasmuch as the Cary Automatic Recording Quartz Spectrophotometer combines excellent resolution in the ultraviolet region with an enhanced spreading out of the wave length scale through suitable combinations of scanning and chart speeds, a reinvestigation of the gadolinium spectrum with this instrument was deemed advisable. Studies with both chloride and perchlorate solutions have effected resolutions beyond those previously reported and have shown adherences of the data to Beer's relation providing the wave lengths employed are accurately fixed.

Experimental

Materials Used.—Atomic weight gadolinium oxide (Inventory No. GD-5)[6] was converted to chloride and perchlorate by treatment with the appropriate acid and evaporation to remove excess acid. Acid-free solutions were standardized by the usual oxalate precipitation procedure and diluted to 0.5 *M*. Further dilutions were made as necessary.

Absorption Spectra Measurements.—All measurements were made with the Cary Spectrophotometer. The instrument was adjusted to zero optical density with blank cells containing distilled water, and these settings were used: scanning gear, small (1.0 Å. per sec.), "Lo" position; chart drive gear, 80 driving and 40 driven (4 in. per min.);

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(1) For the preceding communication in this series, see T. Moeller and D. E. Jackson, *Anal. Chem.*, **22**, 1393 (1950).

(2) W. Prandtl and K. Scheiner, *Z. anorg. allgem. Chem.*, **220**, 112 (1934).

(3) T. Moeller and J. C. Brantley, Technical Report, Office of Naval Research Contract N6ori-71, T. O. VII, University of Illinois, September 1, 1949.

(4) T. Moeller and J. C. Brantley, *Anal. Chem.*, **22**, 433 (1950).

(5) D. C. Stewart, United States Atomic Energy Commission Declassified Document 2389, September 22, 1948.

(6) C. W. Naeser and B. S. Hopkins, THIS JOURNAL, **57**, 2183 (1935).

"slit control," scale division "10"; optical density range, 0–2.5. In all cases, 1-cm. quartz cells were used with distilled water as a reference. Measurements in the region 2400–3150 Å. were entirely reproducible with both salts both as to wave length and optical density values.

Results and Discussion

The absorption spectrum of a 0.500 M gadolinium perchlorate solution is given in Fig. 1. The spectrum of a chloride solution of the same concentration was identical except for a somewhat enhanced background. Comparison of Fig. 1 with other recorded plots of the gadolinium spectrum[4,5] indicates clearly the greater resolution obtained in the entire ultraviolet region and particularly in the 2720–2765 Å. range. A total of eighteen well-defined absorption peaks and two additional inflections indicative of other unresolved peaks can be distinguished. The wave lengths of all of these are easily ascertained and reproducible to the nearest ångström.

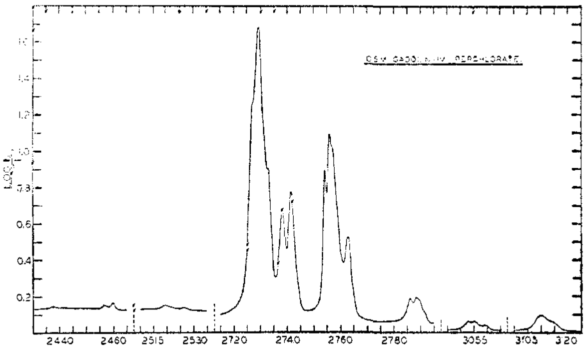

Fig. 1.—Absorption spectrum of aqueous gadolinium perchlorate solution.

Numerical data characterizing both the perchlorate and chloride spectra are summarized in Table I, together with corresponding values obtained by other workers.[2,3,4,5] Agreement among wave length values is excellent. In general, every band found by previous workers has been detected in the present investigation, and, in addition, several bands not obtained even by the photographic technique have been characterized. Agreement among molar extinction coefficients for both chloride and perchlorate solutions is quite generally good, as is also agreement between the chloride data and those obtained by Moeller and Brantley.[3] More significant differences are noted between the perchlorate data and those of Stewart.[5] These differences are not unreasonable, since all of the present data have been corrected for background absorption and are, therefore, absolute for the gadolinium ion. The enhanced resolutions effected here and the use of acid-free solutions probably contribute further to these differences.

Adherence to Beer's law was tested using solutions varying in concentrations from 0.125 to 0.500 M. From the data recorded in Table II, it is apparent that significant deviations from this relation at the major absorption peaks occur only at concentrations above 0.25 M, with chloride solutions giving smaller deviations than perchlorate solutions. For practical purposes, deviations at concentrations up to at least 0.375 M are unimportant. It follows, therefore, that gadolinium can be

TABLE I

ABSORPTION SPECTRA DATA FOR GADOLINIUM ION IN AQUEOUS SOLUTION

Present work		Moeller and Brantley[3,4]		Prandtl and Scheiner
Wave length, Å.	Molar extinction coefficient[a]	Wave length, Å.	Molar extinction coefficient	Wave length, Å.
		Gadolinium Chloride		
2438	0.03			2436
2457	.04			2457
2460	.10	2460	0.22	
2520	.06	2520	0.229	2421
2527	.04			
2727	[b]			
2729	3.20	2727	3.43	2729
2732	1.72			[c]
2738	1.15	2737	1.16	[c]
2741	1.48	2740	1.31	
2754	1.49			
2756	2.11	2755	2.04	2756
2757	[b]			
2763	0.97	2760	0.884	2762
2786	.24	2786	0.370	2791
2788	.30			
3053	.09	3052	0.127	3051
3055	.11			3055
3058	.05			
3110	.17	3109	0.207	3108
		Gadolinium Perchlorate		
		Stewart[5]		
2438	0.03	2436	0.145	
2457	.05			
2460	.08	2460	0.158	
2520	.07	2522	0.147	
2527	.03			
2727	[b]			
2729	3.20	2727	2.04	
2733	1.64			
2738	1.21			
2742	1.40			
2754	1.66			
2756	2.04	2756	1.22	
2757	[b]			
2763	0.90	2762	(0.572)[d]	
2786	.27	2785	0.204	
2788	.28			
3052	.10	3050	0.042	
3055	.10			
3059	.06			
3110	.18	3108	0.086	

[a] Calculated as $\epsilon = (\log_{10} I_0/I)/(cl)$, where c = molar concentration, l = 1 cm. [b] Inflection. [c] Indicated, but no wave length assigned. [d] Lost in adjacent 2756 Å. peak.

