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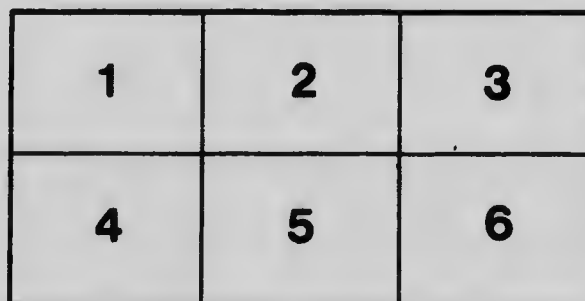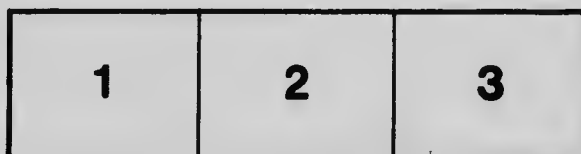The copy filmed here has been reproduced thanks to the generosity of:

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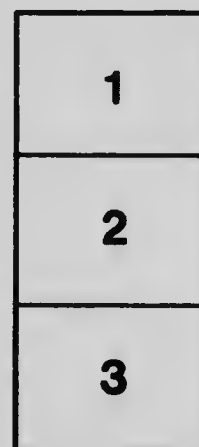
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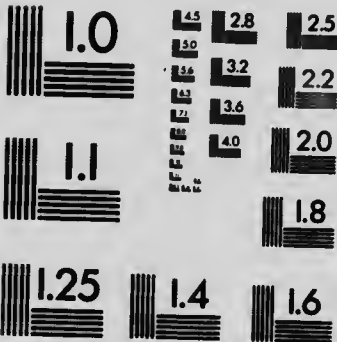
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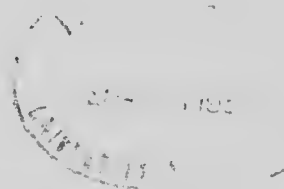
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THE INDUCTION BY FERROUS SALTS OF THE REACTION BETWEEN CHROMIC AND HYDRIODIC ACIDS

BY ROSS A. GORTNER

THE INDUCTION BY FERROUS SALTS OF THE RE ACTION BETWEEN CHROMIC AND HYDRI- ODIC ACIDS.

BY ROSS A. GORTNER

The reaction between chromic acid, ferrous salts and hydriodic acid, studied here some years ago by Miss C. C. Benson,[1] presents many points of interest which invite further investigation: the great influence of the acid concentration on the rate, the retarding action of ferric salts, and the observation that less iodine is liberated per second at 30° C than at 0° C, are all most unusual. Mr. Green's work on catalysis by ferric salts, recently published,[2] which shows that nothing similar to the retardation observed by Miss Benson is to be met with in the behavior of reactions otherwise closely analogous, adds interest to this exceptional case.

My own measurements, described in the present paper, show that the lessened retardation observed when "aged" portions of the oxidation product were added to the reaction mixture is quantitatively ascribable to the hydrolysis of the ferric salts, and that colloids and colloidal ferric hydrate in particular have but little effect on the rate. Sulphuric acid may be replaced by hydrochloric acid without changing the general nature of the results, but the addition of fluorides, chlorides or bromides retards the liberation of iodine and accelerates the oxidation of the ferrous salt. This observation may be accounted for very naturally by an explanation in keeping with Miss Benson's Ferroiodion theory; it may therefore be regarded as furnishing independent evidence in support of the latter. Miss Benson's observation that the rate of liberation of iodine at 30° C is less than at 0° C, is confirmed and supplemented by experiments which show that the rate of oxidation of the iron is greater at the higher temperature.

[1] Jour. Phys. Chem., 7 .903); 7, 356 (1903); 8, 116 (1904).
[2] Ibid., 12, 389 (1908).

