

## Exchange Reactions with Deuterium II. The Photochemical Exchange Between Deuterium and Hydrogen Chloride

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Citation: [The Journal of Chemical Physics](#) **6**, 345 (1938); doi: 10.1063/1.1750267

View online: <http://dx.doi.org/10.1063/1.1750267>

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## Exchange Reactions with Deuterium

### II. The Photochemical Exchange Between Deuterium and Hydrogen Chloride

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(Received February 18, 1938)

The exchange reaction between hydrogen chloride and deuterium, initiated photochemically, is found to be a chain reaction with quantum yields ranging from 2 to 19 under the experimental conditions employed. The rate determining step is the reaction  $\text{Cl} + \text{D}_2 \rightarrow \text{DCI} + \text{D}$ . The proportions at the photostationary state are shifted from those at thermal equilibrium in a direction which indicates a somewhat stronger absorption by HCl than by DCI in the region 2000–2150Å.

WHEN mixtures of hydrogen chloride and deuterium, or of deuterium chloride and hydrogen, are exposed to light absorbed by the hydrogen chloride or deuterium chloride, an exchange reaction is observed which proceeds rapidly at first, then approaches a photostationary state (Fig. 1) at which the equilibrium proportions are near to, yet definitely different from, the proportions corresponding to thermal equilibrium at the temperature concerned. Using the apparatus previously described,<sup>1</sup> we have studied this exchange with respect to both the initial rate and the photostationary state.

#### EXPERIMENTAL

The hydrogen chloride-deuterium or deuterium chloride-hydrogen mixtures were exposed, in the quartz reaction vessel *R* (Fig. 1 of reference 1), to the light of a zinc spark; the effective radiation consisted of the four strong lines in the region 2000–2140Å. Quantum yields were obtained by actinometric comparison with the rate of decomposition of ammonia. Measurements of the absorption of hydrogen chloride and ammonia<sup>2</sup> show that for the system used (average light path ~25 mm) absorption of the zinc lines at 2000–2140Å may be taken as complete (>95 percent) at ammonia pressures of *ca.* 50 mm or over, while HCl absorbs even more strongly.

The rate of ammonia decomposition was observed through the pressure change, with the as-

sumption that each molecule decomposing produces an increase of one molecule in the gas. The rate of the HCl–D<sub>2</sub> exchange was determined through the analysis, using the gas density balance, of the hydrogen-deuterium mixtures obtained. The quantum yield of the exchange reaction (number of H atoms exchanged per quantum absorbed) over any exposure interval is then given by

$$\Phi_{\text{obs}} = \frac{2(F_2 - F_1)P_{\text{D}_2 + \text{HD} + \text{H}_2}\Phi_{\text{NH}_3}}{(t_2 - t_1)(I_{\text{HCl}}/I_{\text{NH}_3})(dP_{\text{NH}_3}/dt)}, \quad (1)$$

where  $F_1$ ,  $F_2$  are the fractions of hydrogen in the hydrogen-deuterium mixture at the beginning and end of the exposure interval,  $t_1$  to  $t_2$  (minutes);  $P_{\text{D}_2 + \text{HD} + \text{H}_2}$  is the total pressure of the D<sub>2</sub>+HD+H<sub>2</sub> mixture;  $\Phi_{\text{NH}_3}$  is the quantum yield of the ammonia decomposition at the pressure used;  $dP_{\text{NH}_3}/dt$  is the observed rate of pressure increase, in mm/min., when ammonia is

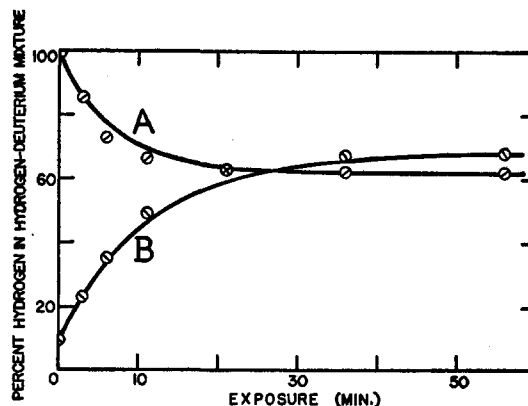


FIG. 1. Hydrogen-deuterium analyses as a function of exposure time. Curve A, for a starting mixture of H<sub>2</sub>+DCI, curve B, D<sub>2</sub>+HCl.

