

# A CRITICAL INVESTIGATION AND DEVELOPMENT OF THE "DIFFUSION METHOD" FOR DETERMINING SPEEDS OF ATOMIC REACTIONS.

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## PART I.

The "diffusion method" developed by Hartel and Polanyi<sup>1</sup> for the determination of rates of slow atomic reactions is based on the following principle: sodium vapour is introduced through a nozzle at an initial pressure  $p_T$  into the gas with which it is to react, and the distance from the nozzle is determined at which the partial pressure of sodium has reached a given value  $p_0$  (i.e., the radius of the "flame"). In the stationary state the following general differential equation holds:—

$$D\Delta p + v \text{ grad } p - K \cdot p \cdot p' = 0 \quad (1)$$

where  $p$  is the pressure of sodium,  $p'$  that of the reacting gas (halogen),  $D$  the diffusion coefficient of sodium from the nozzle,  $K$  the velocity constant of the reaction, and  $v$  the streaming velocity.

This equation is solved by assuming (1) that  $v$  (and hence the middle term) can be neglected; (2) that  $p'$  is constant throughout the reaction zone. Geometrical simplifications were also introduced (the spherical diffusion of sodium vapour from the nozzle, etc.). Hartel and Polanyi<sup>1</sup> examined the integrated equation so obtained:—

$$K = \frac{(\ln p_T/p_0 - \ln R/r)^2}{(R-r)^2} \cdot \frac{\delta}{p'} \cdot \frac{1}{T} \quad (2)$$

(where  $K$  is the velocity constant,  $r$  the radius of the nozzle, and  $\delta$  the diffusion constant of the sodium vapour in the gas mixture). Apparently this equation was adequately fulfilled. Hartel, Meer and Polanyi,<sup>2</sup> by more accurate measurements, showed systematic deviations from the relationship between  $p'$  and  $R$  given by equation (2) and rejected the quantitative use of the method. In the present work the method has been improved and the conditions for obtaining quantitative results have been determined.

## 1. Apparatus and Method.

(1) **The Circulation Apparatus.**—The apparatus (Fig. 1) consists of a circulation and distillation system. The carrier gas Tr ( $H_2$  or  $N_2$ ) circulated by the pump  $P_1$ , is introduced into the apparatus at E, and streams in the direction of the arrows  $a_3 \rightarrow a \rightarrow a_1 \rightarrow a_2 \rightarrow a_3$ . The remainder of the halogen compound which is not removed by reaction in the reaction vessel is condensed in the liquid air traps  $F_1$  and  $F_2$ , and if necessary removed by molten sodium in trap  $F_3$ . The circulation speed

<sup>1</sup> Hartel and Polanyi, *Z. physik. Chem.*, B, 1930, **11**, 97.

<sup>2</sup> Hartel, Meer and Polanyi, *ibid.*, 1932, **19**, 139.

of the carrier gas is regulated by a glass membrane valve  $V_1$  constructed by v. Bogdandy, and is measured by the double McLeod  $M_1$  (from the fall in pressure across the capillary  $K_1$ ,  $K_2$  or  $K_3$ ). Two buffer volumes,  $H_2$  and  $N_2$  (each 30 litres, *i.e.*, ten times the volume of the apparatus) serve to prevent fluctuations in pressure in the reaction vessel.

## (2) The Distillation Apparatus.—

For reasons discussed later, we also introduced a distillation system which permitted the use of pentane as a carrier gas, and enabled the total pressure to be increased above 10 mm. without any disturbance or fluctuation of the streaming speed. The two systems can be interchanged without interruption of the experiments.

The carrier gas coming from the reservoir  $C_5H_{12}$  ( $V_2$  is a metal needle valve for regulation of the streaming speed) flows in the direction of the arrows  $a_0 \rightarrow a \rightarrow a_1 \rightarrow b$ , through the capillary  $K_4$  and the glass valve  $V_3$  (for the production and regulation of the pressure in the reaction zone) to the liquid air trap  $F_4$ , where it is condensed. The streaming rate is determined from the pressure difference between the manometer Man and the McLeod gauge  $M_2$ . (The McLeod reading gives at the same time the pressure in the reaction vessel.)

The pentane fraction used (boiling-point  $29^\circ$ – $30^\circ$ ) was purified by further distillation in the apparatus by complete removal of the dissolved gases (by using  $V_2$ ,  $P_2$ ,  $F_4$ ,  $H_2$  and  $H_3$ ).

**(3) The Introduction of the Halogen Compound.**—The halogen compound  $HI$  or  $HI'$ , completely air free, enters the reaction vessel at  $E$ , through capillary  $K_6$ ,  $K_8$  or  $K_7$ . Fine capillaries were used in order to keep the halogen partial pressure as low as possible; (see later, they were so fine that there was considerable inertia in building up the pressure before and behind them). To overcome this in front of the capillaries a buffer volume  $HI''$  was included in the halogen system to diminish fluctuations in pressure, and after the capillaries a by-pass of the carrier gas stream ( $1/10$  of the main stream) was caused to flow in the direction  $E_3$ —(or  $E_5$ )— $E$ , carrying with it the halogen coming out of the capillary. Frequent calibration of the constancy of the diameter of the fine capillaries was necessary, since even the formation of a film of only  $5\mu$  thick in a capillary of radius  $0.1$  mm. would produce a 19 per cent. decrease in the amount of gas streaming. To effect the calibration, a sample of  $Tr-HI$  mixture (sodium being absent) was removed through a long capillary  $K_8$ , running along the interior of the reaction vessel into the adjoining apparatus between taps  $H_4$  and  $H_7$ . From the total pressure and the  $HI$  partial pressure (obtained by freezing out  $HI$  in  $F_6$ , pumping off the  $Tr$  gas, and re-evaporation of  $HI$ ) and further data, we obtained the value of  $\eta_{HI}$  for a definite pressure difference, thus obtaining a very sensitive indirect check on the constancy of the capillary radius.

**(4) Introduction of the Sodium Vapour.**—To obtain a pure sodium surface, the metal was freed from hydrocarbons,  $Na_2O$ , and  $Na_2CO_3$  by

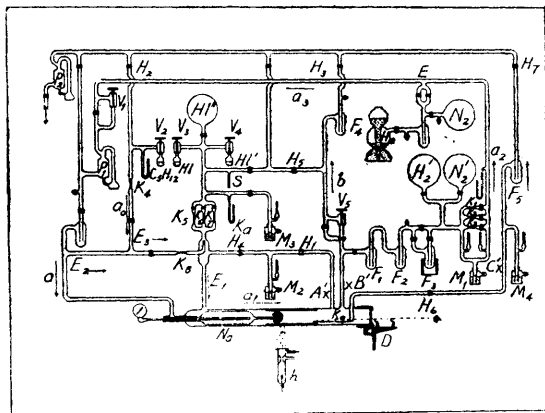


FIG. 1.

