XXXIX.—CONTRIBUTIONS FROM THE LABORATORY OF
GONVILLE AND CAIUS COLLEGE, CAMBRIDGE.No. 1.—*On conditions affecting the Equilibrium of certain Chemical Systems.*

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It is well known that a given chemical system is capable of assuming more than one stable configuration, each configuration being conditioned by certain physical circumstances. Temperature, time, mass, &c., &c., all exert a more or less marked influence upon the chemical distribution, at any moment, of the masses of matter which comprise a given system.

When all the members of such a system are free to act and react, the influence of extraneous physical forces upon the stability of the system is very marked (see Gladstone, this Journal, **9**, 54; Harcourt, *ibid.*, **20**, 460; Lemoine, *ibid.*, 1877, ii, 828, &c., &c.).

But even in cases where one, or more of the compounds produced during the change from one configuration to another is partially removed from the sphere of action, we find that the points of maximum stability vary with variations in physical conditions.

If one of the products of the change be gaseous, and if the change be allowed to proceed in an enclosed space, a series of states of stable equilibrium is attained, each marked by a different tension of the gaseous product of the change. The conversion of phosphorus α into phosphorus β , and the oxidation of phosphorus, in pure oxygen, only under diminished pressure, are cases in point.

If each chemical system be characterised, as it undoubtedly is, by the possession of a definite amount of energy, then any force which tends to alter that energy will also tend to disturb the chemical equilibrium of the system.

Such forces are time, temperature, mass, concentration, nature of the containing vessel, &c., &c. If any, or several, of these conditions be largely exaggerated, abnormal results may be obtained. Thus Troost and Hautefeuille (this Journal, 1877, ii, 273) state that if oxygen be submitted to the action of the silent discharge at a temperature of 1300° , while the outer portions of the oxygen are cooled to a moderate temperature, ozone is produced.

If the passage from one configuration to another be attended with a loss of energy, that passage usually occurs. Thus Berthelot (this Journal, 34, 108) shows that dry BaO_2 is stable, while moist BaO_2 slowly changes to BaH_2O_2 ; now the change $\text{BaO}_2 = \text{BaO} + \text{O}$ would involve an absorption of about six units of heat, but the change $\text{BaO}_2 + \text{H}_2\text{O} = \text{BaH}_2\text{O}_2 + \text{O}$ is accompanied by the evolution of nearly three units of heat.

If the view be adopted that in a chemical system which is in stable equilibrium, atomic interchanges are constantly occurring to a greater or less extent, and that so long as the molecular decompositions and recompositions are equal in unit of time, the configuration remains stable, but that any action which tends to increase the former without directly influencing the latter, tends to disturb the equilibrium, then I think we are presented with a fairly workable hypothesis to guide us in our examination of the conditions which influence chemical equilibrium.

It is the object of the present paper to examine in some detail the conditions which affect two cases of chemical equilibrium, with the view of arriving at general results concerning these conditions, and, if possible, of throwing some light upon the general conditions affecting the equilibrium of such chemical changes as result in the production of comparatively insoluble compounds.

1. The action formulated $\text{BiCl}_3 + x\text{H}_2\text{O} = \text{BiOCl} + 2\text{HCl} +$

INFLUENCE OF MASS.

Nº 1. Solution. — Initial state = $\text{BiCl}_3 : \text{HCl} : \text{H}_2\text{O} = 1 : 2.6 : 192$ mols. Temperature = ordinary.

Nº 2. Solution. — Initial state = $\text{BiCl}_3 : \text{HCl} : \text{H}_2\text{O} = 1 : 2.5 : 37.5$ mols.

Temperature = ordinary.

$x\text{H}_2\text{O}$, presents us with a chemical change, the investigation of which seemed likely to throw light upon the subject of chemical equilibrium. The products of this change, viz., hydrochloric acid and bismuthyl chloride, are not without chemical action upon each other: the change is one which admits of tolerably accurate measurement without the introduction of a foreign body, the entrance of which might disturb the equilibrium of the reacting system.

2. Solutions of pure bismuthous oxide in hydrochloric acid (containing known amounts of the acid and water) were prepared, and the proportion between bismuthous chloride, hydrochloric acid, and water molecules in each solution was calculated. A measured volume of each liquid was placed in a suitable vessel, and a quantity of water, representing a determinate number of molecules, was run in from a measuring vessel. The liquid was thoroughly shaken, and then allowed to remain at rest for a fixed number of minutes, hours, or days. At the expiry of the proper time, the whole or a portion of the clear supernatant liquid was withdrawn, run through a dry filter if necessary, and the amount of bismuth remaining in solution was determined in an aliquot portion of this liquid. Many of the experiments were made in duplicate.

From the results obtained the proportion of bismuthous chloride which had been converted into oxychloride was calculated.

3. The following tables, I to IV, comprise the more important numerical results, as these bear upon the question of the disturbing influence of mass of water and of bismuthous chloride.

TABLE I.—*Influence of mass.* (Compare curves of Table A.)

13.816 grams Bi_2O_3 dissolved in 239 c.c. aqueous HCl (1 c.c. = 0.2701 gram HCl and 0.8519 gram H_2O) and 1.8 c.c. H_2O added.

After solution have	18.687 grams BiCl_3 .	Solution No. 1.
	58.095 „ HCl .	
	207.852 „ H_2O .	

or in molecular proportion, $\text{BiCl}_3 : \text{HCl} : \text{H}_2\text{O} = 1 : 26 : 192$.

10 c.c. solution used for each experiment: Time = 76 hours. Temperature = ordinary (summer).

	Molecules.			
	$\text{BiCl}_3 : \text{HCl} : \text{H}_2\text{O}$			Percentage of BiCl_3 decomposed.
<i>a</i>	1 : 26 :	3,500		70·84
<i>b</i>	1 : 26 :	4,000		81·94
<i>c</i>	1 : 26 :	4,500		86·58
<i>d</i>	1 : 26 :	5,000		91·46
<i>e</i>	1 : 26 :	5,500		94·17
<i>f</i>	1 : 26 :	6,000		94·82
<i>g</i>	1 : 26 :	6,500		98·19
<i>h</i>	1 : 26 :	7,000		97·93
<i>j</i>	1 : 26 :	7,500		98·22
<i>k</i>	1 : 26 :	8,000		98·38
<i>l</i>	1 : 26 :	9,000		98·69
<i>m</i>	1 : 26 :	10,000		99·02
<i>n</i>	1 : 26 :	12,500	{ trace only unde- composed.	
<i>o</i>	1 : 26 :	15,000		100·00

TABLE II.—*Influence of mass.*

52·727 grams Bi_2O_3 dissolved in 170·3 c.c. same aqueous HCl.