<sup>1</sup> P. C. Cross and P. A. Leighton, *J. Chem. Phys.* **4**, 28 (1936).

<sup>2</sup> S. W. Leifson, *Astrophys. J.* **63**, 73 (1926). H. E. Bacon and A. B. F. Duncan, *J. Am. Chem. Soc.* **56**, 336 (1934). H. S. Taylor and J. C. Jungers, *J. Chem. Phys.* **2**, 375 (1934). L. Farkas and P. Hartek, *Zeits. f. physik. Chemie* **B25**, 257 (1934).

TABLE I.

A. Initial rates in HCl+D <sub>2</sub> mixtures								
$P_{D_2+HD+H_2}$ mm	$P_{HCl}$ mm	$\frac{I_{HCl}}{I_{Std}}$	$t_2-t_1$ min.	$F_1$	$F_2$	$F_\infty$	$\Phi_{obs}$	$\Phi_0$
31	79	1	3	0.153	0.270	0.72	1.4	1.9
50	81	1	3	0.153	0.268	0.61	2.2	3.1
53	126	1	3	0.095	0.230	0.68	2.8	3.5
54	330	1	5	0.095	0.295	0.875	2.5	3.2
56	49	1	4	0.095	0.232	0.42	2.2	3.2
62	234	1	5	0.095	0.286	0.775	2.8	3.6
63	176	1	10	0.111	0.432	0.725	2.3	3.7
75	85	0.33	5	0.095	0.198	0.48	5.4	7.0
76	84	0.063	10	0.095	0.200	0.475	14.7	19.0
78	137	0.118	14	0.095	0.275	0.60	9.9	13.5
80	53	1	5	0.095	0.234	0.36	2.6	4.1
113	203	1	5	0.210	0.344	0.64	3.5	5.4
161	82	1	3	0.125	0.203	0.335	4.9	7.0

B. Initial rates in DCl+H <sub>2</sub> mixtures								
$P_{D_2+HD+H_2}$ mm	$P_{DCl}$ mm	$\frac{I_{DCl}}{I_{Std}}$	$t_2-t_1$ min.	$F_1$	$F_2$	$F_\infty$	$\Phi_{obs}$	$\Phi_0$
90	175	1	3	1.000	0.853	0.62	5.1	6.5
91	90	1	3	1.000	0.907	0.76	3.3	4.2
175	74	1	3	1.000	0.921	0.85	5.3	7.6

placed in the reaction cell; and  $I_{HCl}$ ,  $I_{NH_3}$  are the incident intensities of 2000–2140Å when HCl and  $NH_3$  were in the cell, with complete absorption assumed in both cases.

Since the quantum yield of ammonia decomposition varies with pressure,<sup>3</sup> a standard ammonia pressure of 600 mm was adopted, at which  $\Phi_{NH_3}$  was taken as 0.18. Runs with ammonia were made at a standard light intensity at which  $dP_{NH_3}/dt = 0.31 \pm 0.01$  mm/min.<sup>4</sup> When using HCl–D<sub>2</sub> mixtures, intensities other than this were obtained by varying the distance of the source and assuming the inverse square law. Introducing these modifications, (1) becomes

$$\Phi_{obs} = \frac{1.16(F_2 - F_1)P_{D_2+HD+H_2}}{(t_2 - t_1)(I_{HCl}/I_{Std})}, \quad (2)$$

where  $1.16 = (2 \times 0.18)/0.31$ ,  $I_{Std}$  is the intensity

<sup>3</sup> E. O. Wiig, J. Am. Chem. Soc. **57**, 1559 (1935).

<sup>4</sup> With a cell volume of 150 cc this corresponds to the absorption of  $1.4 \times 10^{17}$  quanta/sec.

for which  $dP_{NH_3}/dt = 0.31$  mm/min. and  $I_{HCl}$  is the intensity used in producing the exchange.

