116. *The Persulphate–Iodide Reaction. Part II. The Critical Increment, and the Catalysed Reaction in the Presence of Neutral Salts.*

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The reaction has been studied in the presence of different cations. The critical increment appears to be unaffected by interchange of cations; the velocity change observed is probably due to change in collision number. Increase in ionic strength is accompanied by an appreciable increase in the critical increment. The observed velocity has been compared with that calculated from the collision equation, and the probability factor is of the order 10^{-4}. The reaction catalysed by iron and copper ions has been examined from the standpoint of Brönsted's theory, and qualitative agreement with this theory is evident.

The materials used and the experimental procedure have been described in Part I (Howells, J., 1939, 463). Determinations of velocity constants were made in slightly acid solutions (0·005N-sulphuric acid) since such solutions appear to give more consistent results than neutral solutions. The reaction may be regarded as $S_2O_8'' + I' = S_2O_8I'''$, followed by the rapid reaction $S_2O_8I''' + I' = 2SO_4'' + I_2$.

The constants were calculated from the bimolecular equation $k = x/at(a - x)$, a being the initial concentrations of persulphate and iodide in g.-equivs./l., and x the number of g.-equivs./l. of iodine liberated in t minutes. The reaction is affected by light (see von Kiss, *Rec. Trav. chim.*, 1927, **46**, 230). In these experiments, and also in those described in Part I, the interior of the thermostat was only weakly illuminated—in almost all cases by artificial light.

The Critical Increment.—Velocity constants for the reaction were determined at two temperatures in the presence, separately, of potassium, ammonium, and sodium ions.

The results are recorded in Table I. The critical increment, with which is associated the energy of activation of the reaction, has been calculated from the relation

$$E = 2{\cdot}303\boldsymbol{R}T_1T_2 \log (k_{25^\circ}/k_{20^\circ})/(T_2 - T_1).$$

TABLE I.

$0{\cdot}0333\text{N-}R_2S_2O_8 + 0{\cdot}0333\text{N-}RI + 0{\cdot}005\text{N-}H_2SO_4$.

R.	$k_{25^\circ} \times 10^3$.	$k_{20^\circ} \times 10^3$.	E, cals.
K	188	131	12,520
NH_4	167	117	12,330
Na	139	97	12,470

Experimental errors may well account for the variation in the value of E. The critical increment is the same, or nearly so, for the reaction in the presence of the cations considered and at the concentrations involved. According to the collision theory, $k = pZe^{-E/\boldsymbol{R}T}$. The differences in the k values in Table I are probably due to different collision numbers.

The Collision Equation.—Potassium persulphate and iodide being used, determinations of the reaction velocity were made at four temperatures. The results are recorded in Table II (a). The temperature coefficient $k_{25^\circ}/k_{15^\circ} = 2{\cdot}14$; this is well below the average value, approximately 2·5, for so-called normal reactions. The plot of log k against $1/T$ approximates to a straight line, thus conforming to the Arrhenius equation.

TABLE II.

(a) $0{\cdot}0333\text{N-}K_2S_2O_8 + 0{\cdot}0333\text{N-}KI + 0{\cdot}005\text{N-}H_2SO_4$.

Temp.	28°	25°	20°	15°
k	0·233	0·188	0·131	0·088

(b) $0{\cdot}0333\text{N-}K_2S_2O_8 + 0{\cdot}0333\text{N-}KI + 0{\cdot}005\text{N-}H_2SO_4 + 0{\cdot}5622\text{N-}NaCl$.

Temp.	28°	25°	15°
k	0·564	0·442	0·199

(c) $0{\cdot}0166\text{N-}K_2S_2O_8 + 0{\cdot}0166\text{N-}KI + 0{\cdot}005\text{N-}H_2SO_4 + 0{\cdot}5622\text{N-}NaCl$.

