The relation of the ionic potential to certain properties of compounds will be shown in subsequent papers, in which it will appear that the numerical values of the potentials may be used to indicate the order of variation of numerous effects.

Summary

1. A periodic classification of ions has been developed, with provision for all valence forms of all the elements. It is shown that no single atomic characteristic is an adequate basis for a periodic classification, and the new arrangement takes account of the charge, structure and radius of the ions. For this purpose a new function, the ionic potential, is introduced and used as a quantitative basis for the classification.

2. It is shown that the ionic potential is related to many of the characteristics of ions and their compounds, and that the new arrangement satisfactorily represents the behavior of hydrogen, the eighth group elements and the rare earths.

3. It is also shown that the properties of the ions are definitely related to the structure of their outermost electronic shells, with respect to the completeness or incompleteness of these shells. On this basis a new definition of the periodic families is given.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

STUDIES ON THE PERIODIC SYSTEM. II. THE IONIC POTENTIAL AND RELATED PROPERTIES[1]

BY G. H. CARTLEDGE

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In the preceding paper[2] it has been shown that the ratio of charge to radius is an important periodic property of the ions and may be made the basis of a quantitative classification. This function has been called the ionic potential. In the present paper the relation between the ionic potential and several related properties of substances will be developed, and it will be shown that the periodic classification presented in the preceding paper is able to indicate the order of variation of many properties which may not readily be related to the older forms of representation.

Ionic Hydration and Associated Effects

When a polar crystal is placed in water the lattice becomes disrupted under the influence of the attraction between the ions and the polarized water molecules. Following Fajans,[3] the measured heat of solution, Q_s,

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[1] In memory of Ira Remsen.

[2] Cartledge, THIS JOURNAL, **50**, 2855 (1928).

[3] Fajans, *Ber. physik. Ges.*, **20**, 712 (1918); *ibid.*, **21**, 549, 714 (1919).

plus the lattice energy, U, is equal to the sum of the heats of hydration of the ions. According to Born[4] the molal heat of hydration of an ion (W_h) is equal to the decrease in its electrostatic energy when the gaseous ion is placed in water; that is

$$W_h = \frac{\overline{N}Z^2e^2}{2r}\left(1 - \frac{1}{D}\right) \tag{1}$$

in which $\overline{N}$ is Avogadro's number, e the electronic charge, Z the ionic valence, r the radius of the ion and D the dielectric constant of water.

The situation is more complicated than this relation assumes in equating the decrease in electrostatic energy to the heat of hydration, since a portion of this energy goes into an increased intramolecular energy of the water molecules as a consequence of their distortion. In the case of cations an additional heat *evolution* is also undoubtedly caused by the effect of the outer electronic region of the ion in attracting the hydrogen ends of the water molecules. If the Born relationship were correct, the heat of hydration *per equivalent* should be linearly proportional to the ionic potential, ϕ, since from (1)

$$\phi = \frac{Z}{r} \propto \frac{W_h}{Z} \tag{2}$$

For the ions of the alkalies the linear relation is found to hold, although the equation is of the form

$$\frac{W_h}{Z} = a\phi + b \tag{3}$$

and the constant a does not correspond to that given by Born's equation when the crystal radii of Pauling are used for the calculation.[5] The ionic potential may be used in general, therefore, only to indicate the *order of variation* of the heats of hydration. For the alkali ions the equation $W_h = 60\phi + 30$ (kg. cal. per equivalent) represents the values of Fajans quite closely.

Since the heat of hydration of the ions of a salt is equal to the lattice energy plus the heat of solution and since, for salts with a common anion, the electrostatic energy of the cation varies inversely as the cation radius r_c, while the lattice energy varies inversely as the interionic distance $r_c + r_a$, the electrostatic energy increases more rapidly than the lattice energy as the radius is decreased. As a consequence, in a series of salts such as the alkali or alkaline earth chlorides, the heat of solution (evolution) of the anhydrous salt in sufficiently dilute solution should vary in the same order as the varying ionic potential. Table I includes data from the Landolt-Börnstein "Tabellen" which show that this conclusion is in accordance with the facts. The only exceptions to the rule are in cases in which the ions are very unlike in size, mutual repulsion of the larger ions

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[4] Born, *Ber. physik. Ges.*, **21**, 679 (1919).

