No. IV.—*On the Influence of Temperature upon the Decomposition of Barium Chloride by Potassium Oxalate in Aqueous Solution.*

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1. The influence of temperature upon the reaction formulated as—

was considered in outline in the first of these contributions (*loc. cit.*).

The general result, deducible from the curves of Table G in that paper, is, that the amount of chemical change in unit time increases as the temperature is varied, and this more rapidly with the earlier than with the later increments of temperature.

The initial state of the chemical system in these experiments was approximately $\text{CaCl}_2 : \text{Na}_2\text{CO}_3 : \text{H}_2\text{O} = 1 : 1 : 1,500$ mols.

If more concentrated solutions be employed, the influence of temperature is less marked: this is shown by the following numbers:—§

* See especially Tilden, "Theory of Solution, &c.," a lecture delivered to the Bristol Naturalists' Society, Feb., 1878.

† "Liquid Diffusion applied to Analysis," *Phil. Trans.*, 1861.

‡ "On Hydrated Salts and Metallic Peroxides," by Graham; *Brit. Assoc. Reports*, 1834.

§ The numbers given are all the means of at least two closely agreeing experiments.

PLATE IX. (TABLE XIII).

 $\text{BaCl}_2 : \text{K}_2\text{C}_2\text{O}_4 = 1:1$ molecules. 30 minutes.*Influence of Temperature.* *Journ. Chem. Soc. Feb. 1880*

TABLE XII.

10 c.c. calcium chloride solution used = 320.27 mgrms. CaCl_2 + 8.1 c.c. sodium carbonate solution = 305.54 mgrms. Na_2CO_3 .
 Initial condition = $\text{CaCl}_2 : \text{Na}_2\text{CO}_3 : \text{H}_2\text{O} = 1 : 1 : 330$ mols.
 Each 25 c.c. water added = 470 mols. Time = 10 mins.

Water added. c.c.	Mean percentage of CaCl_2 decomposed.		
	20°.	50°.	80°.
50	89.1	89.4	89.6
100	85.5	83.5	88.2
250	83.8	89.0	88.8
Time = 60 mins.			
50	91.2	91.4	94.6
100	90.3	91.9	94.2
200	87.9	89.3	—
300	85.2	87.2	—
500	72.6	77.6	82.9

Several other series of experiments were carried out with a similar result, viz., that temperature exerts little influence on the course of the change, except when somewhat dilute solutions are employed, and that the influence is then regular.

In place of continuing these experiments with much more dilute solutions, as was originally intended, I determined to examine in a little more detail the influence of temperature on the reaction between barium chloride and potassium oxalate, as from the results contained in the preceding paper, facts of more general interest might reasonably be expected from this study.

2. The solutions used and the experimental methods employed were the same as those described in the preceding paper.

TABLE XIII.

$\text{BaCl}_2 : \text{K}_2\text{C}_2\text{O}_4 : \text{H}_2\text{O} = 1 : 1 : 360$ mols.
 Each 100 c.c. water added = 1840 mols. Time = 30 mins.

c.c. water added.	Mean percentage of BaCl_2 decomposed.			Numbers actually obtained.				
	3°.	20°.	80°.	3°.	20°.	80°.		
100	74.8	79.8	85.0	74.8	—	79.8	—	85.0
300	51.1	70.8	76.0	50.1	52.2	73.2	68.5	75.7
600	7.8	8.3	51.1	7.8	—	8.9	7.8	52.0
700	1.0	3.7	33.7	1.0	—	3.7	—	33.7

Curves A, B, C, and D of Plate IX represent these results in graphic form.

TABLE XIV.

Details as before. *Pipetting.* Time = 90 mins.

c.c. water added.	Mean percentage of BaCl ₂ decomposed.				Numbers actually obtained.											
	3°.	20°.	50°.	80°.	3°.			20°.			50°.			80°.		
100	91.6	93.5	95.0	94.8	91.6	92.1	91.1	—	—	—	94.5	92.5	—	95.0	94.7	—
300	67.8	80.0	82.0	85.9	67.8	68.4	67.2	—	—	—	80.0	80.0	—	82.0	85.5	—
400	58.0	65.9	80.4	83.4	58.0	58.3	57.8	—	—	—	63.7	63.7	—	80.4	83.4	—
500	41.8	44.3	63.7	78.7	41.8	42.8	40.8	—	—	—	42.8	45.8	—	63.7	79.1	78.4
700	15.0	20.6	59.0	60.9	12.9	16.6	10.2	18.1	17.2	—	18.6	18.9	24.4	59.0	60.9	60.9
800	5.0	4.5	24.2	44.1	4.5	5.5	—	—	—	—	4.0	4.0	5.1	23.3	25.1	43.9
900	—	3.1	7.5	42.1	—	—	—	—	—	—	3.1	—	—	8.7	6.4	42.0
1000	—	5.3	9.6	30.5	—	—	—	—	—	—	5.3	5.3	—	9.6	—	28.0

Curves A to H, Plate X, represent these results graphically.

