

TABLE I.

Temperature of reaction vessel (°C)	Extent of thermal decomposition (dark reaction) (%)	H ₂ O ₂ vapor entering reaction vessel (molecules per sec)	CO ₂ formed during irradiation (molecules per second per cc)
132	20.5	69 × 10 ¹⁷	8.7 × 10 ¹⁶
120	15.3	77 × 10 ¹⁷	8.1 × 10 ¹⁶
97	14.3	47 × 10 ¹⁷	6.8 × 10 ¹⁶
105	12.0	55 × 10 ¹⁷	10.5 × 10 ¹⁶

CO Flow rate = 3.7 cc/sec

water. In neither case could the organic products be identified. Ammonia was also investigated, but the saturated solution in 99.6 percent H₂O₂ became unstable on standing and subsequent agitation produced a violent explosion. It is proposed to make further investigations with these gases.

Our thanks are due to the Buffalo Electrochemical Company, Inc., for a generous gift of concentrated hydrogen peroxide,

* Commonwealth Fund Fellow, 1950-51. Present address: Department of Chemistry, University of Bristol, Bristol, England.

¹ Urey, Dawsey, and Rice, *J. Am. Chem. Soc.* **51**, 1371 (1929).

² von Elbe, *J. Am. Chem. Soc.* **55**, 62 (1933).

³ D. H. Volman, *J. Chem. Phys.* **17**, 947 (1949).

† von Elbe (see reference 2) reported almost twice as much reaction at 40°C as at 27°C. However, as the yields were lower than those reported here by a factor of a thousand, it is likely that the probable error was large.

‡ Recombination of OH does of course occur, but its effect will be similar whether the carrier is active or inert and so it will not modify the number of OH radicals available for reaction.

⁴ Frankenburger, *Z. Elektrochem.* **36**, 757 (1930).

⁵ Faltings, Groth, and Harteck, *Z. physik. Chem.* **B41**, 15 (1938).

⁶ Geib and Harteck, *Z. physik. Chem.* **A170**, 1 (1934).

The Second Virial Coefficient of Benzene

P. G. FRANCIS and M. L. MCGLASHAN*
Chemistry Department, Reading University, England

AND

S. D. HAMANN and W. J. MCMANAMEY
C.S.I.R.O., High Pressure Laboratory, Sydney University, Australia
 (Received May 26, 1952)

EVERETT and Penney¹ have recently reviewed the experimental data on the second virial coefficient (*B*) of benzene and drawn attention to the disagreement between the results of different experimenters. This is apparent in Fig. 1 where the values of $-B$ found by Eucken and Meyer² and by Baxendale and Enüstün³ are seen to be considerably larger than those of

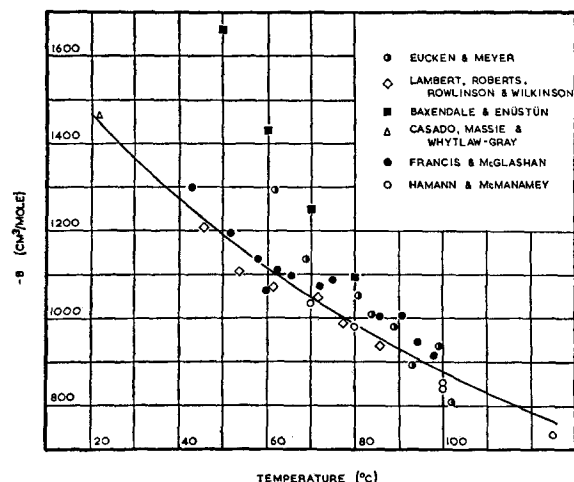


FIG. 1. Second virial coefficient of benzene.

Lambert, Roberts, Rowlinson, and Wilkinson⁴ and of Casado, Massie, and Whytlaw-Gray.⁵

In this note we report two independent series of measurements aimed at resolving these discrepancies.

The measurements at Reading were made in a "Boyle's apparatus" similar to that described by Alexander and Lambert.⁶ Two different samples of benzene were used. The first of these was prepared at Reading by treatment with sulfuric acid followed by fractional distillation and then by repeated fractional crystallizations. The purity of the sample so prepared was calculated from the shape of the freezing point curve and was found to be 99.95 ± 0.05 moles percent. The second sample was kindly supplied by Professor J. Timmermans from the Bureau International des Etalons Physico-chimiques in Brussels. Considerable care was taken to de-gas the liquid so as to ensure that a gas-free sample of vapor was introduced into the burette. The results are given below.

Reading sample:
 t°C: 43.1 51.9 60.0 62.9 65.7 75.1 85.9 94.2 99.1,
 $-B/\text{cm}^3 \text{ mole}^{-1}$: 1300 1198 1064 1112 1099 1090 1004 947 916.

Brussels sample:
 t°C: 58.1 72.1 90.8,
 $-B/\text{cm}^3 \text{ mole}^{-1}$: 1137 1075 1006.