[5] Pauling, THIS JOURNAL, **49**, 765 (1927).

then becoming a complication. With lithium fluoride the lattice energy is large and decreases very rapidly as either ion is changed in the alkali or halogen series. The decrease in the lattice energy more than compensates the decrease in the heat of hydration of the varying ions, and an increase in the heat of solution is observed (LiF to LiI or LiF to CsF). In the alkaline earth group this effect is more marked as the anion is varied. The solid arrows in Table I show the order of increasing potential and heat of solution in accordance with the rule. The broken arrows indicate increasing heat evolution with decreasing potential. The data give the heat evolution (lower figure) attending the addition of 1 mole of the anhydrous salt to the number of moles of water given by the upper figure.[6]

TABLE I

HEAT OF SOLUTION (KG. CAL. PER MOLE)

	Li	Na	K	Rb	Cs	Be	Mg	Ca	Sr	Ba
	—	400	—	—	—			—	—	—
F					→			←		→
	−1.04	−0.6	+3.6	5.8	8.37			2.70	−2.10	−1.90
	↓	↑	↖ ↑	↑	↑			↓	↓	↓
	230	100	200	100	—	—	800	300	400	400
Cl	←					←				
	8.37	−1.2	−4.4	−4.4	−4.75	44.5	35.92	17.41	11.14	2.07
	↓	↓	↑	↖ ↑	↑		↓	↓	↓	↓
	—	200	200	—	—		—	400	400	400
Br	←						←			
	11.25	−0.19	−5.08	−5.96	−6.73		43.3	24.51	16.11	4.98
	↓	↓	↑	↑	↖ ↑		↓	↓	↓	↓
	—	200	200	—	—		—	—	—	—
I	←						←			
	14.76	1.22	−5.11	−6.5	−8.25		49.8	28.12	20.12	10.3

	Ca^{++}	Cr^{++}	Mn^{++}	Fe^{++}	Co^{++}	Ni^{++}	Cu^{++}	Zn^{++}
	300	—	350	350	400	400	600	300
Cl		→ ←				→		
	17.41	18.6	16.01	17.85	18.34	19.17	11.08	15.63

The development of acidic properties is obviously closely associated with an increase in the ionic potential. If the potential is sufficiently high, not only is the hydration greatly increased but the increase in the intramolecular energy of the bound water molecules may exceed the heat of ionization of water into hydrogen and hydroxyl ions. In such a case the change may be expressed,

$$M^{m+} + nH_2O \longrightarrow M(H_2O)_n^{m+} \longrightarrow M(H_2O)_{n-1}(OH)^{(m-1)+} + H^+$$

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[6] The effect of the *relative* size of the ions in a crystal in producing "abnormal" variations in properties in a series of compounds has been quantitatively treated for certain cases since the completion of the present paper. See Pauling, THIS JOURNAL, 50, 1036 (1928).

This corresponds to the hydrolysis of chlorides of non-metals, such as PCl_5, or to the acid character of hydrated ions, such as the cation of hexa-aquochromic chloride, $Cr(H_2O)_6^{3+}$, the ionization of which according to the scheme

$$Cr(H_2O)_6^{3+} \rightleftarrows Cr(H_2O)_5OH^{++} + H^+$$

has been recently studied by Brönsted and King.[7]

As a matter of fact, according to Fig. 1 of the preceding paper, *the exclusively basic ions have values of $\sqrt{\phi}$ falling below 2.2; between 2.2 and 3.2 the ions are amphoteric, and above 3.2 all ions are acidic in character.*[8] The similarity of Be^{++}, Al^{3+} and Ti^{4+} from this point of view is strikingly suggested, corresponding to the well-known diagonal relationship of the Mendelejeff system. The relative positions of B^{3+}, Si^{4+} and P^{5+} are also apt.[9]

Another aspect of the view of hydration effects here presented is in connection with the existence of oxy-ions, such as UO_2^{++}. Compounds derived from ions of this type are stable in acid solution only if the potential of the simple cation U^{6+}, for example, exceeds the minimum value requisite for the ionization of a bound water molecule. If the potential is sufficiently high, complete hydrolysis to an acid occurs. The occurrence of ions which form such stable oxy-salts is, therefore, limited to the amphoteric region of potentials.