Method of working and of recording the results

In the composition of the solutions, in the methods of manipulation, and in the temperatures worked at, I closely followed the details described by Miss Benson;[1] and after a little practice found that on repeating her experiments I obtained identical results. In tabulating the measurements, also, the symbols and arrangement described on page 359 of the paper referred to have been adopted;[2] for convenience it may be repeated here that the numbers after the symbols Ac, Cr, KI, Fe, are very closely proportional to the number of equivalents of the various reagents present in the reaction solution—one formula-weight of bichromate being equivalent to seven of sulphuric acid and to six of ferrous sulphate or potassium iodide.

To facilitate reference, my tables and experiments are numbered consecutively with those of Miss Benson's last paper.

Effect of chlorides, bromides, and fluorides on the rates

When hydrochloric acid is substituted for sulphuric acid (Table XXXVI) *the rate of liberation of iodine is somewhat reduced,* but still remains proportional to a high power of the concentration of the acid. The retardation cannot be ascribed to the action of the ferric salt, for, as is shown on page 636, ferric chloride and ferric sulphate have the same effect on the rate; it is explained by the experiments of Table XXXVII, which show that addition of sodium chloride, potassium bromide, or potassium fluoride reduces the rate of liberation of iodine; potassium sulphate is without effect.

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[1] Ac 10 represents 10 cc of 0.059 F sulphuric acid (*i.e.*, acid containing 0.059 formula weights H_2SO_4 per litre); Cr 10, 10 cc of 0.0083 F potassium bichromate (including unreduced bichromate, if any, in the oxidation product); KI 10, 10 cc of 0.0479 F potassium iodide; Fe 1, 10 cc of 0.05 F ferrous sulphate; Ox 5, the product of oxidation of 5 cc of 0.05 F ferrous sulphate. The duration of the reaction in minutes is entered in the tables under Θ; the number of cc of N/100 sodium arsenite equivalent to the iodine liberated, under As; and the number of units of ferrous salt oxidized, under x, 10 cc 0.05 F ferrous salt being taken as the unit. As = 5y.

[2] Jour. Phys. Chem., **7**, 357 (1903).

The measurements of Table XXXVIII[1] show that *the rate of oxidation of iron is increased* by addition of fluoride. These observations may be explained very naturally by assuming that the halogen and the ferro-ion unite to form a complex FeF' (analogous to the ferroiodion FeI' of Miss Benson's hypothesis);[2] this substance on oxidation would yield ferric salt but no iodine, the induction factor should therefore fall off with increase in the concentration of the fluoride, as observed. To account for the increased rate of oxidation of the iron, it is only necessary to assume that the complex FeF' is more rapidly oxidized than Fe'' (or FeI').

The effect of colloids on the rate

The fact that under certain circumstances ferric hydrate can exist in the colloidal form, suggested experiments with other colloids. Agar-agar in one-tenth percent solution has no effect. Egg albumen, two-tenths percent solution, retards the oxidation, but this is probably due to its action as a weak base,[3] the retardation being proportional to the amount of albumen used. "Dialyzed iron" (colloidal ferric hydrate) retards a little, but nothing like as much as the same quantity of ferric sulphate or chloride—see Table XXXIX.

On the whole, therefore, the colloids experimented with have no retarding action to be compared with that of the ferric salts.

Diminished retardation by "aged" ox. prod.

When the product of oxidation of ferrous sulphate by chromic acid (ox prod) is allowed to stand, it gradually de-

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[1] The values of x in this and other tables of this paper are obtained by interpolation from the data of part B of the table, as explained in this Journal, **7**, pp. 3 and 364 (1903).

[2] Undissociated FeI_2, FeF_2, etc., or the corresponding acids might be assumed; the type of the reaction however is fixed by Miss Benson's measurements. See Jour. Phys. Chem., **11**, 9 (1907).   W. L. M.

[3] Ber. chem. Ges. Berlin, **28**, Ref. 858 (1895).

posits a yellow brown precipitate and its retarding power is lessened.[1] Similar changes in solutions of ferric chloride have been studied by Goodwin,[2] who showed by conductivity measurements that the "ageing" of the solutions was due to hydrolysis. In solutions of the strength of my "ox prod" this hydrolysis is accompanied by the formation of a precipitate, so that the concentration of the ferric salt is reduced, and that of the acid is increased—both changes tending to accelerate the liberation of iodine. The experiments of Tables XL and XLI show that the increased rate actually observed when "aged" ox prod is used can be completely accounted for if these changes in acidity and ferric concentration are taken into consideration.

