On the Variation with Temperature of the Rate of a Chemical Change

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VI. *On the Variation with Temperature of the Rate of a Chemical Change.*

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With an Appendix

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In a study of the laws of connexion between the conditions of a chemical change and its amount, whose results have been communicated at intervals to the Royal Society, one of the conditions varied was the temperature of the solution in which the change took place.*

On considering the numerical results, our first observation was that the increase of rate due to increase of temperature could be nearly represented for equal increments of temperature by a geometric progression. The rate was approximately doubled by each rise of ten degrees in the temperature of the solution. But the ratio of the series gradually diminished as the temperature rose, and a formula had to be found giving a series of this kind. For the way in which such a formula was found, see 'Phil. Trans.,' Series A, vol. 186, pp. 855–866.

Using for the rate of change the symbol k, recently adopted by a committee of the Chemical Society, the formula was

$$\log k_t = \log k_0 + m \log \frac{273+t}{273}, \quad \text{or} \quad \frac{k_t}{k_0} = \left(\frac{273+t}{273}\right)^m,$$

where k_0 is the rate at 0° C., k_t the rate at any other temperature t, and m a constant for each particular case of chemical change.

This equation implies that at $-273°$ C. the rate of change is nil. It has long been accepted that at this point, which is the zero of temperature, gases have no tension because molecules are at rest; and from our observations it appears that at the same point atoms are at rest and no contact between any kinds of matter brings about chemical change.

The discovery by Esson of this natural law seems, as has happened in other cases,

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* 'Phil. Trans.,' vol. 156 (1865), p. 193; vol. 157, p. 117; and series A, vol. 186 (1895), p. 817.

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to have attracted less attention than it deserves, for, as will be seen in the Appendix, most of the Chemists who have made observations on the variation with temperature of the rate of chemical change have calculated from other formulæ which give numbers agreeing less well with their experimental results.

The following account of work done relates to an attempt to measure the influence of temperature in another case of gradual chemical change.

When solutions of ferric chloride and stannous chloride are mixed, ferrous chloride and stannic chloride are formed more or less gradually according to the concentration and temperature of the solution. Stannic chloride is decomposed by water, hydrogen chloride and a gelatinous precipitate of stannic hydroxide being formed; but if hydrogen chloride has been added in sufficient quantity the liquid remains clear. If the liquid is hot, a larger proportion of hydrogen chloride is needed to resist the action of water than when it is cold. For the observation of a colour change, it is necessary that the liquid should remain clear. A ferric salt loses its colour when it is reduced, but the colour is too pale, and therefore the change of colour too little, to serve for observation; but when a sulphocyanide has been added the fading of the blood-red colour can be followed by the eye from minute to minute, or at less intervals of time when the rate of change is greater.

With stannous chloride in excess the whole of the ferric salt is reduced and the liquid becomes colourless; but it is not possible to fix with any approach to accuracy the time when this final stage is reached, for the rate of change continually decreases as the residue of ferric chloride grows less and less, becoming at last indefinitely slow. The plan followed was, therefore, that of the police-trap, namely, to have two fixed stations or standards and to take as accurately as possible the time at which the change passed each of these. Glass cylinders were used of about 100 c.c. capacity, as similar as possible; one was the reagent glass, two served as standards, filled with a darker and with a paler red liquid. Into the reagent glass, for each observation, water with a small proportion of hydrogen chloride, solutions of ferric chloride and of potassium sulphocyanide, were delivered from pipettes, making up a total volume of 75 c.c., and lastly, when the liquid had been brought to the desired temperature, 5 c.c. of an acid solution of stannous chloride. Exactly the same routine was followed for each observation, the only difference being of the temperature of the liquid.

The darker standard was made by filling one of the glasses to the level at which 80 c.c. stood in the reagent glass, with a mixture of a few drops of ferric chloride with a large proportion of hydrogen chloride and potassium sulphocyanide, such as to produce a colour sufficiently translucent to be well distinguished, and considerably less deep than that of the mixture in the reagent glass. In the absence of an excess of hydrogen chloride and potassium sulphocyanide, ferric sulphocyanide is gradually bleached when exposed to sunlight, but the presence of an excess of one or other or both of these substances seems to increase its stability. If the conditions of this action of light have not been investigated that would be worth doing. Many attractive by-paths have to be left unexplored. For the purpose of these observations it was only necessary to make sure that the dark standard, made in the manner described, would not change appreciably, the tube being corked and kept in the dark except when in use, by exposure to diffused daylight. A set of observations only occupied five or six hours, and the same standard was in use for several weeks without any noticeable change.