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several distillations in high vacuum. Before an experiment the oven was heated to a temperature  $30^{\circ}$  to  $50^{\circ}$  higher than that used in the experiments ( $270^{\circ}$  C.) in order to avoid delay in building up the pressure due to a surface film, and in attaining the adsorption equilibrium of the carrier gas on the sodium surface as it exists at the experimental temperature. Special experiments showed that, if these precautions are neglected,  $pT$  varies and the reproducibility of the experiments is lowered to 50 per cent.

**(5) Increase of the Intensity of the Sodium Resonance Lamp.**—A self-reversal of the D-line was prevented, by changes in the sodium vapour lamp, and, at the same time, the intensity of emission was increased so that a sodium pressure of even  $10^{-6}$  mm. could be observed. The emission of a continuum, through traces of foreign gases, was suppressed by baking out the electrodes in the arc, and by the use of rigorously purified sodium. The lamp, surrounded by an electric oven of constant temperature, provided sodium light which remained of constant intensity for months, as was shown by the reproducibility of the velocity constants. The special conditions are: 240 volts, 0.1 amp. 2-3 mm. Argon,  $100^{\circ}$ - $110^{\circ}$  C.

**(6) Measurement of Flame.**—The flame was measured by the device D, mounted on the end of the reaction tube, which was closed by a plane parallel glass plate. The upper and lower edges of the flame were observed in line with two thin threads of different colour, which were dimly illuminated, and could be moved vertically by a micrometer screw. The error in measurement was 4 per cent. in the most unfavourable case, corresponding to an uncertainty in the velocity constants of  $\pm 2$  to 3 per cent.

Absorption or scattering of light by the deposit on the reaction vessel was avoided by placing in the reaction vessel a glass cylinder, to the end of which a semicircle of iron enclosed in glass was fixed, so that the cylinder could be moved by an external electro-magnet. In this way an uncoated surface could be obtained between the reaction zone and the lamp and frequent cleaning of the reaction tube was unnecessary.

The "blinding" effect of the relatively intense resonance at the centre of the flame ( $10^{-3}$  mm. sodium pressure) makes the limiting intensity of  $10^{-6}$  mm. imperceptible. We found rather that a pressure of  $10^{-5}$  mm. corresponds to the actual concentration of sodium vapour on the visible edge of the flame. This is the value chosen for  $p_0$ .

**(7) Total Error in Velocity Constants Obtained by the New Method (in so far as they are of a Purely Technical Nature).**—The reproducibility of the measurements has been improved to 15 per cent. in unfavourable cases, as shown by a large series of analogous measurements taken at different times (over months and years). It is only in the determination of the flame size that the unknown error has technical significance. With a flame of 4 cm. diameter an error of  $\pm 3$  mm. would produce a systematic error or  $\pm 50$  per cent. in the velocity constants, but the error seldom exceeds 25 to 30 per cent. Finally, the extinction of the sodium resonance by the carrier gas need not be considered as a source of error in the pressure region used.

## 2. The Partial Pressure of the Halogen Compound before its entry into the Reaction Zone.

The rate of streaming of the halogen compound ( $n_{HI}$ ) calculated from the pressure fall  $\Delta p$  across the capillaries by application of Poiseuille's Law was found to be inaccurate. The increase of  $n_{HI}$  with  $\Delta p$  was far less than was to be expected and, if  $\Delta p$  was kept constant,  $n_{HI}$  altered with the mean pressure  $\bar{p}$ . Hartel, Meer and Polanyi,<sup>2</sup> by a somewhat different method, confirmed our results. This source of error causes a perceptible "drift" in the velocity constants with the size of the flame and with the total pressure. We therefore calculated  $n_{HI}$  from calibration experiments, using the same method as that used as a check of the capillary radius (sec. 1 (3)). It is, however, necessary to avoid a "diffusion error"

due to the fact that the quantitative composition of the gas mixture in the reaction vessel is not necessarily the same as that of the sample of gas mixture sucked into the adjoining apparatus. As a result of two hundred calibrations, we find that the calibrations are perfectly correct only if they are carried out exclusively with a heavy carrier gas ( $N_2$ ) and for a  $\bar{p}'$  of not less than 3 mm. ( $\bar{p}' = \frac{1}{2}(\bar{p}_{\text{reaction vessel}} + \bar{p}'_{\text{adj. apparatus}})$ ) and for a  $\Delta\bar{p}'$  of not less than 2.5 mm. ( $\Delta\bar{p}' = (\bar{p}_{\text{reaction vessel}} - \bar{p}_{\text{adj. apparatus}})$ ).

We cannot, therefore, explain the dependence of  $k$  upon  $\bar{p}$  and  $\Delta\bar{p}$  by turbulence in the halogen capillaries. In fact, the highest streaming speed used in the halogen and carrier gas capillaries was still less than half the critical speed which is given by the Reynold's number 2000 (relative to the diameter of the capillaries). (Since only very short capillaries with conical ends were used, the Reynold's number is in our case even greater.)

The inapplicability of Poiseuille's Law is due rather to the existence of slip in the gas streaming across the capillaries. In Fig. 2 the shape of

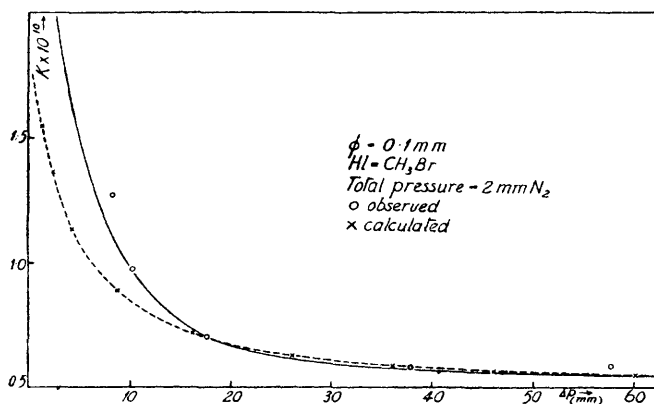


FIG. 2.

an experimental calibration curve is compared with a corresponding theoretical curve on the assumption of a coefficient of slip of  $\zeta = 100 \times 10^{-7}$ . The ordinates show the "capillary constant"

$$k = \frac{\pi r^4}{8\eta l 2RT}$$

The theoretical curve is based on a value of  $k$  of  $0.454 \times 10^{-10}$  ( $\bar{p}$  in mm.), obtained from calibrations on the assumption that  $\zeta$  is  $100 \cdot 10^{-7}$ . Fig. 2 shows that the character of the calibration curves is satisfactorily explained by the slip. The larger discrepancy at small  $\Delta\bar{p}$  values is due to uncertainty in the experimental determination of the amount of HI streaming if it becomes smaller than  $1/1000$  mm.

