

tion products considered. Also, analytical examination of Eq. (1) reveals that as V_0 is decreased the minimum in p vs T at constant V_0 will again occur. This unphysical behavior reduces confidence in the equation of state, particularly if it is to be extended to smaller volumes.

This equation of state is probably fairly reliable if its use is restricted to explosives which are similar to those included in a determination of its parameters, and to pressures and volumes not too different from those existing at the Chapman-Jouguet point. There

would seem to be little justification for its use in an extended extrapolation of any sort.

An investigation similar to the one reported here using the Lennard-Jones-Devonshire free-volume equation of state is in progress at this laboratory.²³ Results will be published at a later date.

7. ACKNOWLEDGMENTS

The authors are indebted to Frederick R. Parker for help with the machine computations, and to W. W. Wood for several helpful discussions.

THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 24, NUMBER 5

MAY, 1956

Rate of Recombination of Radicals.* I. A General Sector Theory; A Correction to the Methyl Radical Recombination Rate

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(Received July 5, 1956)

We have derived a rotating sector theory applicable to simple photochemical decompositions involving both first-order and second-order removal of radicals. This theory gives the behavior of radicals under intermittent illumination as a function of two parameters: α , the ratio of first- to second-order removal rates, and β , a function of flash time. We use this theory to recalculate the experimental data on the methyl radical recombination rate. We find the constant k_2 to be 2.2×10^{13} cc moles⁻¹ sec⁻¹ in the temperature range 125°C to 175°C.

1. INTRODUCTION

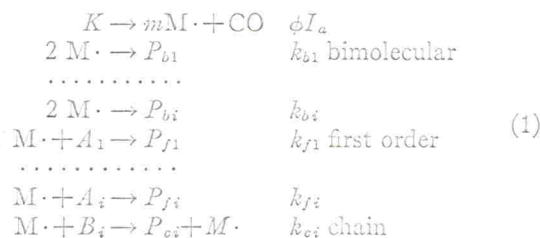
IN this laboratory we have undertaken the further study of the recombination rates of radicals by the rotating sector technique, using ketones as the radical sources. To account properly for the steps involving first-order removal of radicals, we have reinvestigated the sector theory, deriving complete equations whose form is a simplification over previous work. These equations apply not only to ketones, but to a rather general gas phase photochemical mechanism. In this paper we present the theory and use it to correct the recent results obtained for the methyl radical recombination rate. The following paper presents results on the recombination of trifluoromethyl radicals. A future paper will present results on the recombination of ethyl radicals.

If, in a photochemical decomposition, the steady-state concentration of a certain radical is proportional to the square root of the absorbed light intensity, the recombination rate of these radicals may be studied by photolyzing under intermittent illumination (conveniently produced by a rotating sector whose dark to light ratio is β), for then the steady state concentration will vary from $(\beta+1)^{-1}$ to $(\beta+1)^{-1/2}$ times the unsectored

value, as the sector speed varies from zero to infinity. Assuming simple square root dependence (removal of radicals only by recombination) Dickinson¹ and others^{2,3} have developed a complete theory. Assuming one first-order (in radicals) removal step, O. K. Rice⁴ and others^{5,6} have developed theories. We present a new treatment applying to a general mechanism, and offering simplified final equations.

2. THEORY

Consider the following gas phase mechanism:



¹ R. G. Dickinson: see W. A. Noyes, Jr., and P. A. Leighton, *The Photochemistry of Gases* (Reinhold Publishing Corporation, New York, 1941), pp. 202-209.

² F. Briers and D. L. Chapman, *J. Chem. Soc. (London)* 1802 (1928).

³ G. M. Burnett and H. W. Melville, *Proc. Roy. Soc. (London)* A189, 470 (1947).

⁴ O. K. Rice, *J. Chem. Phys.* 10, 440 (1942).

⁵ G. M. Burnett and W. W. Wright, *Proc. Roy. Soc. (London)* A221, 37 (1954).

⁶ Dainton, James, and Kutschke (to be published).

* Contribution from the Division of Pure Chemistry, National Research Council of Canada, Ottawa. Issued as NRC No. 3912.

† National Research Council of Canada Postdoctorate Fellow 1953-1955.

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γ^* [Eq. (17)]	α^* (Fn.29)
2.92 ^b	0.32
2.79	0.30
3.15	0.49
3.01	~0.34
3.44 ^b	0.68
2.88	0.25
3.78	0.30
4.20	~0.84
2.59	0.18
4.12	0.41
2.96	0.21
4.81	1.26

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