

352. *The Photo-expansion of Bromine.*

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Investigation has been made of the photo-expansion of bromine. An equation has been developed, in which the relationship between the photo-expansion, the thermal conductivity, the total pressure, and the light absorbed is shown.

The effect on the photo-expansion of bromine of adding various foreign gases has been examined. The addition of such gases, in general, increases the photo-expansion by facilitating the homogeneous recombination of bromine atoms. The series representing the efficiencies of the triple collision process is given by $\text{CO}_2 > \text{O}_2 > \text{N}_2 > \text{H}_2 > \text{A}$.

The variation of the thermal conductivity with the pressure of bromine has been examined.

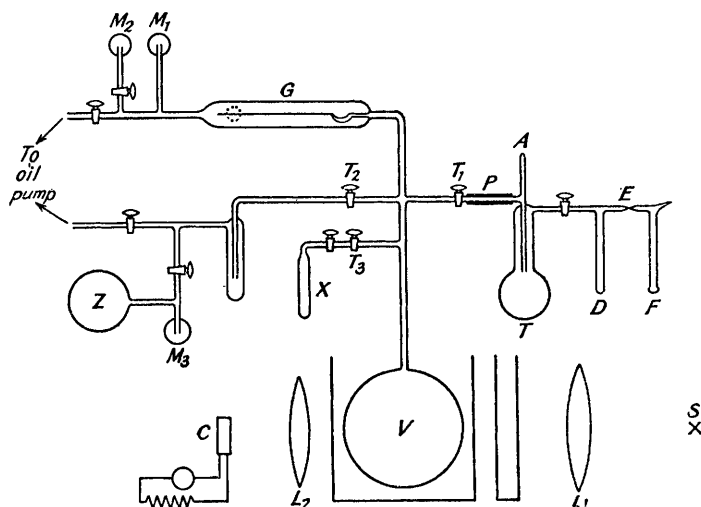
Addition of water vapour after very careful drying did not produce any marked effect in the expansion.

THE present work was undertaken with the object of studying the effect of foreign gases on the expansion of bromine when exposed to light. It was hoped to draw definite conclusions as to the part played by dissociation of the bromine into atoms, the diffusion of these to the walls, their recombination in the gas phase and on the walls of the vessel, and finally to clear up what may be called the mystery of the contradictions which exist as to the effect of moisture and of careful drying on the magnitude of the expansion.

Since this work was begun papers have been published by Rabinowitch and his co-workers which have added considerably to the quantitative knowledge of the dissociation and recombination. Their experimental method was quite different from ours, depending on the photo-electric cell measurement of the decrease in the absorption of the molecular bromine when a portion had been converted into atoms, whereas we were concerned to explore the effect of inert gases by measuring direct expansion which would enable more direct comparison to be made with earlier work.

Apparatus.—The apparatus used is shown diagrammatically in Fig. 1. The spherical insulation vessel *V*, made of soft glass, had an internal volume of 1500 c.c. and was connected to the

FIG. 1.



Bourdon gauge as shown. The vessel was immersed in water contained in a bath which had plane glass walls. (The temperature of the water was that of the room, which did not vary by more than 1° in the course of a day.)

The gauge G had a sensitivity such that 1 division of eyepiece scale = 0.210 mm. mercury. D was the bromine reservoir and Z a reservoir for inert gases, M_3 being a mercury manometer used to give an indication of the amount of gas in Z .

P was a tube about 4 cm. in diameter, loosely filled with pure phosphoric oxide. This was used to ensure that the moisture content of the bromine was at a minimum. As fairly high pressures were used, the taps were lubricated with apiezon grease which had been exposed for several days to bromine vapour.

The light source S was a 500 watt projector lamp. As shown by a voltmeter, the lamp was run at 220 volts from a 230 volts A.C. mains by hand-controlled resistance. By means of a condenser lens L_1 , a convergent beam of light was made to fall upon the insolation vessel. Since the latter was spherical, a convergent beam seemed preferable to a parallel beam. Before entering the vessel, the light was passed through a 14 cm. layer of a 2% solution of copper sulphate. The emerging beam of light was focused upon a Weston Photronic cell C , by means of a condenser lens L_2 . The cell, shielded from external radiations, was connected in series with a Weston galvanometer and a fixed resistance. This system always gave perfectly reproducible results.

Preparation of Materials.—Bromine, bought as pure, had the last traces of chlorine removed by distillation from a solution of potassium bromide. Any traces of hydrobromic acid were removed by shaking the bromine with a very dilute solution of potassium hydroxide, separating it, and finally distilling it from moist zinc oxide. It was kept over phosphoric oxide. Before use, it was fractionally distilled at low pressure several times. This was done by cooling F in carbon dioxide-acetone, and cooling the receiving tube D in liquid air. The initial and the final fraction were in each case removed by pumping off. The final sample was collected in D , and the constriction at E sealed.

Before being collected in the reservoir, argon (99.5%), nitrogen (99%), oxygen (97%), carbon dioxide, all supplied in cylinders by the British Oxygen Company, sulphur dioxide (from a siphon), and air were bubbled slowly (2 bubbles per second) through two wash-bottles containing concentrated sulphuric acid and then passed through a tube, about 20 cm. long, loosely packed with phosphoric oxide. Before use, argon, nitrogen, oxygen and air were passed through a liquid air trap.