In the relatively wide carrier gas capillaries, also, the influence of slip, though naturally much less, must not be neglected when  $\bar{p}$  is smaller than 2 mm. For instance  $\bar{p} = 1$  mm. the slip correction for the widest capillary (3.3 mm. diameter) amounts to 18.5 per cent. (For the smallest halogen capillary of diameter 0.1 mm. the deviation obtained for the same  $\bar{p}$  would be greater than 500 per cent.) This correction eliminates the apparent pressure dependence of the reaction velocity.

The most important result of these experiments, however, is that these calibrations are no longer necessary to obtain the true  $p_{HI}$ . It can be calculated by the formula:—

$$n_{HI} = \frac{1}{8} \frac{\pi r^4}{\eta l} \cdot \frac{1}{2RT} \cdot (p_1^2 - p_2^2) \left( \frac{1 + 4\zeta \cdot 2 \cdot 760}{\pi(p_1 + p_2)} \right),$$

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in which the only uncertainty is  $\zeta$  for halogen-glass. From theoretical considerations, however, the true value must lie between 70 and  $100 \times 10^{-7}$ , involving a maximum error in the calibration of  $\eta_{\text{HI}}$  of 10 per cent. Thus,

TABLE I.

Substance.	$\eta \times 10^7$ (20°).	$\eta \times 10^7$ (20°) (Landolt-Bornstein).
$\text{CH}_3\text{Br}$ .	1485	1327
$\text{CH}_3\text{Cl}$ .	1106	1061
$\text{CH}_2\text{Cl}_2$ .	1156	991
$\text{CCl}_4$ .	1177	1000
$\text{SiCl}_4$ .	1144	—
$\text{C}_2\text{H}_5\text{Cl}$ .	1050	1050
$\text{C}_3\text{H}_7\text{Cl}$ .	1071	—

to replace the tedious calibrations we must, however, know the exact values of  $\eta$  for the halogen compounds used. Table I shows the results of some determinations of  $\eta$  for the principal substances we shall examine. The relative values obtained were converted into absolute values by using the well-known value of  $\eta$  for  $\text{C}_2\text{H}_5\text{Cl}$  as reference. For simple halogen compounds we can use a mean value so far as the halogen atoms are

the same, but not when they are different; moreover, there is a noticeable increase in viscosity with the number of substituted halogen atoms.

### 3. The Concentration Distribution of Halogen Compound in the Reaction Zone.

The assumption in equation (1) that the gas reacting with the sodium vapour has a zero partial pressure inside the nozzle but the constant partial pressure  $p'$  in the reaction zone cannot be exactly true. We have sought to establish how far this condition is actually fulfilled, and to discover the streaming conditions for which we can assume constant concentration distribution of the reaction gas in the reaction zone, and the minimum back diffusion into the nozzle.

**1. The Method.**—A stream of sodium-free carrier gas and of reaction gas ( $\text{C}_2\text{H}_5\text{Cl}$  or  $\text{C}_2\text{H}_4\text{Cl}_2$ ) was introduced into the reaction vessel in concentrations corresponding generally to those used in velocity measurements. Samples of the gas mixture formed in this way were removed through fine capillaries and the concentration of the reaction gas in these samples was determined as previously described (sec. 1). The "diffusion error" (sec. 2) was avoided by using a high streaming speed of the gas in the suction capillaries. The ends of the capillaries (which could be moved by turning a ground glass joint) were so arranged, that from a series of sample analyses the concentration distribution in the reaction zone could be determined (Fig. 3). The samples of gas removed were small, so as not to disturb the concentration distribution in the reaction zone.

**2. The Halogen Distribution Directly in front of the Nozzle in a Plane Normal to its Axis.**—Examining the distribution in a circular plane normal to the nozzle axis, whose centre is about 2 mm. from the nozzle mouth, it was found that  $p_{\text{HI}}$  decreases on approaching the axis. This decrease was not gradual, a fairly rapid drop in  $p_{\text{HI}}$  occurring at about 15 to 10 mm. from the edge of the nozzle, as appears from Table II ( $d_*$  (in mm.) is the distance normal to the nozzle axis). Furthermore, this "HI impoverishment" increases ( $p$  constant)

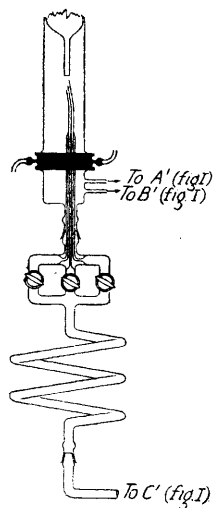


FIG. 3.

TABLE II.—HALOGEN IMPOVERISHMENT IN FRONT OF THE NOZZLE.

(Ethyl Chloride in  $H_2$ . Experiments Nos. 67-73. Temp.  $270^\circ C$ .)

Total $p$ , mm. Hg.	$n_{H_2}$ , mol./sec. $\times 10^8$ .	$\bar{v}$ , m./sec.	$\delta$ , Na/ $H_2$ .	$v/\delta$ , $\times 10^2$ .	$d_r$ , mm.	$p_{H_1}$ , mm. Hg.	HI Distribn.	HI Im- poverishment $d_1 \approx 2$ mm.
5.17	12,600		349		2.0	0.071	40.6	
5.03	11,600		359		3.9	0.103	58.8	
4.97	11,600		363		7.8	0.139	79.5	
4.94	10,600	40.8	366	11.37	11.6	0.158	90.2	59.4
4.93	10,800		366		15.4	0.171	97.8	
4.90	10,800		369		19.1	0.166	95.0	
4.91	11,300		368		22.5	0.175	100.0	

with the linear streaming speed  $v$  in the nozzle (Fig. 4), and increases with  $p$  ( $v$  const.). Thus the increase of  $p$  and  $v$  retard penetration of halogen towards the axis. Since a diffusion process is involved, the halogen impoverishment is, under similar conditions, obviously greater when  $N_2$  instead of  $H_2$  is used (Fig. 7).

We can express these phenomena by the equation :—

$$\frac{p_R}{p_R - p_Z} = k \cdot \frac{\delta}{v} \quad . \quad . \quad . \quad (3)$$

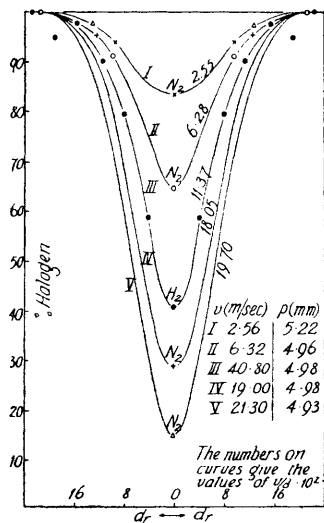


FIG. 4.