In these experiments, three ferric solutions were used. The first was that employed in most of my work at $0°$ and is referred to in the tables under the title "Ox": it was prepared fresh by making up 200 cc acid, 600 cc bichromate and 20 cc ferrous sulphate (the undiluted solutions were used) to two liters; 50 cc contained the oxidation product of 5 cc decinormal ferrous sulphate, and in addition, 10 cc $F/120$ bichromate unreduced,[3] but no free acid. The second was prepared from the first by boiling for about half a minute, filtering hot and cooling; the third was obtained by allowing some of the first to stand 64 days at room temperature and filtering. The ferric salt in each of these three was determined volumetrically. by stannous chloride and bichromate; the bichromate was determined by titration with ferrous sulphate; and the acid by adding excess of volumetric potassium hydrate, and titrating back with sulphuric acid (without filtration) using methyl orange as indicator. The last determination gave both the free acid and that combined with the ferric salt; the latter was calculated from the ferric determination and subtracted. Fifty cc of each of the three preparations contained respectively:

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[1] Jour. Phys. Chem., **7,** 362 and Table 15 pp. 384.

[2] Zeit. phys. Chem., **21,** 1 (1896).

[3] Jour. Phys. Chem., **7,** 359 (1903).

	I	II	III
Ferric salt...........	5.0	1.0	2.87
Bichromate...........	10.0	10.0	10.0
Free acid............	0.0	5.0	2.6

in the units defined on page 633.

In Table XL the volume and the distinguishing number of the ferric solution used in each experiment is given under Ox, also the ferric salt and the free acid contained in it ("Ae from Hydrol"); under "acid added" is entered the amount of acid from the stock solution; the "total acid" is obtained by adding the last two.

Hydrolysis of the ferric solution (ox prod) can be completely prevented by making it up with excess of acid instead of with excess of bichromate; and further experiments (Table XLI) show that an acid solution of ferric chloride may be substituted without affecting the rates. The solutions used contained, in 50 cc:

	IV	V
Ferric (sulphate)	5.0	0.0
Ferric (chloride).....	0.0	5.0
Free acid.........	10.0	10.0
Bichromate.......	0.0	0.0

Experiments at 30.5° C

Miss Benson has shown that by titrating as directed on page 357 of her paper, the amount of iodine liberated by the reaction may be determined accurately if both reaction and titration are carried out at 0° C; experiments of my own confirm this conclusion. At 30° C, however, owing no doubt to the fading of the blue color of iodide of starch at high temperatures, a considerable excess of iodine—from 0.6 to 0.8 cc N/100 iodine in the 700 cc of solution—is necessary to produce the permanent tint taken as end point. When any arsenite was required in the "blank" experiment (without ferrous salt) the same correction for the end point would

apply there; and in these cases the net arsenite (after sub-
tracting the "blank") would be free from error. When
"As = o" in the blank experiment however, *i. e.* when the
iodine liberated in the blank experiment was less than enough
to give the blue with starch, the numbers are too low. This
is the case with most of Miss Benson's measurements from
Table XXIV onward. I have consequently repeated the
determinations at 30° C; the results are contained in Tables
XLV to XLIX. While confirming Miss Benson's conclusions
as to the effect of the concentrations of the various reagents
on the rate of liberation of iodine, they show that the rate of
oxidation of the iron in the solution is much more rapid at
the higher temperature, and that in many cases all the iron
is oxidized within two minutes; this result was checked by
addition of potassium ferricyanide.