The pale standard made by diluting some of the dark standard was less constant, and differed in colour from the liquid in the reagent tube which had faded to a similar depth of colour. This difference of colour made the observations less easy, and therefore less exact, than they would otherwise have been. The cause was found to be that the constancy and precise tint of ferric sulphocyanide, which in dilute solutions varies between pink and orange, depends not only upon the relative proportions of iron, sulphocyanide, and acid, which dilution leaves unaltered, but also upon the concentration of the latter two. In the reagent tube the concentration of these two influential bystanders is practically if not wholly unchanged.

By several preliminary testings a degree of concentration of hydrogen chloride was found which would prevent the formation of a cloudiness by hydrolysis of stannic chloride without increasing unduly the rate of change. The margin is rather narrow.

To maintain a constant temperature the reagent tube was placed on an iron tray covered by white paper, which was heated beneath at one end by a small gas flame, while the liquid was stirred by the passage of large bubbles of carbonic acid from an inverted thistle-funnel. By moving the tube nearer to or further from the heated end of the tray, or by moving the gas burner, the mean temperature of the liquid was regulated during intervals varying from five minutes to three-quarters of an hour within about 0°·05 C. Four or five bubbles a minute stirred the liquid sufficiently when the desired temperature was near that of the room, but for temperatures above 20° C., and during the delivery of stannous chloride from a pipette, a more rapid stream was used.

The colour on mixing was very deep, the excess of ferric chloride being such as to allow at least two or three minutes for adjustment of temperature before the depth of colour approached that of the dark standard. To make the comparison, the cork holding the thermometer and thistle-funnel was replaced by a plain cork, and the dark standard was placed close alongside the reagent tube. The observer looked at the two, watch in hand, closing his eyes at intervals for a few seconds to get a fresh impression, till the colours seemed undistinguishable, made a mental note of the time, and continued to watch till the contents of the reagent tube seemed the paler of the two. Then thermometer and thistle-funnel were quickly replaced, and any disturbance of temperature estimated as having prevailed after the time of agreement, which is the start of the race, was compensated by causing a similar divergence on the opposite side of the thermometer line.

By and by the contents of the reagent tube were only a little darker than the pale standard, then the second observation was made in the same way. The comparison was more difficult because the rate of change was less. It was found helpful to have two similar standard tubes, one on each side of the reagent tube. Generally speaking, the first observation was not liable to an uncertainty of more than 10 seconds; but when the rate was slow the uncertainty attaching to the second observation extended over a minute or more. By a repetition of a set of observations or of a particular observation, and taking the mean of the intervals observed, the error is lessened; but the method does not admit of an accuracy approaching that of observing the appearance in a colourless liquid of the intense colour of the iodide of starch, whose results led to the discovery of what we believe to be a general law. The present observations furnish only another case of agreement within the limits of experimental error with numbers calculated from the formula already established.

The following are the times in which at different temperatures the depth of colour changed from that of the dark to that of the pale standard, that is to say, in which a definite piece of chemical work was done :—

	Temperatures . . .	9°	12°	15°	18°	21°	24°	27°	30°
Time in minutes	Set I.	50·0	37·25	27·75	20·5	15·17	11·1	8·62	6·5
	Set II. . . .	44·7	34·2	26·2	18·2	14·5	10·83	7·83	5·8
	Set III. . . .	47·0	33·3	23·7	18·67	14·0	10·33	7·5	5·92
	Mean . . .	47·2	34·9	25·9	19·1	14·6	10·8	8·0	6·1

The corresponding numbers calculated by the method explained below, and set forth in the following table, are

47·2 34·9 25·9 19·3 14·4 10·8 8·1 6·1.

