Catalytic efficiencies were obtained in this study as soon as temperature equilibrium was reached and it has been shown that magnetic changes occurred during this short interval of time even for the mixed catalyst with a pre-treatment of 6 hours at 670°. On this basis it does not seem reasonable to attach any significance to Hüttig's results for α-Fe_2O_3–ZnO catalysts which were pretreated below 500° and it is not surprising to find that our results do not agree with his above 500°; in particular, no indication of an active intermediate phase can be found in the present experimental results as the maximum in catalytic activity for a pretreatment temperature of 650° was not observed.

If we assume, as Hüttig did, that upon the formation of zinc ferrite from the two solid oxide components, the mobility of the ferric oxide is greater than that of the zinc oxide, then the ferrite structure would be formed by the diffusion of the ferric oxide into the zinc oxide lattice, the diffusional rate increasing in a regular manner with temperature. Similarly, the decrease in surface of the finely divided components should follow from the diffusion of ferric oxide into zinc oxide and be augmented by the simultaneous coagulation of associated particles. The rate of this phenomenon should likewise be a regular function of temperature. It is not possible at present to attribute the catalytic efficiency of these mixtures to the extent of total surface area exposed, to the extent of α-Fe_2O_3 oxide remaining as such in the mixture or to the decrease in structural strains which the increasing temperature treatments would cause, but any of the three effects offer a logical explanation of the regular decrease in catalytic efficiency with pretreatment temperature.

The physical dilution of the α-Fe_2O_3 with inactive ZnO, prior to any heat treatment, should reduce the time for which the gases were in actual contact with the α-Fe_2O_3, though a calculation of the decrease in efficiency to be expected would hardly be justified in view of uncertainties in the way the two materials would pack together, and in the extent of change in the mixture during the efficiency measurement at 500°. Actually, Fig. 2 shows that to obtain a given efficiency the contact time for the mixture was about four times that for the pure α-Fe_2O_3.

It has been pointed out that the magnetic susceptibility of the catalyst mixtures changed appreciably during some of the tests conducted. This observation points to the danger of correlating the catalytic efficiency of such mixtures with magnetic susceptibility measured at room temperature on a separate portion of the same mixture. Unless such correlations can be assigned to significant changes in the magnetic susceptibility measured simultaneously or consecutively they are not felt to be justifiable. No such correlation of catalytic efficiency to magnetic changes in the catalyst was found in this study. However, the value of the magnetic susceptibility measurements to indicate physical or chemical changes in the solid catalyst phase is readily apparent.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO]

II. The Efficiency of the Primary Photochemical Process for Halogens in Water. The Photochemical Reaction of Mn(II) and Br_2

BY AARON C. RUTENBERG AND HENRY TAUBE

The quantum yields of the photoreaction of Br_2, Br_3^- and Br_2Cl^- with Mn(II) in the presence of pyrophosphate under a variety of conditions have been measured. The kinetic behavior of the system indicates that the quantum yields are the values of the primary efficiency for the absorbing substances. The primary efficiencies for the three substances at 19° and λ = 4360 Å. are 0.043, 0.122 and 0.142, respectively. The primary efficiency increases with temperature, the energy per quantum, and for Br_3^-, with increase in concentration of Br^-. The activation energies for Br_2 and Br_3^- are very nearly the same, about 7 kcal. An interpretation is given of the effect of bromide ion on the primary efficiency, and of the effect of changing temperature, wave length and ionic strength. Data for other halogens in water are also discussed.

The chemical method described in an earlier paper[1] for measuring the efficiency of the primary photoreaction for chlorine in water has been applied to bromine in water solution. The reducing agent Mn(II) in the presence of pyrophosphate serves as an efficient reactant for the primarily produced species also in the bromine system.[2] The results of experiments performed with light of wave lengths 4360 Å. and 3650 Å. with bromine (and derivatives) as absorbing species are presented and discussed. Some discussion is also made of observations recorded for chlorine and I_3^- as absorbing species.

Experimental

The general procedure described in the earlier paper[1] was followed in the present study. The extent of reaction was measured by iodimetric determination of the amount of manganic ion formed, after bromine was extracted with carbon tetrachloride.

The Br_2–Mn(II) system is much more manageable than is the Cl_2–Mn(II) system previously described. Thermal reactions were found to make negligible contributions to the over-all change under the experimental conditions, and no corrections were necessary for hydrolysis of the halogen. In addition, the absorption by bromine species was so high relative to that of manganipyrophosphate that the correction due to the inner filter effect of this product was always slight, amounting to only 3% in the most extreme case. Duplicate experiments agreed to better than 2%. The absolute values of quantum yield are considered to be accurate to 5%.

