VI.—CONTRIBUTIONS FROM THE LABORATORY OF GONVILLE AND CAIUS COLLEGE, CAMBRIDGE.

No. III.—*On the Influence exerted upon the Course of Certain Chemical Changes by Variations in the Amount of Water of Dilution.*

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1. In a paper by one of us (this Journal, 1879, Trans., p. 311) an experimental examination was made of some of the conditions which affect the equilibrium of the system $\text{CaCl}_2 + \text{Na}_2\text{CO}_3 + x\text{H}_2\text{O}$. It was there suggested that a study of the changes undergone by this system under conditions such that the action of the various forces might be more disentangled from one another would be advisable.

The present paper contains the results of experiments undertaken with the object of determining the influence on the equilibrium of the system of variations in the quantity of water present.

2. The solutions used contained respectively 320·7 mgrms. CaCl_2 in 10 c.c., and 305·54 mgrms. Na_2CO_3 in 8·1 c.c. The sodium carbonate

CaCl_2 and Na_2CO_3 . 1:1 molecules. 30 minutes. 18°

was added to the calcium chloride solution, and the whole was then shaken up.

Initial condition was $\text{CaCl}_2 : \text{Na}_2\text{CO}_3 : \text{H}_2\text{O} = 1 : 1 : 330$ mols.

Each 25 c.c. water added = 470 mols. Time = 30 minutes. Temp. = $16-18^\circ$.

TABLE I.

Water added.		Mean percentage of CaCO_3 produced.	Actual numbers obtained.					
In c.c.	In mols.							
0	330	97.8	97.5		98.2			
25	800	96.3	96.8		96.1	96.03	96.03	
50	1270	96.0	95.1	96.03	96.03	96.08	95.8	95.8
75	1740	95.5	95.7	95.4				
100	2210	93.8	94.6	93.1	94.3	93.3		
200	4090	91.2	91.2	91.2	91.2			
300	5970	86.3	85.9	85.9	87.1			
400	7850	85.8	85.8	85.8	85.6			
500	9730	82.1	78.7	78.7	85.3			

Another solution was used after this point. 10 c.c. $\text{CaCl}_2 = 55.5$ mgrms.

Initial state = $1 : 1 : 2700$ mols. Each 25 c.c. water added = 2700 mols.

Water added.		Mean percentage of CaCO_3 produced.	Actual numbers obtained.	
In c.c.	In mols.			
100	12,500	75.0	75.0	
175	20,600	66.5	66.0	67.0
200	23,300	62.2	62.2	
225	26,000	52.0	52.0	

The results contained in this table are graphically represented in the curve of Plate I.

3. These results show that in the special case considered the amount of chemical change decreases regularly as the amount of water of dilution increases. The water which is added appears to exert a purely mechanical influence on the change under consideration.

We may suppose that the chances of collision between the molecules of sodium carbonate and calcium chloride are decreased the greater the number of inactive water molecules interposed.

4. In the second series of experiments which we conducted the influence of water on the reaction $\text{SrCl}_2 + \text{H}_2\text{SO}_4 = \text{SrSO}_4 + 2\text{HCl}$ was studied. The results obtained were very discrepant, and seemed to allow of no reasonable generalisation being deduced. These results will be referred to in the sequel.

5. The reaction $\text{BaCl}_2 + \text{K}_2\text{C}_2\text{O}_4 = \text{BaC}_2\text{O}_4 + 2\text{KCl}$ appeared to

present a chemical change well adapted for the study of the influence of dilution.

Barium oxalate is tolerably insoluble in water, and the amount of change can be quickly and accurately determined by measuring the quantity of undecomposed potassium oxalate by titration with standardised permanganate.

The experiments were conducted by adding a measured volume of potassium oxalate solution to the proper quantity of solution of barium chloride previously diluted with a measured volume of water, shaking up, and then allowing to remain at rest. At the close of the time allowed for the change to proceed, a portion of the clear liquid was drawn off and run through a dry filter into a dry beaker, and the amount of potassium oxalate in solution was determined in an aliquot portion of this filtrate.

TABLE II.

10 c.c. BaCl_2 solution used = 627.04 mgrms. BaCl_2 : 9.35 c.c. $\text{K}_2\text{C}_2\text{O}_4$ solution used = 501.03 mgrms.

Initial condition = BaCl_2 : $\text{K}_2\text{C}_2\text{O}_4$: H_2O = 1 : 1 : 360 mols.

Each 25 c.c. water added = 460 mols. Time = 30 mins. Temp. = 16—18°.