Temp.	25°	15°
k	0·409	0·183

The average of the six possible E values, calculated from the k values given in Table II (a), is 12,840 cals. From Lewis's collision equation (J., 1918, **113**, 471) for a reaction between two unlike molecules, the equation

$$k = \frac{N_0}{1000}\sigma_{12}^2 \left\{8\pi \boldsymbol{R}T\left(\frac{1}{M_1} + \frac{1}{M_2}\right)\right\}^{\frac{1}{2}} e^{-E/\boldsymbol{R}T}$$

in l. g.-mol.$^{-1}$ sec.$^{-1}$ has been derived (see Moelwyn-Hughes, " Kinetics of Reactions in Solution," 1933). The author is indebted to Dr. Moelwyn-Hughes for advice on the proper use of this equation. Originally intended for gaseous reactions, it has been successfully applied to various reactions in solution. The reactions under consideration are those given on p. 641. The sum of the radii of the persulphate and the iodide ions has been taken as $\sigma_{12} = 5 \times 10^{-8}$ cm., a sufficiently accurate approximation. With $E = 12{,}840$ cals., k at 25° is calculated to be $5{\cdot}079 \times 10$ l. g.-mol.$^{-1}$ sec.$^{-1}$. The experimental value, at the concentrations given in Table II (a), is $k_{25^\circ} = 0{\cdot}188$ where concentrations are expressed in g.-equivs./l. and time in mins., or $k_{25^\circ} = 3{\cdot}14 \times 10^{-3}$ when time is expressed in secs. At zero ionic strength the extrapolated experimental value is about one-third of this (see Part I).

The use of the unit g.-equiv. instead of g.-mol. does not alter the order of the k value. Hence, the probability factor p is of the order 10^{-4}. This large deviation from unity may be attributed to several causes. A high percentage of collisions occur between reacting ions and water molecules, and, since the latter greatly exceed the former in number, the frequency of such collisions will be high. Also, the reaction is not a normal bimolecular one; a fugitive complex is formed, and it is possible that its formation involves an appreciable absorption of energy, which would otherwise be available for activation. There are, too, reasons, resulting from the phenomenon of solvation, for expecting low p values for reactions between ions of like sign (see Bell, *Ann. Reports*, 1939).

Critical Increments at Different Ionic Strengths.—Tables II (*b*) and II (*c*) record the results of determinations made at different temperatures in solutions of higher ionic strength than that indicated in Table II (*a*). The reaction rate in each determination at high concentration decreases as the reaction proceeds—this is partly due to loss of iodine during removal of solution by means of a pipette, and may also be due to a slight side reaction (see Jette and King, *J. Amer. Chem. Soc.*, 1929, **51**, 1034). Therefore, the extrapolated initial rates are given in Tables II (*b*)—(V).

The k values in Table II (*b*) give an average value of $E = 13{,}950$ cals.; those in Table II (*c*) give $E = 13{,}710$ cals. Comparing these values with $E = 12{,}840$ cals.—found for the reaction in the absence of sodium chloride [Table II (*a*)]—we find some evidence that the critical increment increases with ionic strength. Moelwyn-Hughes (*op. cit.*) has derived a quantitative expression for this increase.

TABLE III.

$0{\cdot}01666\text{N-}K_2S_2O_8 + 0{\cdot}01666\text{N-}KI + 0{\cdot}005\text{N-}H_2SO_4 + RCl.$

NaCl, N	0	0·0333	0·3000	0·5622	1·000	1·250	2·000	2·500	3·000
k	0·143	0·163	0·287	0·409	0·594	0·691	1·135	1·510	1·906
				($F = 6{\cdot}82$)			($F = 18{\cdot}91$)		
KCl, N	0	0·0333	0·1610	0·5622	1·208	1·500	2·000		
k	0·143	0·191	0·344	0·694	1·285	1·547	2·071		
				($F = 11{\cdot}57$)			($F = 34{\cdot}5$)		
NH_4Cl, N	0	0·0333	0·5622						
k	0·143	0·182	0·579						
HCl, N	0	0·0333	0·3000	0·5622					
k	0·143	0·158	0·252	0·337					
LiCl, N	0	0·0333	0·3000						
k	0·143	0·162	0·262						

Determinations at High Ionic Concentrations.—Determinations at concentrations comparable with those indicated in Table III have been made by von Kiss (*Z. physikal. Chem.*, 1928, **134**, 26). They have been re-determined for the sake of uniformity and for comparison with results (Table V) for the catalysed reaction. The log k–$\sqrt{I}$ curve for the reaction in sodium chloride solutions is nearly straight; in potassium chloride solutions the convex nature of the curve is more pronounced. The values of F, the kinetic activity factor, have been calculated on the basis $k_0 = 0{\cdot}06$ (see Part I). It was shown in Part I that F values decrease in the series from cæsium to lithium. Table III shows that in concentrated solutions the kinetic activity factor in potassium chloride is nearly double that in sodium chloride solutions.

