The Conditions of the Evolution of Gases from Homogeneous Liquids

V. H. Veley

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IX. *The Conditions of the Evolution of Gases from Homogeneous Liquids.*

By V. H. Veley, *M.A., University College, Oxford.*

Communicated by A. Vernon Harcourt, *M.A., F.R.S., Lee's Reader in Chemistry, Christ Church, Oxford.*

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I. *Introduction.*

The evolution of a gas, as a product of a chemical change, from a homogeneous liquid is among the earliest and most common experiences presented to a student of chemistry. Thus, oxygen and nitrogen, among the elementary gases, and nitrous oxide, nitric oxide, carbonic oxide, and hydrogen sulphide, among the compound gases, can be readily prepared either from certain salts in a state of fusion, or from aqueous or acid solutions of certain compounds. The effects produced on the rate and magnitude of these changes by varying the conditions of mass, temperature, pressure, and material of the containing vessel have not, hitherto, attracted the attention of investigators. In preference, similar dynamical problems have been studied of chemical changes occurring either between two or more gases, forming a gaseous product, or between homogeneous liquids, or between solutions of solids.

In all these instances the reagents and their products are in the same physical condition, gaseous or liquid, as the case may be. Of such a character are the investigations of Bunsen, v. Meyer, Horstmann, and the more elaborate researches of Dixon on the conditions of chemical change occurring between hydrogen and certain combustible gases. While among changes between homogeneous liquids or solutions of solids, should be mentioned the experiments of Berthelot and Péan de Saint Gilles, and of Menschutkin, on the formation of ethereal salts from organic acids and alcohols, of Harcourt and Esson on the reactions between oxalic and permanganic acids, and between hydrogen iodide and hydrogen peroxide, and of Gladstone on the reaction between ferric salts and sulphocyanides.

Experience thus far has shown that a chemical change from which a gas results is often complicated in itself, or is accompanied and modified by other changes yielding products not susceptible of convenient estimation. Sometimes, also, some portion of the compound whose rate of decomposition is being measured is vaporised unchanged. In the present paper I have the honour of laying before the Royal Society an account of experiments on the rate of formation of gases from liquids. For convenience, the paper will be divided into three parts. In Part I. the effect produced by the presence of finely divided particles is investigated; in Part II. the result of variation of pressure is studied; in Part III. the particular case of the decomposition of formic acid into carbonic oxide and water, under the influence of concentrated sulphuric acid, is investigated, the only conditions varied being those of temperature and mass. The mathematical representation of this change is also discussed, and the results observed are compared with those calculated according to the hypothesis adopted.

Before passing on to details, I should wish at once to state that these investigations were commenced at the instigation of Mr. HARCOURT, who was kind enough to devise for me the various apparatus herein described, and without whose constant co-operation and advice this research could not have been completed. The experiments were conducted in the laboratory of Christ Church, Oxford.

II. *Previous Experiments on the Evolution of Gases from Liquids in which they are formed.*

The principal chemical changes of this nature, at present investigated, are the decomposition of ammonium nitrate into nitrous oxide and steam, of potassium chlorate into potassium chloride and oxygen, and of hydrogen peroxide into water and oxygen.

The first of these changes has been studied from the thermo-chemical side by BERTHELOT,* and from a chemical point of view by myself.† BERTHELOT concludes from his experiments that ammonium nitrate, when heated to 200° C., is decomposed initially into ammonia and nitric acid, which in some degree distil in the gaseous form, recombining in the cooler parts of the apparatus to reproduce the original salt, but to a greater degree react together to form nitrous oxide and steam. These changes are represented as follows:—

$$\text{(i.)}\ NH_4NO_3 = NH_3 + HNO_3.$$
$$\text{(ii.)}\ NH_3 + HNO_3 = N_2O + 2H_2O.$$

My investigations established that the rate of the second change is conditioned by the extent of the first: that is to say, the rate of formation of nitrous oxide, taken as the measure of the decomposition, depends upon the proportion either of ammonia or of nitric acid present in excess over the quantities of base and acid required for their complete neutralisation. Thus, an excess of ammonia, other conditions remaining the same, retarded, or even completely stopped, the decomposition, and an excess of nitric acid produced the same effect, though to a less marked degree. Unpublished

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* 'Annales de Chimie,' [4], vol. 18, pp. 68–82, and [5], vol. 10, pp. 362–365.

† 'Chem. Soc. Journ.,' 1883, pp. 370–383.

investigations also point to the conclusion that the rate of decomposition of ammonium nitrite in solution, into nitrogen and water, is also conditioned by the presence of free nitrous acid. The decomposition of potassium chlorate into potassium chloride and oxygen has been studied by Teed and P. F. Frankland with Dingwall,* whose investigations were published while the present research was being carried on. The results show that of the two changes commonly represented in the text-books, namely—

$$\text{(i.)}\ 2KClO_3 = KClO_4 + KCl + O_2\,;$$
$$\text{(ii.)}\ KClO_4 = KCl + 2O_2$$

—the former at the temperature of boiling sulphur is incomplete, not more than 6·3 to 8·76, instead of 13·05, parts of oxygen being evolved for every 100 parts of potassium chlorate originally taken. Frankland and Dingwall noticed that when the chlorate is mixed with *half its weight of powdered glass* the decomposition of the chlorate according to equation (i.) is practically realised. The effect of certain metallic oxides in favouring the evolution of oxygen from potassium chlorate has been studied by W. A. Miller and by Mercer. The former writes,† "Other oxides produce a similar effect (to that of manganese peroxide); thus, I find when the chlorate is mixed with ferric oxide it requires a temperature of about 260° C., with plumbic oxide a somewhat higher temperature is needed, whilst magnesia and zinc oxide do not aid the decomposition at all. *I have found also that powdered glass and pure silica are equally inert.*"

Mr. Harcourt, in the course of his investigations on the rate of chemical change made several years ago, studied the decomposition of hydrogen peroxide into water and oxygen, of ammonium nitrite in aqueous solution into water and nitrogen, of oxalic acid into carbonic oxide, carbonic anhydride, and water, and of the formation of nitric oxide from a gently warmed mixture of potassium nitrate, ferrous sulphate, and dilute sulphuric acid. The observations made in the course of these unpublished investigations, and those especially on the effect of roughened surfaces on the decomposition of hydrogen peroxide, led to several experiments detailed in this paper, and will be alluded to in the sequel.

III. *The Apparatus used.*

The method adopted in most of the experiments for collecting a definite quantity of gas, taken as the measure of the velocity of the chemical change, may briefly be designated "*the twin* U*-tube method.*" Though described in my paper "On the Rate of Decomposition of Ammonium Nitrate," it will be convenient here to add a brief description. The apparatus consists of two inverted U-tubes (U fig. 1, page 288), made

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[*] 'Chem. Soc. Journ.,' 1887, pp. 274–286.

[†] 'Elements of Chemistry,' fifth edition, vol. 2, p. 847.

from the same piece of glass tubing; the two limbs of each are in close contact, being wired together above and below. Joined to the centre of the upper part of one of these tubes is a stopcock, through which, by means of flexible tubing connecting it with an aspirator, the collected gas can be drawn out till the tube is filled with water when the open ends are standing in a pneumatic trough. Into one limb of this tube the gas is delivered in minute bubbles from the open end of a capillary tube, joined to the decomposition flask; in the other limb the unbroken surface of the water falls steadily. The twin tube contains a quantity of air, measured once for all; the level of water in one limb serves to mark the point at which an equal volume of gas has been collected in the other tube, the level of water in the adjoining tubes being the same. The actual volume varies with conditions of temperature and atmospheric pressure, but, since the contents of both tubes are under precisely the same conditions, this variation is immaterial.

The standard quantity of air taken throughout these experiments was 10 *c.c. of dry air under standard conditions of temperature and pressure.* This was measured out as follows:—The volume occupied by 10 c.c. under the conditions of temperature and pressure on the day of measurement was at first calculated; this was corrected for diminution of pressure due to tension of aqueous vapour and the dip of the delivery tube under the surface of the water. This volume was delivered into the U-tube by means of a capillary tube, from a flask in which that volume of air was displaced by water dropping from a burette. The temperature of the flask was kept constant by immersing it in a vessel of water; while the effect of draughts was minimised by using the capillary tube. In reactions in which a gas insoluble in water was formed, the small volume of gas evolved between each observation of level and the refilling of the tube by means of the aspirator was collected in a separate tube (C, fig. 1), and decanted up during the interval between this and the next observation. Thus the whole process was continuous. In cases in which the gas was partially soluble in water, suitable modifications were introduced or different methods of collection adopted. The observations were made with the help of a clock, beating seconds, stationed close to the apparatus; and, by counting, the exact second could be noted at which the slowly descending water was at the same level as the similar column of water in the twin U-tube. The flask in which the reaction was carried on was heated in an air or water bath, the temperature of which was kept constant by means of an automatic mercury and oil gas-regulator; in most cases the variation of temperature did not exceed one-tenth of a degree. Long-range thermometers were used, graduated to tenths of degrees, in which differences of a twentieth of a degree could easily be noted; some of the thermometers were calibrated according to the method of BESSEL.

PART I.

EFFECT OF FINELY DIVIDED PARTICLES ON THE RATE OF EVOLUTION OF GASES, RESULTING FROM A CHEMICAL CHANGE OCCURRING IN A HOMOGENEOUS LIQUID.