Ionic Potentials and Electrochemical Behavior

While the ionic potentials are obviously most closely related to the ionizing potentials of the atoms in the gaseous state, there is a qualitative connection also with the electrode potentials in electrolysis. In the alkali element family lithium has the highest ionization potential, corresponding to the order of increase in the ionic potentials. In aqueous solutions, however, lithium has also the highest electrode potential, which may be due to the existence of a smaller concentration of unhydrated ions, since the

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[7] Brönsted and King, *Z. physik. Chem.*, **130**, 699 (1927).

[8] An apparent exception is zinc, which is in the basic region of potentials. As a matter of fact, zinc is not certainly amphoteric [Hantzsch, *Z. anorg. Chem.*, **30**, 289 (1902); Britton, *J. Chem. Soc.*, **127**, 2120 (1925)], and seems to be more basic than magnesium in the extent of hydrolysis of its chloride in solution and in the readiness with which the chloride may be dehydrated by heating. Zinc and mercuric salts are, however, anomalous in other respects also (see p. 2869).

[9] The theoretical potentials of the ions of series II (B^{3+} – N^{5+}) are somewhat higher than corresponds to their observed acidic character. This is no doubt due to the fact that these ions are very small and in their hydroxyl compounds the oxygen ions are very close together. Mutual repulsion of these hydroxide ions would be equivalent to a decrease in the potential of the positive central ion and a weakening of the acidic character would result. To this cause may be ascribed the low coördination number of these ions (4) and the corresponding instability of higher hydrates (H_3NO_4 $C(OH)_4$, $R_2C(OH)_2$ compounds, etc.).

extent of the ionic hydration is, in general, greater the stronger the field of force about the ion. In comparing elements of the alkali and alkaline earth families, the ionic potential increases with the valence, corresponding to a decrease in the electrode potentials. The increase in the heat of hydration is not sufficient in these cases to counteract the increase in the ionization potential.

Even more striking results are obtained by considering the discharge potentials of the cations from fused electrolytes. Data for a number of ions are given by Neumann and Richter.[10] The discharge potential should be greater the lower the ionic potential. That this is true is strikingly shown in Fig. 1, in which univalent, bivalent and tervalent ions are included. It is obvious that lithium has a normal discharge potential in fused salts.

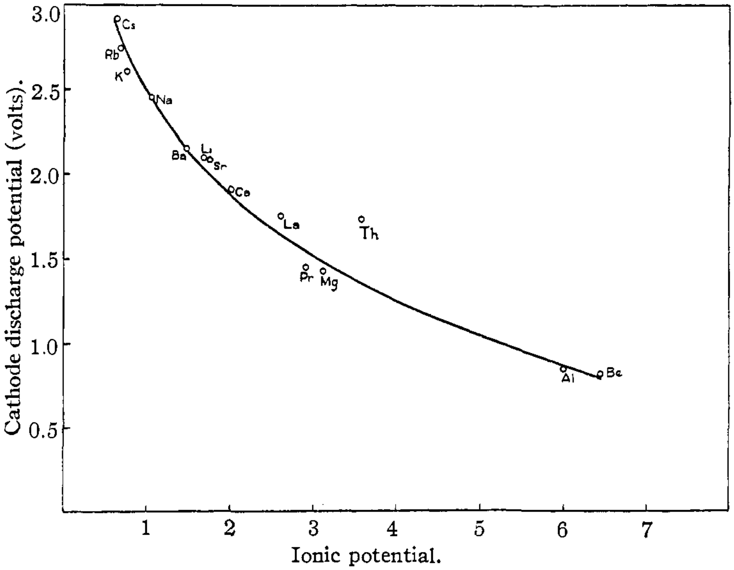

Fig. 1.—Ionic potentials and cathode potentials in the fused chlorides.

The roughly estimated ionic potential of the H^+ ion is in satisfactory agreement with the electrode potential of hydrogen. Considering only cations with inert gas structures, it will be seen from Fig. 1 of the preceding paper that all ions having lower ionic potentials than H^+ may be formed by displacement of hydrogen from acids or superheated steam. This is not the case with those having potentials greater than that of H^+, and in the case of equipotes of H^+, solution of the metal generally takes place sluggishly and oftentimes only with hydrofluoric acid, which forms a complex fluo-ion giving very low concentrations of the simple cation, as in the case of vanadium, columbium and tantalum.

[10] Neumann and Richter, *Z. Elektrochem.*, **31**, 287, 296 (1925).