After solution have 71·317 grams BiCl_3 . Solution No. 2.
 21·325 „ HCl.
 151·162 „ H_2O .

or in molecular proportions, $\text{BiCl}_3 : \text{HCl} : \text{H}_2\text{O} = 2 : 5 : 75 = 1 : 2·5 : 37·5$.

Series A.—10 c.c. solution used for each experiment. Time = 48 hours. Temperature = ordinary.

Molecules.			Percentage of BiCl_3 decomposed.
	$\text{BiCl}_3 : \text{HCl} : \text{H}_2\text{O}$		
<i>a.</i>	1 : 2·5 :	100	23·16
<i>b.</i>	1 : 2·5 :	500	93·22
<i>c.</i>	1 : 2·5 :	1,000	99·08
<i>d.</i>	1 : 2·5 :	1,260	99·65

Series B.—5 c.c. solution used for each experiment; other details as before.

e..	1	: 2·5 :	100	28·49
f..	1	: 2·5 :	500	93·11
g..	1	: 2·5 :	1,000	99·34
h..	1	: 2·5 :	1,250	99·67

TABLE III.—*Influence of mass.*

13·4682 grams Bi_2O_3 dissolved in 46 c.c. prepared acid.

After solution have 18·2166 grams BiCl_3 . Solution No. 3.
 6·1222 „ HCl .
 40·7414 „ H_2O .

or in molecular proportions, $\text{BiCl}_3 : \text{HCl} : \text{H}_2\text{O} = 1 : 3 : 40$.

10 c.c. solution used for each experiment. Time = 76 hours.
 Temperature = ordinary.

Molecules.		
$\text{BiCl}_3 : \text{HCl} : \text{H}_2\text{O}$		Percentage of BiCl_3 decomposed.
1 : 3 : 245.....		56·12
1 : 3 : 490.....		95·45
1 : 3 : 735.....		97·47
1 : 3 : 1,000.....		99·12

TABLE IV.—*Influence of mass.*

3·757 grams BiOCl dissolved in 13 c.c. prepared acid.

After solution have 4·547 grams BiCl_3 . Solution No. 4.
 2·4625 „ HCl .
 11·3337 „ H_2O .

or in molecular proportions, $\text{BiCl}_3 : \text{HCl} : \text{H}_2\text{O} = 1 : 4 : 40$.

Molecules.		
$\text{BiCl}_3 : \text{HCl} : \text{H}_2\text{O}$		Percentage of BiCl_3 decomposed.
1 : 4 : 500.....		67·93
1 : 4 : 1,000.....		98·53
1 : 4 : 1,500.....		99·62

4. The number of water molecules present exerts a most marked influence upon the course of the chemical change. It is very probable that the addition of a small quantity of water to a solution containing bismuthous chloride and hydrochloric acid, causes the decomposition of a few of the former molecules, but if this be so, it is evident that the reverse action ($\text{BiOCl} + 2\text{HCl} = \text{BiCl}_3 + \text{H}_2\text{O}$) takes place, the result being an apparent maintenance of the original state of equilibrium. In order that the primary action shall preponderate over the reverse action, the number of water molecules must be very large as compared with that of hydrochloric acid molecules present.

5. If the initial and final states of the reacting system be alone taken into consideration, a definite proportion is found to hold between the number of hydrochloric acid and of water molecules.

Certain of the intermediate states of the system will be considered in the sequel.

To find the proportion existing between the numbers of the various molecules present, when the whole of the bismuthous chloride is converted into oxychloride, it is of course requisite that the hydrochloric acid produced in the reaction (BiCl_3 produces 2HCl) be taken into account. This being done, the general result is that from 450 to 460 molecules of water must be present for each molecule of hydrochloric acid, in order that one molecule of bismuthous chloride may be completely converted into bismuthyl chloride. In No. 1 solution the molecular proportion at the close of the action was $\text{BiCl}_3 : \text{HCl} : \text{H}_2\text{O} = 1 : 1 : 450$; in No. 2 = $1 : 1 : 460$; and in No. 4 = $1 : 1 : 450$. As the reaction was not carried to entire completion in No. 3 solution, the numbers obtained with that liquid are omitted in this calculation.

When it is remembered that the three liquids contained very different absolute quantities of the reacting bodies, and also when the results detailed in Table II, Series A, are compared with those in the same table, Series B, I think it is evident that the general result just stated holds good, independently of the original degree of concentration of the liquids, and of the absolute amount of liquid used.

Some of the results detailed in Tables I to IV are graphically represented by the curves of Table A.

6. Let me consider the influence of time upon the reaction under consideration. The numerical results obtained are arranged in Tables V, VI, and VII, and graphically in the curves of Table B. The broken curves of Table C represent some of the numerical results of Table VII.

It is apparent from these numbers that when comparatively few water molecules are present chemical change proceeds with no great velocity, and that when, in round numbers, three-fourths of the total decomposition is accomplished, the velocity of the change greatly diminishes. If, however, large numbers of water molecules be present, the total change is accomplished in an exceedingly short space of time, the amount of change being indeed independent of the time of action. If the amount of water added be sufficient to decompose the greater part but not the whole of the bismuthous chloride present, then it is found that a state of what appears to be stable equilibrium is very quickly established in the reacting system, and that this state is maintained for periods of time amounting certainly to 14 days. My experiments do not allow me to say positively whether this equilibrium is finally disturbed or not, but I am inclined to believe that the action of time alone is insufficient to produce any larger amount of chemical change. When 8,000 water molecules are present for each molecule of bismuthous chloride and of hydrochloric acid, a state of practically

stable equilibrium is attained in ten minutes, by the system of bismuthous chloride, bismuthyl chloride, hydrochloric acid, and water molecules, and this state is scarcely changed after the expiry of 14 days. Experiments with solutions of calcium chloride and sodium carbonate, to be detailed in the sequel, show that the state of equilibrium attained in this case, after two or three hours, is maintained unchanged after the expiry of 39 days.

TABLE V.—*Influence of time.* (Compare curves of Table B).

Solution No. 1. $\text{BiCl}_3 : \text{HCl} : \text{H}_2\text{O} = 1 : 26 : 192$ mols.