The effect of finely divided particles or of roughened surfaces in promoting the evolution of gases from their solutions in liquids, and that of vapours from liquids in a state of ebullition is well known. The former phenomenon has been investigated by OERSTED, SCHÖNBEIN, LIEBIG, GERNEZ, SCHRÖDER, and TOMLINSON, and the latter by WATT, GAY LUSSAC, MARCEL, MAGNUS, DONNY, and GROVE. GERNEZ* attributes the effect of these particles in increasing the evolution of carbonic acid from its supersaturated solutions to air bubbles contained within them, an explanation shown to be inadequate. TOMLINSON,† by similar experiments, distinguishes between surfaces which are and are not "*chemically clean.*" From clean surfaces, such as that of a freshly broken flint, or of a metal carefully washed with alcohol, no gas bubbles are given off; but when these surfaces are rubbed with a cloth and reintroduced into the solution of carbonic acid, they are immediately studded with bubbles of gas. He writes, "Make the solids chemically clean, and the solution adheres to them without any disengagement of gas; make them unclean, and then the adhesive force of the solid becomes more energetic for the gas than for the liquid, and there is a consequent separation of gas from the liquid." The experiments of SCHRÖDER‡ are of a similar kind. These phenomena, though analogous to those to be described below, are in this sense different, that in the one case we are dealing with a ready-made solution of a gas, but in the other with a gas in the course of manufacture from the material contained in a solution.§

In an experiment an aqueous solution of sodium formate, containing 1 gram of the salt, was added to such a previously-made mixture of sulphuric acid and water that the composition of the whole, before the reaction set in, was in the ratio $1H_2O : 3H_2SO_4$. An evolution of carbonic oxide resulting from the chemical change—

$$HCOOH = CO + OH_2$$

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* 'Compt. Rend.,' vol. 63, 1866, p. 883.

† 'Phil. Mag.' vol. 34, pp. 136 and 229; vol. 38, p. 204; vol. 43, p. 205; and vol. 45, p. 276.

‡ 'POGGENDORFF, Annalen,' vol. 137, p. 76; and Ergänzungsband 5, p. 87.

§ Mr. HARCOURT tells me that his attention was called to this subject nearly thirty years ago, when, in attempting to concentrate hydrogen dioxide under the receiver of an air-pump, he found that the decomposition of the liquid was hastened by removing the atmospheric pressure. Subsequently, he tried to measure the rate of decomposition of hydrogen dioxide under constant conditions, and had, finally, to abandon the attempt, in consequence of the impossibility of fixing one condition, namely, the state of the surface of the glass vessel which held the liquid. If the vessel was scrupulously cleaned, the decomposition took place more quickly than if any trace of grease adhered to the glass, and more quickly with some kinds of glass than with others.—July 26th, 1888.

occurred at a temperature of 35°·8–35°·9. But some finely divided particles, afterwards shown to be silica, were suspended in the solution of sodium formate; these were, doubtless, due to some process adopted by the manufacturer for obtaining the salt. It was observed that these particles were continually being borne up by the bubbles of gas, and seemed to serve as nuclei for their formation.

The experiment was then repeated under conditions precisely the same, with the exception that *the solution of the sodium formate was filtered into the sulphuric acid*, to free the solution from the coarser and visible particles. No appreciable quantity of gas was given off at 35°·8, and it was found necessary to raise the temperature about 38°, viz., to 73°·8, to obtain a rate of evolution of gas similar to that in the above experiment.

As these results appeared to be similar to those which Mr. HARCOURT had observed in the decomposition of hydrogen peroxide, he conducted the two following experiments. A mixture was made of 300 c.c. sulphuric acid (sp. gr = 1·7877) and 130 c.c. of water; to this, when cool, was added 10 c.c. of a filtered aqueous solution of sodium formate (containing 1 gram of the salt). Of this mixture two portions of 200 c.c. were taken, and introduced into two similar flasks, of which one contained a quantity of well-washed, recently ignited pumice suspended in 10 c.c. of water, the other 10 c.c. of pure water. The flasks, fitted with delivery tubes, were heated side by side in a water bath, and the carbonic oxide gas collected in two graduated tubes, standing in a pneumatic trough. The intervals of time between successive observations were approximately equal; the volumes collected in the two tubes were read simultaneously; the temperature varied throughout the experiment from 75°·8 to 76°·2.

Mixture, with pumice, c.c. of gas collected.		Mixture, without pumice, c.c. of gas collected in same time.	
Total.	Difference.	Total.	Difference.
10	..	5	..
15	5	5·8	·8
20	5	7·1	1·3
25	5	8·5	1·4
30	5	10	1·5
35	5	11·9	1·9
41	6	14·3	2·4
45	4	15·9	1·6
50	5	18·1	2·2

The first observation includes the volume, probably about 4 c.c., given off in consequence of the expansion of the liquid and of the enclosed air.

The rate of evolution of gas from the mixture containing the pumice is to that from the mixture without the pumice in approximately the ratio 5 : 2.

In order to determine the effect produced by variation of the mass of pumice, an experiment precisely similar to the one described above was conducted; in one flask was placed ·1 gram, in the other 5·0 grams of pumice. Temperature 76°.

Mixture with ·1 gram.		Mixture with 5 grams.		Interval of time in minutes and decimals.
Collected in each interval.	Total.	Collected in each interval.	Total.	
c.c.		c.c.		′
5·0	5·0	4·5	4·5	4·0
5·0	10·0	4·5	9·0	3·85
5·0	15·0	6·0	15·0	4·02
5·0	20·0	5·4	20·4	4·12
5·0	25·0	4·7	25·1	4·28
5·0	30·0	4·9	30·0	4·47
5·0	35·0	5·0	35·0	4·85
5·0	40·0	5·0	40·0	5·4
5·0	45·0	5·1	45·0	6·05

The rate of evolution of gas from both mixtures is proceeding *pari passu;* thus the mass of pumice added, whether ·1 gram or fifty times that amount, makes no difference.

The effect of finely divided particles, not only upon the decomposition of formic acid into carbonic oxide and water, but also upon other chemical reactions in which a gas is evolved, was studied more fully by aid of the twin U-tube apparatus.

Decomposition of Formic Acid into Carbonic Oxide and Water.

$$HCOOH = CO + OH_2.$$

Effect of Graphite.

Mixture taken . . . 175 c.c. sulphuric acid.
75 ,, water.

Into this was filtered slowly 50 c.c. of an aqueous solution of sodium formate, containing 5 grams of the salt. From this quantity 165 observations of 10 c.c. each are obtainable, so that in the earlier stages of the decomposition the effect due to loss of mass in each successive observation is inconsiderable.

After a preliminary stage of initial acceleration (see Part II.), the rate of evolution of gas became constant; when this point was reached, the cork through which passed the thermometer was taken out and about half a gram of finely-powdered graphite was introduced into the mixture; the containing flask was shaken, the cork restored to its former position, and observations recommenced at the same temperature.

Temperature 80°·5–80°·7.

Intervals in minutes and decimals required for evolution of 10 c.c. carbonic oxide.			
Before introduction of graphite.	After introduction of graphite.		
′	′	′	′
4·35	·83	3·03	3·25
4·20	2·37	3·12	3·25
4·40	2·80	3·13	3·22
4·30	2·77	3·22	3·37
4·17	2·83	3·15	3·40
4·17	2·87	3·0	3·35
4·22	3·03	3·15	3·42
4·22	3·15	3·25	

From these observations it appears that the rate of evolution of carbonic oxide is much accelerated by the presence of the graphite, for even after twenty-three observations, corresponding to a loss in mass of nearly 14 per cent., the rate was quicker than that observed before the addition of the graphite. At the conclusion of the experiment the graphite was found to be uniformly distributed throughout the acid liquid, and there was no perceptible odour of sulphurous oxide, thus indicating that no reduction of the sulphuric acid had occurred.

Effect of Silica.

The experiment above was repeated with silica, obtained by decomposition of silicon fluoride with water, which had been dried and recently ignited; it was in the usual form of a fine fluffy powder.

Variation of temperature 80°·4–80°·6.

Intervals in minutes.		
Before introduction of silica.	After introduction of silica.	
′	′	′
5·28	1·9	3·06
5·0	2·62	3·17
5·08	2·85	3·06
5·1	2·66	3·37
5·08	2·7	3·33
	2·56	3·33
	3·06	3·33

On adding the silica and agitating the flask containing the decomposing mixture an effervescence of gas took place, so tumultuous that some small quantity of liquid frothed over; it was necessary to wait a few minutes until this had subsided sufficiently to allow of observations being taken.

Effect of Glass Dust.

A quantity of glass dust was obtained by breaking Rupert's drops, and sifting the finely divided glass through a sieve.

A mixture was made up as follows :—

300 c.c. sulphuric acid,
130 ,, water,

into which was filtered slowly 85 c.c. of water containing 10 grams of sodium formate. Two portions, each of 175 c.c., of this mixture were taken, placed in two flasks, which were heated in a water bath side by side.

Mean temperature 79°·5. The observations are divided into sets of 50 c.c. each; the volumes collected in the two tubes were read simultaneously.

Mixture with glass dust.		Intervals in minutes for each difference.	Mixture without glass dust.	
Total.	Difference.		Total.	Difference.
c.c.	c.c.		c.c.	c.c.
10	10	10·45	1·0	1
20	10	9·47	3·0	2
30	10	7·85	5·0	2
40	10	7·95	8·5	3·5
50	10	8·02	12·5	4·0
10	10	7·95	5·5	5·5
20	10	7·13	12·5	7·0
30	10	7·05	18·0	5·5
40	10	7·28	24·5	6·5
50	10	7·43	31·5	7·0
10	10	7·55	7·5	7·5
20	10	7·78	15·0	7·5
30	10	7·92	22·5	7·5
50	20	14·37	38·7	16·2
10	10	7·5	8·0	8·0
20	10	7·87	16·5	8·5
30	10	7·83	24·5	8·0
40	10	7·4	32·5	8·0
50	10	7·7	40·5	8·0
10	10	7·33	8·5	8·5
20	10	7·5	16·5	8·0
30	10	7·67	24·5	8·0
40	10	7·93	32·5	8·0
50	10	8·35	40·5	8·5

From the above results it is evident that the rate of evolution of gas from the mixture with the glass dust is greater than that from the mixture without the glass; the difference between these rates diminishes as the change proceeds, owing, partly, at least, to the greater diminution of mass in the former case than in the latter, for from the one 25 observations of 10 c.c. each were taken, out of a possible 165; from the other only 16 or 17, out of the same number.

