A COMPARISON OF CATALYTIC ACTIVITIES OF SOME SOLID SALTS IN THE RECOMBINATION OF HYDROGEN FREE ATOMS AND HYDROXYL FREE RADICALS.

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It is often observed that some salts, such as potassium chloride, have remarkable retarding effects in the combustion reactions of hydrogen and of organic compounds.[1] These reactions are chain reactions, and it is usually considered that H–atoms and OH–radicals are chain-carriers in the reactions. Since a retarding action of some negative catalyser is in many cases due to an ability of killing the chain-carriers, it is significant to study the recombination of H–atoms and OH–radicals on the surface of some solid salts.[2] In this investigation the relative catalytic activities of some solid salts are determined by measuring the rises in temperature of a thermometer, the mercury-bulb of which was covered with thin layer of solid salt to be tested, and which was inserted into a stream of water vapour involving H and OH. Though the analogous investigation was already made by H. S. Taylor and his collaborators[3], the samples used were limited only to several salts. The present author intended to make the same experiment on more samples and more systematically than they did.

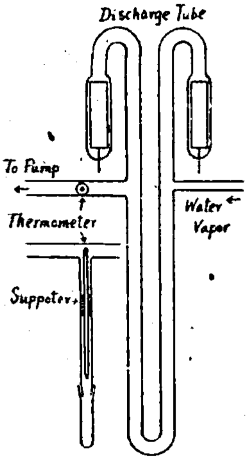

Fig. 1.

Experimental Method.

The apparatus used is simple and only the main part is shown in Fig. 1. The discharge tube is an ordinary Wood's discharge one. The diameter of the tube is 25mm and the whole length about 1m. The diameter of the reaction tube is also 25mm. The water vapour was generated in a small bulb containing distilled water, and passed through the discharge tube, the reaction tube and a trap cooled with dry-ice and alcohol, and finally pumped out by a mercury diffusion pump and a rotary oil pump. The discharge current was kept constant at 3.0 amp in

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[1] See, for example, N. Semenoff, Chemical kinetics and chain reactions.

[2] Three surface reactions involving H–atoms and OH–radicals are possible, that is, $H+H=H_2$, $H+OH=H_2O$ and $OH+OH=H_2O_2$, in which the second is supposed to be most probable.[*]

[3] H. S. Taylor and G. I. Lavin, *J. Am. Chem. Soc.*, 52, 1910 (1930).

[*] Refer to 3) and O. Oldenberg, *J. Chem. Phys.*, 4, 642 (1936).

the primary of a transformer. A thermometer was inserted perpendicularly into the reaction tube at a place 10cm apart from an exit of the discharge tube. The thermometer, the surface of the mercury-bulb of which was cleaned throughly with NaOH–solution, warm chrom-mixture, water and distilled water, was dipped as far as a constant depth into aqueous solutions of sample salts, the concentrations of which were 1% in most cases. The thermometer was, then, drawn up and dried by heating gently above a soft flame of Bunsen-burner so as to make the deposit to be as homogeneous as possible. After setting the thermometer in the reaction tube, the apparatus was evacuated and then the water vapour flowed through it. After the flowing-rate attained a stationary state, the discharge was started and the temperature rises with times were read. The pressure of water vapour in the tube was 7mm of dibutylphthalate.

Experimental Results.

The experimental results obtained are shown in Tables 1, 2, 3 and 4. Figures in the tables denote the rises in temperature of thermometer.

Table 1. Series I. Alkali halides I.

Exp. No. t (min.)	1 KF	2 KCl	3 KBr	4 KI	5 KCl	6 NaCl	7 RbCl	8 LiCl
0	25	22	25	25	25	29	26	25
1	29	48	50	44	—	46	—	37
2	32	—	94	(78)[4]	—	—	88	44
3	—	97	108	98	—	—	97	—
4	—	104	115	110	96	—	103	—
5	36	107	119	117	103	90	106	—
6		109	121	122	107	93	109	—
7		111	122	124	110	93	111	—
8		113	123	126	112	93	112	—
9		114	123	127	113	93	115	—
10		114	123	127	115	93	115	(75)
11		115		128	115			
12				128	116			
13					117			

In every series KCl was taken as a standard. The reproducibility of the rise in temperature is satisfactory in the same series, as shown in the experiments on KCl of Series I. and III. For reference the experimental results for Pt were also listed in the table; the reproducibility in the successive runs is almost perfect.