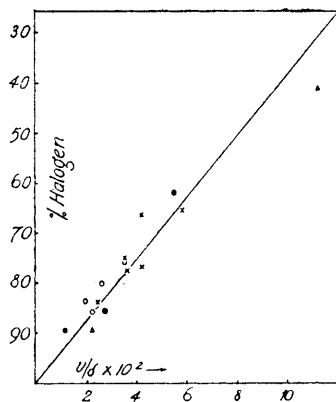


FIG. 5.

Ethyl Chloride :—

X : with  $N_2$ ; without Na range of pressure : 2.04–9.70 mm.

● : with  $N_2$ ; with Na range of pressure : 2.14–2.34 mm.

O : with  $H_2$ ; without Na range of pressure : 4.80–9.82 mm.

Ethylene Chloride :—

Δ : with  $H_2$ ; without Na range of pressure : 1.98–5.17 mm.

where  $p_R$  is the value of  $p_{H_1}$  on the edge of the flame where the "HI impoverishment" is zero.  $p_Z$  that at the place of greatest "halogen impoverishment."  $\delta$  is the diffusion coefficient of sodium vapour in the carrier gas, and is used as a measure of the alteration of  $\delta'$  (the diffusion

coefficient of HI in the carrier gas) with the total pressure and the type of carrier gas.\*

The results shown in Fig. 5 confirm equation (3). The experiments include a variation of  $v$  between 2 and 40 m/sec. of  $p$  between 2 and 10 mm., the use of hydrogen and nitrogen as carrier gas, and  $C_2H_5Cl$  and  $C_2H_4Cl_2$  as halogen. Since equation (3) is valid for this last variation it is clear that, to a first approximation, the nature of the halogen can be neglected. There is an upper limit to  $v/\delta$  of approximately  $15 \times 10^{-2}$ , for equation (3) to be valid, corresponding to a limiting halogen impoverishment of about 90 per cent. Above this value the halogen impoverishment decreases instead of increasing with increasing  $v/\delta$  (for  $v/\delta = 16.5 \times 10^{-2}$  the impoverishment should be 100 per cent., but actually it is smaller than 90 per cent., and for  $18 \times 10^{-2}$  it is nearly 75 per cent.), possibly due to the formation of whirls.†

### 3. The Halogen Distribution in Different Planes Normal to the Nozzle

**Axis.**—Moving along a straight line  $l$  in the direction of the nozzle axis, we find a rapid decrease of the halogen impoverishment. This is seen from Fig. 6, where the halogen distribution is given for five circular planes

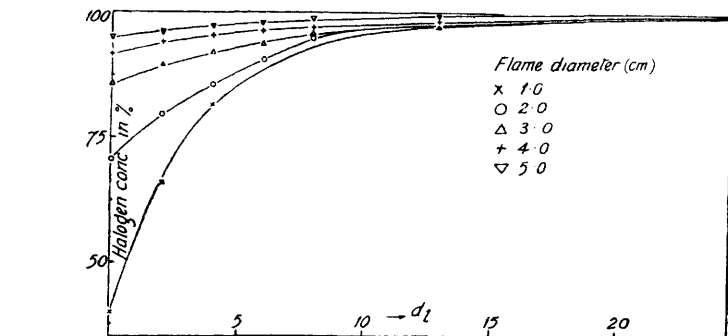


FIG. 6.

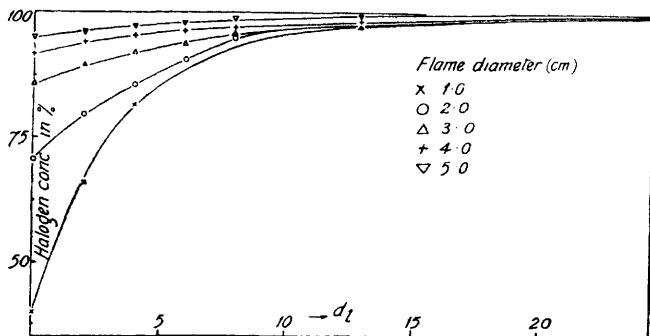


FIG. 7.—Variation with  $d_l$  of the halogen conc. in different cross-sections of the flame hemisphere perpendicular to the axis of the nozzle (for different size of flames).

normal to this line. The distance  $d_l$  of these planes from the nozzle mouth is equally graduated, and the  $v/\delta$  value is  $4.3 \times 10^{-2}$  ( $p = 5$  mm. :  $v = 4.6$  m/sec.).  $N_2$  was used as carrier gas.

\* We use  $\delta$  instead of  $\delta'$  since the value of the latter is unknown. This has also practical advantages. It is assumed that the relative variation of  $\delta$  and  $\delta'$  with the total pressure and the type of carrier gas is constant and that under our experimental conditions the mixture ratio does not influence  $\delta'$ .

† The whirls cannot occur in the nozzle. For streaming in the nozzle the critical  $v/\delta$  value would be  $800 \times 10^{-2}$  ( $270^\circ$ ). The whirls occur in front of the nozzle, where there are two streams of different speed side by side (for a central streaming speed of the Na—Tr gas mixture of 40 m./sec. for instance we calculate an outside streaming velocity of the Hal-, Tr gas mixture of  $1.4 \times 10^{-5}$  m./sec.). The mixing of these two streams directly in front of the nozzle will lead to whirl formation on hydrodynamic principles.



Considering the different values of the HI-concentration along a cross-section, we obtain the mean halogen concentration in different cross-sections of the flame hemisphere, of which the centre is the nozzle mouth. These calculated results are given for different sphere radii in Figs. 7 and 8 ( $v/\delta = 4.3 \times 10^{-2}$ ). We see from Fig. 7 that by decreasing the flame radius below 3 cm. the spacial inhomogeneity of  $p_{\text{HI}}$  increases rapidly.

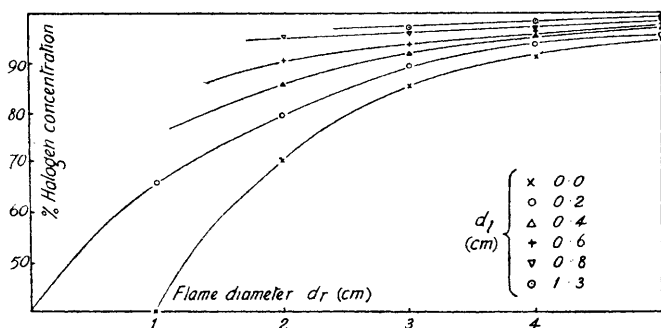


FIG. 8.—Variation with the size of the flame of the average halogen conc. in different cross-sections of the flame hemisphere perpendicular to the axis of the nozzle (for different values of  $d_l$ ).