Molecules.		Time.	Percentage of BiCl_3 decomposed.
BiCl_3	$\text{HCl} : \text{H}_2\text{O}$		
1 : 26 :	3,500	53 mins.	30·03
		48 hours	67·85
		76 „	70·84
		9 days	70·70*
1 : 26 :	5,500	76 hours	94·17
		14 days	94·95
1 : 26 :	6,000	76 hours	94·82
		14 days „ ..	95·71
1 : 26 :	6,500	76 hours	98·19
		14 days	96·47
1 : 26 :	7,500	30 mins.	97·09
		8 hours	97·55
		18 „	98·08
		76 „	98·22
1 : 26 :	8,000	10 mins.	95·39
		76 hours	98·38
		14 days	97·78
1 : 26 :	9,000	76 hours ..	98·69
		14 days	99·31
1 : 26 :	10,000	10 mins.	98·48
		76 hours	99·02
		14 days „ ..	99·40
1 : 26 :	12,500	76 hours	{ trace only unde- composed.
		14 days	

* In this experiment the BiCl_3 solution was added, in small successive portions, to the water.

TABLE VI.—*Influence of time.*Solution No. 2. $\text{BiCl}_3 : \text{HCl} : \text{H}_2\text{O} = 1 : 2.5 : 37.5$ mols.

Molecules.		Time.	Percentage of BiCl_3 decomposed.
BiCl_3	$\text{HCl} : \text{H}_2\text{O}$		
1 : 2.5 :	500	48 hours	93.22
		14 days	93.99
1 : 2.5 :	1,000	48 hours	99.08
		14 days	99.36
1 : 2.5 :	1,250	48 hours	99.65
		14 days	99.68

TABLE VII.—*Influence of time.* (Compare broken curves of Table C.)Solution No. 1. $\text{BiCl}_3 : \text{HCl} : \text{H}_2\text{O} = 1 : 26 : 192$ mols. "Surface addition" (see p. 322).

Molecules.		Time.	Percentage of BiCl_3 decomposed.
BiCl_3	$\text{HCl} : \text{H}_2\text{O}$		
1 : 26 :	2,900	3 mins.	12.19
		35 "	23.26
		24 hours	46.99
		76 "	60.20
1 : 26 :	3,000	3 mins.	18.61
		35 "	27.09
		24 hours	50.91
		76 "	64.45
1 : 26 :	3,500	3 mins.	50.26
		35 "	50.52
		48 hours	68.85

7. The following equation presents a general statement of the action of water upon bismuthous chloride, in presence of hydrochloric acid:—

The greater the value of x'' on the left-hand side of the equation—the values of x and x' being constant—the more rapidly will a condition of equilibrium be attained among the reacting molecules; the smaller also will be the value of n ; if x'' be very large, the element of time may be neglected. If x'' have a small value, the value of n will vary at different moments, and this value will always remain somewhat large.

8. I have already considered the case in which n becomes equal to zero, and have shown that the value of x'' varies from 450 to 460 times

TABLE B. (For numerical details see Tables V and VI.)

INFLUENCE OF TIME.

N^o 1 Solution. Temperature = ordinary. Initial state = $\text{Bi Cl}_3 : \text{HCl} : \text{H}_2\text{O} = 1 : 26 : 192$ mols.

Percentage of Chemical change.

TABLE C. (For numerical details see Tables VII and X.)

INFLUENCE OF MANNER OF MIXING.

N^o 1. Solution. — Temperature = ordinary.

Percentage of Chemical change.

INFLUENCE OF RELATION BETWEEN ACID AND WATER MOLECULES UPON COURSE OF CHEMICAL CHANGE.

Bismuthous Chloride molecules=1.

x' . I now wish to consider the case in which n is approximately equal to x , that is, I wish to consider the distribution of mass when the permanent formation of bismuthyl chloride just commences. The numerical results bearing upon this subject are arranged in Table VIII. The numbers obtained are merely approximate. Small differences in the method of adding water cause considerable differences in the results. This will be apparent by comparing the numbers of Series A with those of Series B. "Surface addition" will be explained in the sequel. These results show that in order to establish permanent production of bismuthyl chloride molecules, the value of x'' must be increased in a more rapidly increasing ratio (referred to the value of x) than that of x' , that is to say, if x be equal to 1, and if x' be increased from 1 to 2, the value of x'' must be more than doubled.

The numbers showing the proportions required to exist between x' and x'' in different experiments are to be found in Table VIII. The curves of Table D graphically represent the principal results detailed in Table VIII, Series A and B.

TABLE VIII.—*Equilibrium of mixtures of BiCl_3 , HCl , and H_2O molecules.* (Compare curves of Table D.)

Solutions of BiCl_3 in aqueous HCl ; H_2O added until permanent precipitate of BiOCl just formed.

Series A.—"Mass addition" of H_2O .

Precipitation permanent.				Proportion of HCl to H_2O mols.	
	Molecules.				
	$\text{BiCl}_3 : \text{HCl} : \text{H}_2\text{O}$				
<i>a.</i>			=	1 : 1	38
<i>b.</i>	"	"	=	1 : 2.5	120
<i>c.</i>	"	"	=	1 : 3	150
<i>d.</i>	"	"	=	1 : 4	300
<i>e.</i>	"	"	=	1 : 10	1,300
<i>f.</i>	"	"	=	1 : 17.5	2,670
<i>g.</i>	"	"	=	1 : 23.5	4,120
<i>h.</i>	"	"	=	1 : 35	7,230

Series B.—"Surface addition" of H_2O .

<i>j.</i>	$\text{BiCl}_3 : \text{HCl} : \text{H}_2\text{O}$	=	1 : 1	38	1 : 38
<i>k.</i>	" " "	=	1 : 2.5	103	1 : 42
<i>l.</i>	" " "	=	1 : 3	120	1 : 40
<i>m.</i>	" " "	=	1 : 4	275	1 : 69
<i>n.</i>	" " "	=	1 : 26	3,090	1 : 119

The proportions found to exist between x' and x'' are further developed in Table IX.

TABLE IX.—*Equilibrium of BiCl₃, HCl, and H₂O molecules (continued).*

Proportions between HCl and H₂O mols.—for one mol. BiCl₃—in order that BiOCl may be permanently formed. (Compare results of preceding Table.)

Series A.—Table VIII.

HCl mols. (x') in		×	= HCl mols. in	H ₂ O mols. (x'') in		×	= H ₂ O mols. in	Proportion between numbers by which HCl and H ₂ O mols. must be multiplied =
Exp. a	2.5		Exp. b	Exp. a	3		Exp. b..	1 : 1.2
„ a	3		„ c	„ a	4		„ c..	1 : 1.3
(„ b	1.2		„ c	„ b	1.25		„ c)	
„ a	4		„ d	„ a	8		„ d..	1 : 2
(„ c	1.3		„ d	„ c	2		„ d)	
„ a	10		„ e	„ a	34		„ e..	1 : 3.4
(„ d	2.5		„ e	„ d	4.3		„ e)	
„ a	17.5		„ f	„ a	70		„ f..	1 : 4
(„ e	1.75		„ f	„ e	2.05		„ f)	
„ a	23.5		„ g	„ a	109		„ g..	1 : 4.6
(„ f	1.35		„ g	„ f	2.7		„ g)	
„ a	35		„ h	„ a	190		„ h..	1 : 5.4
(„ g	1.5		„ h	„ g	1.75		„ h)	

Series B.—Table VIII.

