and gives rise to a second boundary whose velocity yields information as to the concentration adjustment occurring in the region of the solution which contains pure potassium chloride between the two boundaries. From data on both boundaries it is shown that within this latter region the hydrogen ion has been quantitatively separated from the potassium ion and that the concentration of the potassium chloride residue is accurately determined by the "regulating" function of Kohlrausch,[5] a derivation of which is given.

It is shown experimentally that the mobility of the chloride-ion constituent varies linearly between its slightly different values in 0.1 normal hydrogen chloride and 0.1 normal potassium chloride.

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SURFACE REACTIONS OF ATOMS AND RADICALS. I. A NEW APPROACH TO THE PROBLEM OF SPECIFIC SURFACE ACTION

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The problem of specificity in the action of surfaces is still the outstanding problem of chemical reactivity at solid surfaces. The solution of the problem will contribute materially to the explanation of the varied phenomena grouped under the title of contact catalytic action. Hitherto, discussion of this problem has been confined mainly to the reactions which molecules undergo at various surfaces. Little attention has been paid to the influence of surfaces on reactions of atoms and of radicals. Frequently it has been implicitly assumed that, for reactions between atoms and radicals, a surface only was necessary; little regard has been paid to the influence of the nature of the surface. It is the purpose of the present communication to demonstrate that the surface is of importance in atom–radical reactions as in molecular reactions; that great differences in velocity of such reactions at different surfaces occur, though the actual time of reaction is many orders less than with molecules; that the available data, together with other experimental data presented herewith, indicate a connection between the activity of surfaces in atomic reactions and corresponding processes involving molecules. The evidence already in the literature is diffuse and only assumes important proportions when coördinated. It suggests, however, an extended experimental program of which the first results will be here detailed.

The Recombination of Halogen Atoms at Surfaces.—The specific influence of surface in the rate of recombination of halogen atoms is well illustrated by a recent publication of Senftleben and Germer.[1] In this

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[1] Senftleben and Germer, *Ann. Physik*, **2**, 847 (1929).

work, atomic halogens were produced by illumination with light of wave length within the region of continuous absorption and the existence of atoms was demonstrated by measuring the increase in thermal conductivity of the vapor under illumination. This involved the use of a heated platinum wire which decreased in temperature and resistance when dissociation of the halogen occurred. The platinum wire showed a marked tendency to produce recombination of chlorine atoms; the efficiency of the surface in this respect could be materially diminished by glowing the wire in chlorine, a treatment which undoubtedly covered the surface in part with the metal chloride. In this manner the efficiency of the wire in causing recombination was so far diminished that the effect of illumination in producing dissociation was successfully demonstrated. With bromine the success was less great, it being found difficult to poison the wire so as to prevent recombination of bromine atoms. With iodine a new surface factor became of importance. The glass surface of the containing vessel caused rapid recombination of iodine atoms. To reduce this effect quartz was substituted for glass and proved to have a lower order of efficiency in this respect.

These direct observations may now be supplemented by others, somewhat less direct, involving additional types of surface. The low quantum yields in the photochemical hydrogen–chlorine combination found by Marshall[2] at pressures below 60 mm. could be explained by the influence of the walls on the recombination of atoms taking part in the chain reaction of the secondary processes succeeding the absorption process. This conclusion was more directly confirmed by the work of Trifonoff[3] using vessels of various sizes at low pressures, and by Chapman and Grigg[4] using capillary tubes at normal pressures. This effect of capillaries on atom recombination accounts for the failure of Bodenstein and Taylor[5] and later of Marshall[6] to obtain reaction by illuminating the chlorine alone and passing it directly (but, owing to experimental requirements, through capillaries) to unilluminated hydrogen. No reaction was observed even when the time interval between illumination of the chlorine and admixture with hydrogen was 10^{-4} seconds.

A varying influence of surfaces in this same reaction was demonstrated by Polanyi and Bogdandy[7] who found that when the hydrogen–chlorine combination was initiated by the reaction of chlorine with sodium vapor, $Na + Cl_2 = NaCl + Cl$, the chain length of the hydrogen–chlorine combination was short when a clean glass surface was present, but increased

[2] Marshall, *J. Phys. Chem.*, **29**, 1453 (1925).

[3] Trifonoff, *Z. physik. Chem.*, 3B, 195 (1929).

[4] Chapman and Grigg, *J. Chem. Soc.*, 2426 (1929).

[5] Bodenstein and Taylor, *Z. Elektrochem.*, **22**, 202 (1916).

[6] Marshall, *J. Phys. Chem.*, **30**, 757 (1926).