**4. The Average Halogen Distribution in the Hemisphere in front, of the Nozzle for Flames of Different Diameters.**—The average halogen concentration in the total flame space before the nozzle was obtained by integration of six different cross-sectional concentrations. The results are given in Fig. 9 for various flame radii and a constant  $v/\delta$  value of  $4.3 \times 10^{-2}$ . For this value, in spite of the pronounced halogen im-

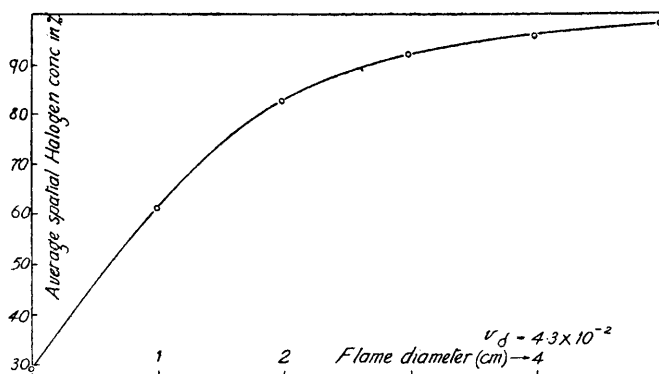


FIG. 9.—Mean halogen conc. in the flame hemisphere in front of the nozzle.

poverishment near the nozzle, the halogen distribution in the total space for large flames approximates to the conditions assumed in equation (1). This value, however, as we will show later (sec. 4), is approximately the lower limit below which the back diffusion of the HI into the nozzle introduces an increasing error of another nature. It is therefore important to know to what extent equation (1) holds if  $v/\delta$  increases, and approaches the upper limiting value of approximately  $15 \times 10^{-2}$ . For want of experimental evidence we made an indirect calculation on the justifiable



assumption that equation (3), found to be valid for a single point in space, holds also for a collection of points in space :—

$$\frac{p_R}{p_R - p_L} = k_n \frac{\delta}{v} \quad (3a)$$

Where  $k_n = f(d_r, d_i)$ . In this way we can determine the change of HI impoverishment with increasing  $v/\delta$  along the axis of the hemisphere (Fig. 10). The value of  $k_n = f(d_i)$  results from the fact that by undisturbed

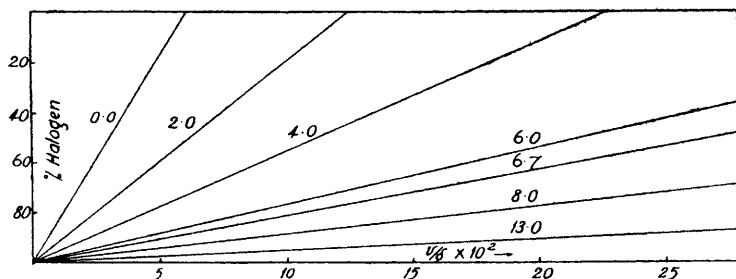


FIG. 10.—Change in halogen impoverishment (with  $d_r$ ) with  $v/\delta$  for different  $d_i$ . Numbers on curve give values of  $d_i$ .

diffusion ( $v = 0$ ) equation (3a) becomes for all points in space :—

$$\frac{p_R}{p_R - p_L} = 0.$$

and that the HI distribution along the hemisphere axis is known for  $v/\delta = 4.3 \times 10^{-2}$ . Further, we determined by integration the mean halogen concentration in the axis of the flame hemisphere, and used this as a measure of the mean halogen concentration in the total hemisphere. With this simplification, the homogeneity of all distributions appears to

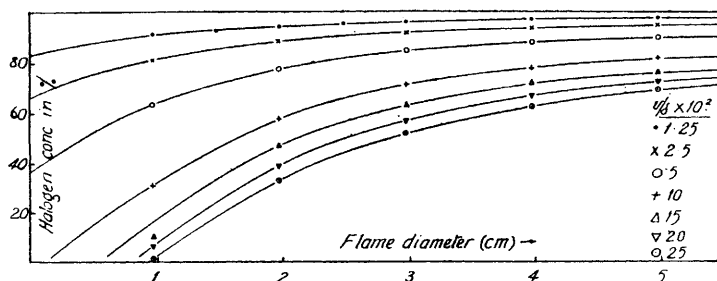


FIG. 11.—Dependence of halogen conc. along the axis of the flame hemisphere on the size of the sphere for different  $v/\delta$  values.

be worse than it actually is, and we may assume that, for all practical considerations, equation (3a) is valid. Figs. 11 and 12 contain the results. (The relationship for  $v/\delta > 15 \times 10^{-2}$  is actually more favourable on account of whirl formation.)

The exact calculation of the aerodynamical relationship in the flame for various values of  $v/\delta$ , which is of great theoretical interest, involves consideration of  $k_n = f(d_r)$ . This function can be deduced in all particular cases from the general nature of the curves given in Fig. 6. Table III shows the results of the exact and of the simplified calculation for one  $v/\delta$  value.

TABLE III.—COMPARISON OF THE EXACT AND APPROXIMATE CALCULATION OF THE HI DISTRIBUTION IN THE WHOLE FLAME.

$$v/\delta = 4.3 \times 10^{-2}.$$

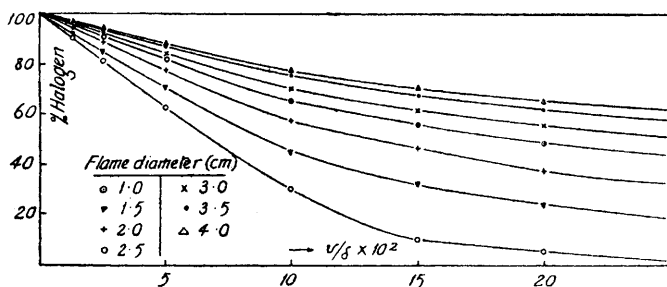
Diameter of flame in cm. . . . .	2.0	3.0	4.0	5.0
Average HI conc. in per cent. in the flame hemisphere . . . . .	82.3	91.8	95.4	97.8
Average HI conc. in per cent. along the axis of the flame hemisphere . . . . .	80.2	86.2	89.3	91.3

**5. The Validity of the Results in the Presence of Other Streaming Gases and of Sodium Vapour.**—The stationary spacial condition in the flame hemisphere in front of the nozzle is given by the differential equation :—

$$\Delta p - \frac{\omega}{D} \text{grad } p = 0 \quad . \quad . \quad . \quad (4)$$

which obviously bears a direct relationship with equation (3), which refers to the stationary appearance at a point in the space. Undoubtedly, also, one may assume that the ratio of the velocities, *i.e.*,  $\omega(x, y, z)$ , is constant, so the stationary spacial condition for any carrier gas is the same, if  $v/\delta$  is the same.