Using the formula $x/x' = (\mathrm{T}'/\mathrm{T})^m$, x, x' being consecutive observed values of the times at temperatures T, $= 273+t$, and T′, $= 273+t'$, a value of $\log m$ is calculated from the derived formula

$$\log\log x/x' - \log\log \mathrm{T}'/\mathrm{T} = \log m.$$

In the table, column 7 contains the values of $\log m$ calculated by subtracting the values of $\log\log \mathrm{T}'/\mathrm{T}$ in column 6 from the corresponding values of $\log\log x/x'$ in column 5. The mean of these values of $\log m$ is taken to be the true value of $\log m$. Assuming this value of $\log m$, values of $\log\log x/x'$ are calculated from the formula

$$\log\log x/x' = \log\log \mathrm{T}'/\mathrm{T} + \log m.$$

Column 8 in the table contains the values of $\log\log x/x'$ calculated by adding the corresponding values of log log T′/T in column 6 to the constant mean value of log m at the foot of column 7. From these values of log log x/x' are derived the values of log x/x' in column 9. If the times of the first, second, … observations are x_1, x_2, …, values of log x_1/x are obtained as the sum of the values of log x_1/x_2, log x_2/x_3, … .

Column 10 in the table contains these values of log x_1/x, as the sum of the values of log x/x' in column 9. Values of log x_1 are obtained by adding to the values of log x_1/x the values of log x. These values of log x_1 in column 11 of the table are calculated by adding the values of log x_1/x in column 10 to the corresponding values of log x in column 3. The mean of these values of log x is taken to be the true value of log x_1, which is given at the foot of column 11.

1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.
t.	x.	log x.	log x/x'.	log log x/x'.	log log T′/T.	log m.	log log x/x'.	log x/x'.	log x_1/x.	log x_1.	log x.	x.
° C.												
9	47·2	674	—	—	—	—	—	—	—	674	674	47·2
12	34·9	543	131	117	662	455	117	131	131	674	543	34·9
15	25·9	413	130	114	658	456	113	130	261	674	413	25·9
18	19·1	281	132	121	653	468	108	128	389	670	285	19·3
21	14·6	164	117	068	649	419	104	127	516	680	158	14·4
24	10·8	033	131	117	644	473	099	126	642	675	032	10·8
27	8·0	903	130	114	639	475	094	124	766	669	908	8·1
30	6·1	785	118	072	635	437	090	123	889	674	785	6·1
					log m (mean) . . .	1·455			log x_1 (mean) . . .	674		
					m (mean) . . .	28·5						

Assuming this value of log x_1, the values of log x in column 12 of the table are calculated by subtracting from this constant value of log x_1 the corresponding values of log x_1/x in column 10; and from these values of log x are derived the values of x in column 13 of the table. Thus x is calculated from the formula $x = x_1 (T_1/T)^m$, m and x_1 being the means of values obtained from the observations, namely, $m = 28{\cdot}5$, $x_1 = 47{\cdot}2$.

The following is another way of presenting the fundamental equation. Reckoning the time required at 0° C., x_0, from the observed times at other temperatures, it is found to be 118·3 minutes. The relation between this time and that at any other temperature, x_t, is $\dfrac{x_0}{x_t} = \left(\dfrac{273+t}{273}\right)^{28\cdot5}$, whence $x_t = x_0 \times \left(\dfrac{273}{273+t}\right)^{28\cdot5}$.

The mixture made for each observation was an aqueous solution, 80 c.c. in volume, of four substances, in the following masses and molecular proportions :—

	Gram.	Mol. props.
Ferric chloride, $FeCl^3$	·0145	1·0
Potassium sulphocyanide, KCNS	·312	36·1
Stannous chloride, $SnCl^2$	·106	6·3
Hydrogen chloride, HCl	·289	88·8

No simple numerical relations were aimed at. A large excess of sulphocyanide was taken in order to increase the depth of colour, Dr. GLADSTONE having shown that this increase extends to a proportion thirty or more times that of the ferric salt. The proportions of hydrogen chloride and of stannous chloride were chosen, after many trials, such as to avoid separation of a stannic compound, and to give rates convenient over the whole range of temperatures. The stannous chloride was taken in large proportion relatively to the ferric chloride, so that the rate of decrease of depth of colour when the change was passing the pale standard might be mainly that due to the diminution of one only of the acting substances.

The conditions were now varied by increasing the amount of hydrogen chloride; the rate was nearly trebled. The short-time observations were made by removing the cork and thistle-funnel and stirring with the thermometer. One set only was made, and gave the following times of change at the same series of temperatures as before :—

Temperatures . .	9°	12°	15°	18°	21°	24°	27°	30°
Minutes	15·8	12·2	8·8	6·8	5·0	4·1	2·8	2·2
(Calculated) . . .	16·35	12·26	8·99	6·82	5·02	3·83	2·91	2·19

The numbers in the lower line are calculated from the equation

$$x_t = 40{\cdot}14 \times \left(\frac{273}{273+t}\right)^{28},$$

40·14 being the estimated number of minutes in which the portion of change would be completed at 0° C.

