

Determination of Calcium in Alkali Halide Crystals

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J. Chem. Phys. **1**, 643 (1933); 10.1063/1.1749344



TABLE I.

Temp. °K	[Acetone] $\times 10^{-17}$ moles/cc	CO	CH ₄ micromoles	C ₂ H ₆ $\times 10^{12}$ (molecules/ cc/sec) [†]	$RCH_4/R^1C_2H_6$ [Acetone] $\times 10^{12}$ (molecules/ cc/sec) [‡]
388	15.10	2.64	0.560	2.100	0.361
414	14.20	3.05	1.067	2.025	0.744
439	13.42	3.21	1.820	1.670	1.480
448	13.20	4.45	2.608	2.28	1.865
483	12.18	3.87	3.82	1.065	4.75
499	5.95	2.30	2.165	0.825	5.65

extent to which this has been achieved is shown by the complete undetectability of mercury sensitization of the lower alkanes when irradiated with the 2537 Å mercury resonance line. The results obtained for the photolysis of purified acetone at 60 mm pressure from 100°C to 230°C are tabulated in Table I. In these experiments a Corning filter No. 7910 was used to remove the 1849 Å line; most of the absorbed light was of λ 2537 Å. The illuminated volume was taken to be the cell volume, 252 cc, and the reaction time was 1200 seconds for all runs.

A least squares Arrhenius plot of the data yields the rate expression

$$13 + \log(k_{\text{methane}}/k_{\text{ethane}}) = 6.14 \pm 0.05 - (2.164 \pm 0.021) \times 10^3/T,$$

or

$$(k_{\text{methane}}/k_{\text{ethane}}) = 1.4 \times 10^{-7} \exp(-9900 \pm 100)/RT,$$

in excellent agreement with the results of Trotman-Dickenson and Steacie.² We can only conclude that mercury does not influence methyl radical reactions to any significant extent.

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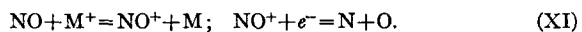
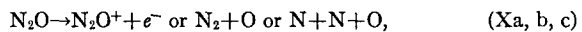
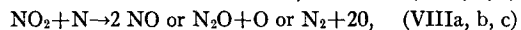
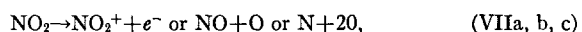
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[‡] A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.* **18**, 1097 (1950).

Fixation of Nitrogen by Ionizing Radiation as Nitrogen Dioxide and Nitrous Oxide*

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UPON irradiation of a mixture of oxygen and nitrogen in a nuclear reactor, the nitrogen is fixed as nitrogen dioxide and nitrous oxide to an extent considerably greater than anticipated. Investigations involved the radiation effects on mixtures of nitrogen and oxygen from 1% nitrogen-99% oxygen to 99% nitrogen-1% oxygen; pressures from 0.01 to 50 atmos; temperatures from -193 to 300°C, and intensities from 5×10^6 R/hr to 3×10^8 R/hr. The techniques used have been previously described.¹⁻³ The reactions, indicating the mechanism, are as follows:



The complex reactions with ozone are omitted.

In a nuclear reactor, the nitrogen and oxygen become ionized and decomposed by the fission fragments (when U^{235} used in direct contact with gas; and by the beta and gamma rays, and by fast neutrons, into nitrogen and oxygen atoms, as shown in reactions (Ic) and (IIc). Reactions (III) and (VIIIa) are the important reactions as the first step in the fixation of nitrogen. Nitrogen dioxide is formed predominantly through reaction (V). Nitrous oxide is formed by reaction (VIIIb).¹ Reaction (IX) is to be avoided for it tends to consume one fixed nitrogen atom (in the nitric oxide) and one free nitrogen atom. Reaction (XI) should also be avoided since nitric oxide has the lowest ionization potential of the group.