Biltz and Klemm[11] have shown that there is a sharp decrease in the electrical conductance of the fused chlorides in passing from left to right in the several periodic series, and have pointed out that where the conductance becomes very low there is also an abrupt decrease in the melting point. This break in properties has been ascribed to a progressive deformation of the anion with increasing charge or decreasing radius of the cation,[12] as revealed by the decrease in the molal refraction of the anions in such a series as CaO–MgO–BeO. The deformation is regarded as finally reaching such a value that there is a transition from a polar, ionic lattice to a non-polar, molecular lattice.[13]

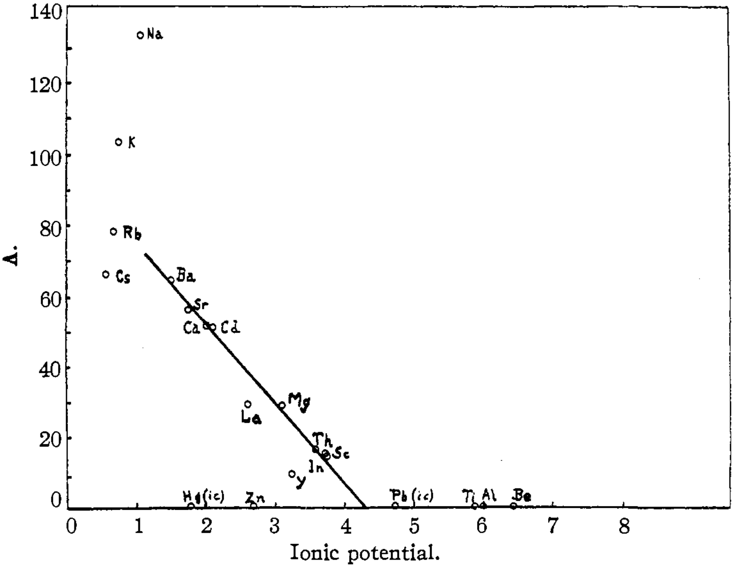

Fig. 2.—Ionic potential in relation to the equivalent conductance of fused chlorides at the melting point.

The deformation of the anion is closely related to the ionic potential of the cation, and it is found that *the zigzag line of Biltz and Klemm dividing the high melting, conducting chlorides from the volatile, non-conducting chlorides corresponds to an equipotential line* drawn at $\sqrt{\phi} = 2.2$. At lower ionic potentials the melting point of the chloride is high (generally > 600°); the equivalent conductance of the fused chloride increases rapidly as the cation potential becomes less than 4.2, according to the relation $\Lambda = 98 - 23\phi$ in the case of the chlorides of Mg^{++}, Ca^{++}, Sr^{++}, Ba^{++}, Cd^{++}, Th^{4+}, Sc^{3+} and In^{3+}; La^{3+} and Y^{3+} have a distinctly lower conductance

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[11] Biltz and Klemm, *Z. physik. Chem.*, **110**, 318 (1924); *Z. anorg. allgem. Chem.*, **152**, 225, 267 (1926); Klemm, *ibid.*, **152**, 235, 252, 295 (1926).

[12] Fajans and Joos, *Z. Physik*, **23**, 1 (1924).

[13] Fajans, *Naturwissenschaften*, **11**, 165 (1923).

than this relation would indicate and the conductances of the alkali chlorides increase in the reverse order (Fig. 2). As suggested by Biltz, in the case of the alkali chlorides the variation is no doubt to be ascribed to the variation in ionic mobility rather than to any incompleteness of ionization as a result of the electrostatic effects, whereas in the other cases the ionic field of force is the important factor. The low conductance and melting point of mercuric and zinc chlorides are striking exceptions to the general rule.

Considering only the quadrivalent ions, the melting points of the chlorides of both *A* and *B* families increase in the same order as the ionic potential decreases, excepting carbon and zirconium

Element	Si^{4+}	Ge^{4+}	Ti^{4+}	Sn^{4+}	Zr^{4+}	Pb^{4+}	Th^{4+}
M. p., °C.	−70	−49.5	−30	−30.2	..	−15	820
$\sqrt{\phi}$	3.13	2.74	2.43	2.36	2.24	2.18	1.90

The volatility and non-conductance of liquid hydrogen chloride are in accordance with the estimated potential of H^+, and the sharp contrast between the high melting, conducting thorium chloride and the chlorides of other quadrivalent ions is particularly striking.