The correction for the end point (which in all the tables
has been added to the observed numbers before entering
them under "As") is given at the head of each table; it varies
slightly from case to case, and was obtained as follows: The
amounts of acid, bichromate, and "ox. prod." indicated at
the head of the table were mixed at 30° C with water and
10 cc of a saturated solution of iodine in water, the ferrous
sulphate was then added with enough water to bring the
whole to a volume of 700 cc; one minute later ammonium
bicarbonate was added, then 5 cc normal potassium iodide,
and starch, and then N/100 arsenite to the "end point." In
order to find the arsenite equivalent of the iodine employed,
10 cc of the same iodine solution was then added, and arsenite
to the end point again; in every case 1.90 cc arsenite was re-
quired. Table XLII shows that the "correction" does not
depend on the length of time the reacting solution remained
in the bath, loss of iodine from evaporation is therefore not
to be feared.

The induction factor at 0° and at 30°

Miss Benson has shown[1] that the induction factor—or

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[1] Loc. cit., page 369.

the number of equivalents of iodine liberated per equivalent of iron oxidized—varies, at o° C, from 1.2 to 1.8. To make the evidence for this as clear as possible, I have calculated the induction factor, *viz.*, the fraction y/x, from the data of her Table XVII, and present the results in Table XLIII. At 30° the induction factor is much lower than at o°; as shown in Table XLIV it falls as low as o.4, and never rises above 1.0.

The influence of the concentrations of the various reagents on the factor is in accordance with the supposition[1] that both Fe″ and FeI′ (FeI$_2$, etc.) are simultaneously undergoing oxidation in the solution; increase in the concentration of the acid, for instance, affects the rate of the second reaction much more than that of the first,[2] and consequently increases the induction factor. A quantitative test of this assumption is postponed until conductivity measurements furnish data for a plausible assumption as to the formula of the addition product (see foot-note, page 634).

My thanks are due to Professor W. Lash Miller, at whose suggestion these measurements were carried out in the Winter of 1907–8.

TABLE XXXVI (HYDROCHLORIC ACID)

Cr, 20; KI, 20; Ox, 5; Fe, 1.0; V, 700; t, o° C

θ	Expt. 49 HCl, 10	Expt. 5a[3] H$_2$SO$_4$, 10	Expt. 50 HCl, 20	Expt. 9a[3] H$_2$SO$_4$, 20
	As	As	As	As
0.25	—	—	2.35	4.05
1.0	1.35	1.90	—	7.15
2.0	2.35	3.10	7.70	8.00
4.0	3.90	4.30	—	—

[1] Loc. cit., p. 374.

[2] Ibid., p. 366.

[3] In Expts. 5a, 9a, etc., the composition of the solution was the same as in Miss Benson's Expts. 5, 9, etc.

TABLE XXXVII (SALTS)

Ac, 10; Cr, 20; KI, 20; V, 700; t, 0° C

Expt.	Salt added	Ox	Fe	θ	As	Blank	No. of blank Ex.
51	0.88 g. K_2SO_4	o	1.0	1.0	4.90	5.00	23a
52	0.5 g. NaCl	o	1.0	0.5	3.30	3.90	23a
53	do	o	0.5	0.5	2.30	2.60	54
55	1.0 g. NaCl	o	1.0	0.5	2.85	3.90	23a
56	do	o	0.5	0.5	2.10	2.60	54
57	1.0 g. KBr	o	1.0	0.5	3.30	3.90	23a
58	0.03 g. $KF.2H_2O$	5	1.0	4.0	4.40	4.35	5a
59	0.1 do	5	1.0	4.0	4.25	4.35	5a
60	0.5 do	o	1.0	1.0	0.80	5.00	23a
61	1.0 do	o	1.0	1.0	0.20	5.00	23a

TABLE XXXVIII (POTASSIUM FLUORIDE)

Ac, 10; Cr, 20; KI (after θ), 20; Ox, o; V, 700; t, 0° C

θ	Expt. 62 KF, o		Expt. 63 KF, 1.0[1]		Expt. 64 KF, 3.0		Expt. 65 KF, 5.0		Expt. 66 KF, 10.0	
	As	x	As	x	As	x	As	x	As	x
0.25	3.20	0.65	2.80	0.71	1.60	0.82	0.75	0.90	0.15	0.98
0.50	2.35	0.75	1.80	0.83	0.80	0.91	0.30	0.96	—	—
1.0	1.60	0.84	1.15	0.90	0.40	0.95	—	—	—	—
2.0	1.05	0.90	0.60	0.94	—	—	—	—	—	—
4.0	0.60	0.94	—	—	—	—	—	—	—	—