The production of nitrogen dioxide and nitrous oxide from a mixture of nitrogen and oxygen, is dependent on the temperature, pressure, radiation intensity and ratio of the amounts of nitrogen and oxygen. The optimal conditions have been found to be at a pressure about 20 to 25 atmos of a nitrogen-oxygen mixture approximating the ratio in air; a temperature between 175 and 200°C and a dose of about 3×10^8 R/hr or higher. Thus, in one of our demonstration experiments, a 100-cc quartz vessel containing dry air, at 25 atmos pressure, was irradiated in the BNL pile at 200°C. After the irradiation, and dipping in cool water the liquid nitrogen tetroxide could be readily observed as a few tenths of a cubic centimeter, indicating that almost one-half of the oxygen of the air had been consumed to form nitrogen tetroxide. This did not include the amount of nitrous oxide formed. From other precise experiments, the G-value for the production of nitrogen dioxide under the most favorable conditions is about 6 and for the nitrous oxide, about 3. These results were determined by comparison with the nitrous oxide dosimeter.³ Thus, assuming two-thirds of the fission energy stopped in the gas, the burnup of one mole of U^{235} , would produce about 6×10^6 moles of nitrogen dioxide.

The only publication we found concerning nitrogen fixation in a reactor is by W. Primak and L. H. Fuchs [*Nucleonics* **13**, 3, 39 (1955)], which involves the reaction of wet oxygen and nitrogen to coat nitric acid susceptible metals.

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Determination of Calcium in Alkali Halide Crystals*

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(Received January 13, 1956)

THE properties of alkali halide crystals containing divalent cation impurities are of use in constructing theories of ionic conductivity, diffusion, and electron trapping in ionic crystals.

Unfortunately, there has heretofore been no convenient analytical method for an ion such as calcium when present in a concentration within the range of interest, namely, about 10^{17} ions/cc. Some workers have used the data of Kelting and Witt,¹ who found for KCl crystals grown very slowly from the melt that the calcium concentration in the crystal was about 10% that in the melt, and have estimated the crystal composition from the melt composition. This requires that the crystal be grown very slowly and that its volume be small compared to the melt volume; for practical reasons these requirements are not often met. Kelting and Witt precipitated calcium as the oxalate and strontium and barium as sulfates. Using crystals from 2 to 5 cc in size with divalent cation concentrations above 5×10^{17} ions per cc, they stated the uncertainty to be about 20%.

Etzel and Maurer² determined cadmium concentrations, in sodium chloride crystals, as low as 2.5×10^{17} ions/cc by polarography.

The method presented here is based upon that of Williams and Moser.³ It has been used to determine calcium concentrations as low as 1.3×10^{17} ions/cc KCl. For this concentration, crystals having a volume of only 0.12 cc were required. This allows samples to be taken which are quite representative of the actual crystals used in an experiment.

With murexide solution (ammonium purpurate), calcium forms a colored complex sufficiently stable in basic solutions to permit the estimation of calcium spectrophotometrically. KCl decreases the absorption peak height and shifts the peak toward longer wavelength, and if present in solution in concentration greater than 25 g/liter the method is ineffective. This imposes the lower limit on the concentration of calcium in KCl crystals that can be measured.

The absorbance of the colored complex follows Beer's law reasonably well up to 2 mg Ca/liter even in the presence of a large excess of KCl. The murexide itself absorbs in the same region. The maximum difference between the absorbance of the complex and of the murexide itself in solutions containing 25 g KCl/liter is at 505 m μ . The absorbance of standard solutions containing 25 g KCl, 16 mg murexide, and known amounts of calcium in the range 0–2 mg per liter were used to make a calibration curve. A standard solution without calcium was used as a reference in the Beckman Model B spectrophotometer. The absorbance per cm was 0.098 for a calcium concentration of one mg/liter.

The size of crystals for analysis was made such that the calcium concentration in solution was less than 2 mg/liter; for this purpose the crystal composition was estimated from the melt composition. The sample was dissolved in 25 ml H₂O and the KCl and murexide concentrations brought to their standard value. The absorbance was compared with the reference solution and calcium concentration was found upon the calibration curve.

Stock murexide solution containing 160 mg/liter was stable for 24 hours if stored in the dark. All more dilute solutions of murexide were stabilized by bringing to pH=11 with NaOH. Even then the decomposition of the dye is sufficiently rapid that the absorbance of all solutions must be determined within an hour after the dilution of the murexide.

From the degree of reproducibility of four calibration curves constructed independently, we estimate the uncertainty to be about 15% for the smallest concentration measured (1.3×10^{17} ions/cc KCl) and about 5% at the greatest concentration (5×10^{17} ions/cc KCl).

* Supported by the Office of Naval Research, Contract N7 onr 37603.