The decadic extinction coefficients for Br_2 at the wave lengths 4360 Å. and 3650 Å. were found to be 127 and 145, respectively; for Br_3^- at the same wave lengths, 183 and 974, respectively. Some measurements of the extinction coefficients of Br_2 in 3 *M* NaCl and 0.1 *M* $HClO_4$ at λ = 4360 Å. were also made. The results were

$(Br_2) \times 10^3$	2.32	3.51	5.32	7.25
$\alpha_{\Sigma Br_2}$	93	99	107	112

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[1] Rutenberg and Taube, THIS JOURNAL, **72**, 5561 (1950).

[2] Taube, *ibid.*, **70**, 3931 (1948).

The trend in the values is considerably outside of experimental error, and shows that in 3 *M* NaCl, other forms of bromine besides Br_2 and Br_2Cl^- are present. A possible interpretation of the behavior is that the equilibrium: $Br_2 + 2Cl^- = BrCl_2^- + Br^-$ also participates. At low total bromine, this would become relatively more important as compared to: $Br_2 + Cl^- = Br_2Cl^-$. At high bromine concentration, $\alpha_{\Sigma Br_2}$ appears to level off. The photo experiments with Br_2 in the presence of Cl^- were done in the concentration region above 7×10^{-3} *M*.

TABLE I

QUANTUM YIELDS OF THE PHOTOREACTION OF BROMINE WITH MANGANOUS ION

ϕ = quantum yield = no. of molecules bromine consumed per quantum absorbed; total pyrophosphate, 0.15 *M*; *p*H, 2.6.

No.	Temp.	(Br^-)	Av. (Mn^{II}) $\times 10^3$	Av. (Br_2) $\times 10^2$	ϕ	Special conditions
			At λ = 4360 Å.			
1	2.5	0.0	2.80	1.53	0.0201	
2	2.5	.0	1.53	1.25	.0200	
3	2.5	.04	3.67	.757	.0394	
4	2.5	.20	3.46	.923	.0779	
5	2.5	.80	3.48	1.91	.1225	
6	2.5	2.00	2.19	1.39	.166	
7	19.0	0.0	3.57	.832	.0428	
8	19.0	.0	3.51	.906	.0433	1.0 *M* $NaClO_4$ added
9	19.0	.0	2.84	.852	.0945	1.0 *M* NaCl added
10	19.0	.0	2.04	.965	.121	3.0 *M* NaCl added
11	19.0	.04	3.35	.967	.0782	
12	19.0	.04	3.57	1.14	.0791	
13	19.0	.20	3.36	.972	.123	
14	19.0	.20	1.53	.919	.121	Low Mn(II)
15	19.0	.20	9.10	.804	.126	High Mn(II)
16	19.0	.20	3.50	13.52	.120	High bromine
17	19.0	.20	2.63	1.54	.1185	High Mn(III) concn.[a]
18	19.0	.20	3.61	1.21	.111	1.0 *M* $NaClO_4$ added
19	19.0	.80	3.23	.578	.1725	
20	19.0	.80	3.60	1.12	.167	Low light intensity[b]
21	19.0	.80	3.45	1.22	.174	1.0 *M* NaCl added
22	19.0	.80	2.05	.948	.1505	1.0 *M* $NaClO_4$ added
23	19.0	.80	2.06	1.15	.153	1.0 *M* $NaClO_4$ added
24	19.0	2.00	3.41	.849	.217	
25	19.0	2.00	1.66	1.44	.218	
26	35.5	0.0	3.60	1.14	0.0781	
27	35.5	.04	3.54	1.33	.133	
28	35.5	.20	3.53	1.24	.174	
29	35.5	.80	3.55	1.23	.236	
30	35.5	2.00	3.20	1.28	.278	
			At λ = 3650 (Å.)			
31	19.0	0.0	3.56	1.43	0.103	
32	19.0	.04	3.53	1.43	.132	
33	19.0	.20	3.39	1.20	.158	
34	19.0	.80	3.65	1.21	.204	
35	19.0	2.00	2.23	1.51	.234	
36	35.5	0.0	3.32	1.10	.165	
37	35.5	.04	3.55	1.46	.226	
38	35.5	.04	3.69	1.10	.228	
39	35.5	.20	3.65	1.51	.227	
40	35.5	.20	3.66	1.41	.231	
41	35.5	.80	3.65	1.20	.265	
42	35.5	2.00	3.22	1.51	.309	

[a] The concentration of Mn(III) developed in this experiment was *ca.* 2.5 times that in the others. [b] In this experiment, the light intensity was 0.28 that obtaining in the others.