As the exposure time is lengthened, or as the photostationary state is approached,  $\Phi_{obs}$  will decrease, and to obtain the true initial quantum yield it is necessary to extrapolate to zero exposure time and zero exchange. The most satisfactory way of doing this was found to be that based upon the empirical relationship

$$\Phi_t \propto (F_\infty - F_t),$$

which leads to the equation

$$\Phi_0 = \frac{1.16P_{D_2+HD+H_2}I_{Std}(F_\infty - F_0)}{I_{HCl}(1 - F_0)(t_2 - t_1)} \ln \frac{F_\infty - F_1}{F_\infty - F_2}. \quad (3)$$

$\Phi_t$ ,  $\Phi_0$  are the quantum yields at the times  $t=t$  and  $t=0$ .  $F_\infty$  and  $F_0$  are the fractions of hydrogen in the hydrogen-deuterium mixture at the photostationary state and at the time  $t=0$ , respectively. The factor  $(1 - F_0)$  corrects for the hydrogen content of the deuterium at  $t=0$ . This equation gives satisfactory constants over different time intervals of a given run, and the  $\Phi_0$  values agree approximately with those obtained by cumbersome semi-theoretical methods. The extrapolations are from concentration ranges in which the reaction  $D_2 + HCl \rightarrow HD + DCl$  predominates over the second-step reaction,  $HD + HCl \rightarrow H_2 + DCl$ , and the precision of the results does not warrant any attempt to apply a correction for the effect of the latter. Values of  $\Phi_0$  are given in Table I. Since  $\Phi_0$  was estimated from the first time interval of each series,  $F_1$  (of Table I) =  $F_0$ .

Experimental determinations of the amount of exchange at the photostationary state,  $F_\infty$ , are compared, in Table II, with the value of  $F$  for the calculated thermal equilibrium at the temperature of the experiments, 25°C. The photochemical values were obtained by exposing the starting mixtures shown until the analyses became

TABLE II. Comparison of photochemical with thermal equilibrium.

$P_{D_2+HD+H_2}$ mm	$P_{HCl+DCl}$ mm	INITIAL ANALYSES		FRACTION OF H IN $D_2+HD+H_2$ AT EQUILIBRIUM (25°C)		RATIO $\frac{F_{photochem.}}{F_{thermal}}$
		$D_2+HD+H_2$	$HCl+DCl$	PHOTOCHEMICAL	THERMAL	
53	126	90.5% D	100% HCl	0.68	0.636	1.07
113	203	79.0% D	100% HCl	0.64	0.610	1.05
90	175	100% H	93% DCl	0.62	0.587	1.06

constant; values of the equilibrium constants used in estimating  $F$  for the thermal equilibrium were

$$\begin{aligned} [\text{HD}]^2/[\text{H}_2][\text{D}_2] &= 3.27, \\ [\text{HD}][\text{HCl}]/[\text{H}_2][\text{DCl}] &= 1.27, \\ [\text{HD}][\text{DCl}]/[\text{D}_2][\text{HCl}] &= 2.58. \end{aligned}$$

### DISCUSSION

The initial quantum yields of greater than unity, together with the effect of light intensity (Fig. 2) indicate without question that the ex-

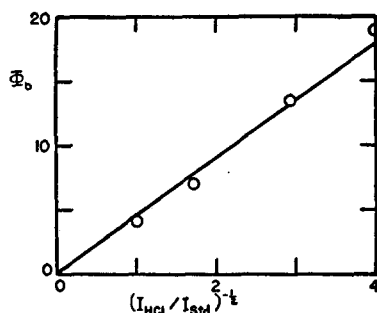
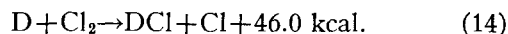
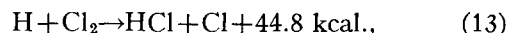
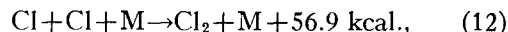
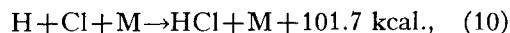
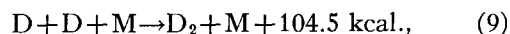
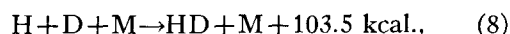
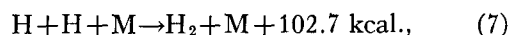
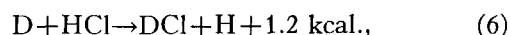
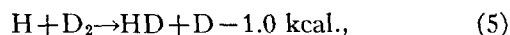
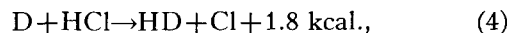
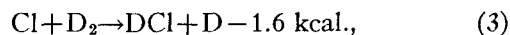
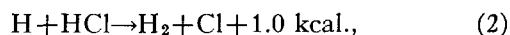