Exp. j	2.5	Exp. k	Exp. j	2.7	Exp. k..	1 : 1.08
„ j	3	„ l	„ j	3.2	„ l..	1 : 1.07
(„ k	1.2	„ l	„ k	1.17	„ l)	
„ j	4	„ m	„ j	7.3	„ m..	1 : 1.82
(„ l	1.3	„ m	„ l	2.3	„ m)	
„ j	26	„ n	„ j	81	„ n..	1 : 3.1
(„ m	6.5	„ n	„ m	11.5	„ n)	

9. It appears, therefore, that if there be a sufficient number of water molecules present to neutralise the action of the acid molecules to such an extent as shall admit of the permanent formation of bismuthyl chloride molecules, and if the number of acid molecules be then doubled, that an equal amount of neutralising action is ensured only when the number of water molecules is more than doubled. When the initial equilibrium of the system is permanently disturbed, but without the production of a new permanently stable equilibrium, the production of this disturbance is dependent, not only upon the relative, but also upon the absolute number of molecules present. On the other hand the production of an entirely new and permanent state of equilibrium

is dependent only upon the relative numbers of molecules present. The study of the course of the chemical change under consideration exhibits molecular phenomena somewhat different from those which are apparent if the initial and final states of molecular distribution be alone examined. It will be shown hereafter that the results obtained from an examination of the action formulated, $\text{MCl}_2 + \text{M}'_2\text{CO}_3 = 2\text{M}'\text{Cl} + \text{MCO}_3$ (page 326), points to a conclusion similar to that just stated.

10. It is evident that our ordinary system of chemical notation expresses only the initial and final distributions of mass of a system, which more or less rapidly passes from one configuration to another; but the final result thus obtained always represents the stable equilibrium of a system acted on by many forces: if an advantage be given to one of these during the process of change, the final distribution of mass may be largely altered. Special instances of the action of such external aids are considered in Part II of the present paper.

11. I have already pointed out (par. 6, p. 316) that, if water be added in quantity sufficient to decompose the greater portion, but not the whole of the bismuthous chloride present, a state of what appears to be permanently stable equilibrium is quickly established in the reacting system.

So far as my experiments extend, they justify the statement that the production of this state is dependent only upon the relative numbers of water and acid molecules. Thus in solution No. 2 the initial molecular distribution in which is, $\text{BiCl}_3 : \text{HCl} : \text{H}_2\text{O} = 1 : 2.5 : 37.5$, the addition of such an amount of water as serves to alter these proportions to $1 : 2.5 : 537.5$ is accompanied with the decomposition of about 95 per cent. of the bismuthous chloride originally present, and this state of equilibrium remains unchanged for a very considerable time. If the molecular proportion in solution No. 3 be $1 : 3 : 650$, a practically stable state of equilibrium (95 per cent. of decomposition) is attained; similarly an analogous condition is ensured in No. 4 solution when the molecular proportion is $1 : 4 : 1,000$; and in No. 1 solution the necessary proportion is $1 : 26 : 6,000$. Now in each of these solutions, the presence of from 200 to 230 molecules of water for each molecule of hydrochloric acid, *independently of the absolute number* of the latter molecules, causes an equal amount of decomposition, which amount marks the assumption of a practically stable condition of equilibrium of the reacting system.

12. It would thus appear that if we allow any system of bismuthous chloride, hydrochloric acid, and water molecules, in which the number of the last-named molecules is large, to act and react until a new and permanent configuration be gained, this configuration will be dependent upon the relation between the numbers of acid and water molecules;

but that if the mutual molecular actions be stopped before such a permanent configuration is gained, the intermediate configuration will be largely dependent upon the absolute number of acid and water molecules present. In the first rush and bustle of the reacting molecules, the water molecules appear to get entangled among the acid molecules, and so to be impeded in their action on the molecules of bismuthous chloride; the greater the number of acid molecules the greater is the amount of this entanglement, although there may be proportionately as many water molecules present as when the number of acid molecules was small. But give the system time, and the water molecules will free themselves from their entanglements; so that the same final state of the system will be attained, whether there be originally many or few molecules of water.

13. In those experiments, the results of which have now been detailed, water was added from a measuring vessel to an acid solution of bismuthous chloride, which was maintained in constant agitation. If the water be poured very cautiously on to the surface of the bismuth solution, and if the whole be then suddenly shaken up, a new set of phenomena present themselves. This method of addition of water I have called "surface addition;" and in Table X I have contrasted the results obtained by this method with those obtained by "mass addition," other conditions being the same in each series of experiments. Some of these results are represented graphically in the curves of Table C.

TABLE X.—*Comparison of results obtained by "surface addition" with those obtained by "mass addition" of water.* (Compare curves of Table C.)

Molecules.		Percentage of BiCl_3 decomposed.	
$\text{BiCl}_3 : \text{HCl} : \text{H}_2\text{O}$	Time.	"Surface addition."	"Mass addition."
1 : 26 : 2,900	3 mins.	12.19	0.00
	35 "	23.26	
	24 hours	46.99	
	76 "	60.20	
1 : 26 : 3,000	3 mins.	18.61	0.00
	35 "	27.09	
	24 hours	50.91	
	76 "	64.45	
1 : 26 : 3,500	3 mins.	50.26	0.00
	35 "	50.52	30.03
	48 hours	68.85	67.85
	76 "	—	70.84
	9 days	—	70.70
1 : 2.5 : 66	48 hours	0.07	0.00
1 : 2.5 : 70	"	9.00	

In the "surface addition" series formation of bismuthyl chloride was apparent at the surfaces of contact of the layers of water and of bismuthous chloride dissolved in hydrochloric acid.

14. These results show that if a few molecules of bismuthyl chloride be allowed to form, it is comparatively very hard to unform these molecules; but that it is possible to arrange the conditions of the experiment so that none of these molecules are permanently produced, although a greater number of water molecules be present than in the first experiment.

At the surfaces of the layers of contact of the two liquids in the "surface addition" experiments, we have such an arrangement as admits of the formation of bismuthyl chloride molecules in the presence of comparatively few hydrochloric acid molecules; it is not until the former molecules have passed downwards towards the lower part of the vessel that there is any chance of their meeting large numbers of acid molecules. If, however, "mass addition" be practised, each bismuthyl chloride molecule so soon as formed finds itself surrounded by a large number of acid molecules, so that its existence is but ephemeral.