Values of the equilibrium $(Br_3^-)/(Br_2)(Br^-)$ were taken from the work of Jones and Baeckstrom,[3] and of Griffith, McKeown and Winn.[4] At 19° the quotient has a value of about 16, the precise value varying slightly with ionic strength.

Results and Conclusions

Table I contains a report of the results which were obtained in a study of the photoreaction of bromine and Mn(II). The variables considered were: wave length of light, temperature, concentrations of Mn(II), bromine, bromide ion, chloride ion, the ionic strength, light intensity and concentration of the product Mn(III).

In general features the rate observed in the bromine–Mn(II) system resembles that of the corresponding reaction with chlorine. The data of Table I lead to the following conclusions about the rate law: The quantum yield ϕ: (a) Is independent of the concentration of Mn(II) (*cf.* no. 1 and 2, and 13, 14, 15). (b) Is independent of the concentration of bromine (*cf.* no. 13 and 16). (c) Is independent of light intensity (*cf.* no. 19 and 20). (d) Is unaffected by the accumulation of Mn(III) (*cf.* no. 17 and others in the series). (e) Is markedly increased by the addition of bromide ion and of chloride ion, but varies only slightly with ionic strength, and not at all when Br_2 is the absorbing substance. (f) Is affected by changes in wave length and in temperature.

The data relating to the variation of ϕ with bromide ion, wave length and temperature are shown graphically in Fig. 1.

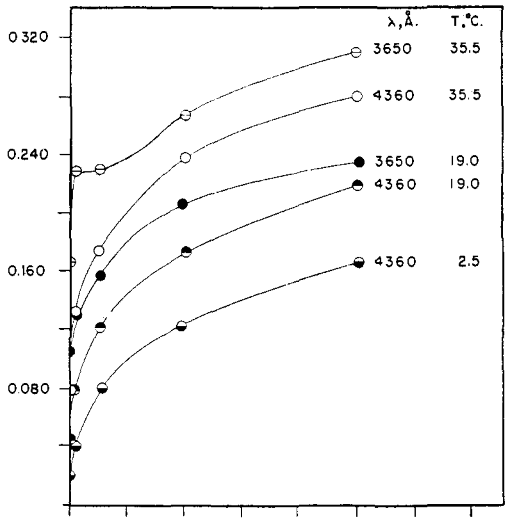

Fig. 1.—Variation of the quantum yield of the reaction of Br_2 with Mn(II) with Br^- concentration.

In Table II are presented the results of some experiments performed on the photochemical re-

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(3) Jones and Baeckstrom, *ibid.*, **56**, 1517 (1934).

(4) Griffith, McKeown and Winn, *Trans. Faraday Soc.*, **28**, 101 (1932).

action of iodine (mainly I_3^-) with Mn(II) in the presence of pyrophosphate. In this system also, ϕ is independent of the concentration of Mn(II) at the levels of concentration used.

TABLE II

QUANTUM YIELD OF THE REACTION OF IODINE WITH MANGANOUS ION

λ = 4360 Å.; temp., *ca.* 28°; pyrophosphate, 0.10 *M*; *p*H 7.5.

(I^-)	Av. (I_2) $\times 10^3$	Av. (Mn(II)) $\times 10^3$	ϕ
0.10	3.6	3.60	0.124
.10	1.9	1.83	.117
.70	4.4	2.16	.208

Discussion

The fact that the quantum yield of the photoreaction of bromine with Mn(II) is independent of the concentration of Mn(II), and the general similarity of the behavior of the system to the behavior of the Cl_2-Mn(II) and Cl_2-Ce(III) systems makes it seem fairly certain that the values of ϕ measure the primary efficiency also in the present system. The values of ϕ measured in the I_2-Mn(II) system can similarly be interpreted to measure the primary efficiency for I_3^- (only a negligible fraction of the light is absorbed by I_2 at the prevailing iodine ion concentrations). Numerous factors have been shown to affect ϕ and therefore the primary efficiency, and in the following discussion, an effort is made to arrive at a detailed mechanism by considering the effects of the variables.