Decomposition of Nitric Acid into Nitric Oxide and Water by means of Ferrous Sulphate.

$$6FeSO_4 + 5H_2SO_4 + 2KNO_3 = 3Fe_2(SO_4)_3 + 2KHSO_4 + 4H_2O + 2NO.$$

A convenient method of preparing pure nitric oxide gas consists in heating ferrous sulphate and potassium nitrate with dilute sulphuric acid. A mixture was made up as follows:—6 grams of potassium nitrate and 36 grams ferrous sulphate were dissolved in 100 c.c. water; the solution filtered to rid it of small quantities of a basic iron sulphate, which invariably separated out; to this solution was added gradually a previously made and cooled mixture of 40 c.c. sulphuric acid and 20 c.c. water. The twin U-tube method was used.

Effect of Pumice.

Temperature 34°·8–35°·2.

Intervals in minutes required for evolution of 10 c.c. nitric oxide.		
Before introduction of pumice.		After introduction of pumice.
6′·05	9′·88	2′·9
6·87	11·37	7·15
7·75		15·08
8·75		

The introduction of the pumice produced a most violent effervescence; some quantity of the liquid frothed over. The above results show that, notwithstanding the loss of mass due to this effervescence, the interval of time in which 10 c.c. of gas is given off is suddenly reduced from 11′·37 to 2′·9.

Effect of Graphite.

The experiment above was repeated, graphite being introduced instead of pumice; the phenomena observed were precisely similar.

Temperature 39°·4–39°·7.

Intervals in minutes.				
Before introduction of graphite.			After introduction of graphite.	
1′·67	3′·77	6′·62	1′·37	4′·97
1·88	4·37	7·43	2·13	6·63
2·4	5·23	8·5	2·87	10·78
3·32	6·05	9·88	3·99	16·67

Thus, on introduction of the graphite the interval required for the evolution of 10 c.c. of gas is suddenly reduced from 9′·88 to 1′·37, notwithstanding the loss of mass due to a tumultuous effervescence of gas.

Effect of Barium Sulphate.

Some barium sulphate was prepared by precipitation of the chloride with sulphuric acid, and washed carefully from all traces of chloride; it was then ignited in the usual manner.

Temperature 37°·6–38°·0.

Intervals in minutes.			
Before introduction of barium sulphate.		After introduction of barium sulphate.	
4′·43	11′·9	5′·08	22′·58
6·88	30·03	10·0	35·1

The interval of time is here reduced from 30′ to 5′ by the presence of the precipitated barium sulphate.

Decomposition of Ammonium Nitrite in Aqueous Solution into Nitrogen and Water.

$$NH_4NO_2 = N_2 + OH_2.$$

The preparation of nitrogen gas by heating together concentrated aqueous solutions of potassium nitrite and ammonium chloride is well known. The effect of finely divided particles in promoting the evolution of nitrogen was studied as affording an example of a case in which there is formed a gas, most sparingly soluble, and thus not likely to be stored in any quantity in the solution of the salts undergoing decomposition.

Effect of Silica.

A mixture was made of 40 c.c. of a concentrated solution of potassium nitrite and 120 c.c. of a cold saturated solution of ammonium chloride, containing about 33 per cent. of the salt.

Variation of temperature, 57°·7–57°·9.

Intervals in minutes required for evolution of 10 c.c. nitrogen.			
Before introduction of silica.		After introduction of silica.	
5′·92	6′·62	3′·0	12′·02
6·03	6·8	4·3	12·8
6·13	7·18	8·72	
5·95	7·77	9·72	
6·13	8·55	10·55	

The interval of time is suddenly reduced to about one-third by the introduction of the silica, as in some previous cases, but the rate of the decomposition quickly resumes its former course.

Effect of Pumice.

This experiment was made with a similar mixture. Temperature, 58°–59°·1.

Intervals in minutes.					
Before introduction of pumice.				After introduction of pumice.	
2′·57	3′·15	6′·23	7′·22	6′·28	10′·7
2·7	4·25	6·03	7·7	6·4	
2·9	4·53	6·03	8·03	9·13	
3·08	5·38	6·65		10·02	

The interval of time is here reduced from 8′·03 to 6′·28 by the introduction of the pumice; otherwise the results are comparable with those of the former experiment.

Decomposition of Ammonium Nitrate into Nitrous Oxide and Steam.

$$NH_4NO_3 = N_2O + 2OH_2.$$

Owing to the solubility of nitrous oxide in water, the twin U-tube apparatus was modified by the interposition between the flask and the U-tube of a bent tube, provided with two bulbs at different levels, the form of which is described at length in my paper "On the Rate of Decomposition of Ammonium Nitrate."* By its means each measure of nitrous oxide was represented by the collection in the U-tube of its corresponding volume of air. The manipulation and processes of purification of the salt were the same as those adopted in the previous experiments. Such a quantity of salt, about 200 grams, was taken that the loss of mass between any two consecutive observations should be far too small to affect the results.

Effect of Pumice.

In this case the temperature of the pumice introduced was as nearly as possible that of the fused salt, so as not to produce local solidification of the salt around the pumice, and thus retard the decomposition.

Temperature, 182°·2–182°·5.

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* 'Chem. Soc. Journ.,' 1883, p. 373.

Intervals in minutes required for evolution of 10 c.c. nitrous oxide.				
Before introduction of pumice.			After introduction of pumice.	
4′·67	4′·63	4′·5	2′·4	3′·65
4·72	4·48		3·35	3·82
4·77	4·5		3·7	3·88
4·7	4·47		3·7	3·85

The interval is reduced from a constant value of 4′·5 to 3′·80 by the introduction of the pumice.

Effect of Barium Sulphate.

The experiment was repeated with precipitated barium sulphate. In order to determine whether the change of atmosphere above the fused salt had any effect upon the rate of the decomposition, the cork, with the thermometer, was taken out, and the superincumbent atmosphere of nitrous oxide, steam, and vapours of the salt was completely blown away. But on restoring the cork the interval required for the evolution of the 10 c.c. of the nitrous oxide was the same as before, which proves that the results obtained in the cases investigated above are not due to the necessary partial change of atmosphere in the process of introducing the finely-divided material. The intervals of time required for the unit of decomposition obtained after the alteration of the atmosphere are given in the second column.

Variation of temperature, 191°·5–191°·8.

Intervals in minutes.						
Before introduction of barium sulphate.			After introduction of barium sulphate.			
5′·4	5′·52	5′·4	2′·32	1′·85	1′·98	1′·88
5·4	5·47	5·4	2·4	1·83	1·93	1·85
5·43		5·53	2·12	1·8	1·95	
5·45			2·02	1·83	1·86	
			1·97	1·87	1·85	

The results show that the constant interval is reduced from 5′·45 to 1′·85, or, practically, to one-third, by the introduction of such a chemically inert substance as barium sulphate.

Effect of Platinum Black.

A sample of platinum black was prepared by reducing the chloride with a slightly alkaline solution of sodium formate; the precipitated metal was washed free from all traces of chlorine and partially dried over sulphuric acid in a vacuum; it was thought advisable not to completely dry the finely-divided metal, so as to avoid a possible absorption of oxygen.

Intervals in minutes.			
Temperature, 200°–205°. Before addition of platinum black.		Temperature, 182°–182°·5. After addition of platinum black.	
4′·92	5′·0	3′·17	3′·17
5·0	5·02	3·2	3·13
5·0	4·98	3·2	3·17
5·02	5·0	3·13	

The effect of platinum black is most striking; the interval of time is reduced practically in the ratio of 5 : 3, even though the temperature was lowered 18°, in order to obtain a rate of decomposition sufficiently slow for convenient observation.

Decomposition of Potassium Chlorate into the Perchlorate, Chloride, and Oxygen.

$$2KClO_3 = KClO_4 + KCl + O_2.$$

It is usually stated in the more recent text-books on chemistry (see page 259), that finely divided chemically inert substances do not accelerate the evolution of oxygen from potassium chlorate. To decide this point a quantity of potassium chlorate was re-crystallised; into two similar-shaped retorts were introduced 70 grams of the salt; to one portion ·7 gram of precipitated barium sulphate was added. The retorts were placed side by side in a small square air bath, provided with two holes in one side, through which the necks of the retorts passed. The air bath was packed with asbestos, to distribute the heat of the lamp as uniformly as possible. After the evolution of oxygen had commenced, but before systematic observations were taken, 104 c.c. of gas were given off from the chlorate containing the barium sulphate, but only 51·2 c.c. from that without the sulphate. The observations are divided into sets of 50 c.c. each, being the capacity of the two graduated tubes which served to collect the oxygen. The time was noted at which each measure of oxygen was evolved from the retort containing potassium chlorate and barium sulphate, and simultaneously the volume which had been evolved from the retort containing potassium chlorate only was read.

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Rate of Evolution of Oxygen.

Mixture of 70 grams potassium chlorate and ·7 gram barium sulphate.		Interval in minutes for each difference.	70 grams of potassium chlorate.	
Total volume.	Difference.		Total volume.	Difference.
c.c.	c.c.		c.c.	c.c,
20	20	3·5	1·0	1·0
40	20	3·53	2·0	1·0
50	10	1·8	2·5	1·5
20	20	4·25	1·5	1·5
40	20	4·6	2·5	1·0
50	10	3·15	3·5	1·0
10	10	5·68	1·5	1·5
20	10	5·32	4·0	2·5
30	10	6·85	7·0	3·0
40	10	6·33	10·0	3·0
50	10	7·43	12·5	2·5
10	10	5·83	2·0	2·0
20	10	7·03	5·0	3·0
30	10	6·13	7·5	2·5
40	10	6·18	10·0	2·5
50	10	6·28	13·5	3·5

From these results it is evident that the evolution of oxygen from the chlorate with which the barium sulphate is mixed not only commenced at a lower temperature, but also was more rapid throughout, though the difference between the two rates of evolution diminishes as the reaction proceeds, owing to a greater loss of mass in the one case than in the other. The whole course of the phenomenon is precisely analogous to that observed in the case of the decomposition of sodium formate by strong sulphuric acid in the presence or absence of glass dust.

In order to determine whether such a chemically inert substance as barium sulphate is as effective a material as manganese peroxide in promoting the evolution of oxygen at a temperature below the point of fusion of the chlorate, two portions of 20 grams of the salt were taken. To the one was added ·2 gram of barium sulphate; to the other, ·2 gram of manganese peroxide, Mn_6O_{11}, H_2O, prepared for a previous investigation, and shown by spectroscopic analysis to be free from any considerable quantities of the oxides of the alkalies and alkaline earths. Each of these mixtures was placed in a piece of combustion tubing, the end of which was drawn out into a capillary. The two tubes were heated side by side in an air bath.