[7] Polanyi and Bogdandy, *Z. Elektrochem.*, **33**, 554 (1927).

30-fold after the glass surface became covered with sodium chloride. The operating pressure was below 10 mm. of mercury with hydrogen in large excess. In the corresponding experiments with potassium in place of sodium the chain length was shorter, pointing to an increased efficiency of potassium chloride over sodium chloride in the breaking of chains.[8] That the effect of the surface was on the recombination of chlorine atoms was indicated by the authors by reason of experience with the effect of surface on chemiluminescences produced by interaction of sodium and chlorine. Polanyi and Schay[9] found that in the interaction of sodium vapor and chlorine, the chemiluminescent flame was at first short and of weak intensity, gradually becoming stronger and longer as the surface of the vessel became coated with sodium chloride. Since the light-producing reactions are initiated by chlorine atoms, by the reaction sequence (1) $Na + Cl_2 = NaCl + Cl$; (2) $Cl + Na_2 = NaCl' + Na$; (3) $NaCl' + Na = NaCl + Na'$; (4) $Na' = Na + h\nu$, it follows that sodium chloride surfaces are less efficient than glass in terminating the activity of chlorine or sodium atoms. Since chlorine atoms are common to this reaction and the preceding, it indicates that it is the recombination of chlorine atoms which is involved at the two surfaces. This conclusion will be strengthened by our own results on the low efficiency of halide surfaces in the recombination of hydrogen atoms. Polanyi and Bogdandy also indicate that a glass surface which has been browned with sodium vapor is more efficient than clean glass surfaces for these atom recombinations.

The efficiency of glass surfaces in the recombination of chlorine atoms is apparent also in the kinetic analysis of the photochemical formation of phosgene[10] and of the photosensitized oxidation of carbon monoxide in presence of chlorine.[11] These studies show that a change from higher pressures to low pressures causes a change in the reaction kinetics directly associable with the changing influence of the wall in the recombination of chlorine atoms. In ordinary reaction vessels in the photochemical formation of phosgene the change manifests itself below 10 mm. of mercury working pressure. If the glass surface of the reaction vessel per unit volume be greatly increased, the change in kinetics is already revealed at 150-mm. mercury pressure. This points indubitably to the action of the glass wall on the reaction $2Cl = Cl_2$. From the cases cited in the

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[8] There is, however, an untested possibility that the difference in chain length between a potassium chloride and a sodium chloride surface was due to impurities in the gases used. This does not apply to the glass–sodium chloride comparison since this was achieved with a given filling. It is evident that there is nothing improbable in the indicated difference in efficiencies of potassium chloride and sodium chloride for atom recombinations.

[9] Polanyi and Schay, *Z. physik. Chem.*, **1B**, 30 (1928).

[10] Bodenstein, Lenher and Wagner, *ibid.*, **3B**, 459 (1929).

[11] Schumacher, *ibid.*, **129**, 241 (1927), and forthcoming papers.

preceding paragraphs it is evident that the kinetics of these photo-reactions would be modified in entirely different pressure intervals were the walls of the reaction vessels coated with alkali halides. This could readily be made the subject of experimental test.

The Recombination of Hydrogen Atoms at Surfaces.—Wood,[12] in his initial work on the production of hydrogen atoms in discharge tubes, drew attention to the desirability of adding water vapor to the hydrogen used, in order to increase the concentration of hydrogen atoms obtained. Langmuir suggested, as a reason for this, the poisoning action of adsorbed water vapor on the surface activity of the glass walls for recombination. This procedure has since been followed and ice has been employed as the containing surface.[13] Recently von Wartenburg and Schultze[14] have further improved the protection of the glass by coating it with hygroscopic materials. Strong solutions of potassium hydroxide and water glass were useful but sirupy phosphoric acid was very efficient. These authors imply that the efficiency may be due to the film of water which such materials hold on the surface. There may be, however, a specific effect of the materials used.

Bonhoeffer[15] demonstrated a varying capacity of surfaces to effect recombination of hydrogen atoms. Metals were especially efficient and the order of efficiency was that of the metals in respect to activity as hydrogenating catalysts. Bonhoeffer states that, besides metals, many salts and especially oxides also catalyze the recombination. Concerning one oxide, Al_2O_3, cited by Bonhoeffer, we shall give experimental data of our own which are in conflict with this view.