TABLE XXXVIII B

Fe	KF, o As	KF, 1.0 As	KF, 3.0 As	KF, 5.0 As	KF, 10.0 As
1.0	7.20	7.70	7.80	6.20	5.40
0.8	6.15	6.55	6.35	5.20	....
0.6	5.10	5.20	....	4.20	3.60
0.4	3.60	3.70	3.50	2.90	....
0.2	2.00	2.10	1.80	1.60	1.40
0.1	1.00	1.05	0.90	0.80	0.70
0.0	0.00	0.00	0.00	0.00	0.00

[1] KF, 1.0 indicates . :c of a solution containing 0.33 gram of potassium fluoride, $KF.2H_2O$ per litre, and is approximately one F-wt of fluoride for one of ferrous salt in the reacting solution.

TABLE XXXIX (COLLOIDS)

Ac, 10; KI, 20; Fe, 1.0; V, 700; t, 0° C

Expt. 67 Agar-agar[1] Cr, 20; Ox, 5; θ, 4.0		Expt. 68 albumen[2] Cr, 20; Ox, 0; θ, 1.0		Expt. 69 Dialyzed iron[3] θ, 1.0				
Agar	As	Albumen	As	Cr	Ox	Dial	Total Fe'''	As
0	4.40	0	5.05	10	0	0	0	2.40
5 cc	4.35	50 cc	2.25	10	0	5 cc	10.8	2.00
25	4.45	100	1.15	10	5	0	5	0.80
50	4.40	150	0.55	20	0	0	0	5.05
100	4.40	—	—	20	0	5 cc	10.8	3.50
—	—	—	—	20	5	0	5	1.90

TABLE XL ("AGED" OX PROD)

KI, 20 ; Cr, 20 ; Fe, 1.0 ; V, 700 ; t, 0° C ; θ, 1.0

Expt.	Ox	Fe'''	Ac from hydrol.	Ac added	Total Ac	As
70	0	0	0	15	15	7.30
71	5 II	1.0	5.0	10	15	6.70
72	1 I	1.0	0	15	15	6.65
73	5 III	2.87	2.6	10	12.5	4.60
74	2.87 I	2.87	0	12.6	12.6	4.00
75	10 III	2.0	10	0	10	3.20
76	2 I	2.0	0	10	10	3.05
77	0	0	0	0	0	0.00
78	5 I	5.0	0	0	0	0.00
79	0	0	0	10	10	5.05
5a	5 I	5.0	0	10	10	1.90
80	10 III	5.74	2.6	0	2.6	0.15

[1] One-tenth percent solution of agar-agar.

[2] One-fifth percent solution of egg-albumen.

[3] 5 cc of the dialyzed iron solution contained 10.8 units.

TABLE XLI (Acid Ox Prod)

Ac, 20; Cr, 20; KI, 20; Ox, 5; Fe, 1.0; V, 700; t, 30.5° C; Corr, 0.75

Expt.	θ	Ox	As
81	0.25	0	3.35
"	0.50	0	4.05
"	1.0	0	4.70
"	2.0	0	5.25
82	0.25	5 IV	1.35
83	0.25	5 V	1.30
84	0.25	5 I	1.35
82	0.50	5 IV	2.00
83	0.50	5 V	1.90
84	0.50	5 I	2.10
82	1.0	5 IV	2.85
83	1.0	5 V	2.85
84	1.0	5 I	2.85
82	2.0	5 IV	3.85
82	1.0	5 IV[1]	2.85
83	2.0	5 V	3.85
84	2.0	5 I	3.85

TABLE XLII (Correction for End point at 30° C)

Expt. 85 : Ac, 20 ; Cr, 20 Ox, 5 ; Fe, 1.0 ; V, 700 ; Iodine 10 cc = As 1.90 ; t, 30.5° C

θ	As found	Corr.
0.25	1.15	0.75
0.50	1.15	0.75
1.0	1.15	0.75
2.0	1.10	0.80
4.0	1.15	0.75
8.0	1.05	0.85

[1] Boiled.