Mixture of 20 grams potassium chlorate and ·2 gram manganese peroxide.		Intervals in minutes for each difference.	Mixture of 20 grams potassium chlorate and ·2 gram barium sulphate.	
Total volume.	Difference.		Total volume.	Difference.
c.c.	c.c.		c.c.	c.c.
10	10	2·22	1·0	1·0
20	10	2·0	2·0	1·0
30	10	2·07	2·5	1·5
40	10	2·43	3·0	·5
50	10	2·03	3·5	·5
10	10	1·13	·5	·5
20	10	·87	1·25	·75
30	10	·92	2·25	1·0
50	20	1·22	3·25	1·0
20	20	1·27	·5	·5
40	20	1·73	2·0	1·5
50	20	·92	3·5	1·0
20	20	2·58	·5	·5
40	20	4·58	1·5	1·0

These results show that, while the evolution of oxygen from the potassium chlorate and manganese peroxide mixture is very rapid while the salt still remained unfused that from the potassium chlorate and barium sulphate is exceedingly small under the same conditions.

The results of the various experiments detailed above all point to the one conclusion, that the rate of evolution of a gas formed by chemical change in an homogeneous liquid is accelerated by the presence of finely divided particles which are chemically inert. Thus, whether the gas is evolved from an aqueous solution or a salt in a state of fusion, whether the gas is soluble in the liquid from which it is being evolved or not, whether the chemical change from which the gas results takes place at a temperature of 37° or 350°, whether the finely divided substance is porous or not, the result is uniformly the same.

PART II.

Phenomenon of Initial Acceleration and Effect of Reduction of Pressure on the Rate of Evolution of Gases.

Before proceeding to discuss the effects produced by reduction of pressure on the rate of evolution of gases from homogeneous liquids, it is desirable to call attention to the phenomenon of initial acceleration. It was observed by Mr. Harcourt some years ago, and confirmed by my experiments on the decomposition of ammonium nitrate and on other chemical reactions detailed in the present communication, that the rate of evolution of gas, external conditions remaining the same, is at first slow, then gradually increases until it reaches a maximum, and for some time constant, rate, from which point it decreases constantly with the diminution of the mass undergoing decomposition. The curve, then, representing the velocity in terms of mass would thus show a point of contrary curvature. This phenomenon of initial acceleration has previously been observed in reactions occurring between two gases giving a third gas as a resultant, as also between two liquids with liquid resultants. Thus BUNSEN and ROSCOE in their photo-chemical researches* pointed out that the combination of hydrogen with chlorine, under the influence of direct sunlight, starts at first slowly, but quickly increases, reaching a maximum; this phenomenon they called "photo-chemical induction." To illustrate their results, they studied the rate of replacement of hydrogen in tartaric acid by bromine, both the reacting substances being in dilute solution; this rate was found to increase slowly, reaching a maximum point. Again, BERTHELOT and PÉAN DE SAINT GILLES† observed the same period of initial acceleration in their studies on the rate of formation of ethereal salts, less marked in the etherification of acetic acid by ethyl alcohol, but most marked in the case of valeric acid. On this point they write as follows‡:—"Pour la concevoir il faut admettre une sorte d'inertie, de résistance à vaincre qui retarde la combinaison dans les premiers instants, et dont les effects compensent et au-delà pendant un certain temps ceux qui résultent d'un état de concentration plus grande dans le système. Cette accélération initielle semble donc constituer un caractère assez général de ce genre de réactions." It is apparently also common to the kind of reactions, here investigated, in which a gas is formed from a liquid. But the intervals of time required for the unit of chemical change do not, however, decrease in any regular uniformity during this period of acceleration; it is probable that the phenomenon is the result of several causes, the peculiar effect of each of which cannot at present be determined by mathematical analysis. In some cases it is due to a storage of gas within the liquid, particularly in the formation of nitric oxide from nitric acid by means of ferrous sulphate, and in others a delay is occasioned by the actual resolution of more complex into simpler molecules, or even atoms, which in their turn react to form the gaseous product. Thus, in the formation of nitrous oxide from ammonium nitrate, the delay may be occasioned by the resolution of the molecule of the salt into ammonia and nitric acid, as observed by BERTHELOT. In the case of the decomposition of potassium ferro-cyanide by sulphuric acid the double salt at first splits up into the separate metallic cyanides, which yield, by the action of the acid, hydrocyanic and subsequently formic acid. This last is then decomposed into carbonic oxide and water. It would appear that hydrocyanic acid is always an initial product in this decomposition. Thus, to put the proposition in a general form, if in any chemical system a

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* 'Phil. Trans.,' 1857, p. 355.

† 'Annales de Chimie,' [3], vol. 66, 1862, pp. 5–153.

‡ *Ibid.*, pp. 26, 65.

compound *abcd* decomposes initially into *ab* and *cd*, which in their turn form *ac* and *bd*, thus

$$\text{(i.)}\quad abcd = ab + cd$$
$$\text{(ii.)}\quad ab + cd = ac + bd,$$

then, if neither of these changes is instantaneous, the rate at which *bd*, the measured compound, is produced would gradually increase until the velocity of change (ii.) is equal to that of change (i.). The reverse case of (i.) may also occur, in which *ab* and *cd* combine to form *abcd*, which is again decomposed thus

$$\text{(i.)}\quad ab + cd = abcd$$
$$\text{(ii.)}\quad abcd = ac + bd.$$

The experiments illustrative of this phenomenon are given below for a variety of chemical changes. In Part I. the intervals of time observed before the maximum and constant rate was reached have in all cases been omitted in order to shorten the tables. To make the results the more comparable, all the observations are reduced on the supposition that the mass of the substances undergoing decomposition remained constant.

Decomposition of Formic Acid into Carbonic Oxide and Water.

Constant mass of sodium formate = 5 grams, corresponding to 3·384 grams of formic acid, and yielding a sufficient volume of carbonic oxide for 160 observations of 10 c.c. each. Temperature 80°·8 to 80°·9. The observations are given up to the point of maximum and constant rate.

Intervals in minutes required for evolution of 10 c.c. carbonic oxide.				
Reduced.			Not reduced.	
18′·98	5′·92	4′·74	6′·53	5′·30
9·47	5·56	4·51	5·67	5·33
6·81	5·17	4·27	5·33	

To determine the effect produced by a temporary lowering of temperature, at the conclusion of the observations recorded in the first column the mixture was cooled by being placed into water at 20°, which caused the temperature to fall to 70°. The flask was then restored to its position and quickly heated up to the former temperature, 80°·8 to 80°·9, when observations were again made; but, as the loss of gas in the interval was not determined, the times recorded in the second part of the table are not reduced. They show, however, that the phenomenon of initial acceleration repeats itself.

Two other series of observations are given below, made under precisely the same conditions of mass of salt, concentration of acid, and with slight differences of temperature.

Intervals in minutes (reduced).				
I. Temperature 80·4–80·5.			II. Temperature 80·7–80·9.	
13′·13	5′·18	4′·18	10′·62	5′·03
8·02	4·50	4·02	7·15	4·93
6·11	4·28		6·02	
			5·26	

Decomposition of Potassium Ferrocyanide by Sulphuric Acid.

$$K_4Fe(CN)_6, 3H_2O + 6H_2SO_4 + 3H_2O = 6CO + 2K_2SO_4 + 3(NH_4)_2SO_4 + FeSO_4.$$

Experiments made in the earlier stages of this research on the rate of decomposition of potassium ferrocyanide with concentrated sulphuric acid in accordance with the above equation also illustrate this phenomenon of initial acceleration. The twin U-tube method was used, but the standard quantity of air taken was such as would correspond to the decomposition of ·058 gram of the salt.

A mixture was made up as follows :—

21	grams	crystallised ferrocyanide, corresponding to 860 observations.
420	,,	sulphuric acid.
2·7	,,	water.

This mixture was heated until the salt had completely dissolved in the acid to form a clear liquid, and then observations were commenced, little or no gas other than small quantities of hydrocyanic acid being given off before the salt dissolved.

Temperature 150°·8–151°.

Intervals in minutes (reduced) required for evolution of standard volume of carbonic oxide.			
7′·27	6′·12	6′·18	5′·70
6·43	6·03	6·16	5·66
6·72	6·13	5·73	
6·35	6·12	5·63	

These results are precisely similar to those given above.

In another set of experiments a mixture was made up as follows :—

31·5	grams	potassium ferrocyanide.
420	,,	sulphuric acid.
1·3	,,	water.

Temperature 150°·8–151°·2.

Intervals in minutes (reduced).		
13′·67	9′·54	6′·83
12·36	8·33	6·44
10·48	7·94	6·01
9·74	7·30	5·84

Decomposition of Ammonium Nitrate.

In my former experiments on the decomposition of ammonium nitrate the same phenomenon was observed; in these the standard volume of air taken was equal to the volume of nitrous oxide given off by the decomposition of ·05 gram of the salt.

Temperature 210°–210°·5.

Intervals in minutes (reduced) required for evolution of standard volume of nitrous oxide.						
17′·7	10′·3	6′·25	4′·2	3′·25	2′·65	2′·35
16·0	8·65	5·75	3·8	3·05	2·55	2·25
14·3	7·9	5·4	3·4	2·8	2·45	2·10
12·0	7·05	4·65	3·35	2·7	2·45	2·15

In other series of experiments a similar very gradual acceleration was observed; of these only one need be quoted in illustration.

Intervals in minutes (reduced).				
6′·57	4′·07	2′·96	2′·87	2′·50
5·20	3·82	3·11	2·76	2·49
4·83	3·58	3·01	2·68	
4·45	3·42	2·99	2·59	

Decomposition of Oxalic Acid by Strong Sulphuric Acid.

$$H_2C_2O_4 - OH_2 = CO_2 + CO.$$

In the course of some experiments made to determine the effect produced by alteration of pressure, the decomposition of oxalic acid into carbonic acid and oxide was selected as a case for investigation. The results obtained also illustrated this phenomenon of initial acceleration. Owing to the solubility of carbonic acid in water some modification of the apparatus was necessary to collect the mixed gases over mercury.

