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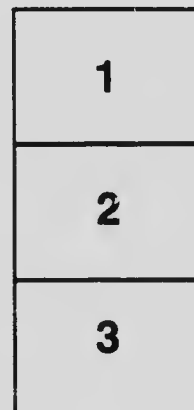
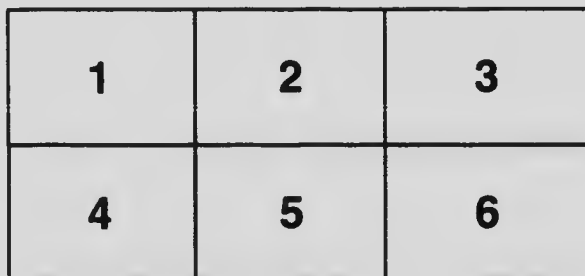
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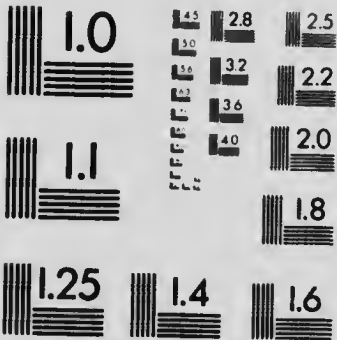
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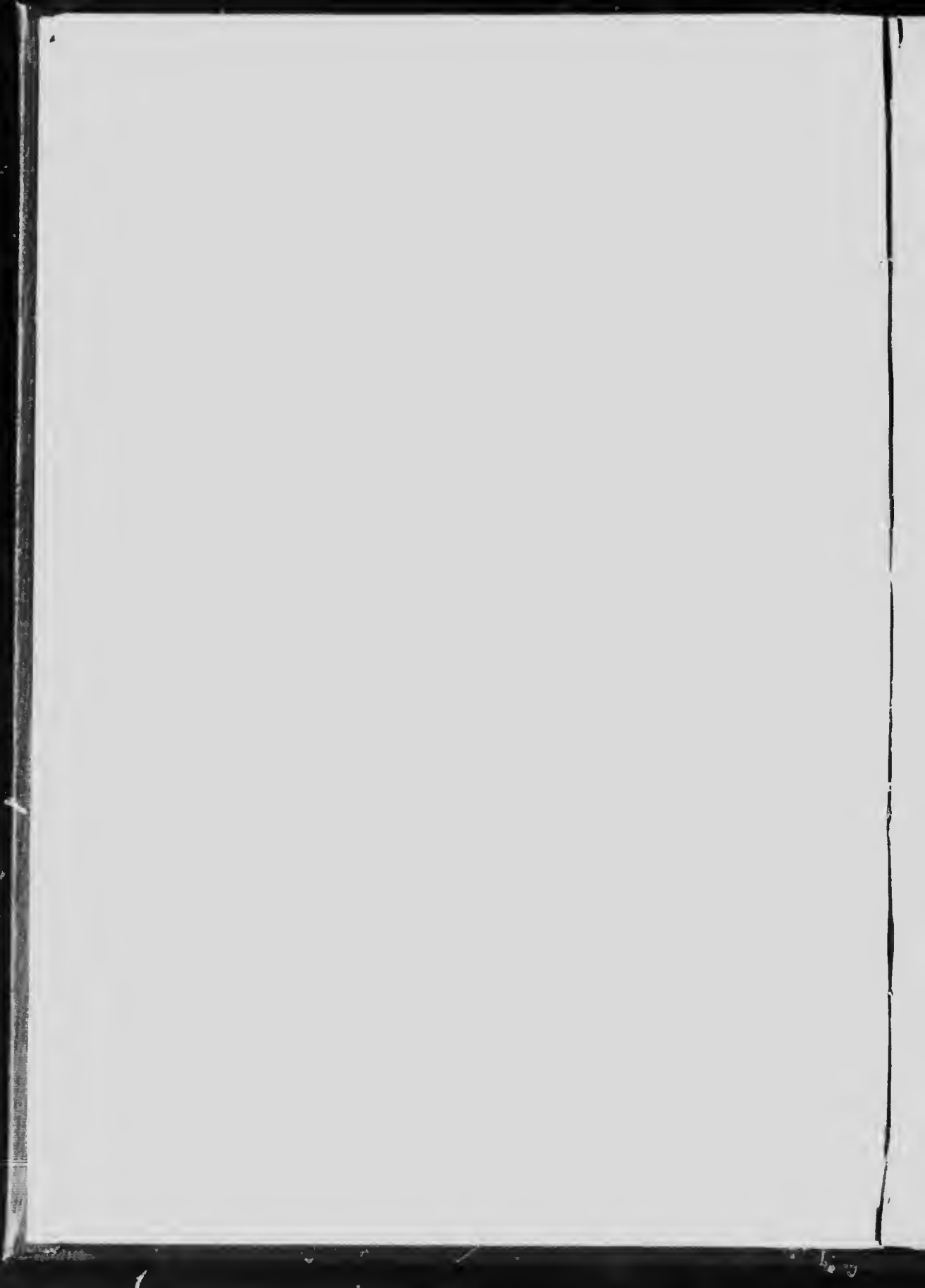
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PAPERS FROM THE CHEMICAL
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No. 44: A REACTION WHOSE RATE IS DIMINISHED BY
RAISING THE TEMPERATURE