15. It is somewhat remarkable that two systems may be obtained consisting of approximately the same absolute and the same relative numbers of water, acid, and bismuthous chloride molecules, that one of these may be perfectly stable, but that the other may undergo a continuous change of molecular equilibrium. Thus the "mass addition" of 2,900 mols. of water to No. 1 solution caused no precipitation of bismuthyl chloride even after 76 hours; while, when the same number of water molecules was added by "surface addition" to an equal volume of the same solution, 12 per cent. of the bismuthous chloride was decomposed in three minutes, and about 70 per cent. in 76 hours. If, however, such an amount of water be added by "mass addition" as causes the permanent precipitation of a small quantity of bismuthyl chloride, and if this solution be compared with a similar solution to which an equal amount of water has been added by "surface addition," the final states of equilibrium are found to be the same in both. Examples of this will be found in the numbers of Table X, some of which are also represented in the curves of Table C. (In one experiment, the bismuthous chloride solution was added to the water in small successive portions, the experiment extending over nine days; the *final* state of equilibrium was, however, the same as that attained in 48 hours under the ordinary conditions.)

16. The amount of bismuthous chloride decomposed in "surface addition" experiments, in short times, is always greater than that decomposed in analogous "mass addition" experiments in long times: the two amounts are equal. We must surely then believe that when

water is added to a solution of bismuthous chloride in hydrochloric acid with constant stirring, molecules of bismuthyl chloride are formed, but are instantly again decomposed; that there are atomic interchanges going on, but that these changes are balanced by those, and that therefore the entropy* of the system is constant. Give one set of changes a small advantage over the other; in other words, disturb the entropy of the system, and a new configuration is produced, and this again is succeeded by another, until a permanently stable state is attained.

If the experiment be so arranged that the entropy of the system is altered in the early stages of the experiment, the chemical change thus produced has evidently a start, so to speak, over another analogous change, which is produced by a change of entropy accomplished towards the later stages of the experiment; but the two changes having been made, the course of decomposition will proceed in each until one and the same final state of equilibrium is attained.

Is there not in these experiments a phenomenon somewhat analogous with that presented by supersaturated solutions?

17. The experiments detailed in Table X also confirm the remark made on page 321, that the study of the course of a chemical change often presents phenomena different from those attendant upon the initial and final stages of that change.

18. In a paper communicated to the Society about a year ago (*Journal*, 1878, *Trans.* 27) I gave some measurements illustrative of the course of the change formulated generally as $[x\text{CaCl}_2 + x'\text{M}_2\text{CO}_3 = (x - n)\text{CaCO}_3 + n\text{CaCl}_2 + 2x' - n'\text{MCl} + n'\text{M}_2\text{CO}_3]$; where $\text{M} = \text{Na}$ or K . Since the date of that paper I have added considerably to the number of measurements made; these measurements I will now discuss.

The method of conducting the experiments was explained in the paper referred to.

Table XI contains the results of experiments bearing upon the influence of mass on the reaction under consideration. Many of these results are represented graphically in the curves of Table E.

TABLE XI.—*Influence of mass.* (Compare curves of Table E.)

Total volume of liquid = 70 c.c. Various solutions of CaCl_2 and Na_2CO_3 (or K_2CO_3) used; average amount of CaCl_2 in mgms. = 100; average amount of Na_2CO_3 in mgms. = 95.5.

* I use this term as meaning "internal energy of position" (see Clerk Maxwell's "Theory of Heat," p. 186), and not in the sense originally given it by Clausius, viz., as expressing energy inconvertible into mechanical work.

TABLE E. (For numerical details see Table XI.)

INFLUENCE OF MASS.

Series A.—Time = 5 mins.

Molecules.		Percentage of CaCO_3 produced, calculated on total theoretical yield.	
$\text{M}_2\text{CO}_3 : \text{CaCl}_2$	Temperature.	M = Na	M = K.
1 : 1	3°	53·5	64·0
2 : 1	„	95·9	92·7
3 : 1	„	96·7	96·0
1 : 1	15°	74·5	81·1
2 : 1	„	92·1	92·5
3 : 1	„	94·3	96·5
1 : 1	40°	83·0	85·5
2 : 1	„	93·2	95·4
3 : 1	„	96·5	96·5
1 : 1	60°	85·0	86·0
2 : 1	„	96·0	99·0
3 : 1	„	100·0	100·0

Series B.—Time = 30 mins.

1 : 1	3°	58·6	80·0
2 : 1	„	92·8	96·0
3 : 1	„	96·8	96·0
1 : 1	15°	85·0	84·7
2 : 1	„	93·2	98·7
3 : 1	„	96·4	98·7
1 : 1	40°	96·0	96·0
2 : 1	„	99·0	99·0
3 : 1	„	100·0	100·0
1 : 1	60°	92·8	100·0
2 : 1	„	100·0	100·0
3 : 1	„	100·0	100·0

Series C.—Time = 60 mins.

1 : 1	3°	76·3	80·0
2 : 1	„	96·0	100·0
3 : 1	„	96·0	100·0
1 : 1	15°	86·0	86·0
2 : 1	„	95·3	100·0
3 : 1	„	96·9	100·0
1 : 1	40°	96·0	96·0
2 : 1	„	96·0	100·0
3 : 1	„	100·0	100·0
1 : 1	60°	99·0	100·0
2 : 1	„	100·0	100·0
3 : 1	„	100·0	100·0

19. These experiments fully confirm the statement previously made, that at ordinary temperatures the change formulated $\text{CaCl}_2 + \text{M}_2\text{CO}_3 = 2\text{MCl} + \text{CaCO}_3$ ($\text{M} = \text{Na}$ or K) is not completed unless the mass of M_2CO_3 molecules be considerably in excess of that shown in the equation. When equal molecules of calcium chloride and sodium (or potassium) carbonate were employed, about 10 per cent. of the chloride remained undecomposed even after 39 days' action.

A practically stable state of equilibrium is quickly attained by the reacting system of calcium chloride, calcium carbonate, sodium chloride, and sodium carbonate molecules: a similar phenomenon has been noticed in the reaction of water upon bismuthous chloride dissolved in hydrochloric acid (see par. 6, p. 316).

20. In both cases it appears that when the number of calcium chloride (or bismuthous chloride) molecules becomes very small compared with the numbers of the other molecules present, the former molecules seldom come within the sphere of action of the latter, or more probably, in the case of bismuthous chloride at any rate, that when they do come within the sphere of action and are thereby decomposed, they are immediately reformed. In other words, we find that before the whole of the internal energy of position of the reacting system has been expended the system has attained a condition of equilibrium. In the case of calcium chloride, as will be shown in the sequel, very small disturbances are sufficient to upset this equilibrium, and to cause the change to proceed to completion (compare par. 23).