A table of molal volumes of chlorides and iodides of alkali metals, and of the radii of the cations, is given by Scott (*J. Physical Chem.*, 1931, **35**, 3379) :

	Li.	Na.	K.	Rb.	Cs.
$r \times 10^8$, cm.	0·60	0·95	1·33	1·48	1·69

The primary salt effect is, therefore, for the series of cations involved, greatest in the presence of the cation of largest radius. An explanation for this has been suggested in Part I (*loc. cit.*). The F values in the presence of potassium and sodium ions are roughly inversely proportional to the square of the radii. It is of some interest to compare these primary salt effects with corresponding secondary salt effects in a different reaction. Dawson and Key (J., 1928, 1239) determined the rate of the acetone–iodine reaction, catalysed by acetic acid, in the presence of chlorides of potassium, sodium, and lithium. The velocity–concentration curves exhibit maxima, and the velocity is highest in the presence of lithium ions and lowest in that of potassium ions. In this case the salt effect is mainly a secondary one. Here the smaller lithium ions exert a stronger attractive force than do the larger potassium ions on the acetic acid anions. Thus the lithium ions are more effective in liberating catalytic hydrogen ions.

TABLE IV.

$0{\cdot}01666\text{N-}K_2S_2O_8 + 0{\cdot}01666\text{N-KI} + 0{\cdot}005\text{N-}H_2SO_4$ + Neutral salt.

Concn., N.	Salt.	Cl.	NO_3.	SO_4.	Concn., N.	Salt.	Cl.	NO_3.	SO_4.
0·0333	K	0·191	0·188	0·180	0·5622	K	0·694	0·634	—
0·0333	NH_4	0·182	0·178	—	0·5622	Na	0·409	0·387	—
0·0333	Na	0·163	0·163	0·160					

Specific Ion Effects.—The velocity constants concerned are given in Table IV, and show that interchange of anions causes a much smaller change of velocity than interchange of cations—as we would expect, for anions have much less influence than cations on the reacting persulphate and iodide ions.

In another experiment, 0·01666N-potassium persulphate, 0·01666N-potassium iodide, and 0·005N-sulphuric acid underwent reaction in presence of 0·4N-solutions of (*a*) sodium chloride and potassium sulphate, (*b*) potassium chloride and sodium sulphate; the values of *k* were nearly identical, *viz.*, 0·661 and 0·656 respectively. The two solutions behave as if they were identical, the salts probably being completely ionised.

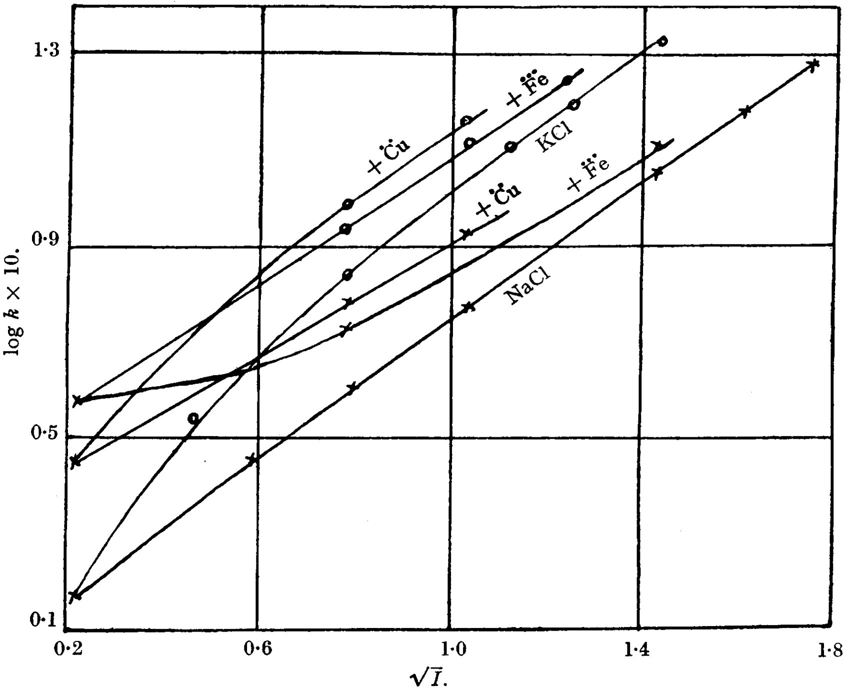

TABLE V.