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[4] Gradulations of thermometer between 70～80 could not be read accurately owing to circumstances of the apparatus.

Table 2. Series II. Alkali halides 2.

Exp. No t (min.)	1 KF	2 KF	3 RbCl	4 KCl	5 KI	6 KBr	7 LiCl
0	34	33	30	30	30	30	27
1	34	33	52	42	40	54	35
2	34	33	—	—	(70)	91	41
3	34	33	96	—	94	105	45
4	34	33	100	93	110	111	51
5	34	33	103	95	118	113	—
6	34	33	105	97	120	115	—
7	34	32	107	98	124	115	65
8	34	31	107	100	124	115	
9	34	30	108	103	124	114	
10	34		108	106	124		
11				109	124		
12				110			
13				110			
14				111			

Table 3. Series III. Miscellaneous salts.

Exp. No. t (min.)	1 NaF	2 LiF	3 KCl	4 Li_2CO_3	5 Na_2CO_3	6 Na_2SO_4	7 $NaNO_3$	8 K_2SO_4	9 NH_4Cl	10 KNO_3	11 $MgCl_2$	12 Glass	13 KCl
0	31	33	26	26	26	27	26	30	28	26	32	26	26
1	33	31	—	34	56	32	56	34	34	60	35	32	—
2	37	35	65	37	—	35	80	38	35	117	38	39	—
3	39	35	—	38	—	37	102	38	36	131	42	42	100
4	39	35	—	38	112	37	120	38	36	135	45	42	112
5	38	35	117	37	120	37	126	38	36	138	46	42	116
6	37	35	120	36	124	37	127		$36^{5)}$	141	47	40	—
7	37	35	—	35	126	35	127			142	—	40	—
8	36	35	124		128	35	123			142	—	39	—
9	35	35	125		128	33	123			141	—		125
10	35		126			33	115			$131^{5)}$	—		
11			126				$110^{5)}$				$50^{6)}$		

Table 4. Series IV. Ca-salts and Pt. Series V. Carbonates.

Exp. No. t (min.)	KCl	$Ca(NO_3)_2$	CaF_2	$Pt^{7)}$	$Pt^{7)}$	KCl	K_2CO_3	Na_2CO_3
0	19	25	26	23	25	23	24	24
1	—	29	27	—	162	—	—	47
2	92	30	27	240	260	97	110	(75)
3	107	29	28	306	320	100	124	(90)

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5) The salts was found after the experiments to have been vapourized.

6) Owing to the hygroscopic property the salt layer did not dry in the atmosphere.

7) Platinized by baking with baking solution.

4	113	29	28	350	358	108	136	100
5	117	29	28	375	377	115	145	112
6	120	29	28	387	387	115	150	119
7	121	29	28	391	395	117	153	124
8	122	28	28	394	395	118	155	127
9	122	28	28	395	396	119	156	129
10	122	28	28	396	396	120	156	130
11				396	396	120		132
12				396	396	121		132

Discusson of Results.

The order of catalytic activeness, which is expressed by the temperature at $t=10$[8], is as follows.

Pt > (K)[9] > (Na)[9] > K_2CO_3 > (KNO_3)[9] > KI > KBr > Na_2CO_3 > ($NaNO_3$)[9] > RbCl > KCl > NaCl > LiCl.

LiF, NaF, KF, CaF_2; Na_2SO_4, K_2SO_4; NH_4Cl, $Ca(NO_3)_2$, $MgCl_2$ have no appreciable catalytic activity.

In these results the regularities of the catalytic activities are found as follows.

(1) Rb– > K– > Na > Li– (for carbonates, halides and nitrates)
(2) Metal > Carbonates > (Nitrates)[9] > Halides (for K– and Na–salts)
(3) –I > –Br > –Cl > –F (for K–salts)
(4) Fluorides and Sulphates are inactive. (for K– and Na–salts)
(5) Salts of alkali-earth metals are inactive, so far as the present experiments are concerned.