21. The influence of time upon the chemical change under consideration is marked: it is illustrated by the numbers of Table XII, many of which are graphically represented in the curves of Table F.

TABLE XII.—*Influence of Time.* (Compare curves of Table F.)

Total volume of liquid = 70 c.c. Other details as before.

Time.		Temperature.	Percentage of CaCO_3 produced.	
			$\text{M} = \text{Na.}$	$\text{M} = \text{K.}$
5 min.	$\text{CaCl}_2 : \text{M}_2\text{CO}_3 = 1 : 1$ mol.	3°	53.5	64.0
30 "	" "	"	58.6	80.0
60 "	" "	"	76.3	80.0
39 days	" "	"	89.6*	—
5 "	$\text{CaCl}_2 : \text{M}_2\text{CO}_3 = 1 : 2$ mols.	"	95.9	92.7
30 "	" "	"	92.8	96.0
60 "	" "	"	96.0	100.0

* This experiment proceeded during the Christmas vacation. The temperature probably did not rise above 5° at any time during the experiment.

INFLUENCE OF TIME.

TABLE XII (*continued*).

Time.		Temperature.	Percentage of CaCO_3 produced.	
			M = Na.	M = K.
5 min.	$\text{CaCl}_2 : \text{M}_2\text{CO}_3 = 1 : 3$ mols.	3°	96.7	96.0
30 "	" "	"	96.8	96.0
60 "	" "	"	96.0	100.0
5 "	$\text{CaCl}_2 : \text{M}_2\text{CO}_3 = 1 : 1$ mol.	15°	74.5	81.1
30 "	" "	"	85.0	84.7
60 "	" "	"	86.0	86.0
5 "	$\text{CaCl}_2 : \text{M}_2\text{CO}_3 = 1 : 2$ mols.	"	92.1	92.5
30 "	" "	"	93.2	98.7
60 "	" "	"	95.3	100.0
5 "	$\text{CaCl}_2 : \text{M}_2\text{CO}_3 = 1 : 3$ mols.	"	94.3	96.5
30 "	" "	"	96.4	98.7
60 "	" "	"	96.9	100.0
5 "	$\text{CaCl}_2 : \text{M}_2\text{CO}_3 = 1 : 1$ mol.	40°	83.0	85.5
30 "	" "	"	96.0	96.0
60 "	" "	"	96.0	96.0
5 "	$\text{CaCl}_2 : \text{M}_2\text{CO}_3 = 1 : 2$ mols.	"	93.2	95.4
30 "	" "	"	99.0	99.0
60 "	" "	"	96.0	100.0
5 "	$\text{CaCl}_2 : \text{M}_2\text{CO}_3 = 1 : 3$ mols.	"	96.5	100.0
30 "	" "	"	100.0	100.0
60 "	" "	"	100.0	100.0
5 "	$\text{CaCl}_2 : \text{M}_2\text{CO}_3 = 1 : 1$ mol.	60°	85.0	86.0
30 "	" "	"	92.8	100.0
60 "	" "	"	99.0	100.0
5 "	$\text{CaCl}_2 : \text{M}_2\text{CO}_3 = 1 : 2$ mols.	"	96.0	99.0
30 "	" "	"	100.0	100.0
60 "	" "	"	100.0	100.0
5 "	$\text{CaCl}_2 : \text{M}_2\text{CO}_3 = 1 : 3$ mols.	"	100.0	100.0
30 "	" "	"	100.0	100.0
60 "	" "	"	100.0	100.0

The influence of time is evidently conditioned by the masses of the reacting bodies, and by the temperatures at which the action proceeds. With a constant temperature and equal numbers of molecules of chloride and carbonate, an increase in the time of action is always accompanied by an increase in the amount of change. The latter increase is most marked after the expiry of the first portion of the time. The only exception to the latter part of this rule (see Experiments 2 and 3, Table XII, and curve 7, Table F) is to be explained either as an experimental error, or possibly as pointing to the forma-

tion of some hydrate of sodium carbonate or calcium chloride at the low temperature of the experiment.

22. When the action approaches that point at which equilibrium is established, the influence of time becomes feebly marked; the molecules of chloride and carbonate, being now few in number, seldom come into collision. Inasmuch as, with an increased mass of carbonate molecules, this state of more or less permanent equilibrium is quickly attained, the influence of time is less marked when 2 or 3 molecules of carbonate are added, than when but a single molecule (proportionately to the chloride molecules) is employed.

23. If the influence of time upon the chemical change considered in the first part of this paper be compared with the influence of the same variable upon the change now under consideration, a difference is at once noticed. In the first case it is necessary to add a very large number of water molecules in order to complete the change, the amount of change is then practically independent of the time: in the second case, a very much smaller number of alkaline carbonate molecules—proportionately to the calcium chloride molecules—is required to complete the change; the amount of change also varies considerably at different moments of time.

In the former case it appears that the production of a small amount of change is accompanied with but small variations in the entropy of the reacting system, the change therefore proceeds slowly and comes to a standstill, while there are yet comparatively large numbers of undecomposed bismuthous chloride molecules present—unless indeed very large masses of water are added, in which case there is a sudden disturbance in the entropy of the system. In the case of the decomposition of calcium chloride it appears that a small amount of chemical change involves a considerable variation in the entropy of the system: hence, give time, and even with *comparatively* small masses, the change will complete itself.

I have been unable to find any exact measurements of the thermal reactions connected with the formation of CaCl_2 and CaCO_3 , and with BiCl_3 and BiOCl respectively; but I think that the facts known concerning the decomposition of CaCl_2 tend to show that in the formation of CaCO_3 there is probably considerably more heat evolved than in the formation of CaCl_2 : while facts which I have myself communicated to the Society concerning the oxidation of BiCl_3 (Journal, 2, 1877, 136, and *Trans.*, 1878, 192) show that this body is not readily decomposed into BiOCl , and that therefore the heat evolution involved in such an oxidation is probably not large.

24. I will now consider the influence of temperature upon the decomposition of calcium chloride by alkaline carbonate. The results

INFLUENCE OF TEMPERATURE.

are arranged in Table XIII, and graphically in the curves of Table G.

TABLE XIII.—*Influence of Temperature.* (Compare curves of Table G.)

Total volume of liquid = 70 c.c. Other details as before.