FIG. 2. Quantum yield as a function of light intensity. Solid line is for inverse proportionality between  $\Phi_0$  and the square root of incident light intensity. Points are experimental.

change is propagated by atomic chains which are stopped by recombinations. Using 102.7 and 101.7 kcal. per mole as the dissociation energies of  $\text{H}_2$  and  $\text{HCl}$ , and taking account of the zero point energies ( $\text{HCl}=4.2$ ,  $\text{DCl}=3.0$ ,  $\text{H}_2=6.2$ ,  $\text{HD}=5.4$ , and  $\text{D}_2=4.4$  kcal. per mole) one obtains the following energetically favorable reactions for starting mixtures of  $\text{HCl}+\text{D}_2$ :



For long chain lengths, these reactions give rise to an expression of the following form for the quantum yield:

$$\Phi_0 = A + \frac{B[\text{D}_2][\text{HCl}](\text{[D}_2] + \alpha[\text{HCl}])}{I^{\frac{1}{2}} M^{\frac{1}{2}} (\sum_{m+n=4} \beta_{mn} [\text{D}_2]^m [\text{HCl}]^n)^{\frac{1}{2}}}, \quad (4)$$

where  $A$  varies between 0 and 2, depending upon the relative velocities of the chain carrying reactions above.  $B$ ,  $\alpha$ , and the  $\beta_{mn}$ 's are also functions of the rate constants of the above reactions. The complicated dependence of  $\Phi_0$  upon the concentrations of deuterium and hydrogen chloride as given by Eq. (4) may be approximated by simpler forms in case certain discrepancies in order of magnitude of the chain carrying rate constants prevail, and provided one may assume that all the recombination rate constants are of the same order of magnitude. For example, if  $(k_2, k_4, k_6) \gg (k_3, k_5)$ ,  $k_2 \gg (k_4, k_5, k_6) \gg k_3$ ,  $(k_4, k_6) \gg (k_3, k_5) \gg k_2$  or  $k_5 \gg (k_2, k_4, k_6) \gg k_3$ ,  $\Phi_0 \propto [\text{D}_2]$ , whereas if the preceding orders of magnitude are reversed,  $\Phi_0 \propto [\text{HCl}]$ .

From the observation that the quantum yield

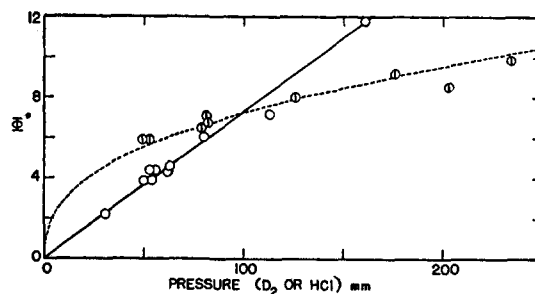


FIG. 3. Quantum yield as a function of the concentration of  $\text{D}_2$  and  $\text{HCl}$ . Solid curve for  $\Phi^* = 0.073[\text{D}_2]$ ; O, experimental values of the quantum yield, corrected to the hypothetical conditions of 100 mm total pressure and 100 mm  $\text{HCl}$  pressure, using  $\Phi_0 \propto [\text{HCl}]^{0.4}([\text{D}_2] + [\text{HCl}])^{-0.5}$ . Broken curve for  $\Phi^* = 1.15[\text{HCl}]^{0.4}$ ;  $\Phi$ , experimental values corrected to 100 mm total pressure and 100 mm  $\text{D}_2$  pressure using  $\Phi_0 \propto [\text{D}_2]([\text{D}_2] + [\text{HCl}])^{-0.5}$ . Corrections are based upon the empirical formula  $\Phi_0^* = 0.115[\text{D}_2][\text{HCl}]^{0.4}$ , where  $\Phi_0^*$  is the quantum yield  $\Phi_0$ , reduced to the basis of total pressure = 100 mm with the assumption that  $M = [\text{D}_2] + [\text{HCl}]$ , i.e., that deuterium and hydrogen chloride are equally effective third bodies for the recombination reactions, and that recombinations at the walls are relatively unimportant.