BY CLARA C. BENSON

(REPRINTED FROM THE JOURNAL OF PHYSICAL CHEMISTRY, VOL. 8, 1904)

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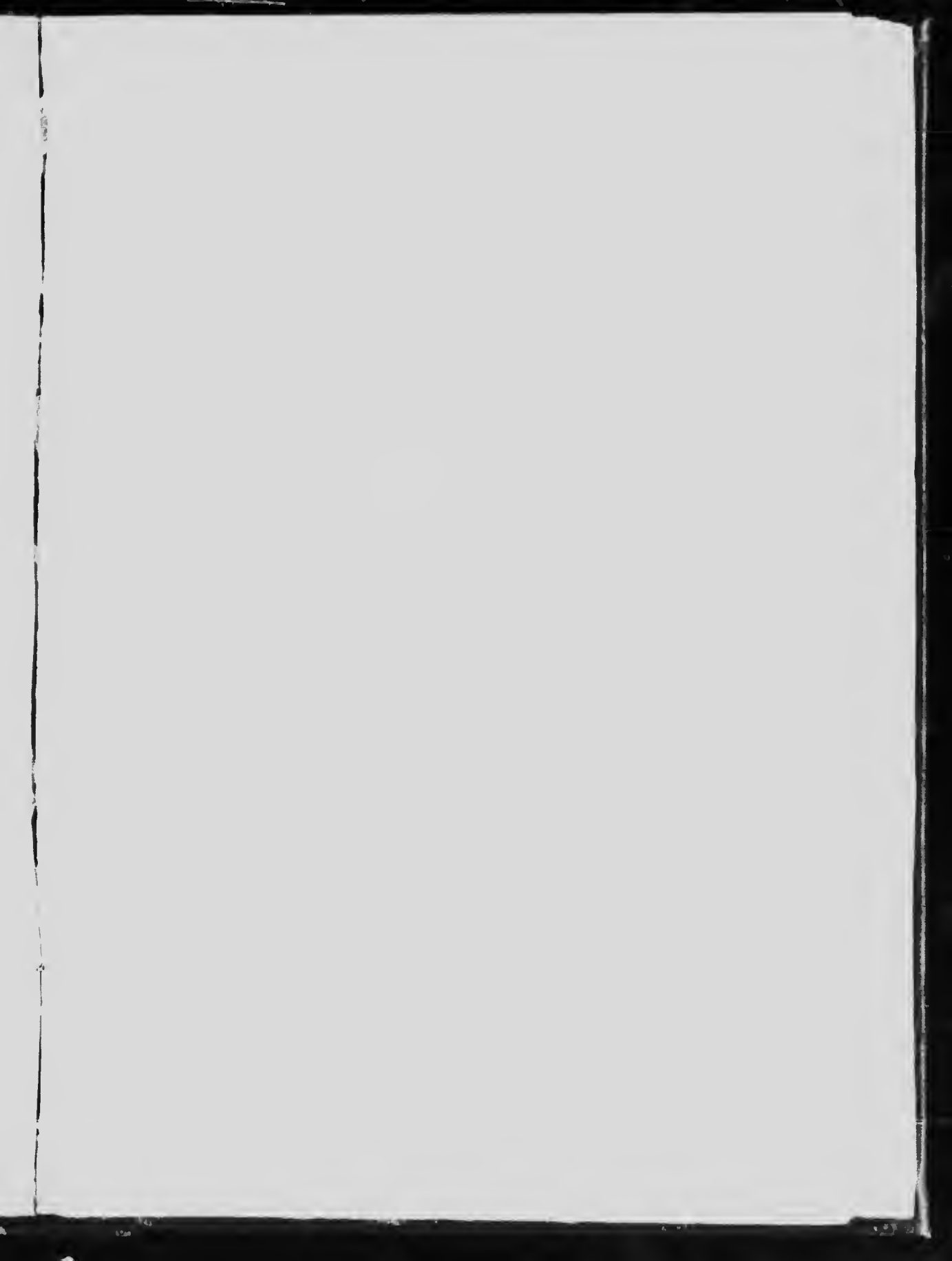
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A REACTION WHOSE RATE IS DIMINISHED BY RAISING THE TEMPERATURE