The presence of sodium (Fig. 5), the partial pressure of which was never greater than  $10^{-3}$ , is without any influence on the diffusion of halogen into the streaming gas.

FIG. 12.—Dependence of halogen conc. along the axis of the flame hemisphere on  $v/\delta$  for different sizes of spheres.

**6. The Practical Application of the Results.**—The results, especially those of Figs. 9, 11 and 12, lead to a series of important conclusions :—

(a) For flames greater than 3.5 cm. diameter, and for values of  $v/\delta$  up to approximately  $10 \times 10^{-2}$ , the deviations of the actual conditions from those assumed in equation (1) appear to be permissible, and the systematic change of the deviations with the size of the flame and  $v/\delta$  is then only relatively small. Thus, the flame sizes to be used experimentally have a lower limit and the  $v/\delta$  values an upper limit.

An upper limit of the flame size is reached at about 5.5 cms. Larger flames have too diffuse an edge for exact measurement. A lower limiting value of  $v/\delta$  is necessary to prevent the back diffusion of halogen into the nozzle (sec. 4); we shall see later (sec. 4) that this is  $5.5 \times 10^{-2}$ . Thus, using the whole permissible range of  $v/\delta$  and  $R$  variations, the maximum variation in the mean spacial halogen impoverishment is between 23 per cent. and 9.5 per cent.

As explained later, this large range of  $R$  and  $v/\delta$  variation cannot be allowed in the case of very fast or very slow reactions, or when  $H_2$  is used as carrier gas. In all other cases, however, one can obtain exact values

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for the *relative* reaction velocity constant  $K$  by working under any experimental conditions within the allowed region.

(b) The *absolute* values of  $K$  can be approximately determined from those obtained for the largest possible flames and the smallest possible  $v/\delta$  values (*i.e.*, the optimum experimental conditions) by extrapolation to the ideal condition,  $v/\delta = 0$ . As to the difference between these two values we conclude experimentally\* that, even if the halogen impoverishment is not taken into account in the  $p_{\text{H}}$  value used for the calculation of the experimental  $K$ , the difference cannot exceed 50 per cent. (in the most favourable part of the allowed experimental range) if the reactions considered have a mean inertia. By introduction of the true mean  $p_{\text{H}}$  and by consideration of the  $p_{\text{r}}$ -error produced by back diffusion of the H1 into the nozzle (sec. 5), this deviation can be reduced to 20 to 30 per cent. This deviation is mainly due to the fact that under the best experimental conditions the assumptions involved in equation (1) cannot be completely fulfilled. The most important part, therefore, of the error in the  $K$  values obtained experimentally with the improved diffusion method is due to the uncertainty of the true flame size (sec. 1).† These two errors give the possible difference between the best experimental and the absolute values of  $K$ . It is scarcely greater than 100 per cent.

(c) The reliability of the diffusion flame method has been greatly increased since the main systematic variations with experimental conditions (the cause and degree of which were previously largely incomprehensible) were found to be a necessary consequence of the aerodynamic relationships in the flame.‡ These conclusions are completely confirmed by the results of experiments.§

\* To be published shortly.

† This error could be reduced by comparing the size of the flame measured visually, and the size as determined photographically. From the latter, using the photometric method of Frommer and Polanyi (*Trans. Faraday Soc.*, 1934, 30, 519), the true value of the sodium pressure on the edge of the visually observed flame could be easily determined.

‡ These are:—

(1) For flame diameters of less than 3 cm. and especially below 2 cm. large variations of  $K$  must occur with variation in flame size as well as with variation in  $v/\delta$ . This appearance of an almost unlimited drift of  $K$  at small flame radii, which was already known from earlier experiments, no longer invalidates the use of the diffusion method, since it occurs under conditions which are not in accordance with equation (1).

(2) Above the  $v/\delta$  value of  $\approx 10 \times 10^{-2}$  (later experiments allow this limit to be extended to  $12 \times 10^{-2}$ ) the variation in  $K$  with  $v/\delta$  can be expected to be small since here (Fig. 12) the variation of the halogen impoverishment with variation in  $v/\delta$  becomes insignificant. The absolute extent, however, of the halogen impoverishment is in this region too great to justify an approximate application of equation (1).

(3) Above the purely aerodynamical critical  $v/\delta$  value of  $15 \times 10^{-2}$  (sec. 3) the reaction velocities may be expected to become still less variable since, as a result of whirl formation, a more uniform halogen distribution occurs, and thus not only the drift of  $K$  with  $v/\delta$  but also the drift with flame size disappears. In this region, therefore,  $K$  becomes practically independent of the experimental conditions. These conditions are unfavourable for exact experiments since the assumption of the spherical nature of the flame is no longer exact.

(4) In the region of the permissible  $v/\delta$  and  $R$  variation, the neglect of the effect of halogen impoverishment in the calculation of  $p_{\text{H}}$  must produce two kinds of apparent variation of  $K$  with experimental conditions. Firstly, there will occur a systematic drift of  $K$  with flame size ( $v/\delta$  remaining constant). The reaction velocity becomes too small with small flames (see Fig. 11). For the limits of  $v/\delta = 5$  and  $10 \times 10^{-2}$  this variation of  $K$  must amount to 6.5 per cent. and 13.5 per cent when the flame diameter varies from 3 cm. to 5 cm. Secondly, there is a systematic and apparent decrease of  $K$  with increase of  $v/\delta$  ( $R$  remaining constant). For a variation of 5 to  $12 \times 10^{-2}$ , this drift will be of the order of 16 per cent. (see Fig. 12) for flames of 4 cm. diameter. (For flames of 2 cm. this drift would reach the value of 26 per cent.)

§ To be published shortly.

#### 4. The Partial Pressure and Concentration Distribution of Sodium Vapour.

The pressure of sodium vapour at the nozzle mouth  $p_T$  is calculated from the temperature of the sodium vessel. The actual  $p_T$  differs, however, from the calculated value in so far as back diffusion of halogen into the nozzle against the carrier gas stream occurs. This back diffusion is governed by the equation:—

$$c_x = c_0 e^{-v/D} \quad . \quad . \quad . \quad . \quad (5)$$

where  $c_0$  is the halogen concentration directly in front of the nozzle, and  $c_x$  that in the nozzle, at a distance  $l$  from the nozzle mouth.