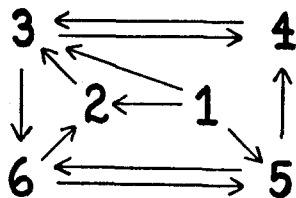


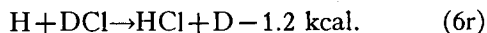
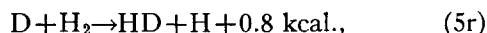
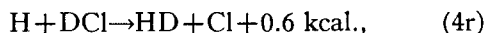
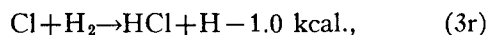
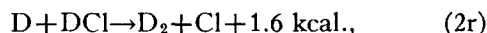
FIG. 4. General scheme for the reaction sequence, showing the various possible chain mechanisms for the exchange. Figures correspond to numbers of the reaction equations (see text).

is pronouncedly more dependent upon the deuterium concentration than upon the hydrogen chloride concentration, as shown in Fig. 3, it is concluded that either (3) is slow compared to (4), or (5) is slow compared to (6), or both; depending upon which of the numerous chains is contributing most to the reaction under the prevailing experimental conditions.

Several investigators have found values near 6.0 kcal. for the activation energy of the reaction  $\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$ .<sup>5</sup> Since this reaction is 1 kcal. endothermic and is the reverse of (2), the activation energy of (2) may be taken as very close to 5.0 kcal. The activation energy of (5) has been reported as 6.5 kcal.,<sup>6</sup> so it is at once indicated that most of the H atoms react by (2), and that chains involving (5) may, with reservations, be excluded from further consideration. The activation energies of the  $\text{Cl} + \text{DH}$  and  $\text{Cl} + \text{D}_2$  exchanges have been estimated to be 0.6 and 1.2–1.4 kcal. higher, respectively, than the activation energy of  $\text{Cl} + \text{H}_2$ .<sup>6, 7</sup> These estimates, combined with the zero point energies, give 7.2 kcal. for the activation energy of (3) and 4.6 kcal. for (4).<sup>8</sup> Having as yet no estimate of the activation energy of reaction (6), which competes with reaction (4) for the deuterium atoms, one must admit the possibility of the two chain processes,  $(2)[(3)(4)] + (3)(4)$  and  $(2)(3)(6) + (3)(6)(2)$ , which remain after the elimination of reaction (5) from the general scheme of reaction sequence shown in Fig. 4. Experimentally, reaction (3) is

the rate determining step, in keeping with the known activation energies for the first chain process. If (6) were slower than (3), the second chain process would be of negligible importance in the exchange, and the dependence upon  $[\text{D}_2]$  would still maintain.

For the exchange between  $\text{DCl}$  and  $\text{H}_2$  the chain carrying reactions are



Taking the activation energy of  $\text{Cl} + \text{D}_2$  as 7.2 kcal.,<sup>6</sup> one obtains an activation energy of 5.6 kcal. for (2r). The observed activation energy of (3r) is 6.0 kcal., while the same value is found for (4r) from  $\text{Cl} + \text{DH} = 6.6$  kcal.<sup>6</sup> The activation energy of (5r) has been estimated as 4.8 kcal.<sup>6</sup> In this case the deuterium atoms should react chiefly by (5r) rather than by (2r). The chain carrying steps obtained by eliminating (2r) from the general scheme of reaction sequence analogous to that shown in Fig. 4, and assuming (5r) relatively faster than (3r) become chiefly (5r)(6r), or (5r)[(4r)(3r)] + (3r)(4r), or both, depending upon the relative speeds of (4r) and (6r).

Although our results on initial mixtures of  $\text{DCl} + \text{H}_2$  are unfortunately meager, they definitely indicate a dependence upon the  $\text{DCl}$  concentration nearly as great as that upon the  $\text{H}_2$  concentration, and a quantum yield of the same order of magnitude as for mixtures of  $\text{HCl}$  and  $\text{D}_2$ . This can be interpreted as favoring the second chain process given above. For the first chain process to give nearly equal dependence upon  $[\text{D}_2]$  and  $[\text{HCl}]$  would require (6r) to have an activation energy near to that of (5r), namely, 4.8 kcal. This would indicate that the exchange between  $\text{DCl}$  and  $\text{H}_2$  should be much faster than that between  $\text{HCl}$  and  $\text{D}_2$ , for which the rate determining step has an activation energy of 7.2 kcal. It appears more plausible that the second process, carried by chains of (3r)(4r), both having activation energies of 6.0 kcal., accounted for the observed exchange. Hence (6r) must have an