BY CLARA C. BENSON

Towards the close of my measurements of the rates of the reactions in solutions containing chromic acid, potassium iodide and ferrous sulphate,¹ I was surprised to find that the amount of iodine liberated in a minute at 30° was less than that set free in the same time at 0° (see Table 21).

Taken by itself, this result does not prove that the rate of liberation of iodine is less at 30° than at 0°, and at first I thought it most likely that at the higher temperature the reaction was over before the minute was up. Analyses at the expiration of two, four and eight minutes, however, showed that, far from being completed within sixty seconds, the reaction was still proceeding after four minutes; and as in blank experiments (no FeSO₄) no iodine was set free inside of eight minutes, the conclusion is unavoidable that the oxidation of potassium iodide by chromic acid in presence of ferrous sulphate is retarded by raising the temperature.

The measurements detailed in the following tables show that the nature of the reaction at 30° is much the same as at 0°. At the higher temperature, as at the lower, the rate is proportional to the first power of the concentration of the iodide (Tables 21 and 25), to the first power of the concentration of the ferrous salt (Tables 24 and 26) and to the 1.7th power of the concentration of the bichromate (Tables 24 and 27). The retarding influence of the products of oxidation (Tables 24, 28, 31 and 30) is somewhat less at the higher temperature, and its "ageing" (Tables 15 and 26) is more rapid. In experiments carried out without addition of the products of oxidation, the rate is proportional to the fourth power of the concentration of the acid (Tables 31 and 32):

¹ Jour. Phys. Chem. 7, 356 (1903).

while in their presence it varies with the second or third power only (Tables 24, 33 and 34). At zero, in the presence of excess of the products of oxidation the rate is proportional to the fourth power, while in the absence of ferric salts the reaction is too quick for accurate measurement. It is a consequence of this difference in the order of the reaction with respect to the acid, that while in Tables 24, 25, 26 and 27 the reaction is four or five times as quick at 0° as at 30.2°, in Tables 33 and 34 where large quantities of the acid were employed, it is seven and fifteen times as quick, respectively.

A single experiment (Table 35) shows that, as was to be expected, the rate of oxidation of ferrous sulphate by chromic acid in absence of potassium iodide is accelerated by heat; Mr. DeLury¹ has found that the same is true for the oxidation of potassium iodide in absence of ferrous salts.

The only reactions hitherto studied whose rates have a negative temperature coefficient, so far as I am aware, are those in which a colloidal catalytic agent is involved; in these cases the rate passes through a maximum as the temperature is increased, and then falls off because of the coagulation of the colloid. In the experiments of the present paper the only colloid present is the ferric salt, and its coagulation instead of retarding, accelerates the reaction.

It seems probable, however, that as the rates in other complex systems came to be studied, further cases of negative temperature coefficients will be met with, and that the present instance may be regarded as typical of a new class. Both ferri-iodion theory and peroxide theory are ready with an explanation of the retardation; the former by assuming that the amount of FeI undissociated is less at high temperatures, and the latter by asserting that as the temperature is raised the peroxide reacts more with the residual ferrous salt, and less with the iodide.

I regret that in the time at my disposal I am not able to undertake the large amount of work necessary to ascertain whether either theory could be brought into accord with quan-

¹Jour. Phys. Chem. 7, 230 (1903).

titative measurements; and at the close of this research I wish to express my sincere thanks to Prof. W. Lash Miller for his interest and assistance.

The University of Toronto
November, 1905.

The experiments were carried out as described in this Journal, **7**, 357, and the abbreviations made use of in these tables are those explained in that paper.

