Chemical Oxidation States of Cl and N Formed by the S34(p, n)Cl34 and O16(p, α)N13 Reactions in Crystals

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The $F_n{}^m$ tabulated by Kihara and Kotani are very simply related to the $W^{(m)}(n)$ which we presented in our publication: $W^{(m)}(n) = (2\epsilon/kT)^{1/6}F_n{}^m$. Table I exhibits typical numerical agreement in the values of the collision integrals.

TABLE I.

	$kT/\epsilon = 1$		$kT/\epsilon = 20$	
	Kihara and Kotani	Hirschfelder, Bird, and Spotz	Kihara and Kotani	Hirschfelder, Bird, and Spotz
$W^{(1)}(1)$	0.7199	0.7197	0.3320	0.3320
$W^{(1)}(2)$	1.806	1.806	0.9442	0.9439
$W^{(1)}(3)$	6.455	6.456	3.631	3.629
$W^{(2)}(2)$	1.590	1.587	0.7437	0.7432
$W^{(2)}(3)$	5.550	5.550	2.866	2.864
$W^{(2)}(4)$	25.15	25.16	13.92	13.90

This excellent agreement obtained by the two independent groups greatly increases our confidence in the accuracy of our respective tables. We are sorry that we were previously unaware of this Japanese publication.

A few values of these integrals were calculated by J. deBoer and J. Van Kranendonk,[3] and excellent agreement was obtained with their results. A few other numerical calculations were made by Rowlinson.[4]

[1] T. Kihara and M. Kotani, Proc. Phys.-Math. Soc. (Japan) 24, 76 (1942); 25, 602 (1943).
[2] Hirschfelder, Bird, and Spotz, J. Chem. Phys. 16, 968 (1948).
[3] J. deBoer and J. Van Kranendonk, Physica 14, 442 (1948).
[4] J. S. Rowlinson, J. Chem. Phys. 17, 101 (1949).

Hydrocarbon Flame Spectra*

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THE combustion of hydrocarbons has been studied intensively for many years because of its theoretical and practical interest. The spectra of hydrocarbon flames were first investigated in detail under low dispersion by Vaidya.[1] He described the appearance of a system of bands called the hydrocarbon (or ethylene) flame bands which are degraded to the red and lie between 2500 and 4100A. These bands were arranged in a vibrational scheme and it was suggested that the emitter of this system was the HCO radical. Since that time many investigations with explosion and various types of stationary hydrocarbon flames have been conducted with the result that the hydrocarbon flame bands have been reported in practically all cases of hydrocarbons burning with air, oxygen or atomic oxygen.[2]

Since most of these flame spectra were investigated with rather low dispersion instruments we have been studying the stationary flames of methane and ethylene under a variety of conditions. A 2-meter Baird grating spectrograph was employed with dispersion 4A/mm and 8A/mm in the regions 3000–4000A and 7000–9000A, respectively.

In a recent note[3] we reported the appearance of the $^1\Pi_g - ^1\Pi_u$ Deslandres-D'Azambuja band system of the C_2 molecule in the spectra of the low pressure stationary flames of ethylene and methane burning with oxygen at stoichiometric proportions. Further studies of these flames reveal, in the region 3000–4000A, bands of the $^3\Sigma_u^- - ^3\Sigma_g^-$ Schumann-Runge system of the O_2 molecule in addition to the C_2 bands mentioned above, as well as various OH and CH bands, e.g., the (0,1) OH band at 3428A and the (1,0) CH band at 3628A. The O_2 bands are stronger the higher the relative concentration of oxygen. These results are similar to those reported by one of us[4] in the $CO+O_2$ explosion flame.

At this point in our investigations we suggest the possibility that the overlapping of the various bands of the diatomic species OH, CH, C_2 and O_2 may produce, in the region 3000–4000A, what has the appearance of a system of bands heretofore ascribed to the HCO radical. Whether or not the above mentioned diatomic species account for all the band structure in this spectral region requires more detailed study.