A few further observations were made upon the influence on the rate of change of other acids.

Phosphoric acid changes the colour of the liquid to a pale yellow. Sulphuric and nitric acids can be used, and have curiously different effects upon the rate of change. The former, instead of increasing the rate, as an addition of hydrogen chloride does, diminishes it greatly. The times of reduction of the same amount of ferric chloride by the same amount of stannous chloride (1) in the mixture, whose composition is given above; (2) in the same mixture with an additional quantity of hydrogen chloride;

(3) in the same mixture with the addition of a corresponding quantity of hydrogen sulphate, were as follows:—

Temperatures . .	12°	15°	18°	21°	24°	27°	30°
Minutes (1) . . .	34·9	25·9	19·1	14·6	10·8	8·0	6·1
,, (2) . . .	12·2	8·8	6·8	5·0	4·1	2·8	2·2
,, (3) . . .	60·0	45·0	36·0	26·8	19·3	16·2	10·7

At each temperature the times in the third set are approximately 1·8 times those in the first set, and 5 times those in the second set.

No complete set has been made with hydrogen nitrate, but enough observations to show that it has an influence on the rate of change quite as unexpected as that of hydrogen sulphate, namely, that its addition makes little if any difference.

The times required for doing the fixed amount of chemical work at 21°, with (*a*) no addition, and then with the addition of equivalent quantities of (*b*) hydrogen chloride, (*c*) hydrogen sulphate, and (*d*) hydrogen nitrate, were as follows:—

a.	*b.*	*c.*	*d.*
14·6	5·0	26·2	13·7 minutes.

Having carried thus far an experimental inquiry which is suggestive of much further work, the author ventures to express a hope that it may attract the attention and pass into the hands of some younger chemist. The mode of working adds to the usual interest of research the particular excitement which attaches to all observations and predictions of time, sporting or scientific, whether it be of the time of a race or of the moment of an occultation.

Lastly, he desires to express his thanks to Dr. Baker and to Christ Church for the welcome and the opportunity of work and the help which he has received.

APPENDIX. *By Prof.* W. Esson, *F.R.S.*

I. The observations recorded in the preceding pages follow the law of connexion between chemical change and temperature with great exactness. This law, first enunciated in the Bakerian Lecture delivered to the Royal Society in 1895, is expressed by the relation

$$k/k' = (\mathrm{T}/\mathrm{T}')^m,$$

k, k' being the rates of chemical change at absolute temperatures T, T′ respectively. This relation is independent of the units of measurement of k and T, and m is a pure number which expresses the ratio of dk/k to $d\mathrm{T}/\mathrm{T}$. This implies that if at a temperature T a small change is made in each unit of temperature, and this change produces a corresponding small change in each unit of chemical change, the latter change is m times the former change. The number m may be regarded as the measure of the effect of heat energy upon chemical energy.

In the Bakerian Lecture it was shown that m is constant for all the temperatures at which the experiments were made, but varies with the medium in which the chemical change takes place. The constancy of m for each medium is secured by making one of the constituents of the medium predominant; m has different values for different predominant constituents in the medium in which the same chemical change occurs; m has also different values for different chemical changes. On p. 879 of the Lecture the values of m are 10, 20·4, 21·2, 24·1 for the predominant constituents $NaHCO^3$, H^2SO^4, HCl, HI respectively in the medium in which the reaction between hydrogen peroxide and hydrogen iodide is taking place. The value of m is 40·5 in the case of the reaction between hydrogen chlorate and potassium iodide, studied by PENDLEBURY and SEWARD, and quoted on the same page of the Lecture.

If the conditions for a stable communication of heat energy to chemical energy are not satisfied the value of m is different at different temperatures. For instance, the predominant constituent of the medium may change its character with a change of temperature, or the nature of the reaction between the substances undergoing change may vary. Examples of this variation of m with temperature are given later. But even when m varies with temperature it is still to be regarded as the measure of the effect of heat energy upon chemical energy at a given temperature, and the value of m is obtained from the experiments by calculating the ratio of dk/k to $d\mathrm{T}/\mathrm{T}$ at each temperature. In the experiments recorded in the preceding pages there are no such disturbing conditions, and m is constant at all the temperatures at which these experiments were made.