The measurements at Sydney were made by a comparative method which has been described before.⁷

Mr. I. Brown, C.S.I.R.O., Melbourne, kindly supplied a purified sample of benzene for these determinations. The pressures were between 15 percent and 75 percent of the saturation pressure of benzene, and in this range no virial coefficients higher than the second are needed to describe the behavior of the vapor. The results are given below:

t°C: 70 80 100 100 125,
 $-B/\text{cm}^3 \text{ mole}^{-1}$: 1035 971 852 839 733.

Both sets of data have been plotted in the diagram. They lie close to the curve

$$B/\text{cm}^3 \text{ mole}^{-1} = 70 - 13.2 \times 10^7 / T^2,$$

which Everett and Penney selected after rejecting Baxendale and Enüstün's results, and they provide further justification for that choice.

* Now at Canterbury University College, Christchurch, New Zealand.

¹ Everett and Penney, *Proc. Roy. Soc. (London)* (to be published).

² Eucken and Meyer, *Z. physik. Chem.* **B5**, 452 (1929).

³ Baxendale and Enüstün, *Phil. Trans. Roy. Soc. (London)* **A243**, 176 (1951).

⁴ Lambert, Roberts, Rowlinson, and Wilkinson, *Proc. Roy. Soc. (London)* **A196**, 113 (1949).

⁵ Casado, Massie, and Whytlaw-Gray, *Proc. Roy. Soc. (London)* **A207**, 483 (1951).

⁶ Alexander and Lambert, *Trans. Faraday Soc.* **37**, 421 (1941).

⁷ Hamann and Pearse, *Trans. Faraday Soc.* **48**, 101 (1952).

A Two-Path Method for Eliminating the Effects of Self-Absorption on Temperature for Isothermal Flames*

S. S. PENNER
*Guggenheim Jet Propulsion Center, California Institute of Technology,
 Pasadena, California*
 (Received June 3, 1952)

IT is the purpose of the present note to outline a two-path method for the determination of flame temperatures. The method is valid for isothermal systems and spectral lines with Doppler contour. All errors arising from self-absorption are eliminated. Practical applications are made by determining the ratio of the total intensity observed when the flame is viewed with a cool blackbody as background to the total intensity obtained with a cool mirror as background. For the sake of simplicity it will be assumed that the reflectivity of the mirror is unity. Spectroscopic studies are made in the usual way, i.e., with a low

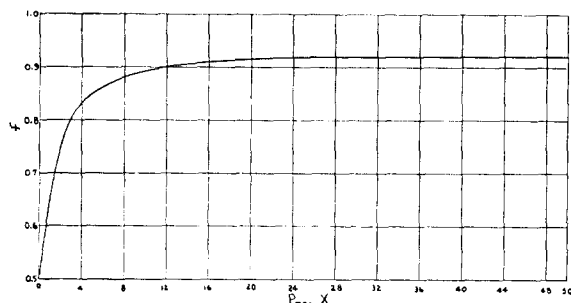


FIG. 1. The quantity $f(P_{\max}X)$ as a function of $P_{\max}X$ for spectral lines with Doppler contour.

resolution spectrograph since only the ratios of total intensities need to be determined. The method is related to a procedure described in a previous publication for spectral lines with resonance contour¹ but differs in so far as it utilizes the fact that observations on visible and ultraviolet spectra are usually made for individual spectral lines. Using the notation of a previous paper,² it is found that for spectral lines with Doppler contour the total observable intensity of the line identified by the index K and with center at the frequency ν_{lu} is³

$$\{A[\nu_{lu}(K)]\}_1 \approx R^0(\nu_{lu})(mc^2/2\pi kT\nu_{lu}^2)^{-1} [P_{\max}(K)X] \times \left\{ \sum_{n=0}^{\infty} [(n+1)!(n+1)!]^{-1} [-P_{\max}(K)X]^n \right\}, \quad (1)$$

if the light reaching the receiver traverses the flame only once. If intensities obtained by allowing the light to traverse the flame twice are identified by the subscript 2, then it is evident from Eq. (1) that

$$\{A[\nu_{lu}(K)]\}_1 / \{A[\nu_{lu}(K)]\}_2 = f(P_{\max}X). \quad (2)$$

The quantity f is plotted as a function of $P_{\max}X$ in Fig. 1. But, for spectral lines with Doppler contour and $h\nu_{lu} \gg kT$,²

$$P_{\max}(K)X = \text{constant} \times X \times [g_u(q_{lu})^2]_K \times \exp[-(E_u - h\nu_{lu})/kT].$$

The recommended procedure, subject to the limitations stated earlier, is seen to involve only the measurement of intensity ratios, the determination of $P_{\max}(K)X$ from Fig. 1, and the calculation of T from the relation

$$\frac{\partial \ln \{P_{\max}(K)X / [g_u(q_{lu})^2]_K\}}{\partial (E_u - h\nu_{lu})} = -1/kT. \quad (3)$$

For isothermal emitters with self-absorption the suggested procedure has the advantage of extreme simplicity. For spectral lines with combined Doppler- and collision-broadening, the quantity f is no longer a universal function of $P_{\max}X$ but depends also on the natural damping ratio.