We have also observed in emission from hydrocarbon flames the heads of the (0,0) and (1,1) bands of the $^1\Sigma_g^+ - ^3\Sigma_g^-$ atmospheric absorption system of O_2 which lie at 7594 and 7685A respectively. In addition we find the (2,0) band at 8751A of the recently discovered $^1\Pi_u - ^1\Sigma_g$ Phillips' system[5] of the C_2 molecule. Since the Phillips' bands involve the lower states of the $^1\Pi_g^1 - \Pi_u$ Deslandres-D'Azambuja and the $^1\Sigma_u^+ - ^1\Sigma_g^+$ Mulliken systems, one would expect both the Deslandres-D'Azambuja and Phillips' bands to be found together in the flame spectrum. The Mulliken bands of C_2 as well as the Fourth Positive bands of CO appear in flames of ethylene and oxygen. These bands have been observed by Gaydon[2] in the oxyacetylene flame Thus, all the known band systems of the C_2 molecule have been observed in hydrocarbon flames except the $^3\Pi_g - ^3\Pi_u$ Fox-Herzberg bands and we are now searching for the latter system which may account for some of the structure in the region 3000–4000A.

We hope in the near future to report the detailed results of these investigations as well as further studies of the hydrocarbon flame spectrum between 2500–3000A.

We wish to thank Dr. G. Herzberg and Dr. J. G. Phillips for their interest and many profitable discussions.

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[2] A. G. Gaydon, Spectroscopy and Combustion Theory (Chapman and Hall Ltd., London, 1948).
[3] G. A. Hornbeck and R. C. Herman, J. Chem. Phys. (to be published).
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[5] J. G. Phillips, Ap. J. 107, 389 (1948).

Chemical Oxidation States of Cl and N Formed by the $S^{34}(p, n)Cl^{34}$ and $O^{16}(p, \alpha)N^{13}$ Reactions in Crystals

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ALTHOUGH many studies have been made of the fate of atoms after radiative neutron capture (Szilard-Chalmers reaction), little has been done in determining the chemical fate of transmuted atoms arising from bombardment with high energy ions, especially in inorganic crystals. Libby[1] has discussed the expected fate of hot transmuted atoms in crystal lattices, and a few investigations of such processes have been made.[2]

We are extending this work of determining chemical states after bombardment of inorganic crystals with high energy ions, and wish to report our work on the chemical state of Cl and N produced by the $S^{34}(p, n)Cl^{34}$ and $O^{16}(p, \alpha)N^{13}$ reactions.

Chlorine was chosen because of the many oxidation states possibly present after bombardment: -1 (Cl^-), 0 (Cl_2), $+1$ (ClO^-), $+3$ (ClO_2^-), $+4$ (ClO_2), $+5$ (ClO_3^-), and $+7$ (ClO_4^-). Production of the higher oxidation states would presumably be favored by bombardment of crystals rich in oxygen,[3] so sulfates and peroxydisulfates were chosen as targets. Powdered anhydrous C.P. Na_2SO_4 and $K_2S_2O_8$ samples were wrapped in thin aluminum foils and bombarded with 14-Mev protons in the circulating beam of the U.C.L.A. 37-in. frequency-modulated cyclotron[4] for 30-min. periods (current ~ 1 μa). The targets showed activities with half-

lives of 10, 33, and 112 min. after the shorter-lived activities decayed out. The 33- and 112-min. activities were shown to be associated with the expected Cl^{34} and $F^{18}(O^{18}(p, n)F^{18})$; the source of the 10-min. activity was puzzling until chemical and absorption tests showed it to be the previously known[5] N^{13}. The only conceivable reaction which would lead to this activity in the targets used is $O^{16}(p, \alpha)N^{13}$. This reaction, as well as the $S^{34}(p, n)Cl^{34}$ reaction, seems not to have been reported before.