TABLE II

ADHERENCE OF ABSORPTION DATA TO BEER'S LAW

Concentration, mole/liter	Gadolinium chloride optical density at			Gadolinium perchlorate optical density at		
	2729 Å.	2741 Å.	2756 Å.	2729 Å.	2742 Å.	2756 Å.
0.125	0.435	0.185	0.28	0.44	0.19	0.275
.250	0.865	.375	0.55	0.87	.375	0.55
.375	1.265	.56	0.815	1.26	.54	0.785
.500	1.615	.76	1.08	1.625	.72	1.04

determined spectrophotometrically at these wave lengths providing sufficient resolution is effected.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Structure of Liquid Aluminum Chloride

BY R. L. HARRIS,[1] R. E. WOOD AND H. L. RITTER

A vacuum X-ray camera is described for obtaining diffraction patterns of liquids at high temperatures using crystal monochromatized X-rays. Diffraction patterns for fused aluminum chloride have been obtained and a radial distribution function calculated according to the method of Warren, Krutter and Morningstar. Most of the coherent scattering is due to molecular Al_2Cl_6. The structure of the Al_2Cl_6 molecule in the liquid state is deduced and agrees well with the structure determined by Palmer and Elliott from the electron diffraction of gaseous Al_2Cl_6.

The identity and disposition of the molecular and ionic species present in molten salts is of considerable interest. It would seem that the methods of X-ray diffraction might be made to yield considerable information about the interatomic geometry of such systems. Lark-Horovitz and Miller[2] have published a very brief summary of their work on molten lithium, sodium and potassium chlorides. Quantitative treatment of the molten lithium and potassium salts showed that the coördination scheme and interatomic distances in each were nearly the same as in the corresponding solid. The similarity between the time-average structure of the liquid and the crystal structure of the solid is, of course, restricted to the immediate vicinity of each atom. These two structures were treated in the X-ray analysis as assemblages of single scattering species; the X-ray scattering of Li^+ being taken as negligible in comparison with Cl^-, and the isoelectronic K^+ and Cl^- being taken as identical. At that time no method was in use for treating the scattering of X-rays from assemblages of two differently scattering atoms. More recently an attack on such systems has been described by Warren, Krutter and Morningstar[3] and applied with considerable success to vitreous[4] and liquid[5] structures. These latter achievements suggest a means for studying the structure of molten salts in general.

We have applied this technique in particular to liquid aluminum chloride. The properties of this liquid are anomalous in many respects, and one might expect an elucidation of the liquid structure to provide a valuable link in understanding the anomalies. For example, the melting point[6] and molar volume[7] of solid aluminum chloride are abnormally high in comparison to the bromide and iodide, while the molar volume of the liquid chloride is about as expected. There is an unusually large decrease in density (about 45%) on melting. The electrical conductivity of solid aluminum chloride increases in the normal rapid fashion as the melting point is approached but falls abruptly nearly to zero on melting.[7] These facts seem to indicate that aluminum chloride undergoes a fundamental and gross change in structure when it melts. Ketelaar, MacGillavry and Renes[8] have shown the crystal structure of aluminum chloride to be based on an ionic bonding scheme. A change to covalent bonding in the liquid would explain these anomalies. Gerding and Smit[9] found their Raman data on liquid aluminum chloride suggestive of discrete Al_2Cl_6 molecules. Just above the sublimation point, moreover, aluminum chloride vapor has been found to consist of Al_2Cl_6 molecules, both from vapor density measurements[10] and by electron diffraction.[11] The fact that the Trouton constant for fused aluminum chloride is normal[12] strongly suggests that the liquid also consists of discrete Al_2Cl_6 molecules. The present research confirms this supposition.

Experimental

The camera (Fig. 1) is designed for obtaining photographic records of diffraction patterns up to Bragg angles of about 85° and up to temperatures of about 900°. The tripod mount A has its plane inclined 6° below the horizontal and rotates about the vertical post B. The axis of rotation coincides with that of the holder C for the crystal monochromator. The cylindrical camera of 57.3 mm. radius carries a collimator D with pinholes 1 mm. in diameter spaced 50 mm. apart. A beam trap E helps to cut down air scattering and is fitted with a fluorescent screen backed with lead glass. The assembly carrying the heater and sample holder is supported from the camera cover. The latter is removable and joins the camera body through a gasketed seal F which permits operation in a vacuum or inert gas. The heating element is constructed by winding helically on a Lavite core G a tight helix of No. 26 nichrome wire (20 ohms). The heater is surrounded by a heavy Lavite insulator, K, and the whole assembly enclosed in a brass can, L. Cooling water is circulated through $^1/_4''$ copper tubing soldered to the outside of the can as well as to the sides and bottom of the camera body. The electrical lead to the heater is passed through a Kovar and glass tube in the lid, H. The temperature is regulated by Variac and measured by a chromel–alumel thermocouple whose junction is placed close to the sample. A monel cylinder I is placed within the heater core and carries a threaded fitting in the bottom.

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