The method adopted was as follows:—Two tubes were wired together above and below, of which one was graduated in cubic centimetres, the other in millimetres. In the former the mixed gases were collected, while the latter served to indicate the pressure in millimetres of the mercury column corresponding to each reading of the other tube, both standing in a small trough filled with mercury. Thus each uncorrected volume of 10 c.c. could be reduced in terms of standard pressure and temperature; due allowance was also made for the tension of aqueous vapour, the tube which served for the collection of the gases being moistened with water. 12 grams of crystallised oxalic acid were dissolved in 120 c.c. sulphuric acid; after complete dissolution of the oxalic acid observations were made; these are divided into sets of 50 c.c. each.

Temperature 67°·4–67°·6.

Intervals of time required for evolution of 10 c.c. of carbonic oxide and acid.	
I.	II.
14′·0	7′·36
12·6	7·50
10·31	7·13
8·12	6·36
7·83	6·27

In other series of experiments precisely similar results were obtained; of these only one need be quoted for illustration, made under conditions precisely similar to that above, with the exception that the temperature was slightly higher, viz., 69°·0.

Intervals of time required for evolution of 10 c.c. of the mixed gases.	
I.	II.
9′·5	5′·39
8·12	5·20
6·71	5·08
6·20	5·03
5·94	5·03

In the above tables the Series II. is practically continuous with the Series I., small quantity of the gases being lost between the last observation of I. and the first of II: in the interval of time during which the collecting tube was re-filled with mercury.

Decomposition of Nitric Acid into Nitric Oxide and Water by means of Ferrous Sulphate.

In the formation of nitric oxide by heating together solutions of ferrous sulphate and potassium nitrate with dilute sulphuric acid, this initial acceleration was not observed under the conditions of the experiments. But when the pale green liquid was warmed at about 40°, it gradually became darker by the solution therein of the nitric oxide, a process which lasted often for half an hour or more. When the liquid had become almost black, then, owing to some indeterminate cause, there was a sudden outburst of gas, accompanied by an evolution of heat, the thermometer rising one to two degrees. From this point the evolution of gas gradually decreased, at a rate probably proportional to the diminution of mass.

Decomposition of Ammonium Nitrite in Aqueous Solution into Nitrogen and Water.

In the few experiments made in the course of the present investigation on the above chemical change the phenomenon of initial acceleration was not observed, but Mr. HARCOURT has informed me that in his previous investigations, on a more extended scale, he always observed the phenomenon, and showed that it could be reproduced by temporary cooling of the liquid, as noted above in the case of the decomposition of formic acid.

Production of Hydrogen from Zinc and Sulphuric Acid.

$$\mathrm{Zn} + \mathrm{H_2SO_4} = \mathrm{ZnSO_4} + \mathrm{H_2}.$$

Though the results obtained in measuring the rate of evolution of hydrogen from zinc and sulphuric acid are not strictly comparable with the evolution of gas from a homogeneous liquid, yet, as SPRING and AUBIN[*] have recently called attention in this case also to an initial acceleration, which they call the "period of induction," it may here be briefly considered.

In the present research, this phenomenon was observed in the course of experiments made before the publication of SPRING and AUBIN's paper. It is probably conditioned by the mechanical adherence of bubbles of gas to the surface of the metal, which is always apparent when sulphuric acid comes in contact with a regular surface of the metal. If these bubbles are removed as fast as they are formed, or if the metal is continuously rolled about within the acid liquid, no such initial acceleration can be observed.

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[*] 'Annales de Chimie' [6], vol. 11, pp. 505–554.

Effect of Reduction of Pressure on the Rate of Evolution of Gases.

The retardation or promotion of certain chemical decompositions and combinations by increase or decrease of pressure has from time to time been the subject of various inquiries; of these, some will be alluded to in the sequel. As the evolution of gas from a liquid might apparently be modified by reduction of the superincumbent atmosphere to which that liquid is subjected, as preventing a possible storage of gas in its initial stage of formation, the effect produced by such a reduction of pressure was considered a subject worthy of particular investigation.

The apparatus employed consisted mainly of three parts, a blown-out flask of stout glass, a SPRENGEL pump with the usual gauge, and a tube serving for the collection of known volumes of the gaseous product. Through the neck of the flask passed a T-piece of glass tubing; the vertical part of this was closed by a rubber cork through which passed the thermometer, while the horizontal part, of stout glass, enclosing a capillary airway, was connected by thick-walled rubber tubing with the SPRENGEL pump. The delivery tube of the pump, resting within a small crucible filled with mercury, was slightly curved up in order to pass the gas into a stout piece of glass tubing of rather larger diameter. To the upper end of this latter was sealed an upright piece of capillary tubing, which served to deliver the gaseous product into some form of collecting apparatus placed upon the working bench of the laboratory. The mercury dropping from the pump overflowed from the crucible into a porcelain dish, and was returned from time to time to the funnel, to which the rest of the pump was connected by a stout piece of rubber tubing, which could be compressed to a greater or less degree by means of a clamp. In order to study the rate of evolution of gas at any desired pressure below that of the atmosphere, a small strip of paper was gummed on the gauge, and the flow of mercury adjusted proportionally to the evolution of the gas, so that the level of the mercury within the gauge varied only a few millimetres on either side of the paper strip marking the reduced pressure. After a little practice this process was found to be easy. In order to test the tightness of the various joints, which were all carefully lubricated, the whole apparatus was exhausted to a few millimetres pressure; if the mercury in the gauge did not rise appreciably after the lapse of several hours, the whole being left generally over night, the apparatus was considered sufficiently air-tight for observations lasting only a few hours.

Decomposition of Oxalic Acid into Carbonic Acid and Oxide.

The method adopted for collecting known volumes of carbonic acid and oxide has been described above. Experiments were at first made under a reduced pressure, then the mixed gases allowed to fill up the vacuum, and observations commenced as before; these are divided into sets of 50 c.c. each, there being a small loss of gas, as observed above, before the last observation of each set and the first of the next.

Mixture used, 12 grams oxalic acid in 120 c.c. sulphuric acid.

Temperature 68°·9–69°·0.

Intervals of time for each 10 c.c. of the mixed gases.					
Pressure 163 mm.			Pressure 785 mm.		
12′·2	3′·9	4′·70	9′·5	5′·39	5′·31
6·02	4·18	4·81	8·12	5·20	5·31
4·5	4·27		6·71	5·08	5·0
4·63	4·64		6·20	5·03	5·0
4·18	4·85		5·94	5·03	

The results at the reduced pressure show an initial acceleration, then a constant, followed by a gradually decreasing, rate; when the mixed gases had filled up the vacuum, which required a volume of 75 c.c., corresponding to a loss of 7·5 observations, the initial acceleration again repeats itself, followed by a constant rate practically equal to that obtained at the point at which the pressure was increased.

These observations do not point to any marked difference in the rate of evolution of gas at pressures below the atmospheric.

Another series of experiments was conducted under nearly identical conditions, which point to the same general result.

Temperature 66°·9–67°·0.

Intervals of time for each 10 c.c.						
Pressure 132 mm.					Pressure 773 mm.	
34′·5	6′·45	5′·78	5′·17	6′·01	14′·0	7′·36
11·9	6·32	6·13	5·20	5·81	12·6	7·50
7·65	6·34	—	5·39	6·58	10·31	7·13
6·59	—	6·00	5·72	6·70	8·12	6·36
6·67	—	5·94	5·95	6·77	7·83	6·27

In the first set three observations were missed, owing to some irregularity in the working of the SPRENGEL pump.

Decomposition of Formic Acid into Carbonic Oxide and Water.

A series of experiments was also conducted to determine the effect produced by variation of pressure on this decomposition; the method of working was the same as that described above, but the twin U apparatus was used, the carbonic oxide being collected over water; the whole process was therefore continuous, with the exception of the interval during which the gas filled up the vacuum, or was pumped out while the pressure was being reduced.

A mixture was made up as follows:—

Sulphuric acid . . . . = 175 c.c.
Water . . . . = 58 „
Solution of sodium formate = 75 „

containing 10 grams of the salt in solution, which corresponds to 330 observations of 10 c.c. each; thus, the difference between successive observations caused by diminution of mass and dilution of the sulphuric acid by the water formed in the reaction is inappreciable.

Temperature 69°–69°·2.

Interval of time required for evolution of 10 c.c. of gas.									
I. At pressure of 155 mm.			II. At pressure of 753 mm.				III. At pressure of 155 mm.		
10′·63	5′·3	5′·61	15′·72	7′·22	7′·26	7′·37	2′·85	7′·13	7′·37
6·73	5·43	5·85	10·33	7·18	7·33		5·3	7·08	7·52
6·4	5·7	6·12	9·38	7·33	7·17		6·27	7·25	
6·03	5·58	6·22	9·15	7·23	7·03		6·77	7·03	
		6·22	8·9	7·40	7·27		6·90	7·47	

The results set forth in the above table are practically continuous; when it was judged that the maximum and constant rate in Series I. was attained, the pressure was suddenly increased by temporarily taking out the cork of the flask containing the acid mixture, and the observations in Series II. commenced; the interval of time between the last observation of I. and the first of II. was 12 minutes, but during this time little, if any, gas was given off. Again, when in Series II. the maximum and constant rate was reached, the pressure was reduced as rapidly as possible to the former point by working the SPRENGEL, a process requiring about 8′·5, during which the pumped-out gas was allowed to escape. The results show that at the reduced pressure there is the usual period of initial acceleration; on increasing the pressure there is a retardation followed by an acceleration, but on again decreasing the pressure the phenomenon is reversed, *i.e.*, there is a period of initial retardation. The intervals of time in the period of maximum rate of Series I. are slightly less than those in Series II., but these latter are equal to those in Series III., thus showing that variations of pressure produce but little variation in the rate of evolution of gases from liquids. It is also to be noted that, as regards the initial acceleration, the effect of a sudden increase of pressure is precisely the same as that of a temporary lowering of temperature.

In other series of experiments results precisely similar were obtained.