Water added.		Mean percentage of BaCl_2 decom- posed.	Numbers actually obtained.			
In c.c.	In mols.					
0	360	90.2	89.09	91.32		
25	820	88.5	88.2	88.8		
50	1,280	87.6	87.5	87.8		
100	2,200	79.8	79.1	80.2	79.3	79.9
200	4,040	74.8	75.0	74.5		
250	4,960	70.3	70.4	70.1		
300	5,880	69.1	70.0	67.8	69.5	
350	6,800	63.2	62.8	63.5		
400	7,720	56.8	57.5	57.5	55.4	
600	11,400	46.0	43.0	49.0		

These results are represented graphically in Curve A, Plate II.

6. The generalisation of par. 3 may, we think, be also deduced from these results. The amount of chemical change decreases regularly as the amount of water of dilution increases.

7. Another series of experiments was conducted similar to the foregoing, save that the beakers in which the change proceeded were surrounded by ice.

TABLE III.

Details as before. Temp. = 3°. Time = 30 mins.

Water added. In c.c.	Mean percentage of In mols. BaCl ₂ decomposed.	Numbers actually obtained.						
0	360	83.7	85.5	82.0				
25	820	81.6	81.5	81.8				
100	2,200	74.8	76.1	77.5	73.1	72.5		
200	4,040	69.6	68.7	69.0	71.0			
300	5,880	61.2	60.5	61.9				
400	7,720	45.8	49.5	43.7	44.1	49.4	44.1	49.4
600	11,400	12.3	12.3					
700	13,240	9.3	9.3					

These results are represented graphically in Curve B, Plate II.

8. In the next series of experiments we made the time longer, still keeping the temperature low.

TABLE IV.

Details as before. Temp. = 3°. Time = 90 mins.

Water added. In c.c.	Mean percentage of BaCl ₂ In mols. decomposed.	Numbers actually obtained.			
25	820	98.1	98.1		
50	1,280	97.5	97.5		
100	2,200	92.0	92.1	91.9	
200	4,040	83.9	83.9	83.8	
300	5,880	71.5	70.7	69.9	73.0
400	7,720	63.7	63.8	65.8	61.5
500	9,560	44.6	46.4	42.8	
600	11,400	30.7	25.8	32.5	33.8
700	13,240	20.1	23.9	16.3	
800	15,080	24.4		24.4	24.4 24.4

These results are represented graphically in Curve C, Plate II.

9. We now raised the temperature, keeping the time the same as before.

TABLE V.

Details as before. Temp. = 18°. Time = 90 mins.

Water added.		Mean percentage of BaCl ₂ decomposed.	Numbers actually obtained.			
In c.c.	In mols.					
25	820	98.2	98.2			
50	1,280	96.3	96.8	96.3		
100	2,200	94.0	95.5	92.5		
200	4,040	88.2	91.2	85.2		
300	5,880	80.5	81.4	79.7		
400	7,720	67.0	68.9	65.1		
500	9,560	49.9	47.4	52.4		
600	11,400	32.5	34.2	32.2	33.7	31.8
700	13,240	24.8	—	24.8		
800	15,080	10.3	10.3	10.8	9.7	

These results are graphically represented in Curve D, Plate II.

10. Curve B (Plate II) seems to us to show that with a low temperature and a short time (30 minutes), the process of chemical change is retarded to a proportionately greater extent by a large, than by a small quantity of water of dilution. Curve C, which exhibits the influence of the water of dilution at a low temperature, but when the change is allowed to proceed for a longer time (90 minutes) shows the same irregularity in the action of the diluting water. And from Curve D we conclude that when the change is allowed to proceed for a considerable time (90 minutes), the retarding influence exerted by large masses of diluting water is proportionately greater than that exerted by small masses, even when the temperature is allowed to rise to 16° or 18°.

11. In order to explain these results we advance the hypothesis that under the conditions of experiment a number of hydrates of barium chloride tend to form in the solution. Among these hydrates we regard the cryohydrate as occupying an important place.

At moderate temperatures (18°) and short times (30 minutes) we suppose that the tendency to formation of cryohydrate is very small; hence the regular action of the water of dilution (Curve A). At low temperatures, however, even if the time be short, the cryohydrate (along with other hydrates, doubtless) tends to form, and being produced in presence of a large mass of one of the products of its own dissociation, this cryohydrate is somewhat stable. The greater the mass of water, the greater the stability of the cryohydrate, other conditions being constant and any secondary action which may be exerted by the water being disregarded.

When we make the time of action longer, the tendency to formation

PLATE II. (TABLES II to V.)
 BaCl_2 and $\text{K}_2\text{C}_2\text{O}_4$, 1 : 1 molecules.
"Filtration curves."