Experimental Procedure.—The apparatus was evacuated by a Hyvac oil-pump, and the transmitted light intensity I_0 at zero pressure of bromine measured by means of the photronic cell system. The levels of the mercury columns in the manometers and the initial position of the gauge pointer image were observed. After "washing" out with bromine vapour, bromine was introduced into the insolation vessel by way of tap T_1 to the desired pressure and illuminated under standard conditions; the deflections of the gauge pointer and galvanometer needle were observed, giving the photo-expansion and transmitted light intensity I at the pressure $[Br_2]$. This process was repeated several times, no appreciable deviations being observed.

In examining the effect of "foreign" gases, the pressures of bromine used were in general 30, 40, and 50 mm. The photo-expansion and the light energy absorbed ($I_{\text{abs.}} = I_0 - I$) for the particular pressure having been recorded, the "foreign" gas was added to the required pressure; the transmitted light intensity was then redetermined, and the photo-expansion measured. Before the latter measurement was made, the bromine-gas mixture was allowed 15 minutes to attain complete mixing; this was found to be necessary, as otherwise incorrect results were obtained.

Theoretical Discussion of the Experiment.

Studies of the photo-dissociation of bromine molecules and of the recombination of bromine atoms have shown that recombination to form the homopolar molecule requires what is virtually a triple collision between the two atoms and a third body acting as a stabiliser (Born and Franck, *Z. Physik*, 1925, **31**, 411; Jost and Jung, *Z. physikal. Chem.*, 1929, **3**, B, 83). The probability of recombination by an immediate reversal of the primary photo-chemical process with emission of radiation has been shown to be small under the conditions of the photo-chemical experiments (cf. Kondratjew and Leipunsky, *J. Phys. Chem.*, U.S.S.R., 1932, **3**, 383).

The concentration of atoms in the gas phase may be considerably reduced by removal of atoms by the walls of the reaction vessel. This effect will be minimised by high pressures of the reactants; the same result will be produced by the addition of an inert gas, but at the same time removal of the atoms by the gas-phase triple collision process will be facilitated, the added gas acting as the third body (Jost and Jung, *loc. cit.*; Jost, *ibid.*, 1929, **3**, B, 95; Ritchie, *Proc. Roy. Soc.*, 1934, *A*, **146**, 828). Absolute velocity coefficients for the triple collision processes with different third bodies have been given by, *inter alios*, Hilferding

and Steiner (*Z. physikal. Chem.*, 1935, B, 30, 399) and Rabinowitch (*Trans. Faraday Soc.*, 1937, 33, 283).

The above considerations refer to bromine atoms obtained by photo-dissociation by light of wave-lengths in the continuous region of the bromine spectrum. Jost (*loc. cit.*) found that the velocity of hydrogen bromide formation in the band region about 5650 Å. was approximately the same as in the continuum, indicating the dissociation by collision of such primarily excited molecules into normal atoms, little distinction being observed between normal and excited atoms in the photo-synthesis.

The bromine atoms produced by the absorption of light may thus be considered in two divisions: (a) those recombining in the gas phase by triple collision, the heat of combination appearing in the gas phase and causing an increase of pressure; (b) those removed by surface action. The above effects may then be represented by the following scheme:

No.	Reaction.	Velocity coefficient.
1	$\text{Br}_2 + h\nu = \text{Br} + \text{Br}$	k_1
2	$\text{Br} + \text{Br} + \text{M} = \text{Br}_2 + \text{M}$	k_M
3	$\text{Br} + \text{wall} = \frac{1}{2}\text{Br}_2$	S

where M is an added inert gas molecule; $S[\text{Br}]$ represents the rate at which atoms are removed from the gas phase at the wall, and includes the rate of diffusion to the wall through the gas mixture, as well as a collision factor depending on the nature of the wall itself.

If the vessel is large and the pressure high, recombination according to mechanism No. 2 will be predominant. The total heat appearing in the gas-phase will be equivalent to the energy absorbed ($I_{\text{abs.}}$) and will be independent of the gases present (except in so far as $I_{\text{abs.}}$ alters with the addition of foreign gases). In the steady state, however, the temperature rise will depend on the rate at which heat is conducted to the thermostated walls of the vessel, *i.e.*, on the thermal conductivity of the gas mixture.

In the photo-stationary state,

$$d[\text{Br}]/dt = k_1 I_{\text{abs.}} - k_M [\text{Br}]^2 [\text{M}] - S[\text{Br}] = 0 \quad (1)$$

On the assumption that the rise in temperature indicated by the increase in pressure Δp is due entirely to heat produced in the gas and that heat produced on the surface does not affect Δp , the heat produced in the gas phase is proportional to $k_M [\text{Br}]^2 [\text{M}]$. In the steady state, the heat transferred to the walls per second will be equal to the heat produced in the gas phase per second, and the rise in temperature will depend on the thermal conductivity of the gas mixture.

In the case of a gas, the thermal conductivity is independent of the pressure when the pressure is sufficiently high (see later experiments; p. 1687). In the present experiments, with a relatively narrow beam, fixed in position, traversing the gas mixture with the walls at a fixed temperature (thermostated), we may apply the general conductivity formula, $Q = K \cdot A \cdot \Delta T/x$ (where Q is the heat quantity transferred per second across an area A , ΔT is the difference in temperature between two planes at a distance x , and K is the thermal conductivity coefficient of the medium between the two planes), in the approximate form $Q \propto \Delta T \cdot K$, where ΔT represents the rise in temperature of the mixture in the illuminated steady state. Since for any gas mixture the increase in pressure is proportional to the rise in temperature, $Q \propto \Delta p \cdot K$. Hence

$$K\Delta p \propto k_M [\text{Br}]^2 [\text{M}], \text{ or } RK\Delta p = k_M [\text{Br}]^2 [\text{M}]$$

where R is a constant.