A mixture was made up of 202 c.c. sulphuric acid, 73 c.c. water, and 75 c.c. of solution of sodium formate containing 10 grams of the salt. Temperature 64°·4–64°·6.

Intervals of time required for evolution of 10 c.c. gas.					
I. At pressure of 763 mm.			II. At pressure of 46 mm.		
23′·37	9′·18	8′·83	3′·52	8′·90	8′·6
10·37	8·75	8·85	7·53	8·8	8·78
9·75	9·03	8·75	8·95	8·83	
9·13	9·1		8·90	8·7	
				8·8	

The observations in Series II. are in accordance with the preceding series, indicating a temporary increase in rate followed by a period of retardation caused by reducing the pressure. This is doubtless caused by the pumping out of some small quantity of gas stored within the liquid, while the retardation followed by a period of acceleration in Series I. is conversely in part due to some increase of storage within the liquid. The carbonic oxide at the moment of its production from the formic and sulphuric acid is somehow or another more soluble in sulphuric acid than ready-formed carbonic oxide, which is practically insoluble.

Decomposition of Potassium Chlorate into the Perchlorate and Oxygen.

A comparative experiment was also made to study the effect of the reduction of pressure on the evolution of oxygen from potassium chlorate, as presenting an example of a fused salt. Into two pieces of combustion tubing were placed 15 grams re-crystallised potassium chlorate; their ends were subsequently drawn out, the one into a capillary, the other so as to form a convenient joint with the SPRENGEL pump. The two tubes were placed side by side in a small iron pot, filled with molten potassium nitrate, heated by a BUNSEN burner. It was found possible to keep the temperature of the molten nitrate fairly uniform. At first the rate was compared of evolution of oxygen from both tubes, that from one passing directly into the collecting tube, that from the other journeying by way of the SPRENGEL pump. As the rates were equal, the pressure on one was reduced to 20 mm.

Volume of gas collected.			
At pressure of 765·4 mm.		At pressure of 768·4 mm.	
Total.	Difference.	Total.	Difference.
c.c.	c.c.	c.c.	c.c.
10	10	8	6
15	5	14·8	6·8
20	5	20	5·2
25	5	24·8	4·8
30	5	29·5	4·7
35	5	34·5	5·0
40	5	39·8	5·3
At pressure of 765·4 mm.		At pressure of 20 mm.	
5	5	8	8
10	5	13·6	5·6
15	5	17	4·6
20	5	21·2	4·2
25	5	25·2	4·0
30	5	28·8	3·6
35	5	33·8	5
40	5	37	3·2
45	5	43	6

The results in the lower table show that on reducing the pressure there is a temporary slight increase in the rate of evolution of gas, but afterwards the decomposition proceeds *pari passu* at the ordinary and at the reduced pressure.

Decomposition of Ammonium Nitrate into Nitrous Oxide and Steam.

The effect of variation of pressure on this decomposition was not completely investigated; one experiment was conducted with an apparatus similar to that described above in the case of the decomposition of formic acid, but with a U-tube interposed between the decomposition flask and the SPRENGEL, and surrounded by a freezing mixture to condense the steam evolved. The fused salt having been heated under a pressure of 20 mm., it was observed that a sudden increase of pressure, caused by opening the decomposition flask by removal of the cork, practically stopped the decomposition for some time; thus, the phenomenon of the retardation, to be followed by a period of acceleration, is much exaggerated.

Evolution of Hydrogen from Zinc and Sulphuric Acid.

Various experimenters have from time to time noticed the complete arrestation by pressure of the displacement of acidic hydrogen by zinc and other metals. Thus, so long ago as 1828, BABINET[*] writes, "Si on opère en vases clos lorsque le gaz (hydrogène)

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[*] 'Annales de Chimie,' [2], vol. 37, p. 183.

acquiert une force élastique suffisante, l'action chimique s'arrête; elle est suspendue jusqu'au moment où l'on donne issue au gaz comprimé." BABINET states that decomposition of zinc by sulphuric acid is stopped by a pressure of 13 atmospheres at a temperature of 0°, and at 33 atmospheres at a temperature of 20° C.; while LOTHAR MEYER* observed that a pressure of 66 atmospheres is required. Experiments made on this subject were more in accordance with the statement of BABINET; to completely stop the reaction at 15° C. a pressure of 28·4 atmospheres was required, this being calculated from the volume of hydrogen which should be theoretically given off by the observed loss in weight of the zinc. The superincumbent pressure was not however equal to this, as a considerable volume of the hydrogen was dissolved in the liquid, and was given off, on releasing the pressure, as carbonic acid from soda water. This subject has also been examined by CAILLETET,† as also from an electric point of view by F. J. SMITH. BEKETOFF‡ also noticed that solutions of certain salts of silver, such as the nitrate or the chloride, in ammonia, though not reduced by zinc and an acid at ordinary pressures, were readily reduced when the materials were confined in a sealed tube. Experiments were made to determine the effect produced by decrease of pressure on the rate at which the hydrogen is given off.

I. *Experiment on the Effect produced by Reduction of Pressure on the Rate of Evolution of Hydrogen.*

The method of experiment was the same as that described above; the twin-U tube method was adopted, 5 c.c. of dry air at 0° and 760 mm. being taken as the standard.

Weight of redistilled zinc = 7·089 grams; 55 c.c. of dilute sulphuric acid, containing 2 grams replaceable hydrogen in 500 c.c., and thus equivalent to 7·15 grams zinc, were mixed with 450 c.c. water. At a pressure of 769·5 mm., at first no appreciable quantity of gas was given off; as soon as a few bubbles were being evolved, observations were made in the usual manner. Temperature 26°·5–28°·7.

Intervals of time required for 5 c.c. of gas.							
I. At pressure of 769·5 mm.			II. At pressure 112 m m.		III. At pressure of 769·5 m.m.		IV. At pressure of 112 m.m.
26′·08	4′·32	3′·67	1′·42	1′·77	2′·27	2′·2	1′·33
11·68	4·1	3·67	1·33	1·7	2·23	2·18	1·53
8·3	3·93		1·67	1·72	2·33	2·22	2·13
6·75	3·83		1·86	1·72	2·45	2·2	1·93
5·8	3·72		1·9	1·7	2·08	2·23	1·93
5·18	3·67		1·92		2·37		1·96
4·72	3·62		1·88		2·23		1·95

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* 'POGGENDORFF, Annalen,' vol. 104, p. 189.

† 'Compt. Rend.,' vol. 68, 1869, p. 395.

‡ 'Compt. Rend.,' vol. 48, 1859, p. 442.

The rate of evolution of gas is at first very slow, and then quickly increases; on reducing the pressure (Series II.) there is a considerable increase in the rate; on allowing the gas to fill up the vacuum the rate is slightly decreased, and on again reducing the pressure the rate is again slightly increased.

Another series of experiments gave precisely similar results, which seems to indicate that in this case the rate of evolution of gas is influenced to a slight degree by reduction of pressure, a result which differs from those observed in previous cases of the formation of a gas in a liquid. But this result may be due either to an acceleration of the chemical change taken in itself, or to the greater agitation of the liquid by the formation of larger bubbles of gas, whereby the liquid already acted upon in the immediate vicinity of the metal is more readily removed, and thus the metal comes more intimately in contact with fresh layers of the acid.

From these results it is apparent that reduction of pressure from one to a fraction of an atmosphere does not permanently alter the rate of evolution of a gas from a liquid, but that an increase of pressure produces *temporarily* a retardation, or even complete stoppage, of the evolution of gas, and, conversely, a decrease of pressure produces an acceleration. The only apparent explanation of these phenomena seems to lie in a storage, to some small extent, of the gas within the liquid, which is increased or decreased temporarily by increase or decrease of pressure; when matters are so equalised that the possible storage of gas has reached its maximum, then the evolution of gas would be the same, whatever be the pressure to which the liquid is subjected. The effect produced by increasing the pressure is the same as that of lowering the temperature.

It would seem, however, that such a gas as carbonic oxide at the moment of its liberation in the so-called nascent state is of a kind different from the same gas ready-formed, in that the one is susceptible of solution in sulphuric acid, while the other is practically insoluble.

PART III.

The Rate of Decomposition of Formic Acid into Carbonic Oxide and Water.

In the introductory sketch, remarks were made on the unsuitability of many chemical changes leading to the formation of a gas for an investigation on the variations in the velocity of such a change produced by alterations in the masses of reacting substances, as also by changes in external conditions, such as temperature, and material of containing vessel. It is difficult also to find cases in which are fulfilled the conditions necessary for such an investigation, namely, that the masses of all but one of the reacting substances should remain constant within small and inappreciable limits. Another difficulty presents itself in the estimation of the residue of unaltered material at the conclusion of any one of the observations, without producing complications in the chemical change itself. Further, the phenomenon of initial acceleration, discussed fully in Part II., and so marked in all the chemical changes investigated, introduces complications. The gas formed must not only be practically insoluble in the liquid from which it is produced, but also in the liquid over which it is collected. The only gases which fulfil the latter condition for the convenient liquid, water, are nitrogen, nitric oxide, hydrogen, and carbonic oxide. Chemical changes leading to the production of the last-named were more particularly investigated. The first trials were made on the rate of formation of carbonic oxide from potassium ferrocyanide when dissolved in concentrated sulphuric acid; but these experiments were soon discarded, for this reaction was found to be complicated initially by the formation of hydrocyanic acid, and, subsequently, by that of sulphurous oxide. The temperature at which this reaction takes place is also inconveniently high.

The decomposition of formic acid into carbonic oxide and water by means of sulphuric acid was then selected as a suitable case for investigation. In preliminary experiments it was ascertained that either from the acid or from its sodium salt the volume of carbonic oxide required theoretically for the equation

$$HCOOH = CO + H_2O$$

was given off at conveniently low temperatures without any separation of carbonaceous matter, and consequent reduction of the sulphuric acid. In fact the determination of volume of carbonic oxide evolved affords a ready method for the estimation of the quantity of formic acid or of a formate, and since these experiments this method has been applied by Messrs. HARCOURT and POULTON to determine the amount of this acid in the secretion from Lepidopterous larvæ.*

The twin U-tube arrangement was used, and, as explained above, 10 c.c. of dry air at 0° C. and 760 mm. pressure was taken as the standard. Thus, each time that the chemical operation represented by the equation

$$HCOOH = CO + H_2O$$

was repeated ·02063 gram formic acid disappeared, with production of 10 c.c. or ·01256 gram carbonic oxide and ·00807 gram of water.