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PLATE III. (TABLES VI and VII)
 BaCl_2 and $\text{K}_2\text{C}_2\text{O}_4$. 1:1 molecules.
'Pipetting curves'

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of cryohydrate might be expected to become greater, and therefore the Curve C might be expected to approach to or even to overlap the Curve B. But long time of action increases the chance of molecular collisions, and hence of molecular decompositions. Curve C keeps always above Curve B, but exhibits the same general form.

But that time does tend to production of cryohydrate (by our hypothesis), even when temperature rather tends to dissociation of the same, provided the presence of a large quantity of the liquid product of such dissociation be insured, is shown by Curve D, which exhibits much the same general form as B and C.

Now the association of water molecules to the molecules of barium chloride must be attended with loss of energy from the entire system, hence the amount of chemical change becomes proportionately less as the velocity of formation of these complex molecules (by hypothesis) increases.

12. In the next series of experiments the condition of time was arranged so that the precipitated barium oxalate should have completely settled down, leaving a clear supernatant liquid, before the close of the action. A portion of the clear liquid was drawn off by means of a pipette and aspirating arrangement, and the quantity of undecomposed oxalate was determined therein without previous filtration.

TABLE VI.—*Pipetting.*

Details as before. Time = 90 mins. Temp. = 3°.

Water added.		Mean percentage of BaCl ₂ decom- posed.	Numbers actually obtained.						
In c.c.	In mols.								
25	820	98.1	98.1						
50	1,280	97.5	97.5	97.5					
100	2,200	91.6	92.1	91.1					
200	4,040	82.0	81.6	82.5					
300	5,880	67.8	68.4	67.2					
400	7,720	58.0	58.3	57.8					
500	9,560	41.8	42.8	40.8					
600	11,400	27.6	26.2	29.0					
700	13,240	15.0	12.9	16.6	10.2	18.1	17.2		
800	15,080	5.0	4.5	5.5					

Curve A, Plate III, represents these results in graphic form.

13. A series of experiments similar to those just detailed was carried out at a higher temperature.

TABLE VII.—*Pipetting.*

Details as before. Time = 90 mins. Temp. = 16—18°.

Water added.		Mean percentage of BaCl ₂ decom- posed.	Numbers actually obtained.				
In c.c.	In mols.						
25	820	98.2	98.2	—	—	—	—
50	1,280	96.4	96.3	96.8	96.0	—	—
100	2,200	93.5	94.5	92.5	—	—	—
200	4,040	88.4	90.9	85.9	—	—	—
300	5,880	80.0	80.0	80.0	—	—	—
400	7,720	65.9	68.2	63.7	—	—	—
500	9,560	44.3	42.8	45.8	—	—	—
600	11,400	31.2	31.4	31.8	30.6	31.0	—
700	13,240	20.6	18.6	18.9	24.4	—	—
800	15,080	4.5	4.0	4.0	5.5	—	—

See Curve B, Plate III.

14. These results are, we think, in keeping with the hypothesis of par. 11.

Curve A shows, it is true, an almost regular retarding influence exerted by the water of dilution, but we believe that the "pipetting method" of estimation is more delicate than the "filtration method," and that the influence of formation of cryohydrate, &c., is shown by the former method in the early as well as in the later portions of the curve.

Curve B, where the temperature is higher, and, therefore, where one of the conditions of formation of cryohydrate is not fulfilled, exhibits the special influence of water of dilution under consideration only when the quantity of water becomes somewhat large. The same general deduction may be made from the analogous filtration Curve D, Plate II.

15. In repeating some determinations in succeeding portions of the same liquid filtered from barium oxalate, we were astonished to find great discrepancies between the results. If 50 c.c. were withdrawn from the filtrate immediately that, or approximately that quantity of liquid had passed through the filter, the quantity of undecomposed oxalate therein was found to be considerably greater than the quantity contained in the succeeding 50 c.c. withdrawn from the filtrate, filtration being continued with little or no intermission.

We, therefore, made a series of determinations of the influence of water of dilution on the change under consideration, the data being obtained from estimation of undecomposed oxalate contained in the second 50 c.c. of liquid which passed through the filter.

PLATE IV. (TABLE VIII)

 BaCl_2 and $\text{K}_2\text{C}_2\text{O}_4$ 1 : 1 molecules.*Journ. Chem. Soc. Feb. 1880.**Comparison of "Pipetting" and "Filtration Curves" at 3°.*

PLATE V. (TABLE VIII).

Journ. Chem. Soc. Feb. 1880. BaCl_2 and $\text{K}_2\text{C}_2\text{O}_4$. 1:1 molecules.*Comparison of "Pipetting" and "Filtration Curves" at 18°*

TABLE VIII.—*Second Filtrates.*

Series A. Details as before. Time = 90 mins. Temp. = 3°.