<sup>5</sup> J. C. Potts and G. K. Rollefson, *J. Am. Chem. Soc.* **57**, 1027 (1935) give 5.8 kcal., and calculate 5.88 kcal. from the data of Hertel, *Zeits. f. physik. Chemie* **B15**, 325 (1931). W. H. Rodebush and W. C. Klingelhoefer, *J. Am. Chem. Soc.* **55**, 130 (1933), give 6.1 kcal.

<sup>6</sup> A. Farkas and L. Farkas, *Proc. Roy. Soc. A* **152**, 124 (1935).

<sup>7</sup> H. W. Melville, *Science Progress*, **123**, 499 (1937).

<sup>8</sup> Arbitrarily assuming that the  $\text{DHCl}$  complex has 0.2 kcal. lower zero point energy than the  $\text{HDCl}$  complex. (Reference 6.)

activation energy  $>6$  kcal. and (6)  $>4.8$  kcal., indicating that reaction between H (or D) and DCl (or HCl) tends to produce HD and Cl rather than HCl (or DCl) and D (or H).

Of the large number of possible mechanisms for the exchange reaction between HCl and  $D_2$ , all of which are of nearly the same order of importance, the results reported here appear to favor chains of reactions (3) and (4) as having the greatest influence on the kinetics of the photochemical exchange under the experimental conditions employed. Similarly, for  $DCl+H_2$  mixtures, chains of (3r) and (4r) are indicated. Before these conclusions can be taken as final there are factors which may require further study. These include the effect of wall reactions, the effect of variations in the rates of the chain terminating reactions, the possible difference in the efficiency of HCl and  $D_2$  as third bodies in the atomic recombinations, and the possibility that the activation energies may be in error by an amount sufficient to alter the conclusions drawn from their relative magnitudes. Also, the entire treatment

has assumed sufficient diffusion to insure that the local and over-all rates are the same.

At the photostationary state the forward and reverse reactions given above, together with the reactions of the H, D, and Cl atoms with HD molecules, reach a state of balance in which the differences in rates should result in the attainment of thermal equilibrium proportions. Actually the photostationary states are displaced in the direction of higher hydrogen content in the  $D_2+HD+H_2$  mixture than that corresponding to thermal equilibrium (Table II). Although it is uncertain just what significance should be attached to this difference, it probably arises from a stronger absorption by HCl than by DCl in the region 2000–2150Å, which is to be expected from the lower zero point energy of DCl. A difference of about 10 percent in the absorption of the zinc lines by HCl and DCl should be sufficient to produce the observed shift of the equilibrium.

The authors are indebted to the Carnegie Institution of Washington for a grant in support of this research.

JULY, 1938

JOURNAL OF CHEMICAL PHYSICS

VOLUME 6

## Nonadiabatic Reactions. Chemiluminescence

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(Received March 29, 1938)

It is pointed out that chemiluminescent reactions are necessarily nonadiabatic, since emission of radiation can only occur by transition from an upper to a lower potential energy surface. The restriction imposed by the second law of thermodynamics on the photon yield is,

$$\varphi \leq \Delta F/E,$$

where  $\varphi$  is the ratio of quanta evolved to molecules reacted,  $\Delta F$  is the free energy decrease in the reaction, and  $E$  is

the energy of the photon emitted. Upper potential energy surfaces are reached either by activation by radiation, which may be that of a black body at the temperature of the reaction, or by the "crossing" of potential energy surfaces. From Audubert's data on the radiation produced by the thermal decomposition of sodium azide approximate surfaces which account for the observations are constructed.

### INTRODUCTION

THE purpose of the present paper is to treat chemiluminescence as a particular example of the general theory of chemical reactions. A general survey of the field is given along with sufficient examples to illustrate the point of view and the method of treatment.

Chemiluminescent reactions are noteworthy because of the wide variation of the ratio of the number of quanta evolved to the number of molecules reacted. Thus reactions are found experimentally with photon yields ranging from about 0.3 to  $10^{-15}$ . The upper limit of 0.3 for the photon yield is reported for the reaction of sodium