$$\text{From equation 1, } [\text{Br}] = (-S \pm \sqrt{S^2 + 4k_1 I_{\text{abs.}} k_M [\text{M}]}) / 2[\text{M}] k_M.$$

k_1 may be taken as 2, and since $[\text{Br}]$ must be positive,

$$[\text{Br}] = (-S + \sqrt{S^2 + 8I_{\text{abs.}} k_M [\text{M}]}) / 2[\text{M}] k_M.$$

But

$$RK\Delta p = k_M [\text{M}] [\text{Br}]^2 = 2I_{\text{abs.}} - S[\text{Br}].$$

Hence, on substituting for $[\text{Br}]$,

$$RK\Delta p = 2I_{\text{abs.}} - S(\sqrt{S^2 + 8I_{\text{abs.}} k_M [\text{M}]} - S) / 2k_M [\text{M}] \quad (2)$$

For mixtures of bromine and one inert gas, $[M]k_M$ must be replaced by $([Br_2]k_{Br_2} + [X]k_X)$, where $[X]$ is the pressure of inert gas. Equation 2 then becomes

$$RK\Delta p = 2I_{\text{abs.}} - S(\sqrt{S^2 + 8I_{\text{abs.}}([Br_2]k_{Br_2} + [X]k_X)} - S)/2([Br_2]k_{Br_2} + [X]k_X)$$

or
$$RK\Delta p = 2I_{\text{abs.}} - Y \dots \dots \dots (3)$$

whence
$$I_{\text{abs.}} = \frac{1}{2}(RK\Delta p + Y) \dots \dots \dots (4)$$

The thermal conductivity K will differ for each gas mixture. Calculation of S for the various conditions was approached as follows. If t is the time taken for a bromine atom to diffuse a given distance through bromine vapour, $t \propto 1/D_{Br_2}$, where D_{Br_2} represents the diffusion factor. For a mixture of gases, we may take (Ludlam and Melville, *Proc. Roy. Soc.*, 1931, A, 132, 108; Ritchie, *loc. cit.*)

$$t \propto 1/D_1 + 1/D_2 + 1/D_3 + \dots$$

and since
$$S \propto 1/t,$$

$$S = m(1/D_1 + 1/D_2 + 1/D_3 + \dots)^{-1}$$

where m is a constant depending on vessel dimensions, nature of the wall, etc., and

$$D \propto 1/[X]\sigma_{AX}^2(1/M_A + 1/M_X)^{-1}$$

Here M_A is the molecular weight of the particle diffusing, *i.e.*, the bromine atom, M_X is the molecular weight of the inert gas, $[X]$ is the pressure of inert gas, and σ_{AX} is the sum of the radii of inert gas molecule and atom.

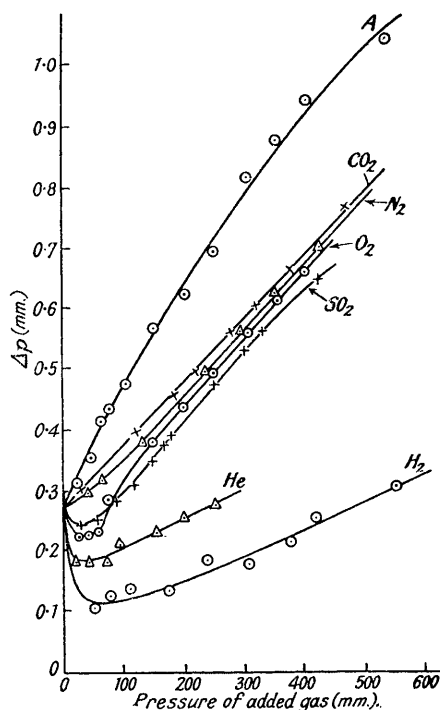
In the above general discussion, no reference has been made to the possible increase in pressure due to the dissociation itself. If the light quantum absorbed is just sufficient to dissociate the molecule into a normal and an excited atom (light of wave-length corresponding to the convergence limit), then the kinetic energy of the resultant atoms will be the same as that of the original molecule and any change in pressure on dissociation will be due to the energy of excitation of the excited atom transferred in collision. This effect will be smaller if the wave-length employed is greater than that of the convergence limit, in which case dissociation will occur only after collision of the excited molecule with other gas molecules. If the quantum be of greater energy than that required for dissociation, the excess energy will appear as kinetic energy of the products, with a consequent increase in temperature. Consideration, however, of the absolute light intensity of the source used indicated that these factors could be of small importance only and showed that the observed pressure increase was due almost entirely to the heat liberated in the atomic recombination.

Possible convection effects have also been neglected for the same reason.

Results and Discussion.

Experimental results and calculations are given in Tables I—VI. In Fig. 2, Δp is plotted against the pressure of added gas. At low pressures there may be no increase but a decrease in Δp , shown most clearly in the cases of hydrogen and helium, an effect which is to be predicted on thermal conductivity grounds alone. The first addition of inert gas will

FIG. 2.



have little effect on the number of atoms combining, but the observed Δp will depend on the thermal conductivity of the gas mixture. If this increases rapidly in the initial stages from a low value to a high one, as it does markedly in the cases of hydrogen and helium, then Δp will be relatively smaller and may fall below the original value. This decrease is more noticeable with lower pressures of bromine, since the increase in conductivity on addition of an inert gas will be greater than in the case where the pressure is initially higher.