$0{\cdot}01666\text{N-}K_2S_2O_8 + 0{\cdot}0166\text{N-KI} + 0{\cdot}005\text{N-HCl} + 0{\cdot}00005\text{M-}FeCl_3$ + chloride.

KCl, N.	*k*.	KCl, N.	*k*.	NaCl, N.	*k*.	NaCl, N.	*k*.
0	0·386	1·000	1·280	0	0·386	2·000	1·348
0·5622	0·842	1·500	1·831	0·5622	0·536		

$0{\cdot}0166\text{N-}K_2S_2O_8 + 0{\cdot}0166\text{N-KI} + 0{\cdot}005\text{N-}H_2SO_4 + 0{\cdot}00005\text{M-}CuSO_4$ + chloride.

KCl, N.	*k*.	KCl, N.	*k*.	NaCl, N.	*k*.	NaCl, N.	*k*.
0	0·280	1·000	1·447	0	0·280	1·000	0·848
0·5622	0·986			0·5622	0·599		

The Catalysed Reaction.—Determinations of the rate of the persulphate–iodide reaction, catalysed separately by iron and copper ions, were made in the presence of potassium chloride and sodium chloride. The concentration of the ferric chloride and copper sulphate used was in each case M/20,000. The results are given in Table V.

That the rate of the reaction is much increased by these ions was shown by Price

(*Z. physikal. Chem.*, 1898, **27**, 474). According to von Kiss and von Zombory (*Rec. Trav. chim.*, 1927, **46**, 225), the ferric ions react thus: (i) $2Fe^{\cdot\cdot\cdot} + 2I' = 2Fe^{\cdot\cdot} + I_2$, (ii) $2Fe^{\cdot\cdot} + S_2O_8'' = 2SO_4'' + 2Fe^{\cdot\cdot\cdot}$. Reaction (i) is almost instantaneous, reaction (ii) being measurable. These reactions are simultaneous with, and superimposed upon, the main persulphate–iodide reaction.

On Brönsted's theory, (ii) may be written $Fe^{\cdot\cdot} + S_2O_8'' = Fe,S_2O_8$, followed by the rapid reaction $Fe,S_2O_8 + Fe^{\cdot\cdot} = 2Fe^{\cdot\cdot\cdot} + 2SO_4''$, whence, for (ii), $k = k_0 f_{Fe^{\cdot\cdot}} f_{S_2O_8''} / f_{Fe,S_2O_8}$. The salt effect in this reaction should, therefore, be negative. By using the expression $-\ln f = \alpha Z^2 \sqrt{I}$ for the activity of an ion—where I is the ionic strength—it may be shown that, for reaction (ii), $\ln k = \ln k_0 - 8 \propto \sqrt{I}$.

Assuming, in the reaction catalysed by copper ions, that the rapid reaction $2Cu^{\cdot\cdot} + 2I' = 2Cu^{\cdot} + I_2$ is followed by the measurable reaction $2Cu^{\cdot} + S_2O_8'' = 2SO_4'' + 2Cu^{\cdot\cdot}$, we may write $k = k_0 f_{Cu^{\cdot}} f_{S_2O_8''} / f_{Cu,S_2O_8'}$. Here, too, the salt effect will be negative, and $\ln k = \ln k_0 - 4 \propto \sqrt{I}$.

These two ln k expressions indicate that the negative salt effect should be greater in the presence of ferric than of cupric ions. That this is so is shown in the accompanying figure by the way in which the log k–$\sqrt{I}$ curves for the catalysed reaction converge upon those for the uncatalysed reaction.

In the experiments concerned, the concentration of ferric and of cupric ions is the same. The results show that in the absence of neutral salts the catalytic effect of the former is greater than that of the latter ions, but that the reverse is true in the presence of high concentrations of neutral salts.

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