Surface Effects in Explosion and Flame Reactions.—Reactions leading to the development of explosions and flames are now known in many cases to be of the chain reaction type.[16] Whether the chains are atom or radical chains or energy chains is not yet known in individual cases with certainty. In many of these reactions, however, the specific effects of surface are well known. The action of metal-organic compounds as "anti-knock" agents in gasoline explosions has been attributed to the effect of the metal particles, produced by thermal dissociation of the compounds, on a chain mechanism produced in the process of gasoline combustion. Egerton[17] seems to favor energy chains but Berl and Winnacker,[18] reasoning from the efficiency of colloidal lead and iron as inhibitors and the

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[12] Wood, *Proc. Roy. Soc.* (London), **102A**, 1 (1923).

[13] Hansen, *Ann. Physik*, **78**, 558 (1925).

[14] Von Wartenburg and Schultze, *Z. physik. Chem.*, 6B, 261 (1930).

[15] Bonhoeffer, *ibid.*, **113**, 199 (1924).

[16] See, for example, Semenoff, *Chem. Rev.*, **6**, 347 (1929).

[17] See, for example, Egerton, "Réunion Int. de Chimie Physique," Paris, **1928**, p. 489.

[18] Berl and Winnacker, *Z. physik. Chem.*, **145**, 161 (1929).

lack of activity of the corresponding dispersed oxides, reject the concept of energy chains and favor some specific chemical reaction (*e. g.*, destruction of peroxide) as the mechanism of inhibition.

Metallic potassium vapor has a marked efficiency as inhibitor in automobile engine combustions and this is to be remembered in conjunction with the well-known use of potassium salts for the prevention of flame at the mouth of cannons firing high explosives.[19] Muraour cites other similar uses of potassium salts.

These latter observations link up with the recent studies of Hinshelwood[20] and of Pease[21] on the influence of surface on the slow combustion of hydrogen and oxygen and hydrocarbons and oxygen. Of especial interest is the observation of Pease that coating the glass surface of the reaction vessel with potassium chloride slows down the rate of reaction approximately 1000-fold. This is not due exclusively to the poisoning of the glass surface for a heterogeneous reaction of combination since an increase of surface by filling with coarse glass powder, either with or without a coating of potassium chloride, *slowed* down the reaction rate. It is evident that, in the oxidation of hydrogen and hydrocarbons, a surface of potassium chloride is *more efficient in breaking chains* than is a clean glass surface. The contrast between this conclusion and the opposite one reached in the case of chlorine atom recombination is compelling evidence of specificity of surface in chain reactions.

In the hydrogen–oxygen reaction the system is sufficiently simple that experimental evidence may be sought to permit a decision as to the nature of the influence of specific surfaces. Hydrogen atoms, oxygen atoms and hydroxyl radicals are the only atoms or radicals that might be involved if the chain is one involving such species. Spectral evidence indicates that hydrogen and hydroxyl are involved.[22] The behavior of these at surfaces may be studied since, in the hydrogen discharge tube, we have a source of atomic hydrogen and, in the corresponding tube, using water vapor, there is now evidence for the production, together with atomic hydrogen, of hydroxyl (with possibly free oxygen atoms).[23]

Experimental

The method employed consisted in an adaptation of that employed by Bonhoeffer in his study of atomic hydrogen. Thermometers whose bulbs were coated with the material to be studied were inserted in positions B, C and D of the exit tube from a dis-

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[19] Muraour, "Réunion Int. de Chimie Physique," Paris, **1928**, p. 502.

[20] Hinshelwood, *Proc. Roy. Soc.* (*London*), **118A**, 170, 591 (1928).

[21] Pease and Chesebro, *Proc. Nat. Acad. Sci.*, **14**, 472 (1928); Pease, THIS JOURNAL, **51**, 1839 (1929), and forthcoming paper.

[22] Bonhoeffer and Haber, *Z. physik. Chem.*, **136**, 263 (1928); Bonhoeffer and Reichardt, *ibid.*, **139**, 75 (1928).

[23] Lavin and Stewart, *Proc. Nat. Acad. Sci.*, **15**, 829 (1929).

charge tube operating either with water vapor or hydrogen (Fig. 1). Since atomic hydrogen was known by spectroscopic observation to persist for longer intervals of time than hydroxyl, positions C and D were ordinarily used for detecting, by temperature rise on the thermometer, any atomic hydrogen recombination. The recombination of hydrogen with hydroxyl was studied at B, position A being used, with a clean glass thermometer bulb, to determine rise in temperature due to the discharge and also the effect of a clean glass surface on the recombination process. As an index of the active material reaching D, the thermometer bulb in this position was normally coated with metallic silver obtained by atomic hydrogen reduction of silver nitrate, since such a surface was shown by Bonhoeffer to act efficiently as a recombination agent for atomic hydrogen. In order to eliminate differences due to the varying efficiency of the discharge tube, the activities at B and C of the surfaces studied were always compared either with clean glass at A or with the silvered surface at D. The results of our experiments are recorded in the accompanying Table I. The data given represent a typical selection from a large number of experiments.