In the experiments recorded in the preceding pages the expression for the progress of the chemical change is, by the law of mass action, of the form

$$f'(y)\,dy/dx = -k,$$

y being the concentration of one of the substances undergoing change, and x the time during which the change takes place. This expression leads to the relation

$$f(y_2) - f(y_1) = kx.$$

The time x is the observed time during which the potential chemical energy expressed by $f(y_1)$ had changed to the potential chemical energy expressed by $f(y_2)$. In the above experiments this change of energy is indicated by the passage of the solution from one given colour to another. At different temperatures this change of energy is constant. Thus if k, k' are the rates of change at temperatures T, T′ respectively, and x, x' are the corresponding observed times,

$$f(y_2) - f(y_1) = kx = k'x'.$$

The relation $kx = k'x'$ is thus independent of the form of the function $f'(y)$, and the method of observation is alike applicable to unimolecular and multimolecular reactions. When this method is used the relation $k'/k = (T'/T)^m$ becomes $x/x' = (T'/T)^m$.

The following table exhibits the agreement of the times calculated from the above relation, the value of m being 28·5 :—

t.	T.	*x.*	
		Found.	Calculated.
9	282	47·2	47·2
12	285	34·9	34·9
15	288	25·9	25·9
18	291	19·1	19·3
21	294	14·6	14·4
24	297	10·8	10·8
27	300	8·0	8·1
30	303	6·1	6·1

The experimental and calculated numbers agree as well as those recorded in the Bakerian Lecture, and show that the method of experiment gives very accurate results.

If the rate of the reaction at zero centigrade is taken to be unity, the following are the rates at the temperatures of the experiments :—

t.	*k.*	*t.*	*k.*
0	1	21	8·17
9	2·51	24	10·96
12	3·37	27	14·59
15	4·56	30	19·28
18	6·12		

At temperatures increasing by 10° the rates are

t.	*k.*	*t.*	*k.*
0	1	20	7·46
10	2·78	30	19·28

The rate at zero centigrade is doubled at 6°·7.

A few experiments made by various authors are appended (II.–XIII.). Most of these (II.–IX.) appear to satisfy the conditions for a stable communication of heat energy to chemical energy at the temperatures of the experiments, and confirm the law of connexion between chemical change and temperature assumed in the previous discussion of HARCOURT's observations. The others (X.–XIII.) show a variation in the value of m which sometimes increases and at other times decreases with temperature. In these cases the values of m are calculated from the formulæ of the authors, which for this calculation are a sufficient approximation to the true values. But the relations thus obtained between m and temperature must be regarded as empirical, and hold good only for the range of temperature of each set of observations. These variations in the values of m are considered to be side effects of temperature which interfere with the main effect of temperatures upon the chemical changes.

II. 'Influence of the Temperature on the Rate of Hydrolysis of Ethyl Acetate by Caustic Soda,' REICHER, quoted by VAN 'T HOFF, translated by EWAN, 1896, p. 130 (4).

The values of k are calculated from the relation $k/k_1 = (T/T_1)^m$, m being 18·9.

t.	k.		
	Found.	Calculated.	Author.
9·4	2·307	2·31	(2·307)
14·4	3·204	3·22	3·2
24·22	6·151	6·10	(6·151)
35·14	12·096	12·00	11·97
44·94	21·648	21·77	(21·648)

The values of k enclosed in brackets are assumed by the author to be correct. The two remaining values of k are calculated from the relation

$$\log k = \cdot 0074T - 1780T^{-1} + 4\cdot 53.$$

The simpler relation

$$\log k = 18\cdot 9 \log (T/T_1) + \cdot 364,$$

in which the constants are calculated by the method of least squares, gives values of k agreeing with those found within the limits of experimental error.

III. 'Influence of the Temperature on the Velocity of the Reaction between Potassium Chlorate and Ferrous Sulphate in presence of Sulphuric Acid,' HOOD, quoted by VAN 'T HOFF, translated by EWAN, 1896, p. 132 (5).