In c.c.	Water added.	Mean percentage of BaCl ₂ decomposed.	Numbers actually obtained.			
	In mols.					
100	2,200	93.4	93.7	93.1		
300	5,880	71.6	70.0	73.2		
500	9,560	52.6	50.8	54.4		
600	11,400	34.9	32.5	37.3		
700	13,240	34.2	32.5	36.0		

Series B. Time = 90 mins. Temp. = 18°.

100	2,200	95.4	96.0	94.8		
200	4,040	89.0	91.5	86.5		
300	5,880	80.8	81.9	79.7		
400	7,720	67.4	69.9	65.0		
500	9,560	51.1	53.8	48.4		
600	11,400	35.3	36.0	34.7		
700	13,240	32.5	35.7	32.3	31.0	30.4

In Plates IV and V these results are graphically represented by Curves A and A' respectively. The Curves B and C of Plate IV, and B' and C' of Plate V, represent the results of "pipetting" and "first filtrate" determinations under the same conditions of time and temperature as those under which the data of A and A' were determined.

16. From the curves of Plate IV it is apparent that the influence exerted by water of dilution on the chemical change under consideration, at low temperatures and moderate degrees of dilution, is much the same whether the data be obtained by analyses of the liquids removed from above the precipitated barium oxalate, by pipetting, or by filtration. When, however, large amounts of water are added, the results show considerable differences, according as the pipetting or filtration process is adopted, the latter process exhibiting the change as proceeding to a greater extent than the former.

We think that these results may be explained by supposing that at a low temperature and with much water the tendency to formation of cryohydrate reaches a maximum, and that under these conditions the whole system of chemical molecules is thrown into a state of strain from which it is partly relieved by the process of filtration, the result of this relief being that the molecular equilibrium is upset, and that the velocity of the decomposition of barium chloride by potassium oxalate is suddenly increased.

If there be elements of truth in this explanation, we should expect to find smaller differences in the results obtained by the methods—

pipetting and filtration—when the conditions of experiment were rendered less favourable to formation of cryohydrate molecules. One less favourable condition is maintenance of higher temperature. The curves of Plate V (when compared with those of Plate IV) show that the results obtained from “pipetted liquid,” “first filtrate,” and “second filtrate” respectively, agree much more closely when the temperature is 18° than when the temperature is 3° .

Again, with small quantities of water of dilution, *i.e.*, with a condition unfavourable to formation of cryohydrate, the differences between the results obtained by the “pipetting,” and those by the “first filtrate” methods are reduced almost to zero, even at 3° ; at this temperature “pipetted” results differ slightly, but only slightly, from “second filtrate” results, while at 18° the results obtained by both methods are almost identical. A small number of experiments carried out at a higher temperature, 50° , showed that identical results are obtained at this temperature by the three methods with a dilution of 400 c.c. and 800 c.c.

It is difficult to foretell what influence would be exerted on the general stability of the system at a low temperature by variations in the time of action. The numbers obtained by us seem to show that the system is in a state of greater strain at 3° , after the expiry of 30 minutes than when 90 minutes have elapsed. Thus the mean percentages of barium chloride decomposed at 3° after 30 minutes' action, as measured by analysis of the first and second 50 c.c. of filtrate, were respectively:—

c.c. water added.	First 50 c.c.	Second 50 c.c.	Difference.
100	74.8	77.3	2.5
300	61.2	71.4	10.2
400	45.8	68.4	22.6

The results obtained under the same conditions, save making time = 90 minutes, are stated for sake of comparison.

c.c. water.	First 50 c.c.	Second 50 c.c.	Difference.
100	92.0	93.4	1.4
300	71.5	71.6	0.1
400	63.7	65.0	1.3

The system would thus appear to be in a state of maximum strain when the conditions favourable for formation of cryohydrate are ensured, *viz.*, low temperature and much water, and when the time of action is short. We are almost inclined to believe that under these conditions the cryohydrate molecules are in process of formation, whilst after a longer time the molecules are, to a great extent, formed,

and that therefore the system, although yet very unstable, is nevertheless more stable than it was under the former time conditions.

17. We do not attempt to propound any exact hypothesis as to the action of the filter in inducing a sudden increase in the velocity of the chemical change. It may be that the reacting molecules are brought into closer contact in the pores of the filter,* or it may be that when a portion of the liquid, the constituents of which are by our hypothesis in a state of strain, is removed from the main liquid, decomposition is induced in the separated portion by the small change of temperature which is undergone by the solution during its passage through the filter, or perhaps by the mechanical action of the surface of paper to which the solution is for a time exposed.