Temperature.		Time.	Percentage of CaCO_3 produced.	
			M = Na.	M = K.
3°	$\text{CaCl}_2 : \text{M}_2\text{CO}_3 = 1 : 1$ mol.	5 mins.	53·5	64·0
15	„ „	„	74·5	81·1
40	„ „	„	83·0	85·5
60	„ „	„	85·0	86·0
3°	$\text{CaCl}_2 : \text{M}_2\text{CO}_3 = 1 : 2$ mols.	„	95·9	92·7
15	„ „	„	92·1	92·5
40	„ „	„	93·2	95·4
60	„ „	„	96·0	99·0
3°	$\text{CaCl}_2 : \text{M}_2\text{CO}_3 = 1 : 3$ mols.	„	96·7	96·0
15	„ „	„	94·3	96·5
40	„ „	„	96·5	96·5
60	„ „	„	100·0	100·0
3°	$\text{CaCl}_2 : \text{M}_2\text{CO}_3 = 1 : 1$ mol.	30 mins.	58·6	80·0
15	„ „	„	85·0	84·7
40	„ „	„	96·0	96·0
60	„ „	„	92·8	100·0
3°	$\text{CaCl}_2 : \text{M}_2\text{CO}_3 = 1 : 2$ mols.	„	92·8	96·0
15	„ „	„	93·2	98·7
40	„ „	„	99·0	99·0
60	„ „	„	100·0	100·0
3°	$\text{CaCl}_2 : \text{M}_2\text{CO}_3 = 1 : 3$ mols.	„	96·8	96·0
15	„ „	„	96·4	98·7
40	„ „	„	100·0	100·0
60	„ „	„	100·0	100·0
3°	$\text{CaCl}_2 : \text{M}_2\text{CO}_3 = 1 : 1$ mol.	60 mins.	76·3	80·0
15	„ „	„	86·0	86·0
40	„ „	„	96·0	96·0
60	„ „	„	99·0	100·0
3°	$\text{CaCl}_2 : \text{M}_2\text{CO}_3 = 1 : 2$ mols.	„	96·0	100·0
15	„ „	„	95·3	100·0
40	„ „	„	96·0	100·0
60	„ „	„	100·0	100·0
3°	$\text{CaCl}_2 : \text{M}_2\text{CO}_3 = 1 : 3$ mols.	„	96·0	100·0
15	„ „	„	96·9	100·0
40	„ „	„	100·0	100·0
60	„ „	„	100·0	100·0

In the experiments made at 3° , beakers containing the proper quantities of water and alkaline carbonate solution, were surrounded by ice until the temperatures of the liquids were nearly constant, calcium chloride solution, at the same temperature, was then added, and the liquids were surrounded by ice until the moment arrived for filtration.

25. In my previous paper I stated that increase of temperature causes an increase in the amount of calcium chloride decomposed in a given time, other conditions being constant. The experiments now detailed confirm this result, but require that it be stated in a somewhat modified form.

The influence of temperature is very marked when equal molecules of calcium chloride and alkaline carbonate are allowed to react upon one another: when, however, two or more molecules of carbonate are employed, the influence of temperature in increasing, or decreasing, the amount of chemical change, although yet perceptible, becomes much less marked. That this is so will be at once apparent from the curves of Table G.

26. It has been already shown that when no excess of either reacting substance is present, a condition of practically stable equilibrium is attained by the system after a comparatively short time; but it is now shown that if energy be added to the system from without, this point of equilibrium is passed and a new equilibrium is attained, when the whole, or almost the whole, of the calcium chloride molecules have been decomposed. In the case of potassium carbonate, decomposition is complete at a temperature of 60° with equal numbers of molecules of carbonate and calcium chloride, and after 60 minutes' action; in the case of sodium carbonate about 1 per cent. of the chloride remains undecomposed under the same conditions.

If, however, the mass of one of the reacting substances be considerably larger than that of the other, then the collisions and decompositions of the molecules are so numerous, even in a short time, that the addition of energy from without the system causes but little change in the final state. That such addition does cause some change in the final state is evident from the numbers detailed, but that this change is small compared with that produced when no excess of either of the reacting substances is employed is also apparent from these numbers.

27. If experiments were conducted in more dilute solutions than those which I have employed, it is probable that the influence of temperature would be more marked in cases where two or more molecules of alkaline carbonate are employed for one molecule of calcium chloride. I am at present conducting experiments to test the truth of this hypothesis.

28. It is worthy of remark that the influence of time is exerted differently from that of temperature in increasing the total amount of

TABLE H. (For numerical details see Table XIV.)

INFLUENCE OF TEMPERATURE COMPARED WITH THAT OF MASS.

Ca Cl₂ and Na₂ CO₃. *Ca Cl₂ and K₂ CO₃.*

change. Confining our attention to those decompositions in which equal molecules of the reacting bodies are employed, it is found that the influence of time is most marked at comparatively low temperatures. At such temperatures the molecular mobility of the system is comparatively small, hence it is necessary that time be given, in order that a new condition of equilibrium may be reached. At higher temperatures, the molecular mobility being greater, the new equilibrium is reached in a shorter time, but if there be no excess of either of the reacting compounds, a certain amount of time is required before this state can be attained; hence the influence of time is considerable even at high temperatures. But it appears that time alone does not suffice to complete the decomposition of the whole of the calcium chloride molecules unless a high temperature be also insured, and if this be insured a comparatively short time only is required. Thus at the ordinary temperature only 86 per cent. of the complete theoretical yield of calcium carbonate is obtained after 60 minutes' action, when equal molecules of potassium carbonate and calcium chloride are employed, and inasmuch as I have shown that in the case of sodium carbonate only 89 per cent. of the total calcium carbonate is formed after 39 days' action, I think I am justified in saying that if the reaction be allowed to proceed at low temperatures, 3—7°, equal numbers of molecules of potassium carbonate and calcium chloride would never succeed in completely decomposing one another; before the decomposition reached completion a condition of permanently stable equilibrium would be attained. But if the temperature be maintained at 60°, the reacting masses being the same as in the previous experiment, complete decomposition is brought about in 30 minutes.

29. If the effects of temperature be compared with those of mass (see Table XIV and curves of Table H), it is apparent that an increase of about 55° causes as great an increase in the amount of decomposition as is effected by doubling the relative number of alkaline carbonate molecules, provided the increased temperature be allowed to act through a somewhat long period of time. In short times, on the other hand, increasing the mass of one of the reacting bodies is more effectual, in accomplishing a greater amount of decomposition, than in raising the temperature.

TABLE XIV.—*Influence of Temperature compared with that of Mass.*
(Compare curves of Table H.)