A, 10, represents ten cc of 0.05*N* sulphuric acid (0.05 gram-formula-weights H₂SO₄ per liter); *C*, 10, ten cc of 0.0083*N* K₂Cr₂O₇ (including unreduced bichromate in the "O₁"); *KI*, 10, ten cc of 0.0479*N* KI; *Fe*, 1.0, one cc of 0.05*N* ferrous sulphate; *O*₁, 5, the product of oxidation of five cc of 0.05*N* ferrous sulphate; *θ* is the duration of the reaction in minutes; *A*_s, the number of cc of *n*/100 sodium arsenite equivalent to the iodine liberated; *V*, the total volume in cc of the reacting mixture.

For the sake of convenience, the tables are numbered consecutively with those of the previous paper, "As₂O₃" (Table 5), for example, referring to Table 3, Jour. Phys. Chem. **7**, 3, 9.

I take this opportunity of correcting the following misprints: Table 22 (Jour. Phys. Chem. **7**, 387), second column, should read: 100, 120, 152, 162, in place of 100, 116, 126, 131. In equation 7 (p. 372) the sign of equality has been omitted after $dy/dθ$, and on page 376 the $+$ sign has been omitted from the expression $a/k(1-a) = 1077$.

TABLE 24

Ac, 10; Cr, 20; KI, 20; O₁, 5; Fe, 1.0; V, 700

<i>θ</i>	0.5	1	2	4	8
As ₂ O ₃ (Expt. 37)		0.55	1.05	1.80	2.40
As ₂ O ₃ (Table 3)	1.05	1.00	3.10	4.30	5.60
Blanks (30.2	<i>θ</i> = 4, As ₂ O ₃ = 0;	<i>θ</i> = 8, As ₂ O ₃ = 0.45			

TABLE 25

Ac, 10; Cr, 20; KI, 10; Ox, 5; Fe, 1.0; V, 700

θ	1	2	4	8
As, 30.2 (Expt. 38)	—	0.80	1.40	1.85
As, 6 ⁰ (Table 8)	1.40	2.20	3.30	4.30
Blank (30.2); θ = 8; As = 0	—	—	—	—

TABLE 26

Ac, 10; Cr, 20; KI, 20; Ox, 5; Fe, 0.5; V, 700

θ	1	2	4	8
As, 30.2 (Expt. 39)	—	0.55	0.90	1.45
As, 6 ⁰ (Table 3)	1.00	1.75	2.50	3.30
Blanks (30.2); θ = 4; As = 0; θ = 8; As = 0.45	—	—	—	—

TABLE 27

Ac, 10; Cr, 30; KI, 20; Ox, 5; Fe, 1.0; V, 700

θ	0.5	1	2	4	8
As, 30.2 (Expt. 40)	—	0.55	1.45	2.30	3.00
As, 6 ⁰ (Table 6)	1.75	2.9	4.15	5.30	—
Blanks (30.2); θ = 5; As = 0; θ = 8; As = 0.60	—	—	—	—	—

TABLE 28

Ac, 10; Cr, 20; KI, 20; Ox, 0; Fe, 1.0; V, 700

θ	0.5	1	2	4	8
As, 30.2 ² (Expt. 41)	0.00	1.45	1.80	2.30	2.60
As, 6 ⁰ (Table 12)	3.95	5.00	5.85	6.30	—
Blank (30.2); θ = 8; As = 0	—	—	—	—	—

TABLE 29

Expt. 42. Ac, 10; Cr, 20; KI, 10; Ox, 5; Fe, 1.0; V, 700;
Temp, 30.2 C

Age of Ox	fresh	fresh	3 days	3 days
θ	2	4	2	4
As	0.80	1.40	1.40	1.35

TABLE 30

Expt. 43. Ac, 20; Cr, 20; KI, 20; Ox, 0; Fe, 1.0; V, 700;
Temp, 30.2 C

θ	0.25	0.5	1.0
As	2.65	3.40	4.40

TABLE 31

Expt. 44. Ac, 10; Cr, 10; KI, 20; Ox, 0; Fe, 1.0; V, 700;
Temp. 39.7° C

θ	2	4	8	16
As	0.30	1.10	1.35	2.25

TABLE 32

Expt. 45. Ac, 20; Cr, 10; KI, 20; Ox, 0; Fe, 1.0; V, 700;
Temp. 39.7° C

θ	0.5	1	2
As	1.40	2.15	2.70

TABLE 33

Ac, 15; Cr, 20; KI, 20; Ox, 5; Fe, 1.0; V, 700

θ	0.5	1	2
As, 30.2° (Expt. 46)	0.55	1.15	2.00
As, 0° (Table 5)	3.00	4.60	6.00

TABLE 34

Ac, 20; Cr, 20; KI, 20; Ox, 5; Fe, 1.0; V, 700.