Inspection of the data on the variation of ϕ with bromide ion shows that this variation cannot be explained merely by accounting for the light absorbed by Br_2 and Br_3^- and assigning a fixed quantum yield to each species. Thus, the fraction of light of wave length 3650 Å. absorbed by Br_3^- in experiments 33, 34 and 35 (temp. 19°, (Br^-) = 0.20, 0.80 and 2.00 *M*, respectively) was 0.96, 0.99 and 0.995; the corresponding values of ϕ were observed to be 0.158, 0.204 and 0.234. It is evident that a pronounced increase in ϕ with (Br^-) takes place even after substantially all of the light is absorbed by Br_3^-, and the conclusion follows that Br^- in some manner enhances the primary efficiency for Br_3^-. The iodine experiments show a similar effect still more strikingly, since even at 0.1 *M* I^-, 99% or more of the light is absorbed by I_3^-. The data at low bromide ion concentration have been used in calculating the primary efficiencies for Br_2 and Br_3^- and the values thus obtained for various conditions are presented in Table III. For convenience in comparison, and in reference, values for Br_2Cl^- (data of experiment 7, 9 and 10, Table I) and for I_3^- (data of Table II) as well as the data for Cl_2[1] and Cl_3^- are included.

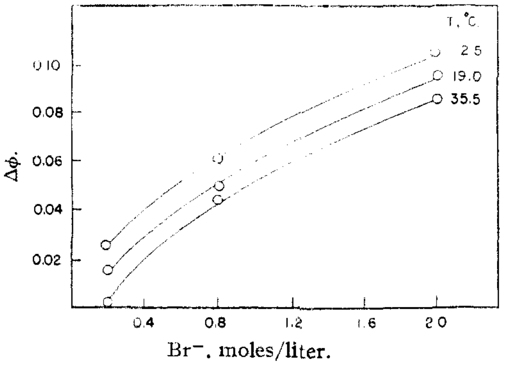

Fig. 2.—Increase in efficiency due to Br^- effect on Br_3^- at λ = 4360 Å.

TABLE III

PRIMARY QUANTUM EFFICIENCIES FOR A NUMBER OF HALOGEN SPECIES

λ, Å.	Temp., °C.	Cl_2	Cl_3^-	Br_2	Br_3^-	Br_2Cl^-	I_3^-
4360	2.5	0.06	...	0.0201	0.0602	...	....
4360	19.0	.09[a]	...	.0428	.122	0.142	0.107[b]
4360	35.5	....	...	.0781	.192	...	....
3650	2.5	0.12	0.34	....	....	...	....
3650	19.0	.155[a]	.40[a]	0.103	0.139	...	....
3650	35.5	....	...	.165	.23	...	....

[a] Calculated from measured values at about 3 and 25°. [b] At 28°.

The excess of the measured quantum yield for solutions at high bromide ion concentration over that computed using the values of primary efficiency for Br_2 and Br_3^- recorded in Table III and the known extinction coefficients for these species is shown plotted against bromide ion concentration in Fig. 2 for the data at λ = 4360 Å. For the experiments with Br_2 in solutions of NaCl, the increase in ϕ with concentration of chloride ion can be accounted for without invoking any effect beyond the participation of Br_2Cl^-. From the values of $\alpha_{\Sigma Br_2}$ in NaCl solution, the extinction coefficient of Br_2Cl^- (at high bromine) at 4360 Å. is calculated as 112. Using this value, the known value for the extinction coefficient of Br_2, and for $(Br_2Cl^-)/(Br_2)(Cl^-)$ the value 1.3 (cited by W. C. Bray), the fraction of light absorbed by Br_2Cl^- in experiment 9 is calculated as 0.534, and in experiment 10 is 0.775. Taking into account the contribution in each experiment by the photoreaction of Br_2, the primary efficiency for Br_2Cl^- in the two experiments is calculated as 0.141 and 0.143, respectively. When $NaClO_4$ is added to a solution containing Br_3^-, complex formation by ClO_4^- presumably does not play a role, and a slight decrease in ϕ is noted (*cf.* no. 18 with 13, 22 and 23 with 19, Table I).

Of the three anions Br^-, Cl^- and ClO_4^-, Br^- is unique in its effect of enhancing the primary efficiency. A similar effect is noted for I^- in the photoreaction of I_3^-. In this system, the effect seems too large to be attributed merely to a salt effect exerted on photo-excited I_3^-. These facts suggest that the influence of Br^- is also not merely a salt effect, but involves chemical participation by the ion. This view is supported further by the observation that the excess in primary efficiency produced by bromide ion is almost linear in bromide ion concentration (*cf.* Fig. 2). The failure of a more perfect linear relationship can be attributed in part to the increase in ionic strength as sodium bromide is added, and in part to the fact that ϕ must level off to a value of unity or less.

