

## NearEquilibrium Criteria for Complex Chemical Reactions during Flow through a Nozzle

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The orthogonality and normalization conditions together with the equation  $a_2 = a_3$  yield

$$c_2 = c_3 = \frac{1}{\sqrt{2}}, \quad (4)$$

$$b_2 = b_3 = (\frac{1}{2} - a_2^2)^{\frac{1}{2}}. \quad (5)$$

The constants  $a_1$  and  $b_1$  can be expressed in terms of  $a_2$  also. The functions  $\psi_2$  and  $\psi_3$  depend on the parameter  $a_2$ . They are strongest when the angle between their maxima,  $\theta$ , equals the tetrahedral angle and their strength,  $S$ , equals that of tetrahedral bonds. This singlet structure does not require the promotion of an  $s$  electron since it requires no contribution from  $p_z$ . Hence it should be more stable than the triplet structure. The conclusion is supported by the experimental work cited by Laidler and Casey.<sup>1</sup>

If we assume  $\theta$  equals  $140^\circ$  in the singlet structure, we find that  $a_2$  equals 0.659 and  $S$  equals 1.962. Now  $S$  equals 2.000 when  $\theta$  equals  $109^\circ 28'$ . The  $140^\circ$  structure might be stabilized by the ionic character of the bonds. An alternative explanation is that Pauling's criterion of strength underestimates somewhat the contribution from the  $s$  orbital to the stability of the bonds.<sup>5</sup>

<sup>1</sup> K. J. Laidler and E. J. Casey, *J. Chem. Phys.* **17**, 213 (1949).

<sup>2</sup> G. H. Duffey, *J. Chem. Phys.* **14**, 342 (1946).

<sup>3</sup> L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1940).

<sup>4</sup> See H. Kuhn, *J. Chem. Phys.* **16**, 727 (1948).

<sup>5</sup> See R. S. Mulliken *et al.*, *J. Chem. Phys.* **17**, 510 (1949). The author has received a private communication (1949) from A. Maccoll of University College, London regarding the same subject.

## Near-Equilibrium Criteria for Complex Chemical Reactions during Flow through a Nozzle\*

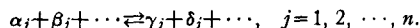
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June 29, 1949

**C**ALCULATIONS of the effect of vibrational and chemical lags on the exhaust velocity of the combustion products formed in conventional rocket motors have been restricted previously<sup>1</sup> to a consideration of individual processes without the introduction of corrections for the interdependence of the chemical reactions or of the vibrational distributions. The approach to chemical equilibrium for a number of interdependent chemical reactions can be handled, at least in principle, by a straightforward generalization of the techniques described previously. Calculations on complex systems require the solution of a number of simultaneous linear and non-linear equations.

**Non-linear relations between the temperature lags in complex systems.** Consider a system of chemical reactions of  $n-1$  individual steps leading to the over-all reaction shown in the  $n$ 'th step, as follows:



The statement that step  $n$  is the sum of steps 1 to  $n-1$  means that

$$\begin{aligned} \alpha_n + \beta_n + \cdots &= \sum_{i=1}^{n-1} \alpha_i + \sum_{i=1}^{n-1} \beta_i + \cdots; \\ \gamma_n + \delta_n + \cdots &= \sum_{i=1}^{n-1} \gamma_i + \sum_{i=1}^{n-1} \delta_i + \cdots. \end{aligned}$$

Furthermore, if  $K_j^0$  ( $j = 1, 2, \cdots, n$ ) denotes the equilibrium constant for the  $j$ 'th step, then

$$K_n^0 = \prod_{i=1}^{n-1} K_i^0.$$

During the adiabatic expansion through a nozzle thermodynamic equilibrium is not maintained with respect to the  $n$  chemical reactions described above. Each of the  $n$  reactions, considered

individually, suffers a temperature lag which is designated as  $T_j - T$  and defined by the relation

$$K_j = \frac{\Pi \text{-molecular concentrations of the species formed in step } j}{\Pi \text{-molecular concentrations of the species reacting in step } j}$$

where  $K_j$  is the equilibrium constant for the  $j$ 'th step not at the true temperature  $T$ , but at a temperature  $T_j$  which differs from  $T$ . If the temperature lag  $T_j - T$  is sufficiently small, then it is said that step  $j$  is in near-equilibrium. From the definition of  $K_j$  it is evident that

$$K_n = \prod_{i=1}^{n-1} K_i. \quad (2)$$

The quantities  $K_j$  may be expressed<sup>1</sup> in terms of the quantities  $K_j^0$  by making use of a Taylor series; if  $T_j - T$  is sufficiently small, all but the first two terms of the Taylor series may be neglected. Therefore