The values of k are calculated from the relation $k/k_1 = (T/T_1)^m$, m being 26·18.

t.	*k*.		
	Found.	Calculated.	Author.
10	1·00	1·00	1·00
12	1·21	1·21	1·21
14	1·46	1·45	(1·46)
16	1·73	1·74	1·76
18	2·11	2·08	2·11
20	2·51	2·49	2·54
22	2·96	2·98	3·02
24	3·59	3·56	3·62
28	5·08	5·05	(5·08)
30	6·04	6·00	6·04
32	7·15	7·13	7·11

The author's values of *k* were calculated from the relation

$$\log_e k = 27{\cdot}189 - 7695\,\mathrm{T}^{-1}$$

or

$$\log k = 11{\cdot}81 - 3342\,\mathrm{T}^{-1}.$$

The constants were found by assuming the observed values of *k* enclosed in brackets to be correct. The relation

$$\log k = 26{\cdot}18 \log (\mathrm{T}/\mathrm{T}_1) + {\cdot}002$$

gives values of *k* which agree with those found within the limits of experimental error.

IV. " On the Dissolution of Metals in Acids," VELEY, 'Journal of the Chemical Society,' LV., p. 361.

The values of *k* are calculated from the relation $k/k_1 = (\mathrm{T}/\mathrm{T}_1)^m$, *m* being 7·28.

t.	*k*.		
	Found.	Calculated.	Author.
21	8·15	8·18	8·15
31	10·38	10·43	10·4
36	12·04	11·76	11·84
41	13·03	13·21	13·4

The author's formula is

$$\log k = {\cdot}685 + {\cdot}0108t.$$

The values of *k* are calculated from

$$\log k = 7{\cdot}28 \log (\mathrm{T}/\mathrm{T}_1) + {\cdot}913.$$

In his subsequent experiments VELEY uses the relation $k/k_1 = (T/T_1)^m$, from which he obtains values of k agreeing with those found within the limits of experimental error.

V. In the observations on "The Rate of Action of Drugs upon Muscle as a Function of Temperature," VELEY and WALLER, 'Roy. Soc. Proc.,' B, vol. 82, 1910, values of m were found to be 26·7, 20·8, 14·3 in experiments with different drugs.

VI. "The Affinity Constants of Bases as determined by the aid of Methyl Orange," VELEY, 'Journal of the Chemical Society,' XCIII., 2, pp. 2122–2144.

In this paper VELEY uses the formula $k/k_1 = (T/T_1)^m$ for his own experiments and applies it to experiments of the same kind by other chemists. Values of m in different experiments were found to be

2, 9, 11, 13, 14, 15, 22·5.

VII. 'Decomposition of Phosphine,' KOOY. These experiments are quoted by VAN 'T HOFF, p. 135 (b), who calculated values of k from the formulæ

$$(a)\ m = (k^{-1}\,dk)/(T^{-1}\,dT) = AT^{-1},$$

$$(b)\ m = (k^{-1}\,dk)/(T^{-1}\,dT) = AT^{-1}+B,$$

$$(c)\ m = (k^{-1}\,dk)/(T^{-1}\,dT) = C.$$

For (a) and (c) he assumes as correct the first and last observation, and for (b) he assumes all the observations except the second. The value of m in (c) is 12·3. The values of k are calculated from the formula

$$\log k = 12{\cdot}3 \log (T/T_1) + \bar{4}{\cdot}681.$$

VIII. "Action of Bromine on Acetaldehyde in Aqueous Solution," BUGARSZKY, 'Zeit. Physikal. Chem.,' 1904, 48, 63–86.

The values of k are calculated from the relation $k/k_1 = (T/T_1)^m$, m being 26·7.

t.	k.		
	Found.	Calculated.	Author.
0	·117	·117	·119
10	·308	·307	·303
20	·790	·777	·772
25	1·205	1·222	1·234

The author's formula is

$$\log k = {\cdot}04068t - {\cdot}9257.$$

This form of relation was rejected by Harcourt and Esson for the reasons given in the Bakerian Lecture, p. 859.

The relation

$$\log k = 26{\cdot}7 \log (\mathrm{T}/\mathrm{T}_1) + \bar{1}{\cdot}07$$

gives values of k agreeing better with those found than the values given by the author.