	Time.	Temp.	Percentage of CaCO ₃ produced.	
			M = Na.	M = K.
a. CaCl ₂ : M ₂ CO ₃ = 1 : 1 mol.	5 mins.	3°	53·5	64·0
b. CaCl ₂ : M ₂ CO ₃ = 1 : 2 mols.	„	„	95·9	92·7

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TABLE XIV (*continued*).

Difference in CaCO_3 produced between <i>a</i> and <i>b</i> .					
M = Na.			M = K.		
42.4			28.7		
Percentage of CaCO_3 decomposed.					
	Temp.		Time.	M = Na.	M = K.
<i>c.</i>	3°	$\text{CaCl}_2 : \text{M}_2\text{CO}_3 = 1 : 1$ mol.	5 mins.	53.5	64.0
<i>d.</i>	60	" "	"	85.0	86.0
Difference in CaCO_3 produced between <i>c</i> and <i>d</i> .					
M = Na.			M = K.		
31.5			22.0		
	Temp.		Time.		
<i>e.</i>	3°	$\text{CaCl}_2 : \text{M}_2\text{CO}_3 = 1 : 1$ mol.	30 mins.	58.6	80.0
<i>f.</i>	60	$\text{CaCl}_2 : \text{M}_2\text{CO}_3 = 1 : 2$ mols.	"	92.8	96.0
Difference in CaCO_3 produced between <i>e</i> and <i>f</i> .					
M = Na.			M = K.		
34.2			16.0		
	Temp.		Time.		
<i>g.</i>	3°	$\text{CaCl}_2 : \text{M}_2\text{CO}_3 = 1 : 1$ mol.	30 mins.	58.6	80.0
<i>h.</i>	60	" "	"	92.8	100.0
Difference in CaCO_3 produced between <i>g</i> and <i>h</i> .					
M = Na.			M = K.		
34.2			20.0		
	Temp.		Time.		
<i>j.</i>	3°	$\text{CaCl}_2 : \text{M}_2\text{CO}_3 = 1 : 1$ mol.	60 mins.	76.3	80.0
<i>k.</i>	60	$\text{CaCl}_2 : \text{M}_2\text{CO}_3 = 1 : 2$ mols.	"	96.0	100.0
Difference between CaCO_3 produced in <i>j</i> and <i>k</i> .					
M = Na.			M = K.		
19.7			20.0		
	Temp.		Time.		
<i>m.</i>	3°	$\text{CaCl}_2 : \text{M}_2\text{CO}_3 = 1 : 1$ mol.	60 mins.	76.3	80.0
<i>n.</i>	60	" "	"	99.0	100.0
Difference between CaCO_3 produced in <i>m</i> and <i>n</i> .					
M = Na.			M = K.		
22.7			20.0		

30. Comparing the influence of time, temperature, and mass upon

the chemical change under consideration, it appears that with equal molecules of the reacting bodies and moderate temperatures the amount of decomposition is greater the greater the time of action, until a certain point is reached short of complete decomposition, after which the equilibrium of the system is undisturbed. That increase of temperature disturbs this equilibrium and brings about the completion of the chemical change; but that the change is more rapidly completed, even without the aid of the energy added in the form of heat, by increasing the mass of one of the reacting bodies.

31. The experiments which have been now described have many points of contact with questions of general chemical theory. I have already alluded to a few of these. I should like now to gather together some of the leading facts established, and to indicate what appears to me to be their bearing upon a few points of general theory.

32. One is very ready to regard the present system of chemical notation as a final system; but such a system it certainly is not. The advantages of the system of notation now generally adopted are many. Among its disadvantages may I think be fairly classed the tendency, which is fostered by continued use of this system, to regard a knowledge of the initial and final distribution of mass as the all important data necessary for solving chemical problems. We too readily neglect to study the course of the chemical changes, the results of which we so assiduously register.

We have been taught by Harcourt and Esson, by Gladstone, and by others, to attend somewhat to the phenomena presented while a chemical system is passing from one state of stable equilibrium to another, in cases wherein all the reacting bodies remain in solution; but we must also attend to these intermediate phenomena in cases wherein solid compounds are produced.

A chemical system may probably be regarded as at all times tending to undergo change, possibly as at all times actually undergoing change. So long as the molecular decompositions and recompositions balance one another, a condition of apparent stability is maintained; but allow the decompositions to gain a little upon the recompositions, the stability is upset, and the change proceeds. I do not see how, but upon some such view as this, the fact is to be accounted for that a solution containing molecules of bismuthous chloride, water, and hydrochloric acid remains clear for some hours, but gradually becomes clouded from the formation and precipitation of bismuthyl chloride molecules; or how else are we to account for the production of conditions of stable equilibrium *before complete* decomposition of the bismuthous chloride (or calcium chloride) molecules, which conditions are again disturbed by the action of "impressed forces?"

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33. It is possible, as has been shown, to assure the existence of a system of bismuthous chloride, water, and hydrochloric acid molecules, which system under other conditions is altogether unstable; but very slight causes suffice to disturb the equilibrium of the system, and when it is once disturbed the chemical change proceeds with considerable rapidity. But even after the change is started the final result is undetermined. Many forces are at work: one may gain a preponderance over the other, and thus modify the future course of the change. If comparatively large masses of one of the reacting bodies be used, we have a large number of one kind of molecules hovering round a small number of another kind of molecules; disturb the entropy of the system, and off goes the chemical change, regardless, to a great extent, of such subsidiary conditions as time and temperature. But let the masses of the reacting molecules be more nearly (chemically) equal, and then the subsidiary conditions come into play and exert most marked effects. The fact that time alone will not accomplish so great a decomposition as is brought about by increased temperature seems to find its explanation in the two principles: (1) that chemical changes are continually proceeding in every system comprising different kinds of molecules; but (2) that if any such system be withdrawn from the action of extraneous forces it will assume an apparently stable condition of equilibrium, which state is disturbed only by the action of "impressed force."

It appears to me that a study of the latter of those chemical changes, a partial analysis of which has been attempted in the present paper, under conditions where the action of the various forces might be more disentangled from one another would be advisable. Such a study I am now pursuing.

34. The fact that the amount of decomposition effected by a given mass of one of the reacting bodies is largely conditioned by the circumstances under which the decomposition proceeds appears to me to militate against the value of those "dynamical units," which have been established for a few substances by Mills, and the number of which that chemist is anxious largely to increase.

35. It is worthy of remark that the amount of chemical change is always somewhat greater when potassium carbonate than when sodium carbonate is employed, other conditions being constant.

36. I reserve the discussion of the bearing of my experiments upon the general question of chemical affinity until I am able to lay more detailed results of the influence of temperature, time, dilution, physical condition of the precipitating vessels, &c., &c., before the Society.