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Electronic Absorption Spectrum of the Thiophosgene Molecule

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(Received January 13, 1956)

A RECENT work by Duchesne¹ on the visible absorption spectrum of thiophosgene showed the interest and importance of a continued study of this molecule. Accordingly, research was undertaken with the main object of identifying new band systems either in the ultraviolet or in the visible part of the spectrum. Table I summarizes the results obtained, which are shown together with those of Duchesne.¹

Weak bands were found on the long wavelength side of the main visible system (path length: 50 cm; lowest pressure: 100 mm Hg). They have been interpreted as belonging to transitions corresponding to vibrational levels of high quantum number of the $^3A_2^*$ excited state. The origin of this system ($A_1 \rightarrow ^3A_2^*$)

TABLE I.

Spectral region (Å)	ν_{0-0} (cm ⁻¹)	Transition	Excited state frequencies (cm ⁻¹) ^a
~7000–5300	~15 000	$^1A_1 \rightarrow ^3A_2^*$ $n \rightarrow \pi^*$	300 (unassigned) $\nu_2 = 400$
5750–3900	17 344	$^1A_1 \rightarrow ^1A_2^*$ $n \rightarrow \pi^*$	$\nu_1 = 914$, $\nu_2 = 423$, $\nu_3 = 240$, $\nu_4 = 610$, $\nu_5 = ?$, $\nu_6 = 365$ $\nu_2 = 468$, $\nu_3 = 310$
2970–2690	33 380 \pm 468	$^1A_1 \rightarrow ^1B_2^*$ $n \rightarrow \sigma^*(CS)$	
2770–2390	36 045	$^1A_1 \rightarrow ^1A_1^*$ $n \rightarrow \sigma^*(CCl_2)$	$\nu_2 = 442$, $\nu_3 = 208$

* Duchesne's nomenclature has been used.¹

cannot be located with certainty, but does not seem to lie beyond 7000 Å.

We have completed Duchesne's assignment of frequencies for the main visible system¹ by the discovery of the excited state frequency $\nu_2 = 423$ cm⁻¹ (instead of 450 cm⁻¹ assumed by Duchesne). This was deduced from the analysis of spectrograms taken in the first order of a 21-foot radius grating, having 15 000 lines per inch. The new value of the frequency does not however modify, in their essentials, the earlier conclusions concerned with the calculation of the potential function. When the substance was dissolved first in *n*-hexane and then in acetone, a blue shift of about 300 cm⁻¹ was observed. This, according to recent considerations,² favors an $n \rightarrow \pi^*$ transition, in agreement with earlier identification.¹ We have measured the oscillator strength, whose low value ($1.26 \cdot 10^{-4}$) also confirms the interpretation of the spectrum as a forbidden transition.

The third system (2970–2690 Å), whose existence was noted by Henri,³ is composed of about 60 sharp bands. Its characteristics, especially the values of the frequencies of the corresponding excited state and the shape of the bands, strongly suggest an $n \rightarrow \sigma^*$ transition localized in the CS group, which makes the visible system allowed.

It is to be presumed that in the first three excited states, the molecule is of C_{2v} symmetry, which has already been shown by Duchesne¹ for the $^1A_2^*$ state.

The fourth system, also noted by Henri,³ contains about 40 diffuse bands, and is the most intense one. On the basis of a discussion of the potential function deduced from the frequencies associated with the excited state, which was assumed to maintain the symmetry of the ground state, it has been possible to identify the spectrum as $n \rightarrow \sigma^*$ transition localized in the CCl₂ group. The solvent effect gave a red shift of 150 cm⁻¹ on going from *n*-hexane to ether, and the oscillator strength amounted to the high value of 10^{-1} . These results indicate the validity of our interpretation of the nature of the system by an $n \rightarrow \sigma^*$ transition of the type $A_1 \rightarrow A_1^*$.

A detailed account of this work will be published elsewhere in the near future.

We are greatly indebted to Professor J. Duchesne for advice and helpful discussion.

* Aspirant du Fonds Nationale de la Recherche Scientifique.

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Erratum: Thermal Diffusion in Polymer Solutions

[J. Chem. Phys. 23, 2252 (1955)]

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IN Eqs. (3), (10), (11), (13), (18), and (20) there appears the expression $X(\partial M/\partial X)$ with various subscripts. In each case, the expression should be $X(\partial \mu/\partial X)$ with the subscripts shown, where μ is the chemical potential.