

Erratum: The Quantum Mechanics of Chemical Kinetics of Homogeneous Gas Phase Reactions. II. Approximations for Displacement Reaction between an Atom and a Diatomic Molecule

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can then be obtained by making use of an adequate number of non-linear equations.

Application to propellant systems. As soon as attempts are made to utilize the general formulas between the temperature lags, difficulties are encountered because of the lack of adequate data for the reaction rate constants. The six simultaneous relations determined from Eqs. (5) to (10) do not necessarily lead to meaningful results unless some of the rate constants k_6 to k_{10} are known with considerable accuracy. This conclusion follows immediately from the well-known loss of significant digits which may be encountered during the inversion of matrices.²

Limited application of the techniques discussed here is of interest, and has been made for the set of reactions given in Eqs. (5) to (10). For example, it is found that the temperature lag ($T_{10}-T$) is of the same order of magnitude as the temperature lags (T_8-T) and (T_8-T) even if the direct reaction between H_2 and F_2 occurs relatively slowly. Similarly, the simultaneous occurrence of reactions (6) and (8) does not produce temperature lags significantly different from those determined on the assumption that these reactions occur independently. Finally, by applying the usual intuitive rules of chemical kinetics to complex systems, the qualitative conclusion may be drawn that near-equilibrium will obtain for a complex set of reaction if some of the possible reactions occur with sufficient speed to maintain nearly complete thermodynamic equilibrium, and these fast reactions are sufficient in number to allow all of the necessary atomic and molecular concentration changes.

In conclusion, the author takes pleasure in expressing his appreciation to Mr. J. Lorell for helpful discussion of various sections of this report.

* This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under U. S. Army Ordnance Department Contract No. W-04-200-ORD-1482.

¹ S. S. Penner, *J. Am. Chem. Soc.* **71**, 788 (1949); See also J. Franklin *Inst.* **245**, 421 (1948); *J. Chem. Phys.* **17**, 56 (1949); *J. App. Phys.* **20**, 445 (1949).

² J. von Neumann and H. H. Goldstein, *Bull. Am. Math. Soc.* **53**, 1021 (1947). The physical reason for the loss of significant figures is associated with the fact that several of the rate-determining reaction rates are of similar magnitude.

The Deslandres-D'Azambuja Band System of the C_2 Molecule in the Ethylene-Oxygen Flame*

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THE Deslandres-D'Azambuja band system of the C_2 molecule has heretofore been obtained in both condensed and uncondensed discharges. These bands were analyzed by Dieke and Lochte-Holtgreven¹ and Kopfermann and Schweitzer.² Most recently, Herzberg and Sutton³ analyzed a number of new bands of the C_2 molecule, which were found to be tail bands of the Deslandres-D'Azambuja system.

Investigators of hydrocarbon flame spectra have reported the Swan (${}^3\Pi_g-{}^3\Pi_u$) and Mulliken (${}^1\Sigma_g^+-{}^1\Sigma_g^+$) band systems of the C_2 molecule.⁴ The purpose of this note is to report the appearance of the Deslandres-D'Azambuja bands (${}^1\Pi_g-{}^1\Pi_u$) as a prominent feature of both the ethylene-oxygen and methane-oxygen flames.

The fuel and oxygen were premixed and burned off a grid orifice at a pressure of about 50 mm. In each case the fuel-oxygen ratio was stoichiometric. Under these conditions an intense blue flat reaction zone was obtained. Spectrograms were obtained in the second order of a 2-meter Baird grating spectrograph (4A/mm) in the region $\sim 3100\text{\AA}$ to $\sim 4100\text{\AA}$.

All the Deslandres-D'Azambuja bands listed by Herzberg and Sutton³ have been identified in the case of the ethylene-oxygen flame except the (5,3) and (4,2) bands. The former is obscured by

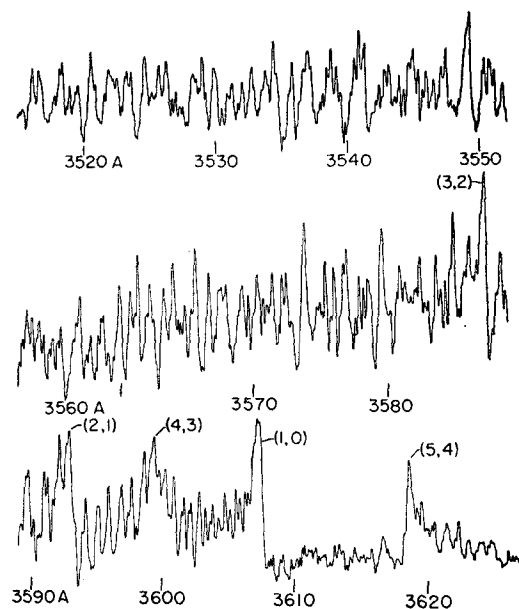


FIG. 1. Densitometer tracing of a sequence of Deslandres-D'Azambuja bands of the C_2 molecule.

the (0,1) band of OH and the latter is headless. While band heads were not measured for the methane-oxygen flame spectra direct comparison reveals the presence of most of these bands. In Fig. 1 is a densitometer tracing of a sequence of Deslandres-D'Azambuja bands.

We wish to express our appreciation to Dr. G. Herzberg, National Research Council, Canada, for his interest and invaluable discussion. We thank Helen S. Hopfield for her aid in making the plate measurements.

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¹ G. H. Dieke and W. W. Lochte-Holtgreven, *Zeits. f. Physik* **62**, 767 (1930).

² H. Kopfermann and H. Schweitzer, *Zeits. f. Physik* **61**, 87 (1930).

³ G. Herzberg and R. B. Sutton, *Can. J. Research* **18**, 74 (1940).

⁴ A. G. Gaydon, *Spectroscopy and Combustion Theory* (Chapman and Hall, Ltd., London, 1948).

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THE designation of ortho and para states for the upper curve of Fig. 3 (labeled $n=1$) should be interchanged. Ortho states are all those having odd rotational quantum numbers, while para states have even rotational quantum numbers.

This means that approximately 40 percent of the contribution to the rate comes from hydrogen molecules in the first excited vibrational states having rotational quantum number $K=3$, instead of $K=4$ as stated in the text. Hydrogen molecules having rotational quantum numbers 2, 3, 4 make up approximately 60 percent of the rate, instead of 75 percent as stated in the text. All other conclusions are not affected.