Following a bombardment the target crystals were dissolved in water, Cl^-, ClO_3^-, and ClO_4^- carriers were added, as well as F^- hold-back carrier, and a Cl^- fraction precipitated with excess Ag^+. The filtrate was treated with SO_2 or NO_2^- to reduce higher valent states, excepting ClO_4^-, to Cl^-, and a second AgCl precipitate removed. Finally, the ClO_4^- was precipitated with methylene blue.[6] All precipitates were filtered onto paper disks, dried, and mounted for counting[7] in a reproducible geometry under a Geiger-Müeller counter and scale-of-64, the 2.5- and 5.1-Mev positrons[5] being used for the detection. Typical results are shown in Table I.

TABLE I. Corrected activities of Cl fractions from $S^{34}(p, n)Cl^{34}$ reaction.

Fraction	Net activity, c/m[a] Na_2SO_4	$K_2S_2O_8$
Cl^-	13743 ± 115	1047 ± 24
ClO_3^- v	22 ± 3	0 ± 2
ClO_4^-	40 ± 3	9 ± 2

[a] Error includes only standard counting error.

These experiments indicate that essentially all of the Cl^{34} activity appears as Cl^- or in a form rapidly exchangeable with Cl^-; thermal exchange between Cl^- and ClO_2, ClO_3^-, and ClO_4^- under the given conditions has been shown[8-10] to be slow, whereas Cl^- and Cl_2 are known[11] to undergo rapid exchange. It is indeterminate whether the Cl^- exists in the crystal lattice as such or arises as a result of dissolving the crystals. The hot chlorine atom may be ejected as a neutral atom or positive ion and take up electrons before it can react with the oxygen in the crystal. Similar results have been reported[8] for the Szilard-Chalmers reaction on ClO_4^-.

An attempt was made to determine the chemical state of the N^{13}, but no quantitative results can be given. The addition of NH_4^+ carrier to the solution (chemically freed from Cl^{34} and F^{18} activities), followed by its precipitation with Nessler's reagent, carried down a moderately large, but unreproducible, fraction of the N^{13} activity. A Kjeldahl reaction experiment indicated higher oxidation states were present. The N^{13} does not exist appreciably in any volatile form in the solution inasmuch as little activity was lost when the aqueous solution was evaporated to dryness. Since it was important to know whether exchange would take place between certain oxidation states in the time required for the experiments, the exchange of NH_4^+ and NO_2^- was investigated briefly. In solutions $0.23f$ in both NH_4^+ and NO_2^-, and $0.012f$ in H^+, 3.3 ± 2.6 percent exchange was found after 92 min. at room temperature, separation being achieved by the use of Nessler's reagent.

[1] W. F. Libby, J. Am. Chem. Soc. 69, 2523 (1947).
[2] See, for example, A. H. W. Aten, Jr., Phys. Rev. 71, 641 (1947); Sherr, Muether, and White, Phys. Rev. 75, 282 (1949).
[3] Aten (see reference 2) found that the radiophosphorus produced by (n, p) or (n, α) reactions with radium-beryllium neutrons on inorganic crystals containing sulfur or chlorine tends to form phosphates in oxygen-rich crystals.
[4] We wish to thank Professor J. R. Richardson and the cyclotron crew for their co-operation in arranging the bombardments.
[5] G. T. Seaborg and I. Perlman, Rev. Mod. Phys. 20, 585 (1948).
[6] F. J. Welcher, Organic Analytical Reagents (D. Van Nostrand Company, Inc., New York, 1948), Vol. IV.
[7] Background, decay, and coincidence corrections were applied. Activities in the precipitates were shown to be due only to 33-min. Cl^{34} by decay measurements. Final filtrates were counted with a dipping counter and no residual Cl^{34} activity was found.
[8] W. F. Libby, J. Am. Chem. Soc. 62, 1930 (1940).
[9] H. Dodgen and H. Taube, J. Am. Chem. Soc. 71, 2501 (1949).
[10] We confirmed that the exchange between Cl^- and ClO_3^- and between Cl^- and ClO_4^- is very slow for our experimental conditions.
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Photo-Chemical Reduction of Water by Europium (II) Ion, and the Magnetic Susceptibilities of Europium (II) and (III) Ions