The kinetic observations on the photochemistry with Br_3^- as the absorbing substance are consistent with the mechanism

$$Br_3^- + h\nu = Br_3^{-*} \qquad \text{Rate} = I$$

$$Br_3^{-*} \xrightarrow{k_2} Br_3^- \qquad (2)$$

$$Br_3^{-*} \xrightarrow{k_3} 2Br + Br^- \qquad (3)$$

$$Br_3^{-*} + Br^- \xrightarrow{k_4} 2Br + 2Br^- \qquad (4)$$

$$Br + Mn(II) = Br^- + Mn(III)$$

A species for which deactivation competes against production of active intermediates induced by bromide ion is necessary to explain the bromide ion effect.

A more detailed description of this species—whether it be an electronically excited state, or atoms trapped in a solvent cage[5]—is not implied by the rate law. The species which reacts efficiently and completely with Mn(II) is assumed to be atomic bromine (or Br_2^- if (Br^-) is high),[2] and the symbol Br represents only those which have escaped the influence of their partners in the original halogen molecule.

The intermediates Br_3^{-*} and Br are the minimum number and the mechanism as represented is the simplest which will explain the observations. An additional possibility to which further reference is made later is that only a fraction of the light quanta produce a species which can yield effective intermediates. A fraction of the light quanta may be wasted and in this event, the maximum value which the primary efficiency can attain will be less than unity.

A series of reactions similar to those represented above presumably function when Br_2 is the absorbing species. However, the data are not extensive enough to separate the step.

$$Br_2^* + Br^- \longrightarrow 2Br + Br^-$$

from the photochemical effect attributed to Br_3^-, and any contribution by this process has been absorbed in the value of primary efficiency ascribed to Br_3^-. With this treatment, only the reaction

$$h\nu + Br_2 \xrightarrow{k_1} 2Br$$

need be added to account for the contribution by Br_2 as the absorbing substance.

The law for the variation of ϕ with (Br^-) when Br_3^- is the absorbing substance is

$$\phi = \frac{k_3}{k_2 + k_3 + k_4(Br^-)} + \frac{k_4(Br)^-}{k_2 + k_3 + k_4(Br^-)}$$

The second term on the right-hand side represents the contribution to ϕ by the bromide ion-induced path. When this contribution remains relatively small, ϕ will vary linearly with the bromide ion concentration. Using the increment between 0.2 *M* Br^- and 0.8 *M* Br^-, Fig. 2, as a measure of initial slope, and for the ratio k_3/k_2 the value of *ca.* 0.07 as determined by ϕ at low concentration of bromide ion, k_4/k_2 is found to be 0.06. If k_4 is assumed to be equal to the collision frequency for a bimolecular process, a lower limit of *ca.* 2×10^{-13} sec. for the lifetime of Br_3^{-*} is calculated. Within the precision of the data, k_4/k_2 is independent of the temperature. This fact implies that the activation energy for step 4 is low. However, a value for k_4 100 or 1000 times lower than the collision frequency is not excluded, and if this is the case, the half life of Br_3^{-*} would be correspondingly greater.

Two distinct mechanisms may be considered for the action of Br^- in enhancing the primary efficiency for Br_3^-. In one mode of action, Br^- may be assumed to become a part of the activated complex including Br_3^{-*}, and the enhancement accounted for by assigning to $Br_4^{=*}$ a high probability for fruitful dissociation. The second possibility is that the halide ion acts by electron exchange through the solvent cage

$$Br^- + (Br, Br, Br^-) \longrightarrow Br + (Br^- + Br + Br^-) \qquad (4a)$$

Of these two, the second appears the more reasonable possibility, and receives qualitative support from the observation that the efficiency of the analogous process for I^- on I_3^- (and as far as can be calculated for Cl^- on Cl_3^-) is about the same as it is in the bromine system (*vide infra*). Another argument favoring the electron transfer interpretation is based on the observation that although Cl^- added to Br_2 raises the primary efficiency, Cl^- does not enhance the primary efficiency for Br_2Cl^-. The difference in behavior of $Br_2 + Br^-$ on the one hand and $Br_2 + Cl^-$ on the other is readily explained by the electron transfer mechanism but not by the complex-formation mechanism.