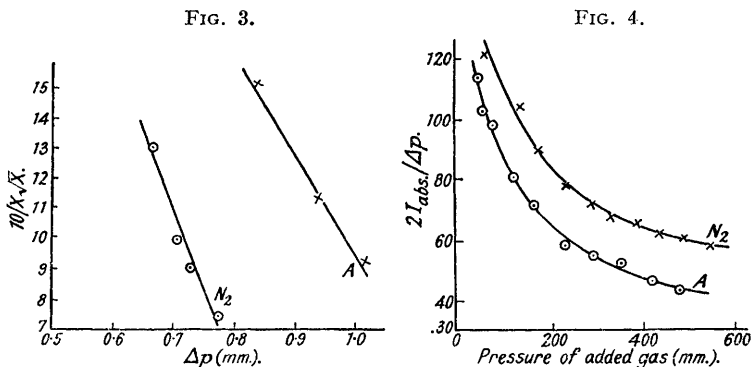
Further addition of inert gas causes K to tend to a constant value, namely, that for the inert gas alone. At the same time, however, diffusion to the walls is prevented and the number of triple collisions increases, the latter effects outweighing the former and an increase in the photo-expansion being observed.

At high pressures of inert gas K and $I_{\text{abs.}}$ are roughly constant and S becomes small. Hence, since $[\text{Br}_2]k_{\text{Br}_2}$ is small compared with $[\text{X}]k_{\text{X}}$, equation 3 becomes

$$RK\Delta p = 2I_{\text{abs.}} - S\sqrt{8I_{\text{abs.}}([\text{Br}_2]k_{\text{Br}_2} + [\text{X}]k_{\text{X}})/2([\text{Br}_2]k_{\text{Br}_2} + [\text{X}]k_{\text{X}})} \\ = 2I_{\text{abs.}} - S\sqrt{2}\sqrt{I_{\text{abs.}}}/\sqrt{[\text{X}]k_{\text{X}}}$$

But $S \propto 1/[\text{X}]$, and therefore plotting Δp against $1/[\text{X}]\sqrt{[\text{X}]}$ gives a straight line (Fig 3).

At very high pressures of added gas $RK\Delta p = 2I_{\text{abs.}}$, i.e., $2I_{\text{abs.}}/\Delta p$ tends to the constant value RK as shown for nitrogen and argon in Fig. 4, where $2I_{\text{abs.}}/\Delta p$ is plotted against the pressure of added gas. The ratio of the limit values for nitrogen and argon is approximately $55/38 = 1.44$, in agreement with the ratio of the respective thermal conductivities $2.28/1.58 = 1.45$ (neglecting the relatively small pressures of bromine present).



By extrapolation, curves such as those of Fig. 4 give the value of R for the experimental conditions. At zero pressure of added gas, on the other hand, the R term becomes small and the value of m in the S factor important; by taking k_{Br_2} as unity, the value of m may be estimated. The intermediate pressures then give the appropriate values of k_{M} in relation to k_{Br_2} .

In the calculations of Tables I—VI use was made of the following constants:— $\sigma_{\text{Br}} = 2.0 \times 10^{-8}$ cm., $\sigma_{\text{Br}_2} = 3.4 \times 10^{-8}$ cm., $\sigma_{\text{A}} = 2.86 \times 10^{-8}$ cm., $\sigma_{\text{N}_2} = 3.10 \times 10^{-8}$ cm., $\sigma_{\text{O}_2} = 2.90 \times 10^{-8}$ cm., $\sigma_{\text{H}_2} = 2.30 \times 10^{-8}$ cm., $\sigma_{\text{CO}_2} = 3.20 \times 10^{-8}$ cm.; $k_{\text{Br}_2} = 1.0$, $k_{\text{A}} = 0.50$, $k_{\text{N}_2} = 0.80$, $k_{\text{O}_2} = 0.90$, $k_{\text{H}_2} = 0.60$, $k_{\text{CO}_2} = 0.90$; $K_{\text{Br}_2} = 0.44$, $K_{\text{A}} = 1.58$, $K_{\text{N}_2} = 2.28$, $K_{\text{O}_2} = 2.33$, $K_{\text{H}_2} = 15.9$, $K_{\text{CO}_2} = 1.37$. The thermal conductivities of the various gas mixtures were taken to be linear functions of the composition; these and values of m and R are given in the Tables. In the final columns are given the ratios of the values of the right hand side to those of the left hand side of equation 4. In any one series, the incident light intensity remained constant, though $I_{\text{abs.}}$ increased with the pressure of added gas (see Tables), corresponding to the broadening of the bromine absorption bands by the added gas molecule (cf. Ribaud, *Ann. Phys.*, 1919, **12**, 208) and due to the perturbation of the molecular forces with consequent absorption over a wider range of frequencies. This effect is particularly noticeable with hydrogen.

The ratios in the final columns of the Tables approximate to unity, indicating that the general equation satisfactorily expresses the experimental data. The values of m and R are sensibly constant for Tables I—V. On the other hand, results for carbon dioxide (Table VI) and sulphur dioxide cannot be so expressed over the entire range of pressures; application of the equation with similar values of m and R gives apparently negative values for

TABLE I.