PLATE X. (TABLE XIV.)

BaCl₂ : K₂C₂O₄ = 1:1 molecules. 90 minutes.*Influence of Temperature.**Journ. Chem. Soc. Feb 1880.*

PLATE XI. (TABLE XV.)

 $\text{BaCl}_2 : \text{K}_2\text{C}_2\text{O}_4 = 1 : 2$ molecules. 30 minutes.*Influence of Temperature.* *Journ. Chem. Soc. Feb. 1880.*

3. Curves A and B (100 c.c. and 300 c.c. water) confirm the results of the experiments with calcium chloride and sodium carbonate.

The influence of temperature begins to be felt when 300 c.c. water of dilution are added; the increase in the amount of chemical change is considerably greater for the rise of temperature from 3° to 20° than for that from 20° to 80° .

But when 600 c.c. and 700 c.c. of water are added (Curves C and D), a different result is observed. The increase in the amount of chemical change is very small for the first rise of 20° , but after that the increase is rapid.

These results are, I think, explicable in terms of the "*strain hypothesis*," developed in the preceding paper. With tolerably dilute solutions, where the formation of cryohydrate molecules is (by hypothesis) small, a moderate increase of temperature is accompanied by a considerable increase in the amount of chemical change; but the system having now very nearly reached the point of most stable equilibrium, further increase of temperature exerts but little influence on the amount of change. If, however, the conditions favourable to formation of hydrated molecules be maintained—much water and low temperature—then a (comparatively) small rise of temperature does not succeed in thoroughly decomposing the loaded molecules. When, however, this decomposition is effected, the chemical change proceeds at an accelerated rate, *i.e.*, when the change is fairly started the curves rapidly ascend.

It is probable that as the point of maximum stability of the system is approached, the influence of temperature on the change would become less and less marked, in other words, the curves would again approach straight lines; if this were so, the curves would exhibit points of contrary flexure.

4. Experiments were now conducted similar to those of Table XIII, except that the time was made 90 minutes (see p. 80).

5. The higher curves of Plate X exhibit the contrary flexure referred to in the last paragraph: but this again disappears when *very* dilute solutions are employed.

Generally, then, it may be said that with concentrated solutions, temperature exerts little influence on the amount of the change under consideration: with more dilute solutions, the first increase of about 20° causes a marked increase in the amount of change, but after this influence of temperature is more regular: with yet more dilute solutions, increase of temperature causes at first a slight increase in the amount of chemical action, but as the temperature continues to rise, the amount of action rapidly increases, until a point is reached after which further increase of temperature but slightly affects the amount of chemical change: and finally, that with *very* dilute solutions the

influence of temperature again becomes nearly regular, the points of contrary flexure being higher up in the curves, and being very much less marked, the curvature of the curves being smaller.

6. A few experiments were carried out in order to determine the effect of increasing the mass of one of the reacting substances.

TABLE XV.

$\text{BaCl}_2 : \text{K}_2\text{C}_2\text{O}_4 : \text{H}_2\text{O} = 1 : 2 : 340$ mols.

Details as before. *Pipetting.* Time = 30 mins.

c.c. water added.	Mean percentage of BaCl_2 decomposed.				Numbers actually obtained.			
	3°.	20°.	50°.	80°.	3°.	20°.	50°.	80°.
800	10.5	16.0	34.0	53.2	10.5	16.0	34.0	51.4 55.1
1000	2.5	18.0	—	24.0	2.5	19.0	17.0	— : 23.0 25.0

7. These results (see Curves A and B of Plate XI) show, that with 2 mols. potassium oxalate to 1 mol. barium chloride and 800 c.c. water of dilution, the effect of increasing temperature upon the amount of chemical change is nearly, if not altogether, regular; but that in a more dilute solution (1000 c.c. water) the effect is similar to that in much less dilute solutions when equal mols. are used, *i.e.*, the first increase of 20° causes a much larger increase in the amount of change than either of the succeeding increments of 30°.

There is, however, in the Curve B no indication of contrary flexure, similar to that of Curves B to H of Plate X.

Let the action be fairly started, then the strained condition is, so to speak, neutralised by the effect of increased mass of potassium oxalate.

8. These experiments, I think, present certain points of analogy with the so-called "*induction*" of Bunsen and Roscoe.

We seem to have certain conditions under which the chemical change proceeds at the normal rate; but by altering these conditions, the rate of change may be accelerated or diminished. If the conditions which diminish the rate of change be somewhat suddenly removed, the change may be abnormally accelerated for a time, after which it may again return to its normal rate.

The conditions which accelerate or diminish the rate of change will probably vary for each chemical reaction: in the present case, dilution and temperature exert opposing actions on the change considered.