θ	0.25	0.5	1	2	4
As, 30.2° (Expt. 47)	—	1.35	2.25	3.40	4.30
As, 0° (Table 5)	4.05	5.75	7.15	8.00	—
Blank (30.2°); $\theta = 4$, As = 0					

TABLE 35 (Expt. 48)

In the mixture Ac = 20, Cr = 10, Ox = 5, Fe = 1.0, V = 700, at 0°, after half a minute, 0.78 cc of the ferrons salt remained unoxidized (Table 19).

In the same mixture at 30.2°, the amount of ferrons sulphate remaining after half a minute caused the liberation (in four minutes) of iodine equivalent to As = 1.15, when KI = 20 was added, and water enough to bring the total volume up to 800 cc.

But in the mixture Ac = 20, Cr = 10, KI = 20, Ox = 5, Fe = 0.75, V = 800, for $\theta = 4$, As = 1.70. Consequently, *less* than 0.75 cc of FeSO₄ must have remained unoxidized after half a minute in the previous experiment (See Jour. Phys. Chem. 7, 1 (1903)).

LIST OF EXPERIMENTS

Expt	Table	Ac	Cr	KI	CN	Fe	Temp	Rate	
1	1	10	10	20	5	1	0	375	
2	1	10	10	20	5	0.5	0	375	See also Tables 16, 17
3	2	15	10	20	5	1	0	375	" " " " " " 17
4	1	15	10	20	5	0.5	0	375	
5	3	10	20	20	5	1	0	376	" " " " " " 16, 17
6	3	10	20	20	5	0.5	0	376	" " " " " " 17
7	4	20	10	20	5	1	0	376	
8	4	20	10	20	5	0.5	0	376	
9	5	20	20	20	5	1	0	377	" " " " " " 16, 17
10	5	15	30	20	5	1	0	376	
11	5	15	20	20	5	1	0	377	
12	6	10	30	20	5	1	0	376	
13	6	10	30	20	5	0.5	0	376	
14	7	10	20	5	5	1	0	381	" " " " " " 16, 17
15	7	10	20	5	5	0.5	0	381	" " " " " " 17
16	8	10	20	10	5	1	0	381	" " " " " " 16, 17
17	8	10	20	10	5	0.5	0	381	" " " " " " 17
18	9	10	20	30	5	1	0	382	
19	9	10	20	30	5	0.5	0	382	
20	10	10	20	20	5	2	0	382	
21	10	10	20	20	5	1.5		382	
22	10	20	10	20	5	0.25		382	
23	12	10	20	20	0	1	0	383	" " " " " " 17
24	12	10	20	20	2.5	1	0	383	
25	12	10	20	20	3.3	1	0	383	
26	12	10	20	20	5.0	1	0	383	
27	12	10	20	20	10	1	0	383	
28	13	10	20	20	0	1	0	384	K ₂ SO ₄ added
29	13	10	20	20	0	1	0	384	Cr ₂ SO ₄ added
30	13	10	20	20	5	1	0	384	Iodine added
31	13	20	10	20	5	0	0	384	Haemoglobin added
32	13	10	20	20	0	0	0	384	Ferrosamrose added
33	13	10	20	20	0	0	0	384	K ₄ FeCN ₆ added
34	15	10	20	20	age	1	0	384	
34	10	10	10	0	5	1	0	386	
35	10	10	20	0	5	1	0	386	See also Table 17
36	10	20	10	0	5	1	0	386	
37	24	10	20	20	5	1	30.2	118	
38	25	10	20	10	5	1	30.2	119	
39	26	10	20	20	5	0.5	30.2	119	
40	27	10	30	20	5	1	30.2	119	
41	28	10	20	20	0	1	30.2	119	
42	29	10	20	10	age	1	30.2	119	
43	30	20	20	20	0	1	30.2	119	
44	31	10	10	20	0	1	39.7	120	
45	32	20	10	20	0	1	39.7	120	
46	33	15	20	20	5	1	30.2	120	
47	34	20	20	20	5	1	30.2	120	
48	35	20	10	20	5	0.75	30.2	120	