TABLE XLIII

(Values of the Induction factor, y/x, calculated from Miss Benson's measurements at $0°$ C; see her Table 17)

Cr, 20; V, 700; t, $0°$ C; Ox, 5 except in Expt 23 Ox, o

Expt.	Ac	KI	Fe	Induction factor					
				$\theta = 0.5$	1.0	2.0	4.0	8.0	∞ [1]
5	10	20	1.0	$y/x = 1.4$	1.4	1.3	1.4	1.4	1.5
6	10	20	0.5	1.3	1.4	1.4	1.4	1.4	1.6
9	20	20	1.0	1.6	1.6	⁻6	1.7	1.8	1.8
14	10	5	1.0	—	0.9	0.9	0.9	1.0	1.2
15	10	5	0.5	—	—	1.1	1.1	1.2	1.4
16	10	10	1.0	—	0.7	0.8	1.1	1.2	1.4
17	10	10	0.5	—	1.2	1.3	1.4	1.6	1.7
23	10	20	1.0	1.4	1.5	1.4	1.4	—	1.5

TABLE XLIV

(Values of the Induction factor, y/x, at $30.5°$ C; from Tables 45–49)

Fe, 1.0; t, $30.5°$ C; V, 700

Expt.	Ac	Cr	KI	Ox	Induction factor				
					$\theta = 0.25$	0.5	1.0	2.0	4.0
86	10	20	20	0	$y/x = 0.40$	0.40	0.40	0.40	0.40
87	—	—	—	2.5	—	—	0.43	0.41	0.42
88	—	—	—	3.5	—	—	0.36	0.34	0.39
89	—	—	—	5.0	—	—	0.38	0.37	0.38
90	15	20	20	0	0.64	0.70	0.73	0.80	0.84
91	—	—	—	2.5	0.51	0.54	0.60	0.65	0.65
92	—	—	—	3.5	—	0.46	0.50	0.57	0.61
93	—	—	—	5.0	—	0.40	0.44	0.49	0.52
94	20	20	20	0	0.85	0.92	0.97	1.02	1.02
95	—	—	—	2.5	0.62	0.71	0.78	0.84	0.84
96	—	—	—	3.5	0.53	0.63	0.69	0.75	0.75
97	—	—	—	5.0	0.69	0.70	0.71	0.72	0.72
98	—	—	—	10.0	0.60	0.61	0.60	0.61	0.61
99	20	20	10	0	0.77	0.82	0.89	0.94	1.01
100	—	—	—	5.0	—	0.52	0.50	0.51	0.51
101	—	—	—	10.0	—	—	0.50	0.50	0.48
102	20	10	20	0	0.68	0.76	0.75	0.82	0.82
103	—	—	—	5.0	0.42	0.61	0.62	0.67	0.71
104	—	—	—	10.0	—	0.61	0.63	0.62	0.64

[1] Values of θ from 30 up.

TABLE XLV
Ac, 10; Cr, 20; KI, 20; Fe, 1.0; V, 700; t, 30.5° C

θ	Expt. 86 Ox 0; Cor. 0.66		Expt. 87 Ox 2.5; Cor. 0.70		Expt. 88 Ox 3.5; Cor. 0.70		Expt. 89 Ox 5.0; Cor. 0.7	
	As	x	As	x	As	x	As	x
0.25	1.30	0.65	—	—	—	—	—	—
0.50	1.65	0.83	—	—	—	—	—	—
1.0	2.00	1.00	1.05	0.49	1.00	0.54	0.93	0.50
2.0	—	—	1.55	0.74	1.40	0.83	1.40	0.75
4.0	—	—	2.10	1.00	1.95	1.00	1.90	1.00
16.0	2.00	1.00	2.10	1.00	1.95	1.00	1.90	1.00