IX. "On the Decomposition of Ozone by Heat," Perman and Graves, 'Roy. Soc. Proc.,' A, vol. 80, p. 366. The values of k are calculated from the relation $k/k_1 = (\mathrm{T}/\mathrm{T}_1)^m$, m being 39·6.

t.	log *k*.		
	Found.	Calculated.	Author.
40	2·86	2·85	2·86
60	3·95	3·91	3·86
80	4·91	4·92	4·86
100	5·74	5·87	5·86
120	6·86	6·77	6·86

The authors' formula is

$$\log k = {\cdot}05t + {\cdot}86,$$

which is of the same form as the authors' formula in V.

The relation

$$\log k = 39{\cdot}6 \log (\mathrm{T}/\mathrm{T}_1) + 2{\cdot}85$$

gives values of $\log k$ agreeing better with those found than the values given by the authors.

The values of m found from the experiments I.–IX. and those given in the Bakerian Lecture (B) arranged in ascending order of magnitude are given in the following table, with the range of temperature for which m has a constant value:—

	m.	*t*.		*m*.	*t*.
VI.	2	10–40	B.	20·4	0–50
IV.	7·3	21–41	V.	20·8	7–24
VI.	9	10–50	B.	21·2	0–40
B.	10	15–19	VI.	22·5	0–60
VI.	11	10–60	B.	24·1	20–30
VII.	12·3	310–512	III.	26·2	10–32
VI.	13	10–60	V.	26·7	7–25
VI.	14	10–60	VIII.	26·7	0–25
V.	14·3	7–24	I.	28·5	9–30
VI.	15	15–60	IX.	39·6	40–120
II.	18·9	9–45	B.	40·5	4–30

The experiments (X.–XIII.) do not satisfy the conditions for the constancy of m. They are quoted by VAN 'T HOFF, translated by EWAN, 1896, pp. 127–135, and are numbered (1), (2), (3), (6). The values of m, the ratio of dk/k to $d\mathrm{T}/\mathrm{T}$ are calculated at each temperature from the formulæ given by the authors.

X. (1) 'Influence of the Temperature on the Rate of Decomposition of Dibromosuccinic Acid.'

The author's formula is

$$\log k = \cdot 0412t - a$$

or

$$\log k = \cdot 0412\mathrm{T} - b\,;$$

hence

$$\log_e k = \cdot 09462\mathrm{T} - c,$$

and

$$m = (k^{-1}dk)/(\mathrm{T}^{-1}d\mathrm{T}) = \cdot 09462\mathrm{T}.$$

t.	m.	t.	m.
15	27·2	70·1	32·4
40	29·6	80	33·4
50	30·5	89·4	34·3
60·2	31·5	101	35·4

XI. (2) 'Influence of the Temperature on the Rate of the Reaction between Sodium Chloracetate and Caustic Soda,' SCHWAB.

The author's formula is

$$\log k = \cdot 0404t - a,$$

or

$$\log_e k = \cdot 093\mathrm{T} - b\,;$$

hence

$$m = (k^{-1}dk)/(\mathrm{T}^{-1}d\mathrm{T}) = \cdot 093\mathrm{T}.$$

t.	m.	t.	m.
70	31·9	110	35·6
80	32·8	120	36·5
90	33·7	130	37·5
100	34·7		

XII. (3) 'Influence of the Temperature on the Rate of Change of Chloracetic Acid in Aqueous Solution,' SCHWAB.

The author's formula is

$$\log k = a - 5202\mathrm{T}^{-1},$$

or

$$\log_e k = b - 13280\mathrm{T}^{-1}\,;$$

hence

$$m = (k^{-1}dk)/(\mathrm{T}^{-1}d\mathrm{T}) = 13280\mathrm{T}^{-1}.$$

t.	*m.*	*t.*	*m.*
80	37·6	110	34·7
90	36·5	120	33·8
100	35·6	130	33·0

XIII. (6) 'Influence of the Temperature on the Rate of Hydrolysis of Ethyl Acetate by Caustic Soda,' WARDER.

The author's formula is

$$\log_e k = a - 5579\mathrm{T}^{-1};$$

hence

$$m = (k^{-1}dk)/(\mathrm{T}^{-1}d\mathrm{T}) = 5579\mathrm{T}^{-1}.$$

t.	*m.*	*t.*	*m.*
3·6	20·2	27·0	18·6
5·5	20·0	28·4	18·5
7·2	19·9	30·4	18·4
11·0	19·6	32·9	18·2
12·7	19·5	34·0	18·2
19·3	19·1	35·0	18·1
20·9	19·0	37·7	17·9
23·6	18·8		