$$K_j = K_j^0 + K_j^0 \frac{d \ln K_j^0}{dT} (T_j - T). \quad (3)$$

Replacing  $K_j$  in Eq. (2) by its value from Eq. (3) it can readily be shown that

$$\begin{aligned} T_n - T &= \sum_{i=1}^{n-1} \frac{d \ln K_i^0 / dT}{d \ln K_n^0 / dT} (T_i - T) + \sum_{i < m=2}^{m=n-1} \frac{d \ln K_i^0 / dT}{d \ln K_n^0 / dT} \\ &\quad (d \ln K_m^0 / dT) (T_i - T) (T_m - T) + \cdots \\ &\quad + \prod_{i=1}^{n-1} \frac{d \ln K_i^0 / dT}{d \ln K_n^0 / dT} (T_i - T). \quad (4) \end{aligned}$$

Equation (4) is the desired result, since it gives an analytic expression for the temperature lag  $T_n - T$  in terms of the temperature lags of the individual  $n-1$  steps provided near-equilibrium is maintained with respect to each of the  $n$  individual reactions.

**Linear relations between the temperature lags in complex systems.** The linear relations between the temperature lags in complex systems involve the individual rate constants for each of the steps of a complex chemical reaction. It is possible to write one equation which is linear in the terms  $T_j - T$  for each of the steps of a complex reaction. The number of independent linear equations is equal to the number of chemical reactions which cannot be constructed by simple additions or subtractions involving other chemical reactions which are known to be independent in this sense.

The linear equations can be obtained by following the procedure outlined previously<sup>1</sup> taking care, however, to allow for the simultaneous participation of a given reactant in several alternative reaction paths. A representative result obtained from Eq. (5) for the set of reactions



is

$$\begin{aligned} [\Delta H_5 - \gamma RT(\gamma - 1)^{-1}](-dT/dt) \\ = k_{f5}(M)(\Delta H_5 - RT)[1/K_5 + 2(\text{H})/(\text{H})](T_5 - T) \\ - k_{f6}(F)(\Delta H_6)[1 + 2(\text{H}_2)/(\text{H})](T_6 - T) \\ + 2k_{f8}(F_2)(\Delta H_8)(T_8 - T) + 2k_{f9}(F)(M) \\ \times [\Delta H_9 - RT](T_9 - T) - k_{f10}(F_2)(\Delta H_{10})(T_{10} - T) \quad (11) \end{aligned}$$

where the contributions to the concentration changes resulting from the change of state during adiabatic expansion have been taken into account. Equations similar to Eq. (11) can be derived readily from Eqs. (6) to (10). However, of the six linear equations involving the temperature lags  $T_5 - T$  to  $T_{10} - T$  only three are independent. This must be true, since it is possible, for example, to derive Eqs. (6), (8), and (10) from Eqs. (5), (7), and (9). A sufficient number of relations between the temperature lags

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.<sup>2</sup>

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.

<sup>1</sup> 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).

<sup>2</sup> 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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July 21, 1949

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-Holtgreven<sup>1</sup> and Kopfermann and Schweitzer.<sup>2</sup> Most recently, Herzberg and Sutton<sup>3</sup> 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.<sup>4</sup> 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  $\sim 3100\text{A}$  to  $\sim 4100\text{A}$ .

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

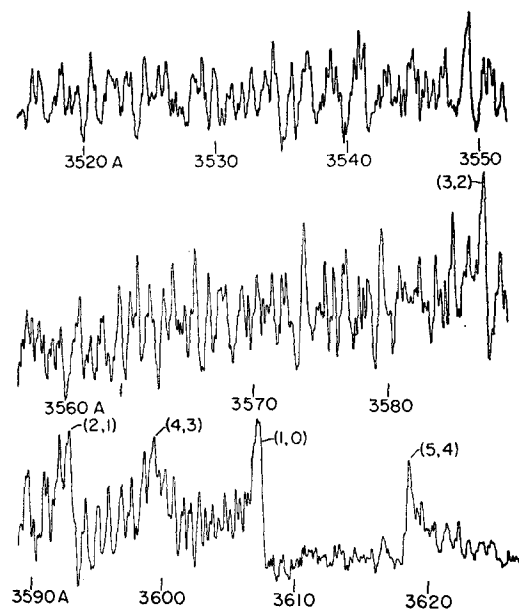


FIG. 1. Densitometer tracing of a sequence of Deslandres-D'Azambuja bands of the  $C_2$  molecule.

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.

\* The work described in this paper was supported by the Bureau of Ordnance, U. S. Navy, under Contract NOrd-7386.

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

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

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

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

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

[*J. Chem. Phys.* **17**, 630 (1949)]

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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.