It can reasonably be expected that if electron transfer is energetically possible,[6] other substances besides the halide ion can function in the manner represented in equation 4a. Presumably there is a contribution by Mn(II) functioning in this way

$$Mn(II) + (Br, Br, Br^-) \longrightarrow Mn(III) + (Br^-, Br, Br^-)$$

However, if the specific rate for this reaction is the same as or less than that of k_4—and the fact that k_4/k_2 is essentially independent of temperature suggests that k_4 is determined largely by collision frequency—a variation in the concentration of Mn(II) at levels of 0.1 *M* and higher would be needed to expose the effect. Owing to the limited solubility of Mn(II) in the pyrophosphate environment, this concentration region cannot be explored in the present system, but probably can in the Ce(III)–Cl_2 system.

The fact that Cl^- does not enhance the primary efficiency for Br_2Cl^- contributes to the conclusion that the excited species should be regarded as atoms trapped in a solvent cage, rather than as a molecule-retaining electronic energy. A system which has retained electronic energy added by a quantum of wave length 4360 Å. has sufficient energy for the process

$$Br_2Cl^{-*} + Cl^- \longrightarrow (Br^-, Br, Cl^-) + Cl$$

and an effect of Cl^- on the primary efficiency for Br_2Cl^- could reasonably be expected. The observed efficiencies in the system are accounted for completely, by assigning fixed values to the efficiencies for Br_2 and Br_2Cl^-. This single observation is not powerful enough to rule out the possibility that the excited states retain electronic energy. However, to simplify the later discussion,

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(5) Rabinowitch and Wood, *Trans. Faraday Soc.*, **32**, 1381 (1936).

(6) Durrant, Griffith and McKeown, *ibid.*, **34**, 389 (1938), found evidence for the process: $I_2^* + NO_2^- \rightarrow NO_2 + I + I^-$ in the photochemical reaction of iodine and nitrite.

the point of view will be adopted that the activated states consist of atoms trapped in a solvent cage.

To discuss the variation of the primary efficiency with the temperature, the values of k_3/k_2 for various absorbing species have been computed and are presented in Table IV.

TABLE IV

VALUES OF k_3/k_2 FOR VARIOUS HALOGEN SPECIES

k_3/k_2 is the ratio of specific rate for fruitful dissociation of the activated species, to the specific rate for deactivation. Values in brackets are ratios of the ratios over a temperature interval of 16.5°

λ,	Temp.,	k_3/k_2 for					
Å.	°C.	Cl_2	Cl_3^-	Br_2	Br_3^-	Br_2Cl^-	I_3^-
4360	2.5	0.06	....	0.0205	0.0640	...	...
		[1.6]		[2.18]	[2.17]		
4360	19.0	.10	....	.0446	.139	0.166	0.099
				[1.90]	[1.71]		
4360	35.5	....	....	.0847	.238	...	...
3650	2.5	$.13_7$	0.51	.....	.....	...	...
		[1.34]	[1.31]				
3650	19.0	$.18_4$	.67	.115	.162	...	...
				[1.72]	[1.85]		
3650	35.5	....		.198	.30	...	...

A significant feature of the data is that the activation energy corresponding to k_3/k_2 is very nearly the same for Br_2 and Br_3^-. This observation suggests that the process requiring activation is the formation in the solvent of holes of size suitable for the escape of the atomic halogen. The escaping entity is the same for Br_3^- as it is for Br_2. This point of view also explains why the primary efficiency is relatively insensitive even to a large increment in the absorbed energy. A decrease in wave length is effective mainly by increasing the time required for the trapped atoms to lose sufficient energy to make recombination possible.

An interesting feature of the data on the variation of ϕ with temperature, is the magnitude of the temperature effect in the case of Br_2 and Br_3^-. The activation energy in the case of Br_2 at 4360 Å. over the interval at the lower temperatures is 7.5 kcal. and over that at the higher temperatures is 7.0 kcal. For Br_3^- these values are 7.5 and 5.9 kcal., respectively. The decrease in the calculated activation energy as the temperature rises is outside of experimental error. A possibility in explaining the variation is that the simple Arrhenius equation does not apply to a system as complex as that constituted by the trapped atoms and the solvent cage; another is that the maximum value of ϕ is not unity as assumed, but that a lower ceiling value impresses its effect, which would be greater, the higher the value of ϕ.

A separate point of interest in the data is that an increase in ionic strength does not affect the primary efficiency for the neutral species Br_2 (*cf.* no. 7 and 8, Table I) but decreases the primary efficiency noticeably when Br_3^- is the principal light absorbing species (*cf.* no. 13 and 18, no. 19 and no. 22 and 23, Table I). Although no change in the sum of the magnitudes of the charges takes place in reaction 3, a slight effect on the rate of a change in ionic environment can be expected, since the geometry of the charge distribution is changed on reaction. The fact that a change in ionic atmosphere exerts an effect shows that the process involved is slow as compared to relaxation effects in the ion atmosphere.