It is concluded that in general *the more positive the positive ion is and the less negative the negative ion is, the more active the salt is.*

The results showing the higher activities of potassium salts than of sodium salts were expected from the fact that the same tendency as in a negative catalyser had also found in some combustion reactions.

In the experiments on the nitrates, as seen in Series III. No. 7 and 10, after attaining maximum values, the temperature began to fall. This may be due to the reduction of the salt to metal and successive evaporation of the metal by the heat of recombination.[10] Thus, the maximum values obtained for these nitrates are those of the evaporating metals. The values of metals themselves would be

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[8] Precisely, it should be expressed by the rise in temperature above room-temperature and not above that at $t=0$, because the latter is not necessarily equal to room-temperature.

[9] See later.

[10] Indeed, the reduction of nitrates by atomic hydrogen was found by H. Kroepelin and E. Vogel, *Z. anorg. Chem.*, 229, 1 (1936).

obtained by the extrapolations of the falling curves after the maximums to t=0. The present data, however, are unfortunately not so accurate as to make it possible, and we are obliged to be satisfied with the results that K-metal[11] and Na-metal next to it, are more active than any other salts of them.

For alkali halides, seeking for the relations between the observed order of activeness and other physical constants, we have arrived at a conclusion that, as shown in Table 5, the smaller the lattice energy is, the greater the catalytic activity is.[12]

Table 5.

	Salts	Mean value of Temp. at t=10	Lattice energy[13] (Kcal)
Dependence on halogen ions	KF	35	191
	KCl	110	161
	KBr	119	158
	KI	126	148
Dependence on alkali ions	LiCl	70	194
	NaCl	90	178
	KCl	110	162
	RbCl	111	156

In an investigation on the influence of alkali halide on the lowest temperature at which a reaction between methane and oxygen is observed, Jorrissen and Lebbink[14] found that the lowest temperature rose in order Li <Na <K <Rb and similary in order F <Cl <Br <I. These orders agree with those of the catalytic activity in the reactions involving H and

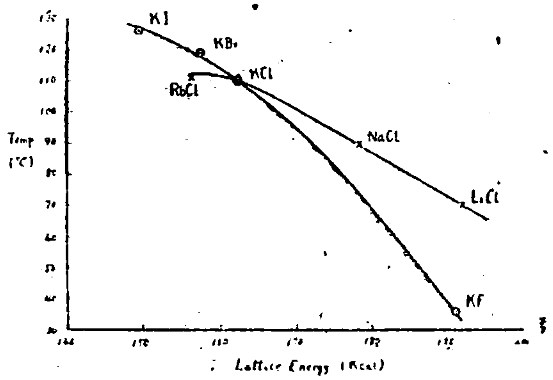

Fig. 2.

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[11] It is noticed that K-metal is well-known as one of the most effective antiknocking substances.

[12] If the temperatures are plotted against the lattice energies (Fig. 2), it is seen that, at first sight, the former increases linearly as the latter does with the exception of the point for KF and the slight deviations of the points for KBr and RbCl. However, the deviations of the points for KBr and RbCl cannot be taken as experimental errors. If we take these points as correct ones and take into account the point for KF also, we find that the points for KI, KBr, KCl and KF fall on one curve and, those for RbCl, KCl, NaCl and LiCl fall on another curve. Therefore, the catalytic activity and the lattice energy are not in a relation of one to one correspondence. In respect to this point more investigations are desired.

[13] E.A. Moelwyn-Hughes, *Physical Chemistry*, P. 601.

[14] W.P. Jorissen and H.O. Lebbink, *Rec. Trav. Chim.*, 58, 959 (1939).

OH in the present investigation. In Table 5 it is seen that the influence of change in halogen ion on the catalytic activity of alkali halide is more pronounced than that of change in alkali ion; similar tendency is also found in the reaction between methane and oxygen. From these facts it is conceivable that the reactions occurring on the surface of alkali halide crystals are the same in both cases. It appears, therefore, that the retarding action of alkali halides in the reaction between methane and oxygen is ascribed to their action of promoting recombination processes involving H and OH.

As seen in the cases of –I, –Br, –Cl and –F, in general, the salt of weaker acid is more active; the high activeness of carbonates and the inactiveness of sulphate may obey this rule.

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