* Supported by ONR under Contract Nonr-220(03), NR 015 210.

¹ S. S. Penner, *J. Chem. Phys.* **19**, 272, 1434 (1951).

² S. S. Penner, *J. Chem. Phys.* **20**, 507 (1952).

³ R. Ladenburg, *Z. Physik* **65**, 200 (1930).

Influence of Light on the Secondary Emission in a Low Frequency Electrodeless Discharge: Joshi Effect

A. P. SAXENA
Holkar College, Indore, India
AND

N. A. RAMAIAH
Chemical Laboratories, Benares Hindu University, Banaras, India
(Received May 26, 1952)

THE present communication reports a few significant observations made during the studies of Joshi effect,¹ viz., an instantaneous photovariation (Δi), usually though not invariably

diminution ($-\Delta i$), of the current (i) in a low frequency electrodeless discharge in water vapor. Cylindrical (glass) tubes containing pure H_2O vapor were excited by 50-cycle potentials, using external sleeve electrodes; the current structure was investigated by a DuMont cathode-ray oscillograph. The accompanying pair of oscillograms represent a typical group selected out of numerous ones obtained over a wide range of pressure p and applied potential V . Above the "threshold potential" V_m , at which the discharge attained a self-maintained nature, there appeared a few pulses on the otherwise smooth sinusoidal current trace; their number increased markedly with p and V . They were of two types: (a) longer pulses produced presumably due to large number of avalanches created by fast moving electrons emitted from the cathode by γ and $\eta\theta g$ processes,^{2,3} and (b) shorter pulses due to avalanches yielded by electrons generated in the vicinity of the cathode by other β processes.^{2,3} It was noticed that irradiation diminished the heights of (a) and enhanced the number of (b); (cf. the action of transverse magnetic field was to reduce the heights of (b) only).⁴ Similar results were recorded in iodine vapor.⁵ Under light, the pulses were remarkably of the same height (Fig. 1) as in the well-known Geiger (not self-maintained) region⁶

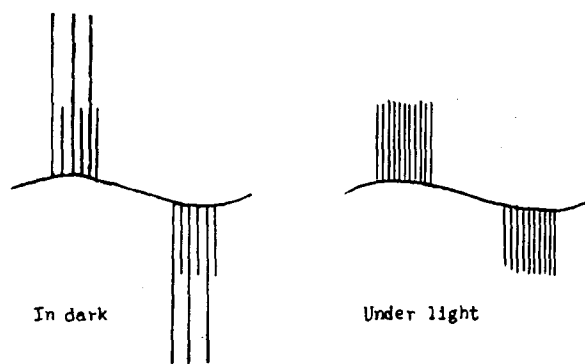


FIG. 1. Current structure in dark and under light ($p_{H_2O} = 13.5$ mm Hg, $28^\circ C$, 1.21 kv).

in which Townsend α -mechanism was but operative. This suggested that the secondary emission from the cathode responsible for the maintenance of the discharge was inhibited by light to give $-\Delta i$; and that the (simultaneous) increase of the number of shorter pulses constituted the positive effect $+\Delta i$. When the rms value of i was observed by current detectors like ac microammeter, vacuo-junction, etc., the resultant, $+\Delta i$ or $-\Delta i$ whichever predominated, was noticed.^{7,8}

These findings follow from a mechanism suggested simultaneously by Harries and Engel⁹ and by one of us¹⁰ (N.A.R.) that surface molecules held by van der Waals forces dissociate under light to yield electronegative atoms or/and radicals which reduce the secondary emission to give $-\Delta i$. The positive effect $+\Delta i$ is the result of photo-ionization of pre-existing gas particles in the neighborhood of (and/or on) the cathode.¹⁰

Grateful thanks are due Professor Joshi of Benares Hindu University for his kind interest in our work.

¹ Joshi, Presidential Address, Proc. Ind. Sci. Congress, Chemical Section (1943).

² Loeb, *Fundamental Processes in Electrical Discharge in Gases* (John Wiley & Sons, Inc., New York, 1939); *Revs. Modern Phys.* **8**, 256 (1936).

³ Townsend, "Electrons in Gases," Hutchinson's Sci. & Tech. Publications (1947).

⁴ Ramaiah, unpublished results.

⁵ Jatar, *Jour. Sci. Ind. Res.* **9B**, 283 (1950).

⁶ Korff, *Electrons and Nuclear Counters* (D. Van Nostrand Company, Inc., New York, 1948).

⁷ Joshi, Proc. Ind. Sci. Congress, Physical Section, Abstract 25 (1947).

⁸ Ramaiah, *J. Phys. Chem.* **52**, 218 (1952).

⁹ Harries and Engel, *J. Chem. Phys.* **19**, 514 (1951); *Proc. Phys. Soc. (London)* **64B**, 916 (1951).

¹⁰ Ramaiah, *J. Sci. Ind. Res.* **10A**, 182 (1951).