TABLE XLV B $\theta = 16$

Fe	Ox, 0 As	Ox, 2.5 As	Ox, 3.5 As	Ox, 5.0 As
0.2	0.40	0.40	0.40	0.40
0.4	0.86	0.80	0.85	0.80
0.6	1.20	1.25	1.20	1.20
0.8	1.65	1.65	1.65	1.65
1.0	2.00	2.10	1.95	1.90

TABLE XLVI
Ac, 15; Cr, 20; KI, 20; Fe, 1.0; V, 700; t, 30.5° C

θ	Expt. 90 Ox 0; Cor. 0.70		Expt. 91 Ox 2.5; Cor. 0.70		Expt. 92 Ox 3.5; Cor. 0.70		Expt. 93 Ox 5.0; Cor. 0.65	
	As	x	As	x	As	x	As	x
0.25	2.30	0.71	—	—	—	—	—	—
0.50	2.80	0.80	1.10	0.43	1.02	0.44	0.90	0.45
1.0	3.10	0.85	1.85	0.65	1.42	0.57	1.35	0.61
2.0	3.85	0.96	2.50	0.83	2.44	0.85	2.20	0.90
4.0	4.20	1.00	3.25	1.00	3.05	1.00	2.60	1.00
8.0	4.20	1.00	3.25	1.00	3.05	1.00	2.60	1.00

Blanks:— Expt 90, $\theta = 8$, Corr 0.20.   Expt 92, $\theta = 8$, As 0.35.
Expt 91, $\theta = 8$, As 0.30.   Expt 93, $\theta = 8$, As 0.80.

TABLE XLVI B $(\theta = 8)$

Fe	Ox, 0, As	Ox, 2.5 As	Ox, 3.5 As	Ox, 5.0 As
0.20	1.40	0.90	0.80	0.70
0.40	2.50	1.60	1.55	1.30
0.60	3.25	2.20	2.20	1.85
0.80	2.80	2.80	2.65	2.20
1.00	4.20	3.25	3 05	2.60

TABLE XLVII

Ac, 20; Cr, 20; KI, 20; Fe, 1.0; V, 700; t, 30.5° C

Corr: Expt 94, 0.75; Expt 95, 0.70; Expt 96, 0.72; Expt 97, 0.75; Ex 98, 0.82

θ	Expt. 94 Ox, 0		Expt. 95 Ox, 2.5		Expt. 96 Ox, 3.5		Expt. 97 Ox, 5.0		Expt. 98 Ox, 10.0	
	As	x	As	x	As	x	As	x	As	x
0.25	3.35	0.79	1.55	0.50	1.47	0.55	1.35	0.39	1.12	0.37
0.50	4.05	0.88	2.70	0.76	2.32	0.74	2.00	0.57	1.77	0.58
1.0	4.60	0.95	3.55	0.91	3.12	0.90	2.85	0.80	2.52	0.83
2.0	5.10	1.00	4.20	1.00	3.75	1.00	3.60	1.00	3.05	1 00
9.0	....	....	4.20	1.00	3.75	1.00	3.60	1.00	3.05	1.00
16.0	5.10	1.00	—	—	—	—	—	—	—	—
Blanks:	θ 16, Corr 0.2		θ 9, As 0.80		θ 9, As 1.05		θ 9, As 1.40		θ 4 9 16 As 0.80, 2.40, 5.00	

TABLE XLVII B

Fe	Ox, 0, As	Ox, 2.5 As	Ox, 3.5 As	Ox, 5.0 As	Ox, 10.0 As
0.20	1.70	1.30	1.15	0.80	0.60
0.40	2.75	2.20	2.10	1.50	1.20
0.60	3.85	3.10	2.75	2.30	1.85
0.80	4.60	3.60	3.25	2.90	2.45
1.00	5.10	4.20	3.75	3.60	3.75