The higher values of ϕ observed for chlorine as compared to bromine, as well as the lower temperature coefficient[7] can perhaps be correlated with the smaller size of atomic chlorine, which would result in a greater probability of escape for it. An additional escape path involving electron transfer with the solvent may be open for atomic chlorine

$$Cl + H_2O \longrightarrow Cl^- + HO + H^+$$

Although equilibrium in this system at reasonable acidity favors Cl and H_2O as products[8] the equilibrium is not so unfavorable that kinetic participation by HO is excluded.

The experiments performed with the system I_3^- + Mn(II) suggest for the primary efficiency of I_3^- at 28° and $\lambda = 4360$ Å. a value of *ca.* 0.10. If the trend in the observed values for the efficiencies of molecular chlorine and bromine as compared to their respective trihalide ions continued with iodine, the value of the primary efficiency for I_2 would be expected to be 0.05 or less. Zimmerman and Noyes[9] have determined the primary efficiency of I_2 in hexane at 25°, with $\lambda = 4360$ Å., to be 0.59. The comparison may imply that the solvent cage in hexane is more labile than it is in the structurally integrated solvent water. The coefficient k_4/k_2 in the I_3^-–Mn(II) system has the value 0.15. The fact that this coefficient is within a factor of 3 the same as it is in the bromine system supports the view that reaction 4 proceeds essentially without activation. Further support is derived from the experiments of Durrant, Griffith and McKeown.[6] The coefficient for the process $I_2^* + NO_2^- \rightarrow I + I^- + NO_2$ competing against deactivation of I_2^* was measured as *ca.* 0.05.

Further work will be necessary to reconcile certain of the results and conclusions of the work with Mn(II) and Ce(III) as reducing agents, with published observations. Hochhauser and Taube[10] concluded on the basis of a comparison of the rate of the chemically induced reaction of chlorine and oxalic acid with the photochemically induced reaction that the primary efficiency in 2 *M* HCl at 25° is 0.6. The work with Mn(II) as reducing agent yielded for the same conditions (HCl replaced by NaCl) the value 0.35. The latter result, derived as it is from a simpler measurement, is more reliable. The discrepancy implies that in spite of the kinetic similarity of the Fe^{++} and photoinduced reactions, iron ions may play a specific role in the chain reactions of chlorine and oxalic acid. The quantum yield of the photochemical reaction of Fe^{++} and iodine has been measured as unity.[11] To reconcile this result with those obtained in the present work, as well as the similar ones of Durrant, Griffith and McKeown, it is tempting to ascribe a peculiarly high efficiency to the reaction of Fe^{++} with the excited species generated by the action of light on iodine. This interpretation is not con-

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[7] A parameter which affects comparisons between different species is the possible variation in ceiling values of primary efficiency.

[8] Taube, THIS JOURNAL, **63**, 2453 (1941).

[9] Zimmerman and Noyes, *J. Chem. Phys.*, **18**, 658 (1950).

[10] Hochhauser and Taube, THIS JOURNAL, **69**, 1582 (1947).

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sistent, however, with the present conclusion that the reactions of the excited species with halide ions (or NO_2^- in the case of I_2^*) proceed with very nearly the maximum rate of the collision frequency.

In some respects the Br_3^-–Mn(II) photoreaction qualifies as a useful actinometer. The reaction is non-chain in character, completely reproducible, and sufficiently free from complication by thermal reactions. It has advantages over the uranyl oxalate system, since the reaction product can conveniently be estimated accurately, and arrangement for complete absorption of light can readily be made at longer wave lengths, but has the disadvantage that more accurate control of temperature is necessary.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Vapor Pressure and Critical Constants of Normal Pentane

BY JAMES A. BEATTIE, SAMUEL W. LEVINE AND DONALD R. DOUSLIN

The vapor pressure of normal pentane, C_5H_{12}, has been measured from 100° to the critical point. The results are represented quite well by the relation $\log_{10} p(\text{atm.}) = 3.752453 - (1225.960/T) + 8.06841 \times 10^{-4}\,T$ ($T = t°\text{C.} + 273.16$). The critical constants were determined by compressibility measurements in the critical region and were found to be $t_c = 196.62 \pm 0.05°$ (Int.); $p_c = 33.31 \pm 0.05$ normal atm.; $v_c = 0.295$ liter/mole (4.09 ml./g.); $d_c = 3.39$ moles/liter (0.244 g./ml.). The uncertainty in the critical volume and density is 1%.