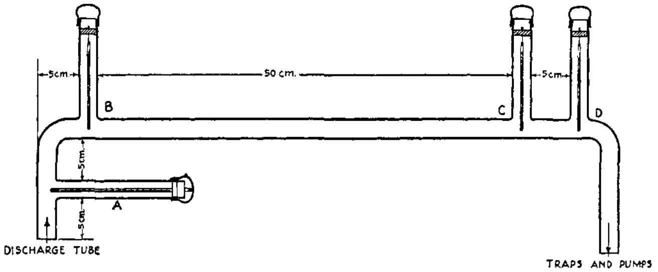

Fig. 1.

TABLE I

RECOMBINATION OF HYDROGEN ATOMS AND HYDROXYL AT VARIOUS SURFACES

Expt.	Nature and position of surface		Gas in discharge tube, *ca.* 0.5 mm.	Thermometer readings at 1-minute intervals				
1	Clean glass[a]	C	Water	22.5	29	29	29	
	Silver	D	Vapor	32.0	52	55	57	
2	KCl	C	Water	27	29	30	30	31
	Silver	D	Vapor	32	75	100	111	128
3	KCl	B	Water	32	110	122	123	124
	Silver	D	Vapor	31	68	81	87	92
4	Clean glass	A	Water	26	27	27	27	28
	KCl	B	Vapor	34	118	127	127	127
5	KCl	C	H_2 +	27	28	29	31	32
	Silver	D	H_2O at 25°	31	79	106	149	169
6	KCl	B	H_2 +	30	32	34	35	37
	Silver	D	H_2O at 25°	27	40	45	48	50
7	KOH	C	Water	29	37	44	54	57
	Silver	D	Vapor	31	64	75	82	85
8	KOH[b]	C	Water	29	62	75	83	93
	Silver	D	Vapor	27	42	47	50	53
9	K_2CO_3	C	Water	25	31	41	54	102[c]
	Silver	D	Vapor	25	41	52	59	69

TABLE I (*Concluded*)

Expt.	Nature and position of surface		Gas in discharge tube, *ca.* 0.5 mm.	Thermometer readings at 1-minute intervals				
10	$ZnO \cdot Cr_2O_3$	C	H_2 +	25	76	94	106	112
	Silver	D	H_2O at 25°	25	29	29	29	28
11	Al_2O_3	C	Water	31	41	46	47	50
	Silver	D	Vapor	37	74	103	135	152
12	Al_2O_3	B	Water	47	95	120	132	..
	Silver	D	Vapor	27	48	64	78	..
13	Al_2O_3	C	Water	28	38	42	44	45
	Silver	D	Vapor	34	91	110	138	165
14	Al_2O_3	B	H_2 +	33	57	68	73	79
	Silver	D	H_2O at 5°	30	72	93	100	104
15	Al_2O_3	B	H_2 +	29	82	109	124	132
	Silver	D	H_2O at 34°	30	96	116	125	130
16	Al_2O_3	B	H_2 +	32	93	129	147	159
	Silver	D	H_2O at 54°	32	106	137	147	152
17	Al_2O_3	B	H_2 +	31	102	138	158	169
	Silver	D	H_2O at 74°	31	118	144	153	158
18	Al_2O_3	C	H_2 +	25	32	35	37	38
	$ZnO \cdot Cr_2O_3$	D	H_2O at 25°	25	100	134	152	163

[a] The bulb of a 360° thermometer with opalescent back and etched scale constituted the glass surface. It was carefully washed in distilled water and dried with a soft cloth.

[b] KOH covered thermometer allowed to stand for one day in air and then again tried in Expt. 8.

[c] Two-minute interval.

Discussion of Experimental Data

It is apparent from Expts. 1, 2, 5 and 6 that neither a clean glass surface nor a potassium chloride surface has any marked efficiency in the recombination of hydrogen atoms either from water vapor at position C or from moist hydrogen at positions A or B. In marked contrast to this is the efficiency of potassium chloride as a reaction surface at position B when water vapor is passed through the discharge tube (Expts. 3 and 4). In this it is markedly superior to a clean glass surface at A (Expt. 4). We associate this efficiency with a recombination of hydrogen and hydroxyl since spectroscopic evidence shows marked concentrations of the latter at B and also for reasons indicated in the subsequent discussion of alumina.