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THE slow reaction of europium (II) ion with hydrogen ion or water to-produce hydrogen and europium (III) ion has been previously reported.[1-4] Prior to an investigation of the aqueous chemistry of europium (II) ion, the study of this reaction was undertaken. It was decided to follow the course of the reaction by observing the change in magnetic susceptibility of the reaction mixture, using a Gouy balance. This method was suggested by the aforementioned work of R. A. Cooley.[4] Preliminary experiments showed that solutions 0.25 m in europium (II) chloride and about 0.3 m in hydrochloric acid were stable over periods of weeks when kept in the dark, but evolved hydrogen and changed susceptibility rapidly when exposed to bright light (either sunlight or a tungsten lamp). One other such system has been reported in the literature. Poterill, Walker, and Weiss investigated the photo-chemical reduction of water by iron (II) ion.[5]

A systematic investigation of this reaction, including the thermal reaction, has been in progress for some time. The apparatus will be described in detail in a future report. It permits the sidewise irradiation, with the 3660A line group of a 20-cm mercury arc, of a Gouy tube containing the reaction mixture and an identical tube containing a uranyl oxalate actinometer. Experiments so far have been confined to solutions 0.50 m in HCl, 0.15 m in $EuCl_2$ and 0.05 m, 1.05 m or 2.05 m in KCl, the ionic strength in these cases being 1.0, 2.0 and 3.0 respectively. Table I contains a summary of some of the results obtained thus far. It is considered that insufficient data are available to elucidate completely the mechanism and so a discussion of this will be deferred.

TABLE I. Quantum yields of photo-chemical reduction of water by europium (II) ion.*

(HCl) =0.50 m		(EuCl₂) =0.15 m		Volume =Ca 12 ml	
(1)	(2)	(3)	(4)	(5)	(6)
					Quantum yield column (4)
Expt. No.	Ionic strength of solution	Change in conc. of Eu (II)	Molecules Eu (II) oxidized	Quanta absorbed	= ——————— column (5)
14-b	1.0	0.0072	5.2×10^{19}	3.1×10^{19}	1.7 ± 0.2
14-c	1.0	0.0071	5.1×10^{19}	2.8×10^{19}	1.8 ± 0.2
16-b	2.0	0.0071	5.1×10^{19}	2.5×10^{19}	2.0 ± 0.2
17-b	3.0	0.0082	6.2×10^{19}	2.7×10^{19}	2.3 ± 0.2

* Activated by the 3660A radiation, of which Eu (II) is the only absorber in these solutions.

With regard to the analytical method, the literature contains many values of the magnetic susceptibility of europium (III) ion. Yost, Russell, and Garner present a summary of these.[6] We have determined the molar susceptibility of europium (III) ion in aqueous solution at 25.0°C to be 4.50×10^3 c.g.s. units; this value is independent of the ionic strength of the solution. The magnetic susceptibilities of a number of compounds of europium (II) is reported[7, 8] but no value for the ion in solution appears in the literature. By working in an atmosphere of carbon dioxide when preparing the solutions, and when carrying out analyses, by the method recommended by H. N. McCoy,[9] we have measured the susceptibility of europium (II) ion in aqueous solution, over the concentration range 0.3 m to 0.1 m, with the following result: $\chi_M = 26.2_5 \pm 0.1 \times 10^3$ c.g.s./g ion. The ionic diamagnetic susceptibilities listed by L. F. Bates[10] were used throughout. This value of χ_M is in good agreement with Van Vleck's[11] theoretical value of 26.1×10^3 c.g.s./g ion for the isoelectronic gadolinium