The vapor pressure of normal pentane has been measured by Rose-Innes and Young[1,2] and by Sage and Lacey.[3] The critical point was determined by Rose-Innes and Young by the disappearance of the meniscus method, and estimated by Sage and Lacey[3] from measurements of the compressibility of the liquid and vapor using the critical temperature determined by Rose-Innes and Young.[1,2]

In continuation of a program of study of the state behavior of hydrocarbons[4] we have measured the vapor pressure of normal pentane from 100° to the critical point and have studied a number of isotherms in the critical region which permit location of the critical constants. The method of making the measurements has been described earlier[5]; the bomb with the glass liner was used.

TABLE I

VARIATION OF THE MEASURED VAPOR PRESSURE OF THE SAMPLE OF NORMAL PENTANE WITH VAPOR VOLUME AT 100°

Vapor vol. ml.	95	74	51	29	6.2	0.26
Measured atm.	5.857	5.857	5.860	5.860	5.864	5.866

TABLE II

VAPOR PRESSURE OF NORMAL PENTANE

Temp., °C. (Int.)	Vapor pressure in normal atmospheres: This work	Observed—Eq. 1		Sage and Lacey	Young
100	5.857	−0.007	−0.12%	5.840	5.80
125	9.902	+ .025	+ .25	9.884	9.79
150	15.730	.000	.00	15.736	15.53
175	23.834	− .072	− .30	23.822	23.57
175[a]	23.838	− .068	− .29		
196.62	33.31	+ .056	+ .17		

[a] Vapor pressure measured after the compressibility runs in the critical region.

TABLE III

ISOTHERMS OF *n*-PENTANE, C_5H_{12}, IN THE CRITICAL REGION

Molecular weight, 72.0924; critical constants from Fig. 1: $t_c = 196.62 \pm 0.05°$ (Int.); $p_c = 33.31 \pm 0.05$ normal atm.; $v_c = 0.295$ liter/mole (4.09 ml./g.); $d_c = 3.39$ moles/liter (0.244 g./ml.). The uncertainty in the critical volume and density is 1%.

Temp., °C. (Int.)		196.20	196.40	196.50	196.60	196.62	196.70
Density moles/liter	Volume liter/mole	Pressure, normal atmospheres					
4.000	0.2500	33.181	33.317	33.380	33.438		
3.900	.2564	33.132	33.249	33.307	33.371		
3.800	.2632	33.104	33.213	33.269	33.332		33.394
3.700	.2703	33.096	33.201	33.257	33.309		33.368
3.600	.2778	33.097	33.199	33.251	33.303	33.312	33.359
3.550	.2817	33.095	33.197	33.249	33.301	33.310	33.354
3.500	.2857	33.096	33.198	33.247	33.298	33.308	33.352
3.450	.2899	33.096	33.198	33.248	33.297	33.306	33.350
3.400	.2941	33.094	33.196	33.248	33.297	33.307	33.351
3.350	.2985		33.197	33.247	33.297	33.305	33.348
3.300	.3030	33.095	33.195	33.247	33.295	33.303	33.349
3.250	.3077		33.196	33.246	33.293	33.303	33.347
3.200	.3125	33.093	33.196	33.244	33.291	33.302	33.345
3.150	.3175		33.194	33.245	33.292	33.302	33.346
3.100	.3226	33.095	33.192	33.243	33.290	33.301	33.344
3.000	.3333	33.088	33.188	33.239	33.286		33.340
2.900	.3448	33.085	33.182	33.236	33.282		33.338
2.800	.3571	33.076	33.176	33.232	33.276		
2.650	.3774	33.060	33.160	33.214	33.253		33.302

TABLE IV

CRITICAL CONSTANTS OF NORMAL PENTANE

Source	t_c, °C. (Int.)	p_c, normal atm.	v_c, liter/mole
This work	196.62 ± 0.05	33.31 ± 0.05	0.295[a]
Sage and Lacey	197[b]	33.6	.315
Rose-Innes and Young	197	33.0	.310

[a] $v_c = 0.295$ liter/mole (4.09 ml./g.); $d_c = 3.39$ mole/liter (0.244 g./ml.). [b] Sage and Lacey used the critical temperature given by Rose-Innes and Young to estimate p_c and v_c from their own measurements of the compressibility of the liquid and vapor.

The normal pentane used in this work was an API–NBS sample made available by the American Petroleum Institute and the U. S. National Bureau of Standards through the API Research Project 44. The sample was purified at the National Bureau of Standards by the API Project 6, under the supervision of Dr. F. D. Rossini, from materials supplied

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