Inert gas effect of nitrogen. $[\text{Br}_2] = 50.0 \text{ mm.}, R = 24.0, m = 5.0 \times 10^{-11}.$

$[\text{N}_2], \text{mm.}$	$\Delta p, \text{mm.}$	$I_{\text{abs.}}, \text{divs.}$	$RK\Delta p.$	$Y.$	$\frac{1}{2}(RK\Delta p + Y).$	$\frac{R.H.S.}{L.H.S.}$
0.0	0.336	21.7	3.54	41.1	22.3	1.02
64.2	0.357	21.9	12.54	33.8	23.2	1.05
136.4	0.420	22.0	17.95	25.4	21.7	0.99
170.7	0.483	22.1	21.2	21.9	21.55	0.98
235.0	0.567	22.2	26.7	17.45	22.1	1.00
284.6	0.609	22.3	29.2	14.75	22.0	0.99
336.5	0.651	22.3	31.9	12.5	22.2	1.00
390.6	0.672	22.4	34.5	10.7	22.6	1.01
441.7	0.714	22.4	35.9	9.4	22.6	1.01
494.1	0.735	22.5	38.8	8.8	23.1	1.02
567.4	0.777	22.5	39.8	8.0	22.9	1.02

TABLE II.

Inert gas effect of nitrogen. $[\text{Br}_2] = 40.0 \text{ mm.}, R = 24.0, m = 3.5 \times 10^{-11}.$

0.0	0.273	19.9	2.9	37.6	20.25	1.02
15.4	0.273	19.9	6.25	36.1	21.2	1.06
41.0	0.294	20.0	9.7	32.9	21.3	1.06
72.7	0.336	20.1	12.9	29.7	21.3	1.06
132.9	0.378	20.5	16.1	22.2	19.15	0.93
187.4	0.462	20.5	21.7	17.3	19.5	0.95
240.0	0.504	20.6	24.3	13.1	18.7	0.92
292.0	0.567	20.9	27.8	12.1	19.95	0.97
348.2	0.630	20.9	31.7	9.7	20.7	0.99
424.7	0.714	20.9	36.2	7.8	22.0	1.05

TABLE III.

Inert gas effect of argon. $[\text{Br}_2] = 40.0 \text{ mm.}, R = 24.0, m = 3.5 \times 10^{-11}.$

$[\text{A}], \text{mm.}$						
0.0	0.273	19.9	2.9	37.6	20.25	1.02
10.6	0.294	20.0	4.8	36.3	20.55	1.02
24.7	0.315	20.0	6.6	35.5	21.05	1.05
39.0	0.357	20.1	8.55	33.8	21.2	1.05
60.2	0.420	20.1	11.35	31.2	21.3	1.06
72.9	0.441	20.2	12.3	30.0	21.15	1.04
101.4	0.483	20.3	14.6	26.5	20.55	1.02
151.8	0.567	20.3	17.6	24.6	21.1	1.04
204.0	0.630	20.6	21.05	17.2	19.1	0.93
253.4	0.756	20.8	25.7	17.45	20.1	0.96
302.1	0.819	20.9	28.5	12.15	20.3	0.96
354.2	0.882	21.0	30.7	10.4	20.55	0.98
401.6	0.945	21.0	33.6	9.05	21.3	1.01
538.5	1.05	21.0	37.8	6.35	22.1	1.05

TABLE IV.

Inert gas effect of oxygen. $[\text{Br}_2] = 40.0 \text{ mm.}, R = 24.0, m = 3.5 \times 10^{-11}.$

$[\text{O}_2], \text{mm.}$						
0.0	0.273	19.5	2.9	37.3	20.1	1.03
79.9	0.315	20.0	12.8	27.0	19.9	1.00
100.0	0.336	20.0	14.4	25.0	19.7	0.98
149.9	0.378	20.1	17.5	18.8	18.15	0.90
202.5	0.441	20.2	21.3	15.0	18.15	0.90
253.1	0.504	20.2	25.2	12.2	18.7	0.93
301.0	0.567	20.2	28.7	10.1	19.4	0.97
352.0	0.630	20.3	32.4	8.6	20.5	1.01
400.0	0.672	20.3	34.9	7.55	21.2	1.04

TABLE V.

Inert gas effect of hydrogen. $[\text{Br}_2] = 40.0 \text{ mm.}$, temp. = 25.0° , $R = 8.0$, $m = 4.0 \times 10^{-11}$.

$[\text{H}_2]$, mm.							
0.0	0.320	24.4	1.15	47.0	24.1	0.99	
24.0	0.128	25.1	3.84	46.6	25.2	1.00	
48.0	0.102	25.5	4.8	45.3	25.0	0.98	
74.7	0.128	25.8	7.7	44.2	26.0	1.01	
109.1	0.141	26.0	10.2	42.5	26.3	1.01	
171.5	0.141	26.1	12.3	38.4	24.7	0.95	
241.0	0.192	26.5	18.3	34.6	26.5	1.00	
313	0.179	26.7	18.5	30.8	24.7	0.93	
374	0.218	26.5	23.4	27.3	25.4	0.96	
421	0.256	26.4	28.2	25.2	26.7	1.01	
482	0.269	26.4	30.3	23.0	26.6	1.01	
570	0.320	26.4	36.8	20.1	28.4	1.07	

TABLE VI.

Inert gas effect of carbon dioxide. $[\text{Br}_2] = 40.4 \text{ mm.}$, $k_{\text{CO}_2} = 0.90$, $R = 30.0$, $m = 8.0 \times 10^{-11}$.