We should, therefore, expect that below the lower critical value of  $v/\delta$  there will be an apparent increase in reaction velocities with decrease in  $v/\delta$  and also with diminution of flame radius (variation of  $c_0$ ). There are two ways of removing these uncertainties: the suppression, as far as possible, of "back diffusion" or the determination of the real  $p_T$  value by calculations on the lines of equation (5). We preferred the first method.

The usual value of  $p_{H_1}$  outside the reaction zone is  $10^{-2}$ . If there is a 90 per cent. impoverishment directly in front of the nozzle, the halogen concentration there will be equal to the theoretical sodium concentration (*i.e.*,  $10^{-3}$ ) and in the case of comparatively slow reactions, the total reaction in the nozzle can then only lead to a small error in  $p_T$ . A 90 per cent. halogen impoverishment according to Fig. 10 corresponds to  $v/\delta$   $5.5 \times 10^{-2}$ , and for this reason we have selected this as the "lower critical" value of  $v/\delta$ .

This lower critical  $v/\delta$  value can be considered only as a standard for reactions of mean inertia (*i.e.*, with a collision number of about  $5 \times 10$  to  $5 \times 10^3$ ).<sup>\*</sup> For collision numbers below  $5 \times 10$  the reaction in the nozzle has considerable influence on  $p_T$ , and the reaction velocities appear much too large. To a certain extent the difficulty can be overcome by the choice of a greater  $v/\delta$  value for the lower limit, but in doing this, the region in which  $K$  is relatively constant is narrowed and this reduces the range of experimental conditions. In the case of high reaction velocities it is also necessary to suppress  $p_{H_1}$  very strongly below  $10^{-2}$  in order to get flames of satisfactory size, and this introduces a further difficulty, since the magnitude of  $p_{H_1}$  outside the reaction zone approaches that of  $p_T$ . If, on the other hand, the collision number is much greater than  $5 \times 10^3$ , then in spite of using heavier carrier gases one is obliged to give  $p_{H_1}$  a value much greater than  $10^{-2}$  to obtain a sufficiently small flame. If  $p_{H_1}$  reaches or exceeds the value  $10^{-1}$ , then the halogen concentration at the nozzle is ten times greater than that of the sodium. The small sodium reaction (for reaction of high inertia) cannot compete with the effect of the great penetration of halogen into the nozzle, since the rapidly occurring wall reaction can here assume great proportions. Here, again, one would expect a very strong decrease in  $K$  with increase in  $v/\delta$ , and this is found to be the case. Thus, in very slow reactions the diffusion method cannot give accurate results.

The distribution of the sodium vapour in the reaction zone is also important, but it cannot be experimentally determined because of its small partial pressure. However, the non-symmetrical distribution of the sodium and halogen are fundamentally bound up with one another and with the permitted  $v/\delta$  region from  $5.5$  to  $12 \times 10^{-2}$ , in which equation (1) is approximately satisfied. We can, therefore, neglect the non-symmetry of the sodium distribution.

<sup>\*</sup> This follows from results to be published later.

### 5. The Influence of the Halogen Compound on the Diffusion Constant.

The last question to be considered is that of the influence of the halogen compound on the diffusion coefficient (see equation (2)).

V. Hartel, Meer and Polanyi have already tried to eliminate this factor ; they studied the influence of pentane (as a chemically inert model substance for organo-halogen compounds) on the diffusion of sodium in nitrogen or hydrogen. Their main results (*loc. cit.*<sup>3</sup> Figs. 3 and 4) showed that the Tr-HI mixture would have great influence on  $\delta$  for the system Na—Tr—HI. The velocity constant  $K$  was corrected by means of the calibration curves obtained with pentane. In this way certain drifts of the  $K$  values with experimental conditions became less, and in some cases disappeared. A more extensive examination of this particular question, however, showed that here one is dealing with the superposition of a real and an apparent drift in opposite directions. The drift of  $K$  with increasing flame size certainly becomes weaker if the mean  $p_{\text{HI}}$  values increase. It, however, not only disappears for certain  $p_{\text{HI}}$  values, but inverts and grows again in the opposite direction if  $p_{\text{HI}}$  increases still further. This is quite incompatible with the actual relationships in the flames. It is comprehensible on the assumption that the variability of  $\delta$  is much higher than is actually the case.

This assumption is strongly supported by the experimental results given in Fig. 5. They show :—

(1) A negligible influence of the mixture ratio on the diffusion constant in the two gas systems  $\text{N}_2 - \text{HI}$ , and  $\text{H}_2 - \text{HI}$ . The values of  $\delta$  were calculated without taking account of the mixture ratio. The  $p_{\text{HI}}$  value varied from 12 per cent. to 40 per cent. in the case of  $\text{N}_2$  and from 2.4 per cent. to 16 per cent. in the case of  $\text{H}_2$ . Nevertheless, the scattering of the points is not systematic, showing that any effect on  $\delta$  due to the mixture ratio is less than the experimental accuracy under the conditions of the velocity constant experiments. Thus our results, as well as those of other authors, do not accord with the classical theoretical conclusion of O. E. Mayer :—

$$\delta : \delta' = m' : m$$

( $m$  = molecular weight).

(2) In the presence of sodium vapour  $\delta_{\text{Tr-HI}}$  remains practically unaltered (two points in Fig. 5 representing a halogen concentration of 45 per cent. and 70 per cent. and a sodium concentration of 0.1 per cent.). The triple system, therefore, behaves like a gas-pair, at least under the conditions of the velocity constant experiments.

This contradiction between our results and those of Hartel, Meer and Polanyi can be explained by the fact that the sodium partial pressure in velocity constant measurements is negligible (0.2 per cent. to 0.02 per cent. of the total pressure), whereas in their calibration experiments so small a value of  $p_{\text{Na}}$  could not be chosen ; it was over 10 per cent. of the total pressure. For the relationship in a triple system we obtain the equation (simplified) :—

$$\delta_{\text{Na-(Tr+HI)}} = \frac{1}{3N} \cdot (c_{\text{Na}} l_{\text{Na}} N_{\text{(Tr+HI)}} + \bar{c}_{\text{TrHI}} \cdot \bar{l}_{\text{TrHI}} \cdot N_{\text{Na}})$$

where  $l$  is the mean free path,  $c$  the molecular velocity, and  $N$  the

A discussion of this equation shows that the superimposed influence of two mixture ratios, though it is small for a gas pair, ought to preponderate in a triple system to give curves like those obtained by Hartel, Meer and Polanyi. But under experimental conditions where  $N_{\text{Na}} < 10^{-3}N$  the above equation takes the simpler form :—

$$\delta_{\text{Na-(Tr+HI)}} = \frac{1}{3} c_{\text{Na}} l_{\text{Na}} N_{\text{(Tr+HI)}}$$

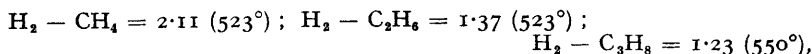
and the complex function of  $l_{Na}$  is simplified to:—

$$l_{Na} = \frac{3\sigma_{Na}^2}{\left[3c_{Na}^2 + \left(\frac{c_{HI} + c_{Tr}}{2}\right)^2\right] N_{(Tr+HI)} \Pi \left[\sigma_{Na} + \left(\frac{\sigma_{HI} + \sigma_{Tr}}{2}\right)\right]^2},$$

where  $\sigma$  is the molecular diameter.