A few determinations were made of the amount of change when calculated from data obtained by analyses of the third 50 c.c. of filtrate. These determinations were almost identical with those obtained from the second 50 c.c., but considerably higher than those obtained from the first 50 c.c. of filtrate.

The results obtained by the pipetting and filtration methods are stated in percentages of total barium chloride decomposed: the rapid change which occurs while filtering under certain conditions of dilution and temperature, occurs in that small isolated portion of the general chemical system which is placed upon the filter, but the amount of change is calculated as if that change proceeded to the same extent within the whole liquid. The exposure of the whole liquid to a very slightly higher temperature, or to passage through a filter, would not necessarily produce a change to the same extent as is produced in the small isolated portion.

Certain experiments, which we have not as yet continued, seemed to show that, if, when strontium sulphate is precipitated from a dilute solution of the chloride by addition of sulphuric acid, and when the liquid above the precipitate is perfectly clear, a portion of this clear liquid be isolated from the main portion by withdrawal in a pipette, the clear liquid so isolated quickly becomes turbid, because of renewed precipitation of strontium sulphate.

18. The individual results contained in many of the foregoing tables show considerable discrepancies among themselves; these discrepancies are not, however, in our opinion, contradictory of the hypothesis which we have advanced.

The method of determining the amount of chemical change which we have used is fitted to give fairly accurate results if the mean of several determinations be adopted, but the occurrence of small differences between the numbers actually obtained is to be expected.

The discrepancies are most marked when dealing with dilute solu-

* In connection with this, compare Bayley, this Journal, 1878, Trans., p. 304.

tions, a low temperature and a short time of action; they become less marked when the temperature is high, the solutions less dilute, or the time longer; further the results obtained by the "pipetting" method show, on the whole, fewer discrepancies than those obtained by the method of "filtration." In other words when the system is, by hypothesis, in a condition of strain, differences between the individual results are noticeable, but when the conditions favourable to production of such strain are removed, the discrepancies among the individual results tend also to disappear.

19. In paragraph 4 it was stated that the influence of water of dilution on the reaction between strontium chloride and sulphuric acid had been examined, but that the numbers obtained led apparently to no general results. We think that the great discrepancies noticed between the numbers obtained may be explained by the hypothesis already advanced. Sulphuric acid forms many hydrates with water, and is doubtless able to attach to itself large numbers of water molecules. If our hypothesis be true, we should expect a system containing sulphuric acid, much water, and such a salt as strontium chloride, to be in an eminently strained condition, and therefore to be capable of having its equilibrium upset by very small amounts of impressed force.

Now, unless very special precautions were taken to maintain the conditions of each experiment altogether unchanged during the whole course of that experiment, and unless a very delicate method of determining the amount of change, under given conditions, were adopted, we should expect to obtain discordant results. But we did not adopt such *special* precaution, nor was the method of measuring the amount of change characterised by extreme delicacy.*

The results obtained were therefore discordant, as indeed we should expect them to be if our hypothesis be correct. We subjoin a few of the actual numbers obtained.

* The method consisted in filtering a portion of the clear liquid, precipitating undecomposed strontium chloride as carbonate, dissolving in standard acid, and determining residual acid by titration with standard alkali.

PLATE VI. (TABLE X).

 Ba_2NO_3 and $\text{K}_2\text{C}_2\text{O}_4 = 1:1$ molecules.

"Pipetting" and "Filtration Curves"

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TABLE IX.—*Strontium Chloride and Sulphuric Acid.*

20 c.c. SrCl_2 solution used = 354.64 mgrms. SrCl_2 . 8.8 c.c. H_2SO_4 solution used = 877.52 mgrms. H_2SO_4 .

$\text{SrCl}_2 : \text{H}_2\text{SO}_4 = 1 : 4$ mols. Temp. = 16–18°.

c.c. water added.	Percentage of SrCl_2 decomposed.				
	Time = 60 mins.			Time = 18 hours.	
25	75.9	—	—	—	—
50	73.6	—	—	—	—
75	62.9	66.1	77.3	78.7	68.5
100	52.8	67.2	64.7	—	—
125	47.7	—	—	—	—
150	33.7	49.6	—	33.7	38.3
175	46.2	—	—	—	—
200	27.4	—	—	—	—
225	29.7	—	—	24.9	43.3
250	27.8	—	—	—	—

Time = 60 mins. $\text{SrCl}_2 : \text{H}_2\text{SO}_4 = 1 : 2.5$ mols.