Cation Potentials and the Deformation of Anions

The varying deformation of anions such as CO_3^{--} and NO_3^- is associated with numerous properties of compounds containing such ions. In a crystalline carbonate the C–O valences are presumably non-polar, the carbonate ion as a whole acting as one of the crystal units in a polar lattice. The firmness of the binding *within* the carbonate ion is less the stronger the electrostatic action of the cation. This effect has been called a *contrapolarization* by Goldschmidt;[14] for a series of salts with a common anion the effect obviously increases with increasing cation potential.

In respect to crystallo-chemical relationships, Goldschmidt has shown that an increase in temperature quite generally acts in the same direction as the substitution of a smaller cation of the same valence, that is, in the same direction as an increase in the cation potential. Thus, in the rare earth oxides the cubic modification is the high temperature form of the cerite earths, while in the yttrium earths (higher potential) it is the low temperature form.

In similar manner, the deformation of the anion may increase to the point of complete dissociation of the compound. It is found, for example, that the ionic potentials indicate the order of increasing dissociability of the carbonates and nitrates. Cations with $\sqrt{\phi} > 2$ do not form stable normal carbonates or nitrates; in cases in which $2 < \sqrt{\phi} < 2.5$, basic carbonates may be precipitated in solution which are generally soluble

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[14] Goldschmidt, *Skrifter Norske Videnskaps-akad., Oslo., I, Matemat.-Natur.-Klasse,* **1926**, No. 2.

in excess of ammonium or alkali carbonate. The greater stability of nitrates as compared with carbonates at not too high temperatures may be associated with the higher potential of N^{5+} as compared with C^{4+}, the result being a greater deformability of the carbonate ion.[15] The instability of bicarbonates in the solid state may in like manner be related to the high value of $\sqrt{\phi_{H^+}}$, only the low potential alkali ions forming stable bicarbonates.

Other properties which have been associated with the deformation of ions may in like manner be related to ionic potentials, such as color[15] and the photoelectric conductance of salts.[16]

Ionic Potentials and the Hardness of Compounds

Goldschmidt[14] has pointed out that the hardness of inorganic compounds of similar composition increases as the inter-ionic distance decreases. In Table II Goldschmidt's data on the hardness of previously fused or sintered compounds are given on Moh's scale, together with the corresponding ionic potential.

Table II

Hardness and Ionic Potentials

$\sqrt{\phi}$	$\sqrt{\phi}$ Ion	2.54 Be^{++}	1.76 Mg^{++}	1.64 Zn^{++}	1.44 Cd^{++}	1.42 Ca^{++}	1.35 Hg^{++}	1.33 Sr^{++}	1.21 Ba^{++}
1.19	O^{--}	9	6.5	5	...	4.5	...	3.5	3.3
1.04	S^{--}	7.5	4.5–5	4	3.2	4.0	3	*ca.* 3.3	*ca.* 3
1.00	Se^{--}	5.5	3.5	3–4	3.0	3.2	2.8	*ca.* 2.9	*ca.* 2.7
0.95	Te^{--}	3.8	..	3.0	2.8	2.9	2.6	*ca.* 2.8	*ca.* 2.6

	NaF	MgO	ScN	TiC
Hardness	3.2	6.5	7–8	8–9
$\sqrt{\phi}$ (cation)	1.02	1.76	1.92	2.43
$\sqrt{\phi}$ (anion)	0.86	1.19	1.32	1.24

It is clear that in a general way there is a parallel increase in hardness and potential.

In a recent paper[17] Noyes and Beckman have presented the results of a study of the ionization potentials for the different valence states of the elements as far as atomic number 26; these authors reach the conclusion that there is no definite relation between the ionization potential for the formation of a particular ion and the tendency of the element to assume that ionic form. While the work described in the present paper was in progress the ionization potential was considered as a possible basis of classification, but was rejected both because of the limitations in the data that are available and because it was realized that the ionic potential as

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[15] Fajans and Scott, *Naturwissenschaften*, **11**, 165 (1923), give the anion refraction per oxygen octet as 3.66 for NO_3^- and 4.08 for $^1/_2$ CO_3^{--}.

[16] Gudden and Pohl, *Z. Physik*, **16**, 42 (1923).

[17] Noyes and Beckman, *Proc. Nat. Acad. Sci.*, **13**, 737 (1927).

here defined is a closer index to the behavior of an ion in compounds than is the ionization potential.