Potassium hydroxide shows a more pronounced efficiency for atomic hydrogen recombination than does the chloride (Expts. 7 and 8 compared with Expt. 2). On standing in the air the potassium hydroxide appeared to improve in efficiency (Expt. 8). We, therefore, were led to try potassium carbonate and thus found it also to have good efficiency in the combination of atomic hydrogen (Expt. 9). When a surface shows marked activity in atomic hydrogen recombination at C, its test at B for the H–OH combination is useless since the present method of test does not distinguish between the two reactions, and at B there is always a higher concentration of hydrogen atoms than at C under given discharge tube conditions.

The specific action of surfaces, thus found for the two reactions, suggested a correlation with the specific behavior of surfaces in similar reactions involving molecules. Thus, the combination of atomic hydrogen and hydroxyl is analogous to the removal of water from organic molecules by means of dehydration catalysts. The recombination of atomic hydrogen is analogous to the removal of hydrogen from organic compounds by dehydrogenation catalysts. It seemed probable, therefore, that a purely dehydration catalyst might promote H–OH recombination without affecting the H–H reaction, while a purely dehydrogenation catalyst might secure the H–H recombination. To test this, we chose alumina as a dehydration catalyst and the now well-known mixture of zinc and chromium oxides (used in methanol synthesis) as a typical oxide dehydrogenation catalyst. The correlation of hydrogen atom recombination on metals with the catalytic activity of the latter has already been indicated by Bonhoeffer.[15] Our expectations were completely realized. It is evident that alumina has high efficiency in position B and low efficiency at position C (cf. Expts. 11, 12 and 13). Experiment 13 was especially conclusive since it immediately succeeded Expt. 12 in which the high activity at B was realized. Nevertheless, in Expt. 13 at C, only the activity associated with a small amount of residual water vapor is to be noted. Its inertness toward atomic hydrogen is also manifest in Expt. 18, where a zinc–chromium oxide surface immediately beyond it revealed a high residual concentration of atomic hydrogen.

We wish also to record one other observation with alumina which bears upon the problem of its surface activity. The oxide was prepared from the precipitated hydroxide which was dried after it had been placed on the thermometer bulb. The product displayed no activity at all in either position B or C until it had been dehydrated by heating in an electric furnace to 300°. A treatment of this kind at 250° was insufficient to activate the surface. This points to a poisoning of the oxide surface by adsorbed water.

It appeared necessary, in view of the observation already recorded by Bonhoeffer as to the efficiency of alumina in atomic hydrogen recombination, to ascertain to what factor Bonhoeffer's observation was due. We accordingly tested alumina at position B, the discharge tube operating with a stream of hydrogen which had been bubbled through water maintained at various temperatures. A perusal of the selection of our results given (Expts. 14–17) will indicate that the temperature rise obtained is dependent on the concentration of water vapor in the gas stream. We suggest, therefore, that Bonhoeffer's results with alumina were due to the hydroxyl content of his atomic hydrogen.

The efficiency of zinc–chromium oxide for the atomic hydrogen recombination in comparison even with silver is shown in Expt. 10 as well as in the Expt. 18 already quoted.

We wish also to record the observation that the active combination of the atoms and radicals in question is associated in many instances with the production of distinctive chemiluminescences at the reaction surfaces. With potassium chloride and water vapor in the discharge, the glow was purple; with potassium hydroxide and potassium carbonate a blue-green. With alumina one obtains also a purple glow. With zinc–chromium oxide and on the silvered thermometer there was no observable light production. We propose to investigate these phenomena in detail later.

Our experiments have demonstrated that the specificity of behavior of dehydration and dehydrogenation catalysts is associable with their activity in producing the recombination of H–OH and H–H, respectively. We plan a further series of investigations to ascertain the factors controlling the activity of surfaces in these simple reaction processes and hope thence to derive the explanation of specific surface action in these molecular processes.[24]

Summary

1. It has been demonstrated that the nature of the surface is of fundamental importance in determining the velocity of atom–radical reactions.
2. Potassium chloride is more efficient than clean glass in H–OH recombination. It is less efficient than clean glass in Cl–Cl recombination. Alumina is very efficient in the H–OH reaction.
3. Potassium chloride and alumina are inefficient in H–H recombination. Potassium hydroxide and carbonate, and especially zinc–chromium oxide, are efficient agents for this reaction as are also metal surfaces.
4. Active recombination of atoms and radicals is associated with the production of distinctive chemiluminescences at several of the surfaces.
5. A correlation of the activity of surfaces in atomic reactions with similar processes involving molecules has been given and the importance of this in the problem of specific surface activity has been indicated.

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[24] It is evident that analogous to this specificity of surface in atom–radical reactions, there should exist specific third-body action in homogeneous systems. Such specificity is fundamental in the kinetics of such reactions, has not been emphasized and yet apparently exists in reactions already studied.