25	70.1	67.5	85.5	—	—	—
50	74.5	60.4	56.4	—	—	—
90	52.0	53.0	—	—	—	—
100	49.5	51.7	55.1	—	—	—
125	45.2	51.1	39.4	50.2	46.0	54.4
150	36.9	22.5	21.5	32.2	—	—
175	14.2	24.8	10.6	—	—	—

20. As a further test of the value of our hypothesis, we carried out a short series of determinations of the influence of water of dilution on the change which occurs when barium nitrate is decomposed by means of potassium oxalate.

TABLE X.—*Barium Nitrate and Potassium Oxalate.*

Used 10 c.c. Ba_2NO_3 solution = 800 mgrms. Ba_2NO_3 , and 9.4 c.c.

$\text{K}_2\text{C}_2\text{O}_4$ solution = 509 mgrms. $\text{K}_2\text{C}_2\text{O}_4$.

$\text{Ba}_2\text{NO}_3 : \text{K}_2\text{C}_2\text{O}_4 = 1 : 1$ mols. *Pipetting.* Time = 90 mins.

c.c. water added.	Percentage Ba_2NO_3 decomposed.	
	3°.	18°.
100	85.4	91.8
300	58.4	76.4
500	39.4	50.3
700	9.1	25.3

Filtration (first 50 c.c.) results. Time = 90 mins. Temp. = 3°.

c.c. water added.	Percentage Ba ₂ NO ₃ decomposed.
0	98·7
25	96·9
50	95·8
100	83·0
300	70·5
500	53·0
700	29·5

These results are represented graphically in Curves A, B, and C, Plate VI.

The "pipetted" results show little or no indication of formation of hydrates: in the "filtered" results on the other hand such indication is clearly shown when the quantity of water of dilution becomes considerable.

21. We subjoin certain data taken from Guthrie's papers regarding the cryohydrates of the salts employed by us.

BaCl ₂ .2H ₂ O cryohydrate solidifies at	— 8°	with 37 mols. of water.
SrCl ₂ .6H ₂ O	"	" —17° " 23 "
CaCl ₂ .3H ₂ O	"	" —37° " 12 "
Ba ₂ NO ₃	"	" — 0·8° " 259 "
K ₂ C ₂ O ₄	"	" + 6·3° " 17 "

In the reaction in which calcium chloride was decomposed by addition of sodium carbonate, the influence of water of dilution on the change was regular; because, on our hypothesis, the tendency to formation of the cryohydrate of calcium chloride is but feebly marked under any experimental conditions realised by us. In the reaction between barium nitrate and potassium oxalate the influence of water of dilution is regular; because, the cryohydrate of barium nitrate tends to be formed in considerable quantity under the experimental conditions employed. But if the determinations of the amount of change are made in the filtered liquid, then the results show large differences from those obtained by the "pipetting" method; because, the equilibrium of the system, although sufficiently stable to resist overthrow by the mere process of pipetting off a portion thereof, is nevertheless disturbed by the process of filtration.

Further, the influence of water of dilution on the change which occurs when barium chloride and potassium oxalate mutually react, is irregular; because—on our hypothesis—the cryohydrate of barium chloride tends to be formed under the conditions of experiment, but not to be formed to such an extent as renders the system, comparatively, stable.

PLATE VII.

BaCl_2 and $\text{K}_2\text{C}_2\text{O}_4$. 1:1 molecules. - 3 and 18°.

Influence of Time.

Journ. Chem. Soc. Feb. 1880.

A comparison of the "filtration" and "pipetted" curves for barium nitrate with those for barium chloride, under the same conditions of temperature and time (A and C, Plate VI, with C and B, Plate IV), shows that the difference between the results obtained by the two methods is much greater in the case of the nitrate than in that of the chloride.

On our view of the influence of water of dilution, the very stability of the barium nitrate solution (because of the large formation of cryohydrate) would be looked on as the reason why, when that stability is overthrown, the velocity of the chemical change is so largely increased.

22. But there is an aspect of the influence of water of dilution other than that which we have hitherto regarded.

The addition of much water might be supposed to bestow upon the reacting system a greater degree of molecular mobility than would be possessed by a more concentrated solution. Chemical change should therefore occur with greater readiness in the former than in the latter liquid. But at the same time the chances of molecular encounters, and therefore of molecular decompositions, occurring in unit time, must be smaller in dilute than in concentrated liquids, notwithstanding the greater mobility of the former system. Therefore we should conclude that the influence on the chemical change of small impressed forces would be more marked in dilute than in less dilute solutions, while at the same time the total amount of change under the same conditions would be greater in the more concentrated solutions.

Dewille (*Phil. Mag.* [4], **32**, 365) has advanced a theory of the influence of dilution, in which he supposes that energy of position is actually gained by the reacting molecules when dilution is increased, and that this energy may be changed into mechanical work, whereby again heat may be evolved sufficient to raise some of the chemically active molecules present to their dissociation-temperature, *i.e.*, to shatter them into their constituent atoms.