CO_2 , mm.							
0.0	0.273	19.1	6.55	35.3	20.9	1.09	
28.1	0.294	19.1	7.22	36.8	22.0	1.15	
44.0	0.336	19.2	9.37	35.8	22.6	1.18	
73.6	0.315	19.5	9.8	34.4	22.1	1.13	
123.4	0.399	19.7	13.5	30.2	21.8	1.11	
173.7	0.399	19.8	14.3	25.5	19.9	1.01	
223.1	0.504	19.9	18.6	21.6	20.1	1.01	
275.2	0.567	20.0	21.25	18.3	19.8	0.99	
327.6	0.609	20.1	23.15	15.6	19.4	0.97	
370.3	0.672	20.1	25.75	13.8	19.8	0.98	
424.0	0.714	20.2	27.6	11.9	19.8	0.98	
467.3	0.777	20.2	30.2	10.7	20.45	1.01	
513.4	0.798	20.2	31.2	9.6	20.4	1.01	

k_{CO_2} and k_{SO_2} , the divergence being such as to indicate removal of bromine atoms by a process which does not give an appreciable heat evolution. This may be chemical reaction in the case of sulphur dioxide, but it is perhaps noteworthy that for pressures of carbon dioxide greater than 150 mm. the theoretical relationship holds for $m = 8 \times 10^{-11}$, $k_{\text{CO}_2} = 0.90$, and $R = 30.0$ (Table VI). It must be remembered that m , involving the rate of removal of bromine atoms at the wall, must depend on the nature of the wall, and this may alter appreciably as the pressure of the easily adsorbed gases sulphur dioxide and carbon dioxide increases. At higher pressures, the value of m may approach a constant value, not necessarily the same as in the case of the less easily adsorbed permanent gases nitrogen, oxygen, etc., and therefore the carbon dioxide coefficient 0.90 is considered comparable with the corresponding coefficients for the other gases. A table of triple collision coefficients has recently been given by Ritchie (this vol., p. 857); the above values may here be compared with values already obtained for the Br-Br combination, k_{N_2} being taken as unity :

Method.	Br_2 .	CO_2 .	O_2 .	N_2 .	A.	H_2 .	Ref.
Absorption decrease ...	—	2.16	1.28	1.00	0.52	0.85	Rabinowitch and Wood, <i>Trans. Faraday Soc.</i> , 1937, 36 , 907.
HBr photosynthesis ...	—	(1.387)	1.38	1.00	0.64	0.51	Ritchie, <i>Proc. Roy. Soc.</i> , 1934, A , 146 , 828.
Budde effect	1.25	1.13	1.12	1.00	0.63	0.75	Present results.

The relative values are in approximate agreement with those determined by the other methods and indicate the general applicability of the treatment.

In the case of helium, under the experimental conditions, the diffusion effect is predominant up to the highest pressure of helium employed (see Fig. 2); this in conjunction with the small triple collision efficiency for helium rendered the accurate determination of k_{He} out of the question.

The above type of calculation cannot be applied to varying pressures of bromine, in that alteration of bromine pressure alters the position of the source of the bromine atoms. With increasing pressure, for example, the region of absorption moves closer to the wall where the light enters; no constant value of m can be expected to apply to different bromine pressures.

The Effect of Pressure on the Thermal Conductivity of Bromine.

Equation 2 is based on the assumption that the thermal conductivity of a gas is independent of the pressure. Maxwell from a consideration of the kinetic theory of gases predicted that there should be no variation over a wide range of pressures; the thermal conductivity will, however, decrease if the pressure is lowered so that the mean free path becomes comparable with the size of the vessel. The results of Senftleben and Riechemeier (*Ann. Physik*, 1930, 6, 112) show that with hydrogen under the experimental conditions the thermal conductivity did not reach a steady value even at a pressure of 100 mm. With argon the thermal conductivity became constant when the pressure was about 10 mm. The variation of the thermal conductivity of bromine was therefore examined for different pressures under our experimental conditions. The experiments performed depended on the fact that, when a hot wire is suspended in a gas-containing vessel the walls of which are at a lower temperature than the wire, heat flows from the wire to the walls. Increase in the conductance causes an increase in the heat flow. This cools the wire and lowers its resistance. Senftleben and Germer (*ibid.*, 1929, 2, 847) have shown that platinum wire may be used with bromine without fear of chemical interaction.

Experiment.—The apparatus used was the same as that shown in Fig. 1 except that the vessel V was replaced by a tube 20 cm. by 3 cm. This was kept in an electrically heated thermostat maintained at $25^\circ (\pm 0.01^\circ)$. A platinum wire 0.015 mm. in diameter and 7 cm. long was suspended in the tube. The leads, pinch-sealed into the tube, consisted of borated copper wire encased in glass capillaries. The copper wire was spot-welded to platinum wire of 0.5 mm. diameter, which in turn was welded to the gauge wire. Before any experimental measurements were made, the gauge wire was glowed for some time in bromine vapour.

The method adopted was to keep the applied voltage constant and measure the change in resistance as the pressure was varied. Bromine, the pressure of which was measured by means of the calibrated Bourdon gauge system, was then admitted to the tube. The resistance of the wire decreased and the change of resistance Δr with different pressures of bromine was thus observed.

The thermal conductivity of bromine reaches a constant value when the pressure is between 2 and 3 mm. Hence with the pressures used in the examination of the photo-expansion of bromine it is safe to say that the thermal conductivity coefficient K_{Br_2} was constant.

The Effect of Water Vapour.

The possible effect of water vapour on the Budde effects in bromine and chlorine has often been investigated. Ludlam (*Proc. Roy. Soc. Edin.*, 1924, 44, 197) concluded that dry bromine exhibited no Budde effect and suggested that the energy absorbed was re-radiated. Lewis and Rideal (J., 1926, 583) maintained that, since the presence of moisture seemed necessary for the expansion, the effect was due to the photo-sensitive hydrate $Br_2 \cdot H_2O$. They showed the photo-expansion to be proportional to the partial pressures of bromine and water vapour, and advanced a mechanism of excitation and decomposition of these hydrate molecules as the explanation of the effect.