The thermochemistry of chemical combination is, in general, too complex to be simply related to the periodic system.[18] In analyzing the heat of formation of polar compounds having a common anion, the ionization potential of the cation and the lattice energy of the compound have opposite signs. They vary in magnitude in the same direction when the cation radius is varied, both quantities increasing as the ionic potential increases. In general, however, the ionization potential increases more rapidly than the ionic potential, while the lattice energy increases less rapidly, being inversely proportional to $r_c + r_a$. In so far as the heat of formation of a compound is determined chiefly by the difference between these two quantities, it will be expected that in a series of compounds with one ion in common the heat of formation (*per equivalent*) will decrease with increasing potential of the varying constituent. This is true in many instances, as seen in the following data for the oxides (kg. cal. per equivalent)

$^1/_2$ MgO	$^1/_6$ Al_2O_3	$^1/_4$ SiO_2	$^1/_{10}$ P_2O_5	$^1/_6$ SO_3
72	63.4	48.7	37.0	17.2

This relationship is not uniform throughout the periodic system, however, but it will be shown in a subsequent paper that the ionic potential may be used to indicate the order of variation in thermochemical effects in the entire periodic classification.

It is proposed in subsequent publications to develop still other relationships between ionic potentials and the properties of matter.

Summary

The following generalizations may be given as a summary of the results of this paper.

1. The heat of hydration of gaseous ions increases with the ionic potential.

2. The heat of solution (evolution) of salts having a common anion increases with the ionic potential of the cation, except in the case of fluorides, with which the order is reversed.

3. Cations having $\sqrt{\phi} < 2.2$ are basic, those between 2.2 and 3.2 are amphoteric and those above 3.2 are acidic in aqueous media.

4. The discharge potentials of cations in fused electrolytes decrease regularly with increasing ionic potentials.

5. Cations having $\sqrt{\phi} > 2.2$ form volatile chlorides which are nonconductors in the liquid state. The conductance increases rapidly as $\sqrt{\phi}$ falls below 2.2, except in the case of the alkali ions, which vary in the reverse order.

6. High temperature and increase in the ionic potential of the cation

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[18] Compare Grimm, "Handbuch der Physik," Springer, Berlin, Vol. 24, pp. 568 ff.

have similar effects in the polymorphic and stability relations of compounds with a common anion.

7. Binary crystals increase in hardness as the ionic potentials of their constituents increase.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

THE CATALYTIC ACTIVITY OF METALLIZED SILICA GELS. V. THE OXIDATION OF ETHYLENE[1]

BY L. H. REYERSON AND L. E. SWEARINGEN

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Previous investigations of the authors[2] have shown that metallized silica gels exhibit considerable activity in certain oxidation reactions. The following investigation is an extension of this work to the oxidation of ethylene. Willstätter and Bommer[3] in their quantitative study of the conditions for the formation of formaldehyde from ethylene showed that, unless dilute, both ethylene and formaldehyde are unstable at temperatures much above 300°. They found that the use of catalysts accelerated the oxidation of ethylene but no formaldehyde was detected when catalysts were used. An osmium catalyst was found to initiate the oxidation of ethylene at about 130°, while copper proved to be effective at 250°. Blair and Wheeler[4] continued these investigations and found that, with a platinum catalyst, formaldehyde was formed at 405° when the gases were streamed through the catalyst very rapidly. As a result of these investigations, it was hoped that the use of metallized silica gels as catalysts would so lower the temperature at which reaction occurred that partial oxidation of ethylene could be effected and a mechanism for its catalytic oxidation obtained.

The experimental procedure was similar to that used by the authors in the study of the oxidation of methane.[5] Samples of the same catalysts were used as in the preceding investigations. Mixtures of ethylene, oxygen and nitrogen were passed over the catalysts at temperatures ranging from about 100 to 310° at varying rates of flow. In no case did the sum of oxygen and ethylene in the mixture exceed 50% of the gas volume. Preliminary experiments showed that the products of oxidation were carbon dioxide and water, so that the gases after passing through the catalyst were analyzed for ethylene, oxygen and carbon dioxide. In no case did tests show the presence of intermediate products of oxidation.

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[1] In memory of Ira Remsen.

[2] Swearingen and Reyerson, *J. Phys. Chem.*, **32**, 113, 192 (1928).

[3] Willstätter and Bommer, *Ann.*, **422**, 36 (1921).

[4] Blair and Wheeler, *J. Soc. Chem. Ind.*, **41**, 303T (1922).

[5] Ref. 2, p. 192.