But without pushing the influence of dilution so far as this, we think we are justified in supposing that in addition to the loss of energy involved in the formation of complex (cryohydrate) molecules, there would be a gain of mobility in the case of those molecules of the reacting bodies which had not thus associated to themselves large numbers of water molecules. Dilution would thus exert two, more or less opposing, actions.

The general result of a series of experiments, carried out by one of us,* is in keeping with the hypothetical deduction that impressed force should produce greater differences in the amount of chemical change when dilute, than when more concentrated solutions, are used.

* See next paper.

23. How should time influence the process of chemical change, specially studied by us, when taking place in dilute solutions, as compared with the influence of the same variable on the same change occurring in more concentrated solutions?

It is not easy to answer this question on *à priori* grounds. The influence exerted by time we should expect to vary, according as a low or a high temperature is maintained. At a low temperature formation of cryohydrate would tend to be increased by increasing time of action; but if dilution act by increasing molecular mobility, as well as by increasing formation of complex (cryohydrate) molecules, we should almost expect that the differences between the total amounts of change, in long, and in short, times, would be less in dilute, than in concentrated solutions.

In a tolerably concentrated solution at a low temperature we have, by hypothesis, a tendency to formation of cryohydrate molecules; water is added, and thereby the tendency aforesaid is increased, but simultaneously molecular mobility is imparted to the system; the greater the amount of mobility the more rapidly will the chemical change proceed: in other words, in dilute solutions the chemical change will complete itself more rapidly than in less dilute solutions. Now if the tendency to formation of cryohydrate be small, *e.g.*, if temperature be somewhat high, the influence of time should probably be less marked than if the tendency to formation of cryohydrate be large.

The results already detailed are arranged in graphic form in Plate VII, with the view of illustrating the influence of time. Curves A and B, which represent results obtained at 3° , show little difference between the action of time in concentrated and in dilute solutions; but Curves C and D show that at a higher temperature (18°) the influence of time is less marked when much water of dilution is present.

If, however, the difference between the times of action were made very considerable, the temperature being somewhat higher than that at which cryohydrate may be supposed to form rapidly, then we think that the curves representing the results at the two times should diverge largely. Now the curves of Plate VIII, representing results after 90 minutes (A), and after 5 hours (B) at 18° , diverge very largely.

The following table contains the results obtained for 5 hours' action at 18° by the pipetting method (Curve B of Plate VIII):—

PLATE VIII.

 BaCl_2 and $\text{K}_2\text{C}_2\text{O}_4$, 1:1 molecules. - 18°.*Influence of Time.**Journ. Chem. Soc. Feb. 1880.*

c.c. water added.	Mean percentage of BaCl ₂ decomposed.	Numbers actually obtained.	
50	97·6	97·6	97·7
100	95·6	95·6	95·6
300	85·2	85·5	84·9
500	75·7	77·4	74·1
700	59·3	60·4	58·1
900	44·7	44·7	—
1100	18·7	18·3	19·1

24. Every chemical system appears to tend towards that condition of equilibrium, the attainment of which is marked by the greatest loss of energy. It may, perhaps, be more correct to say that the entropy of chemical systems, *i.e.*,—that portion of the energy, which, being dependent on the configuration of the parts of the system, is available as mechanical energy,—continually tends to become less.

This tendency to dissipation of energy may be arrested in various ways, among others by impressing upon the system what may perhaps be described as an artificial state of equilibrium.

Thus, the condition of most stable equilibrium for a system originally consisting of barium chloride and potassium oxalate molecules, would be that in which barium oxalate and potassium chloride molecules are produced, but by adding much water a portion of the reacting molecules are, by our hypothesis, loaded with water of hydration. In this loading energy is lost, but less energy than would be lost by the formation of molecules of potassium chloride and barium oxalate; the system is therefore in an unstable condition, but a certain degree of stability is impressed upon it by the presence of a large mass of one of the products of dissociation of the complex and unstable hydrated molecules.

We have thus a system in a state of strain because of the stress between its parts. A small force may be sufficient to relieve the strain, and this relief may be attended with a rapid rearrangement of the parts of the system, and with a large decrease in the entropy of the system.*

25. If the state of the system which we have endeavoured to picture in the foregoing sentences be at all correspondent with the actual state of the system, we should expect small differences in physical conditions to produce much greater variations in the amount of chemical change, in dilute, than in more concentrated solutions.