On the other hand, Brown and Chapman (J., 1928, 560) maintained that drying does not diminish the photo-expansion to any great extent with a mixture of air and bromine, contrary to the results of Lewis and Rideal. Matthews (*Trans. Faraday Soc.*, 1929, 25, 41) found that, although there was a diminution in the Budde effect on drying bromine, it did not disappear entirely, though Ludlam and Mooney later pointed out (*Proc. Roy. Soc. Edin.*, 1929, 49, 256) that, since in Matthews' experiments liquid bromine at constant temperature was in contact with the vapour, any photo-expansion observed would be due to the slight time lag in establishing equilibrium, and the pressure above the liquid would always be the same. They further suggested that in the event of there being no adsorbed film of water on the surface of the containing vessel, then recombination of the halogen atoms would take place on the walls. The heat of recombination would be dissipated, the heat capacity of the walls being very much greater than that of the gas. They also found that the energy absorbed by the bromine was not re-radiated as fluorescence at the pressure used (64 mm.).

Kistiakowsky (*J. Amer. Chem. Soc.*, 1929, 51, 1395) found that careful purification and

drying of bromine and chlorine produced no change in the photo-expansion. Removal of the adsorbed film of water from the walls by "baking-out" the containing vessel at 300° made little or no difference. Inside the vessel was placed an almost hair-fine capillary, through which a platinum wire was drawn. The arrangement was such that only glass was in contact with the halogen vapour, the ends of the wire being carried to the outside of the vessel. The wire was used as a platinum resistance thermometer, the temperature change agreeing fairly well with the expansion on illumination. Martin, Cole, and Lent (*J. Physical Chem.*, 1929, **33**, 148), using chlorine at atmospheric pressure, concluded that careful purification and drying and the "baking-out" of the insolation vessel had no appreciable effect on the expansion.

On the other hand, Narayana (*Indian J. Physics*, 1934, **9**, 91) showed that in pure super-dried chlorine there was no photo-expansion. He further showed that, as the halogens chlorine and bromine were gradually dried, a marked decrease in the photo-expansion could be observed. The Budde effect in iodine (*idem, ibid.*, p. 111) was found to be greater at 200° than at 350°, this being attributed to the fact that at 200° the adsorbed film of water was still present on the walls, whereas at 350° it was assumed absent, the dry walls catalysing the atomic recombination.

Several investigators (Le Blanc, *Z. Elektrochem.*, 1919, **25**, 234; Halban and Siedentopf, *Z. physikal. Chem.*, 1922, **103**, 73; Kornfeld and Steiner, *Z. Physik*, 1937, **45**, 325) have failed to detect any difference between the absorption coefficients of moist chlorine and that which has been thoroughly dried. Martin, Cole, and Lent (*J. Physical Chem.*, 1929, **33**, 148) examined the scattering of light by moist and by dry chlorine. Both scattered it normally, *i.e.*, the intensity of the scattered light agreed with that calculated from the Rayleigh formula, and was a thousandfold less than the hypothetical fluorescence. Kistiakowsky (*J. Amer. Chem. Soc.*, 1927, **49**, 2194) found that extreme drying of chlorine did not appreciably alter the structure of the absorption spectrum or the total amount of energy absorbed. The fluorescence of dried chlorine was at most only a small percentage of the absorbed energy. He concluded that dissociation in the region of continuous absorption was independent of purity. Weigert and Nicolai (*Z. physikal. Chem.*, 1928, **131**, 267) considered that the similarity of absorption in moist and in very dry chlorine indicated considerable fluorescence if the absence of expansion in dry chlorine was proved.

Considering the question on the basis of the previous sections, it is evident that small amounts of water vapour cannot produce any appreciable increase in the number of bromine atoms recombining either through increase in the number of triple collisions with water as a third body, or through a decrease in the rate of diffusion to the walls. The triple collision efficiency of the water molecule will be of the same order as that of the bromine molecule itself. On the other hand, it is evident from Tables I—VI that at the pressure of bromine used in the present experiments (30—50 mm.) a large fraction of the bromine atoms was removed at the surface of the reaction vessel, and it was therefore conceivable that adsorbed water molecules might produce surface changes responsible for the conflicting results recorded by different observers. Discussion of these would involve a knowledge of the dimensions of, and treatment accorded to, the reaction vessels employed. The question was therefore experimentally examined, the reaction vessel earlier described being used.

Particular attention was paid to the purification of the phosphoric oxide used to dry the bromine, the method of Finch and Peto (*J.*, 1922, **121**, 692) being employed. The oxide obtained had no reducing action on silver nitrate or mercuric chloride. Bromine was purified as already described (p. 1681). The apparatus for drying the bromine and measuring its photo-expansion is shown diagrammatically in Fig. 1. *T* was a liquid-air trap which had a volume of approximately 100 c.c. at the lower end. This bulb contained pure phosphoric oxide, introduced by tube *A*. The tap grease used was Apiezon L; it was exposed to bromine for some time before being used to grease the taps *T*₁, *T*₂, *T*₃, any absorption of bromine which might take place during an experiment thus being eliminated. The use of any form of tap grease is not ideal, but the results obtained appear to be quite definite.