TABLE XLVIII

Ac, 20; Cr, 20; KI, 10; Fe, 1.0; V, 700; t, 30.5° C

θ	Expt. 99 Ox, 0; Cor. 0.70		Expt. 100 Ox, 5.0; Cor. 0.75		Expt. 101 Ox, 10.0; Cor. 0.70	
	As	x	As	x	As	x
0.25	2.40	0.62	—	—	—	—
0.50	2.95	0.72	1.05	0.40	—	—
1.0	3.75	0.84	1.50	0.60	1.25	0.50
2.0	4.30	0.91	2.48	0.98	1.75	0.70
4.0	5.05	1.00	—	—	2.05	0.85
8.0	5.05	1.00	2.55	1.00	2.30	1.00
Blanks: $\theta = 8$	Cor. 0.35		As, 0.85		As, 1.35	

TABLE XLVIII B ($\theta = 8$)

Fe	Ox, o As	Ox, 5.0 As	Ox, 10.0 As
0.20	1.60	0.50	0.30
0.40	2.75	1.05	0.80
0.60	3.75	1.55	1.30
0.80	4.35	2.05	1.80
1.00	5.05	2.55	2.30

TABLE XLIX

Ac, 20; Cr, 10; KI, 20; Fe, 1.0; V, 700; t, 30.5° C

θ	Expt. 102 Ox, o; Cor. 75		Expt. 103 Ox, 5.0; Cor. 0.65		Expt. 104 Ox, 10.0; Cor. 0.82	
	As	x	As	x	As	x
0.25	2.55	0.76	0.80	0.38	—	—
0.50	3.25	0.88	1.35	0.44	1.22	0.40
1.0	3.70	0.95	2.10	0.67	1.87	0.59
2.0	4.10	1.00	2.75	0.82	2.67	0.82
4.0	—	—	3.50	0.99	3.20	1.00
8.0	4.15	1.00	3.65	1.00	3.20	1.00
Blanks: $\theta = 8$	Cor. 0.35		Cor. 0.20		As, 0.20	

TABLE XLIX B ($\theta = 8$)

Fe	Ox, o As	Ox, 5.0 As	Ox, 10.0 As
0.20	1.35	1.00	0.65
0.40	2.25	1.80	1.30
0.60	2.95	2.40	1.95
0.80	3.55	3.05	2.60
1.00	4.15	3.65	3.20

LIST OF EXPERIMENTS

Expt.	Table	Ac	Cr	KI	Ox	Fe	Temp.	Page	
49	36	10	20	20	5	1	0		Hydrochloric acid
50	36	20	20	20	5	1	0		"
51	37	10	20	20	0	1	0		0.88 g. K_2SO_4 added
52	37	10	20	20	0	1	0		0 5 g. ...Cl added
53	37	10	20	20	0	0.5	0		"
54	37	10	20	20	0	1	0		"
55	37	10	20	20	0	0.5	0		1.0 g. "
56	37	10	20	20	0	0.5	0		"
57	37	10	20	20	5	1	0		1.0 g. KBr added
58	37	10	20	20	5	1	0		0.03 g. $KF.2H_2O$ ad'ed
59	37	10	20	20	0	1	0		0.1 g. " "
60	37	10	20	20	0	1	0		0.5 g. " "
61	37	10	20	(20)	0	1	0		1.0 g. " "
62	38	10	20	(20)	0	1	0		
63–66	38	10	20	20	0	1	0		KF 1.0, 3.0, 5.0, 10.0
67	39	10	20	20	5	1	0		Agar-agar added
68	39	10	10	20	0	1	0		Albumen added
69	39	10	20	20	5&0	1	0		Dialyzed iron added
69	39	10	20	20	5&0	1	0		
70–80	40	:	20	20		1	0		Various aged ox prods added
81–84	41	20	20	20	5&0	1	30.5		Various acid ox prods added
85	42	20	20		5	1&0.5	30.5		Correction for end point
—	43		20		5&0		0		Values of Induction factor
—	44		:			1	30.5		"
86–89	45	10	20	20		1	30.5		Ox 0, 2.5, 3.5, 5.0
90–93	46	15	20	20		1	30.5		"
94–98	47	20	20	20		1	30.5		Ox 0, 2.5, 3.5, 5.0, 10.0
99–101	48	20	20	10		1	30.5		Ox 0, 5.0, 10.0
102–4	49	20	10	20		1	30.5		"

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