The following results are in keeping with this supposition:—

* We seem to have here an action opposed to that designated "chemical induction," by Bunsen and Roscoe (*Phil. Trans.*, 1857). The state of a system of heterogeneous molecules capable of mutual chemical action is compared by these chemists to that

TABLE XI.—*Pipetting.*

$\text{BaCl}_2 : \text{K}_2\text{C}_2\text{O}_4 = 1 : 1$ mol. Temp. = 20° . Water of dilution = 1100 c.c.

	Percentage of BaCl_2 decomposed.					
	Time = 5 hours.		Diff.	Time = 28 hours.		Diff.
Roughened beaker ..	31.2	34.8	3.8	67.8	66.3	1.5
Broken glass in beaker	9.7	39.8	30.1	66.3	60.6	5.7
Oxalate added with constant stirring....	11.0	37.0	26.0	67.1	59.9	7.2
Oxalate added on surface; after 15 minutes whole stirred up....	14.0	39.1	25.1	62.7	62.1	0.6

Temp. = 20° . Time = 90 mins.

	Percentage of BaCl_2 decomposed.					
	Dilution = 800 c.c.			Dilution = 700 c.c.		
			Diff.			Diff.
Roughened beaker ..	1.5	3.5	2.0	24.3	21.7	2.6
Broken glass in beaker	1.0	3.0	2.0	7.0	11.0	4.0
Oxalate added with constant stirring....	6.8	3.8	3.0	22.4	16.5	5.9
Oxalate added on surface; after 15 minutes whole stirred up....	3.0	1.0	2.0	11.1	11.1	0.0

Temp. = 20° . Water of dilution = 700 c.c.

	Percentage of BaCl_2 decomposed.					
	Time = 90 mins.		Diff.	Time = 24 hours.		Diff.
Roughened beaker ..	24.3	21.7	2.6	81.6	—	—
Broken glass in beaker	7.0	11.0	4.0	79.3	—	—
Oxalate added with constant stirring....	22.5	16.5	5.9	79.3	81.1	1.8
Oxalate added on surface; after 15 minutes whole stirred up....	11.1	11.1	0.0	79.3	—	—

of a wire with a certain weight attached; induction tends to remove the weight. But the addition of water to the system considered by us tends to increase this weight, and so to elongate the wire. Remove the weight, however, and the wire suddenly contracts.

Time = 30 mins.

	Percentage of BaCl ₂ decomposed.	
	Temp. = 20°.	Temp. = 70°.
Dilution = 800 c.c. . .	0·0	1·0
„ = 700 c.c. . .	3·7	33·7

(See also curves of Plate VII.)

26. From these results it is apparent that physical differences affect the total amount of chemical change when much water of dilution is present and the time of action is moderately short (*see 700 c.c. 90 minutes*). Further, that if the amount of dilution-water is made very large, the differences between the results obtained become immense, showing how the action is disturbed by very small alterations in physical conditions (*see 1100 c.c. 5 hours*). But that, if the time of action be prolonged, the results become tolerably concordant, and that those physical conditions which were made the subject of examination, but slightly affect the final amount of chemical change, when that change is allowed to proceed for prolonged periods, even when in exceedingly dilute liquids (*see 1100 c.c. 28 hours, and 700 c.c. 24 hours*).

Further, we conclude from these numbers that, if the amount of water of dilution be so large, and the time of action be such, that but a very small amount of chemical change ensues, then the amount of that change is only slightly affected by the changes in physical conditions to which the liquids were subjected in our experiments (*see 800 c.c. 90 minutes*).

The results of Table XI, bearing upon the influence of temperature corroborate those of par. 22, viz., that in dilute solutions rise of temperature largely increases the amount of chemical change: the experiments made with 800 c.c. of water of dilution, however, show that, if the amount of change at a moderate temperature be almost nothing, a rise of temperature scarcely affects the total decomposition.

27. We think that the experiments recorded in the present paper justify our general hypothesis, viz., that the amount of chemical change which occurs when barium chloride and potassium oxalate are mixed in the proportion of 1 : 1 molecules, is irregularly affected by variations in the mass of water of dilution present, because the entire system is brought into a state of strain due to the stress between its parts; and that the principal forces of which this stress is compounded, are, the force tending to produce cryohydrate—and other hydrated—molecules the force tending to split up these molecules, and the force tending to separate, and so to impart greater mobility to, the chemically active molecules of the system.

The results which we have obtained are, it seems to us, corrobora-

tive of what may be called "the kinetic theory of chemical action," viz., that systems apparently stable are continually undergoing atomic interchanges.

We have spoken of a system of chemically active molecules as being, under certain conditions, in a state of strain; we believe that analogies with this state may be found in supersaturated solutions,* colloidal molecules,† and that "particular condition of bodies in which they are the *débris* of some compound, and not proper chemical compounds of their constituents."‡