The apparatus was evacuated by means of a mercury diffusion pump, backed by a Cenco Hyvac oil-pump. With this system a pressure of 2×10^{-6} mm. mercury (measured by a McLeod gauge) was easily obtained.

The light source was an Osram 500 watt projector lamp, run at 220 volts from 230 volt mains by hand-controlled resistance, and placed at a distance of 40 cm. from the centre of the insolation vessel. Heating rays were removed by interposing a 14 cm. layer of water.

Experimental Procedure.—The apparatus was evacuated, and the insolation vessel washed out with bromine vapour. Re-evacuation was followed by introduction of bromine vapour into the vessel to a pressure of 30 mm. The position of the gauge pointer on the eyepiece scale having been noted, the bromine was illuminated, and the increase of pressure observed. The pointer moved to its maximum reading about 20 seconds after illumination and returned to its original position after the light had been cut off. This process was repeated several times, the mean value of the measured increases of pressure being recorded. Finally the bromine was pumped off.

Meanwhile liquid or solid bromine, in *T*, was in constant contact with phosphoric oxide. (The halogen was frozen out periodically on to the phosphoric oxide with a carbon dioxide-acetone freezing mixture.) This contact was maintained during 3 months, measurement of the photo-expansion obtained with 30 mm. of bromine being made once a week.

The experimental results are in Table VII. All experiments were carried out at room temperature.

TABLE VII.

No. of hours dried.	[Br ₂], mm.	Increase in pressure, mm.	No. of hours dried.	[Br ₂], mm.	Increase in pressure, mm.	No. of hours dried.	[Br ₂], mm.	Increase in pressure, mm.
0	29.4	0.286	704	29.3	0.260	1278	29.9	0.234
72	30.3	0.312	894	30.6	0.260	1538	30.0	0.260
288	29.7	0.234	1134	30.3	0.260	2000	29.9	0.260
392	29.5	0.260	1206	29.8	0.234			

No positive decrease in the photo-expansion of bromine on thorough drying over phosphoric oxide was obtained.

In a second series of experiments the photo-expansion of dry bromine in a "baked-out" vessel was examined. The apparatus was that used above (Fig. 1) with the addition of a side tube (*X*) with two taps to regulate the supply of water vapour. The insolation vessel was heated in an asbestos hot-air bath by a bunsen burner, the flow of gas being regulated by means of a screw-clip. The "baking-out" was done by heating to 350° (this temperature, measured by a thermometer enclosed in the bath, was easily maintained and was considered sufficiently high to remove the adsorbed film of water from the vessel walls) and evacuating continuously with a mercury diffusion pump, backed by an oil pump, for 2 days. The bath was then removed, and dry bromine introduced into the insolation vessel to a pressure of 30 mm.

The results obtained were :—

	[Br ₂], mm.	Photo-expansion, mm.
Prior to drying bromine and "baking-out" insolation vessel	30.0	0.260
After drying bromine and "baking-out" insolation vessel	30.0	0.260

The experiment was repeated, the same result being obtained.

The bromine was then removed from the vessel *V* by freezing out with liquid air. Water vapour from *X* was admitted to *V*, and the pressure measured by the calibrated gauge system. Bromine vapour at a pressure of 30 mm. was now added, and the photo-expansion observed. The bromine-water vapour mixture was then pumped off, more water vapour added, and the process repeated.

Results : [Br₂] = 30 mm.

[H ₂ O], mm.	0	2.1	3.7	6.5
Photo-expansion, mm.	0.260	0.247	0.234	0.260

Thus no increase in the photo-expansion was observed on adding water vapour to dry bromine.

DISCUSSION.

Changes in diffusion and gaseous thermal conductivity would be negligibly small for the small amounts of water vapour added. In general, we may distinguish between two possible primary processes at the wall, the adsorption of single atoms and the recombination of atoms by triple collision with the wall acting as third body. The former is considered predominant for the conditions in question, since the calculations of Tables I—VI are based on a rate of bromine atom removal proportional to the first power of the atom concentration,

and not to the square of that concentration, a conclusion supported by studies of the photo-synthesis of hydrogen bromide, where the rate of HBr formation is proportional to I_{abs} , when surface action is predominant. In any case, the efficiency of a triple stabilising collision such as the above approaches unity (Rabinowitch, *loc. cit.*) and adsorbed film is not likely to reduce it appreciably. On the other hand, the adsorption of a bromine atom by the wall may reasonably be expected to depend on the nature of the wall. The amount of water vapour introduced with the "dry" bromine in our experiments cannot appreciably alter the wall even if every water molecule were adsorbed (1 litre of gas properly dried by phosphoric oxide contains less than 2×10^{-8} g. of water); and hence, if the baking-out procedure employed is regarded as satisfactory, the efficiency of adsorption of bromine atoms on striking the wall must be the same whether the wall be wet or dry. This is then in agreement with the results of Schwab (*Z. physikal. Chem.*, 1934, **27**, B, 452), but offers no explanation of the conflicting results recorded by different workers. It may be pointed out that illumination over a prolonged period may be necessary before equilibrium wall conditions are attained with respect to the bromine atoms, such equilibrium depending on, *inter alia*, the intensity of illumination: the accommodation coefficient of the walls will then depend on the conditions and will thus affect the rate at which heat is conducted away through the wall from the gas mixture. How far such effects show themselves in the observed Budde effect must be a matter for further experiment. The methods of purification of the materials used are of the highest importance, the concentration of atoms being very small and thus affected by correspondingly small amounts of impurity; it is possible that the conflicting results previously recorded are due to traces of impurities introduced with the drying agents.

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