Obviously, for exact observations, it is required to fulfil two rather incompatible conditions, (i.) that the sulphuric acid shall be sufficiently concentrated to effect the decomposition, and (ii.) that it shall be sufficiently dilute for the amount of water formed during the whole course of the operation not materially to dilute the acid. Thus, the mass of dilute sulphuric acid must be relatively large, and that of the formic acid relatively small.

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* 'Brit. Assoc. Report,' 1887, p. 766.

The Formic Acid or Formate used.

In the earlier experiments a solution of a known weight of sodium formate, either ·5 or 1·0 gram, in a given volume of water was used; after the effect of the finely divided particles had been observed, the solution was always filtered into the sulphuric acid. Provided that the solution dropped through the filter at a sufficiently slow rate, and the flask containing the acid was kept constantly stirred, the rise of temperature caused by the admixture of the solution with the already previously diluted acid was not great enough to produce any sensible evolution of gas. In later experiments formic acid was used; this was prepared according to the method proposed by LORIN, viz., by the dry distillation of equi-molecular parts of dry sodium formate and dehydrated oxalic acid. The acid thus obtained was redistilled, when it boiled uniformly at 107°; it contained 76·42 per cent. formic acid. It is thus of the same composition and boiling-point as the rather ill-defined hydrate $HCOOH.OH_2$, which boils at 107°·1 and contains 77 per cent. of the anhydrous acid. Of this, 10 c.c. of a solution containing 3·08 grams of formic acid in 100 c.c. were taken for each set of experiments.

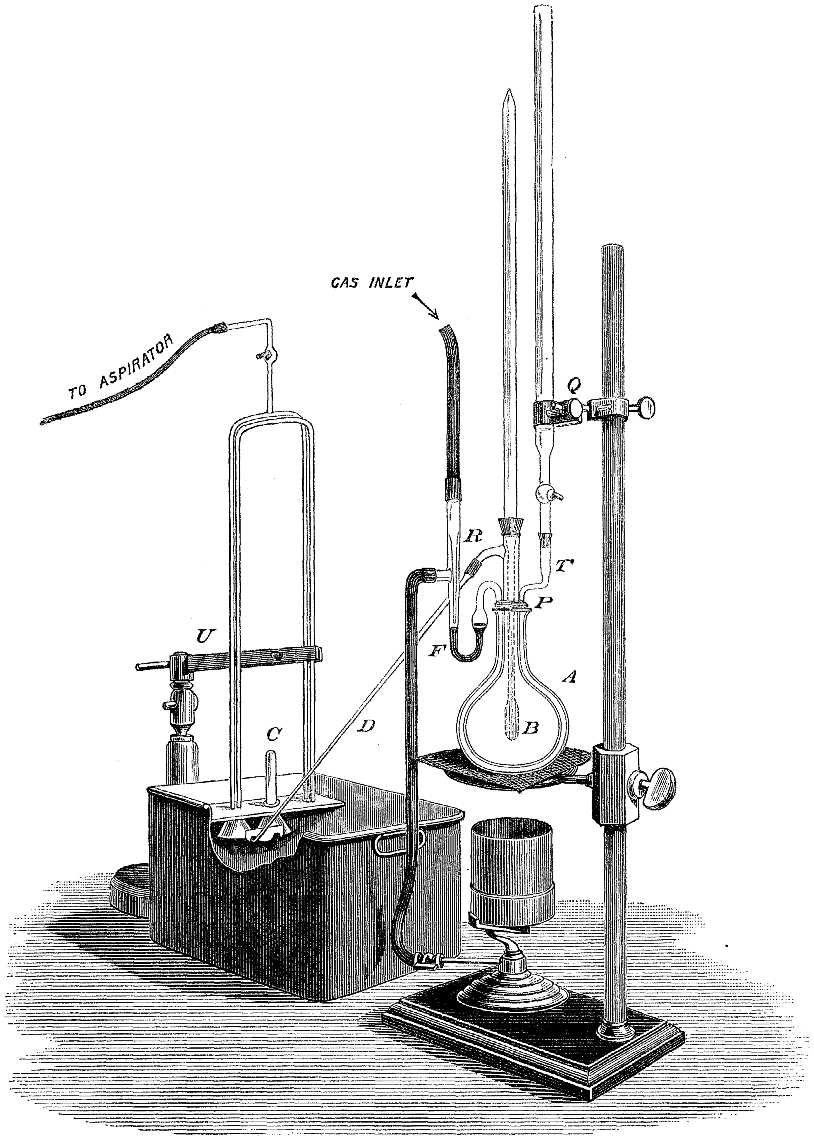
The Sulphuric Acid.

Pure redistilled sulphuric acid was heated in quantities of 1 to 2 litres at a time in a large flask until white fumes began to appear, so as to boil off any dissolved air, and to completely destroy any oxidisable material, which might reduce in the course of the investigations the sulphuric acid into sulphurous oxide. The acid was diluted with a suitable proportion of water, the details of which will be given for each series of observations; and the amount of sulphuric acid per unit volume in these diluted acids was determined either by taking its specific gravity or by precipitation with barium chloride, or in most cases by both methods.

The apparatus (fig. 1) consisted of a flask (A) of about half a litre capacity, within which was blown a bulb (B) of nearly a quarter of a litre capacity, the space between them being completely filled with olive oil. The upper end of the larger flask was closed with a caoutchouc plug (P), through the centre of which the neck of the bulb passed, while through a side hole in the cork passed a smaller piece of tubing (T), bent twice at right angles, the upper end of which was connected with a burette (Q); through another side hole passed a piece of capillary tubing (F), bent twice in a U form. The lower bend of the U was filled with mercury, while at the end furthest removed from the flask was constructed in miniature a gas regulator (R) of the form originally devised by Mr. HARCOURT. The neck of the bulb was closed with a caoutchouc plug, through which the long-range thermometer passed, while a side piece of glass fused on served to connect with the delivery tube. The whole arrangement was enclosed within a double-cased air bath, not represented in the figure, heated by a gas flame issuing from a small jet; the flow of gas was regulated by a governor.

Before a series of observations was commenced the above apparatus was heated to a temperature slightly above that required, the olive oil expanding upwards through the opened tap into the burette. The mixture of sulphuric and formic acids previously made was heated independently in another flask to a temperature slightly below that required; the loss of carbonic oxide during this process was quite inappreciable. The mixture was then poured into the bulb of the decomposition apparatus, and its neck closed with the thermometer-bearing plug. When the temperature appeared to be nearly constant, the tap of the burette was closed; this caused the oil to expand only in the U-tube (F), and to drive the thread of mercury down one

Fig. 1.



limb of the U and up the other until it reached the regulating apparatus, and thus turned the gas jet down, the lowering of which caused the oil to contract until the regulator was opened. This process repeated itself until an equilibrium of temperature was reached. By means of this apparatus the temperature could easily be maintained within a twentieth of a degree on either side of that required. When the temperature was constant observations were commenced, the volume of gas evolved during the preliminary operations being collected in some measuring apparatus. At the end of the observations the mixture was heated to 100° to 110° C., and the volume of the gas given off measured, in order to determine the residue of undecomposed formic acid, the necessary correction being applied for the volume of air displaced by the expansion of the acid mixture. An account of the conditions of one experiment will serve, *mutatis mutandis*, for each of the successive series. A mixture was made up as follows :—

150 c.c. sulphuric acid ;
60 c.c. water ;
10 c.c. water containing 1 gram of sodium formate.

The 1 gram of the salt yields 32·9 observations of the standard unit of chemical change of 10 c.c. dry carbonic oxide with the simultaneous formation of ·2655 gram of water, or a dilution at the completion of the reaction of ·379 per cent. Some quantity of gas was lost before observations were commenced, before a temperature convenient for the purpose was attained; the amount of residue at the conclusion was determined as described above.

In the following Table the results obtained are set forth, in which r represents the residue at the conclusion of each successive observation; $\theta - \theta_1$ the interval of time in minutes and decimals required for that observation; and T the sum of the several values of $\theta - \theta_1$, or the time from the commencement.

SERIES I.

Temperature 73°·7.

r	$\theta - \theta_1$	T
15	25′·47	25′·47
14	28·93	54·4
13	32·73	87·13
12	38·4	125·53
11	44·6	170·13
10	54·12	224·25
9	65·97	290·22
8	88·67	378·89

The relation between the values for r and T is expressible by the general formula

$$\log(T + t) + \log r = \log C,$$

in which t is the interval of time elapsing from the moment at which, the conditions remaining the same, $r = \infty$ and $\theta - \theta_1 = 0$, and the actual commencement of the observations; C is a constant. In the above series the value for t is taken as 378′, and in the following Table are given the values for $\log(T + t)$, $\log r$, and the sum of their values :—

$\log(T + t)$	$\log r$	$\log C$
$\bar{2}\cdot606$	$\bar{1}\cdot176$	$\bar{3}\cdot782$
$\bar{2}\cdot636$	$\bar{1}\cdot146$	$\bar{3}\cdot782$
$\bar{2}\cdot667$	$\bar{1}\cdot114$	$\bar{3}\cdot781$
$\bar{2}\cdot702$	$\bar{1}\cdot079$	$\bar{3}\cdot781$
$\bar{2}\cdot739$	$\bar{1}\cdot041$	$\bar{3}\cdot780$
$\bar{2}\cdot780$	$\bar{1}\cdot$	$\bar{3}\cdot780$
$\bar{2}\cdot825$	$\cdot954$	$\bar{3}\cdot779$
$\bar{2}\cdot879$	$\cdot903$	$\bar{3}\cdot782$

The values for the third column are as concordant as could be desired; taking the mean as $\bar{3}\cdot781$, the observed and calculated values for T will be as follows :—