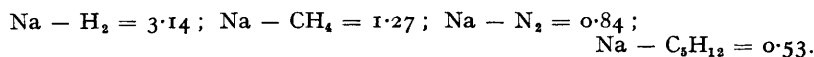
The remaining influence of the mixture ratio (which is practically that of a two-gas system) must disappear completely if there is a great similarity between those properties of the halogen compound and carrier gas which are of interest in this case ( $c$ ,  $\sigma$ ). In this case,  $\delta$  will be nearly invariable in the system Na—Tr—HI, whatever may be the mixture ratio Tr—HI ( $p_{Na}$  being < 1 per cent.).

Although the possible variation of  $\delta$  is far less than was admitted previously, its *drift with the mixture ratio* cannot be completely neglected. This drift will always produce a weak drift of the  $K$  values which must be avoided. The more important fact is that, by calculating with one standard  $\delta$ -value only, the variation of  $\delta$  with the *nature of the halogen compound* would be negligible. For instance, from the following variation of  $\delta$  with increasing length of carbon chain:—



it is easily realised that an observed small variation of  $K$  with rising length of the carbon chain of organo-halogen compounds could actually be due to the error introduced by the neglect of the  $\delta$  variation.

Since the calculation of these  $\delta$  variations on the basis of revised calibration curves is for many reasons excluded, they must be avoided experimentally. To do so we tried to obtain the above-mentioned ideal condition of great similarity between the carrier gas and the halogen compound for  $c$  and  $\sigma$ . As it is impossible to use a different carrier gas for every halogen compound, one was chosen such that  $\delta_{Na-Tr}$  lies *within* the limited range caused by the variation of  $\delta_{Na-HI}$  with the nature of the halogen compound. This condition is fulfilled by pentane. We have the following approximate values for:—



On the other hand, for the lightest halogenated organic compound,  $CH_3Cl$ , we obtain the approximate value:  $\delta_{Na-CH_3Cl} = 0.65$ . Since the lengthening of the carbon chain and also the introduction of more or heavier halogen atoms reduces the value of  $\delta_{Na-HI}$ , pentane is actually situated within the possible range.

A closer examination of the facts shows that the *change of  $K$* , (obtained using a constant  $\delta_{Na-C_5H_{12}-HI}$  value), *with the nature of HI*, seldom exceeds the accuracy of the diffusion method. As regards the *influence of the mixture ratio*, we found that  $\delta$  remains constant within a range of  $p_{HI}$  variation from 0 per cent. to 50 per cent. if  $\delta_{Na-HI}$  is smaller than 0.56; if it exceeds this value, the drift of  $\delta$  is negligible for the variation of  $p_{HI}$  from 5 per cent. to 10 per cent. Using the most unfavourable HI-compound,  $CH_3Cl$ , the drift of  $\delta$  within this range amounts to 6 per cent.

For rapid reactions the pentane pressure must be reduced below 1 mm. to obtain large enough flames. Under these conditions many technical difficulties arise connected with the regulation and maintaining constant of small pressures. Nitrogen and hydrogen therefore were still used as carrier gases, thus also allowing a larger experimental range. To exclude any influence of the halogen on  $\delta$  in this case, it was necessary to keep  $p_{HI}$  sufficiently small compared with  $p_{Tr}$ . In the presence of  $N_2$   $p_{HI}$  must remain below 3 per cent., and in the presence of  $H_2$  below 0.1 per cent. of the total pressure. Within these limits the variation of  $p_{HI}$  remains



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negligibly small. For the most part (principally for  $N_2$ ) this limitation of  $p_{HI}$  is already determined by that necessary to eliminate the influence of back diffusion.

### 6. Conclusion.

The most important result is that the Hartel-Polanyi diffusion method can be used in its now altered form for quantitative determinations of reaction velocities. This holds for reactions of collision number between  $5 \times 10$  and  $5 \times 10^3$ , if the following experimental conditions are fulfilled:

(a) The distribution of the reaction gases in the flame must correspond sufficiently to the assumptions made in equation (2), *i.e.*, for  $v/\delta$  values below  $12 \times 10^{-2}$ .

(b) The halogen partial pressure must be kept so small as to eliminate error through the back diffusion of HI into the nozzle as much as possible. This condition is fulfilled for  $v/\delta$  values greater than  $5 \times 10^{-2}$  if the halogen partial pressure does not exceed a small percentage of the total pressure in the case of  $H_2$  or  $N_2$  and 10 to 20 per cent. in the case of pentane as carrier gas.

(c) Flames must be greater than 3 cm. or better greater than 3.5 cm. diameter. In this case the approximation of the actual conditions to those of uniform halogen distribution in the flame and of the smallest possible back diffusion is the best. Smaller flames, on the other hand, fail in both respects, even if the  $v/\delta$  value lies within the permitted range.

(d) The influence of the halogen compound on the diffusion constant of sodium vapour in the carrier gas has to be completely eliminated. This is possible by the use of pentane as a carrier gas, or in the case of  $N_2$  or  $H_2$  by a stricter limitation of the variation of  $p_{HI}$ .

(e) The accurate determination of  $p_{HI}$  by taking into consideration the effect of slip in the capillaries, and also the reproducibility of the sodium pressure in the sodium oven.

The discussion of the various sources of errors has shown that the reaction velocities obtained by this method ought to differ by little more than 100 per cent. from the absolute values, if the best experimental conditions are used. In this case also, the middle term of equation (1) is negligible, and therefore, experiment is in very good agreement with the theoretical principles of the method.

The above experiments were carried out in the Kaiser Wilhelm. Institut für Physikalische Chemie at Berlin-Dahlem from 1931 to 1933. I should like to express my gratitude to Professor Polanyi for his constant advice in theoretical and experimental matters. I also wish to thank the Liebig Gesellschaft zur Förderung der deutschen Wissenschaft, and the Central British Fund for German Jewry for grants, and Dr. A. G. Evans who translated this paper from the German.

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