Intervals T.		Intervals T.	
Observed.	Calculated.	Observed.	Calculated.
25′·47	24′·72	170′·13	171′·55
54·4	53·52	224·25	223·95
87·13	87·13	290·22	283·43
125·53	125·53	378·89	377·1

The greatest error between the observed and calculated values does not exceed 2 per cent., and is within the limits of experimental error. The curve representing the intervals of time from the commencement of the set, in terms of the residues at each of the several observations, is a portion of a hyperbola. It is apparently illustrative of the law

$$\frac{dr}{dT} = -\frac{r^2}{C},$$

which expresses the rate at which equivalent masses react upon each other; in each experiment $1/C$ is the amount of each unit mass, which reacts with the other per unit time, when an unit mass of each substance is present. It would thus seem probable that in the system of formic and sulphuric acids with water the chemical change taking place does not merely consist in the removal of the elements of water from a molecule of formic acid, with production of carbonic oxide, but rather that one molecule of formic acid acts upon another, probably with formation of an unstable anhydride, which in its turn is decomposed into the second anhydride, or carbonic oxide, and water. The reaction between permanganic and oxalic acids, investigated by HARCOURT and ESSON,* affords an example of a case in which a hyperbolic curve represents the course of a chemical change, while the etherification of acids by alcohol, investigated by BERTHELOT,† is also of a similar nature. If the above explanation of the chemical change occurring within the system is correct, the decomposition of formic acid and its etherification by an alcohol would be chemical changes analogous in kind. Thus the reactions can be represented as follows :—

$$\text{(i.)}\quad HCOOH + C_2H_5OH = \left.\begin{matrix}HCO\\C_2H_5\end{matrix}\right\}O + H_2O\,;$$

$$\text{(ii.)}\quad HCOOH + HCOOH = \left.\begin{matrix}HCO\\HCO\end{matrix}\right\}O + H_2O\,,$$

though the product in the former case is stable in the presence of not too large a quantity of water, while the product of the latter is unstable. The analogy of these two changes is further borne out by the phenomenon of initial acceleration observable in both cases.

Other series of experiments are given below in a series of Tables, in which are set forth the conditions, the observed values for r, $\theta - \theta_1$, and T, the last being compared with those calculated for certain values taken for t, and from the mean number for log C.

SERIES II.

205 c.c. of 1 : 4 sulphuric acid,

10 c.c. of dilute formic acid, containing ·308 gram of the acid, which gives 15 observations, yielding ·12 gram water, or a dilution of ·2 per cent.

Temperature 68°·9 — 69°·0.

r	$\theta - \theta_1$	T observed.	T calculated, $t = 320$, log C $= \bar{3}{\cdot}564$.
10·7	22·82	22·82	22·82
9·7	32·62	55·44	57·6
8·7	44·78	100·22	100·22
7·7	58·33	158·55	156·44
6·7	76·2	234·75	227·02
5·7	95·8	330·5	334·6
4·7	131·08	461·6	461·6

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* ‘Phil. Trans.,’ 1866, p. 201.

† ‘Annales de Chimie’ [3], vol. 66, p. 113.

SERIES III.

Mixture as in Series II. Temperature 75°·6.

r	$\theta - \theta_1$	T observed.	T calculated, $t = 243$, $\log C = \bar{3}\cdot445$.
10·3	27′·57	27′·57	27′·57
9·3	29·67	57·24	57·24
8·3	39·38	96·62	92·8
7·3	47·05	143·67	138·95
6·3	63·18	206·85	201·64
5·3	82	288·9	283·2
4·3	114	403	405·6
3·3	197	600	602

SERIES IV.

Mixture as above. Temperature 82°·1.

r	$\theta - \theta_1$	T observed.	T calculated, $t = 250$, $\log C = \bar{3}\cdot502$.
11·5	26′·55	26′·55	26′·55
10·5	28·28	53·83	52·7
9·5	32·27	86·1	84·2
8·5	40·27	126·37	124·12
7·5	48	174·37	172·68
6·5	64·92	239·3	239·3
5·5	88·5	328·	327·8
4·5	127·4	455·2	456·3

SERIES V.

Mixture as above. Temperature 90°.

r	$\theta - \theta_1$	T observed.	T calculated, $t = 180$, $\log C = \bar{3}\cdot234$.
8·75	17′·02	17′·02	15′·9
7·75	24·2	41·22	41·22
6·75	31·96	73·18	74·1
5·75	44·47	177·85	117·65
4·75	60·16	180·58	180·58
3·75	100·1	277·9	277·1
2·75	167·1	445	443·8

In the four preceding series the only known variable is the temperature; but there is not apparently any immediate correlation between the factor 1/C and the temperature, as the following figures show :—

Temperature.	$1/C$
69°·2	·000272
75·6	·000357
82	·000315
90	·000583

It is probable that the factor $1/C$ is dependent not only upon the temperature, conditions of concentration remaining the same, but also upon the variable and quite unknown condition of the cleanliness of the containing vessel, whereby, in some cases, more nuclei are presented for the evolution of the gas than in others. The method of procedure after the residue had been determined was to siphon off the acid as far as possible, and to keep closed the neck of the decomposition flask with the thermometer-bearing cork between each series of observations; but probably small particles, not discernible by the eye, may have been introduced, producing a considerable acceleration in the rate of decomposition. This is rendered evident by the following series of observations, made with a solution of sodium formate containing particles of silica, which led, as mentioned above, to the investigation of the effect of finely divided particles.

SERIES VI.

Mixture as in Series I. Temperature 35°·9.

r	$\theta-\theta_1$	T observed.	T calculated, $t=335$, $\log C=\bar{3}\cdot778$.
16·75	22′·77	22′·77	22′·77
15·75	23·18	45·95	45·95
14·75	25·82	71·77	71·77
13·75	30·03	101·8	101·8
12·75	34·45	136·25	134·9
11·75	40·18	176·43	175·51
10·75	46·33	222·76	223·48
9·75	56·43	279·19	280·2
8·75	71·63	350·82	350·82

On comparison of the Series VI. with Series I., it is evident that the value for $1/C$ in both cases is practically equal, viz., ·000165 and ·000162; but in Series I. the reaction was effected at a temperature of 73°·7, and in Series VI. at a temperature of 35°·9. But the law governing the rate of this chemical change is still valid in the presence of these finely divided particles, the concordance between the observed and calculated values for T being especially marked in this series.

It will be necessary to quote only one more series, in which observations were carried on almost to the ultimate limit of the reaction.

SERIES VII.

Conditions
190 c.c. sulphuric acid
38·8 c.c. water.
5·0 c.c. water containing ·5 gram sodium formate.
Temperature 68°·6.

r	$\theta-\theta_1$	T observed.	T calculated, $t=300$, log $C=\bar{3}\cdot534$.
		′	′
10·47	28·38	28·38	26·6
9·47	34·88	63·26	61·41
8·47	44·13	107·39	103·65
7·47	53·67	161·06	158·13
6·47	67·87	228·93	228·93
5·47	94·42	323·35	325·18
4·47	131·53	454·88	465·6
3·47	219	673·88	663·8
2·47	392	1065·9	1092·2
1·47	960	2025·9	2025·9

With the exception of the last observation but one, the observed and calculated results are very concordant; thus, whether the time required for the evolution of the 10 c.c. of dry carbonic oxide be rather less than half an hour or sixteen hours, the law governing this chemical reaction is still exemplified.

GENERAL CONCLUSIONS.

(i.) The rate of evolution of gases from homogeneous liquids is accelerated by the presence of finely divided chemically inert particles, not only when the gas is merely dissolved in the liquid but also when it is in a state of formation as a resultant of a chemical reaction.

(ii.) In the earlier stages of a chemical reaction yielding a gas the phenomenon of initial acceleration is observed, the rate of change increasing up to a maximum and constant point, from which it decreases at a rate bearing some immediate relation to the diminution of mass.

This phenomenon of initial acceleration repeats itself when the temperature is lowered temporarily and then restored to its former point, or when the pressure is increased suddenly.

(iii.) Reduction of pressure from one to a small fraction of an atmosphere causes but little *permanent* variation in the rate of evolution of gas from a liquid; though a sudden increase of pressure stops *temporarily* the evolution of gas, and a decrease of pressure produces *temporarily* an increase in the rate of evolution.

(iv.) Increase of pressure diminishes or even stops the evolution of a gas from a liquid.

The chemical changes in the case of homogeneous liquids herein studied are the decomposition of formic acid into carbonic oxide and water; of oxalic acid into carbonic oxide, carbonic acid, and water; of potassium ferrocyanide, forming carbonic oxide and water; of nitric acid into nitric oxide; of ammonium nitrate into nitrous oxide and steam; of ammonium nitrite into nitrogen and water; of potassium chlorate into the perchlorate and oxygen.

The particular case of the formation of hydrogen from zinc and sulphuric acid is also investigated.

The finely divided chemically inert substances include pumice, silica, graphite, barium sulphate, and finely divided glass.

(v.) The particular case of the decomposition of formic acid into carbonic oxide and water is also investigated; the rate of change is shown to be directly proportional to the mass of substance undergoing the change. The curve representing the interval of time required for each unit of chemical change in terms of the mass present is shown to be hyperbolic and illustrative of the law—

$$\frac{dr}{d\mathrm{T}} = -\frac{r^2}{c}.$$

This indicates that the change results between equivalent masses, probably of formic acid itself, the sulphuric acid merely serving to induce the reaction between two molecules of the acid, precisely as it serves to induce the etherification of an organic acid by an alcohol.

The observed values for the sum of the interval of time required for each unit of decomposition taken as the standard are concordant with those calculated according to the hypothesis adopted. So far as the investigation has been carried on no immediate relation has been discovered between the rate of change and the temperature, though the introduction of particles and the cleanliness, or otherwise, of the containing vessel may have introduced errors not readily obviated.

In presence of finely divided particles, as silica, the law governing this chemical change is still valid, though the change itself occurs at a much lower temperature.

In conclusion, I would again allude to my great obligations to Mr. VERNON HARCOURT, and to Mr. W. ESSON, for help in the mathematical portion of Part III., to whom I would express my best thanks. I would also acknowledge, with thanks, the receipt of a grant from the Government Grant Committee of the Royal Society, to assist me in this investigation.