In X. and XI. m increases with the temperature: in X. from 27·2 at 15° C. to 35·4 at 101° C.; in XI. from 31·9 at 70° C. to 37·5 at 130° C. In XII. and XIII. m decreases with the temperature: in XII. from 37·6 at 80° C. to 33 at 130° C.; in XIII. from 20·2 at 3°·6 C. to 17·9 at 37°·7 C. It is remarkable that in the experiments by SCHWAB, XI., XII., the sum of the values of m at each temperature from 80° C. to 130° C. is very nearly constant, having a mean value 70·3. The two experiments taken together give a mean value of $m = 35·17$.

The value of m is the same at the temperature given by $·093\mathrm{T} = 13280\mathrm{T}^{-1}$, *i.e.*, at $\mathrm{T} = 377·9$ or $t = 104·9$. At this temperature $m = 35·14$. It would appear from this that if the conditions for a stable communication of heat energy to chemical energy had been secured in each set of experiments the constant value of m would have been 35·1.

The relation of m to temperature is in X. and XI. $m = c\mathrm{T}$, and in XII. and XIII. $m = b\mathrm{T}^{-1}$. These relations are probably merely empirical, and are used in this paper to obtain approximate values of m at each temperature. VAN 'T HOFF's formula for m is

$$m = (k^{-1}dk)/(\mathrm{T}^{-1}d\mathrm{T}) = b\mathrm{T}^{-1} + a + c\mathrm{T},$$

which he deduces from the principles of thermodynamics. In the experiments discussed by him, a, b, c are made equal to zero in succession, but no reason is given for this process. In the discussion of the experiments, I.–IX., b and c are considered to be both zero, and a is the constant value of m deduced from the observations.

In the series of experiments II.–XII. taken at random from a number of experiments by other authors on the effect of temperature upon chemical change it has been shown that in the majority of cases II.–IX. m has a constant value. The reason for the variation of m with temperature in X.–XIII. has yet to be discovered. The writer intends to discuss at some future time all the experiments upon the subject, and hopes with the aid of HARCOURT to discover an explanation of the variation.

The experiments recorded in the Bakerian Lecture were made upon a simple unimolecular reaction, and the utmost care was taken to eliminate all possible sources of error in the determination of the effect of temperature upon the reaction. On p. 860 the assumption is made that the relation is of the form

$$k/k_1 = \{(c+t)/(c+t_1)\}^m.$$

The value of c, the temperature of no action, is determined from the experiments to be $-272°\cdot6$ C. This agrees closely with the zero of absolute temperature, $-273°$ C. In the subsequent experiments of the Lecture, in HARCOURT's recent experiments, and in the experiments of other authors, the relation is for this reason assumed to be

$$k/k_1 = (\mathrm{T}/\mathrm{T}_1)^m,$$

with the consequent relation

$$m = (k^{-1}dk)/(\mathrm{T}^{-1}d\mathrm{T}).$$

In studying the effect of one phenomenon, A, upon another phenomenon, B, which mutually influence each other, it often happens that the chain of processes from A to B which cause the influence is unknown. It would seem reasonable, in our ignorance of these processes, to assume that when the chain is uniform the ratio of the increase per cent. in B to the increase per cent. in A is constant, and further to assume that if the chain is not uniform, and this ratio, therefore, is no longer constant, the ratio will still be a measure of the effect of A upon B.

In the present case the phenomenon A is the molecular energy of heat, and the phenomenon B is the chemical energy of a reaction which may be energy of atoms or electrons. The mode of influence of the one kind of energy upon the other is unknown, and the measure m of the influence is taken to be

$$m = (\mathrm{B}^{-1}d\mathrm{B})/(\mathrm{A}^{-1}d\mathrm{A}).$$

If A is of the form $\frac{1}{2}mu^2$ and B of the form $\frac{1}{2}nv^2$ another form of the measure is

$$m = (v^{-1}dv)/(u^{-1}du),$$

and m is the ratio of the percentage increase of the average velocity of atoms or electrons to the percentage increase of the average velocity of molecules.

It is possible that this mode of measuring the effect of one phenomenon upon another may have a wider application. In studying the relation between unemployment and pauperism, the proper course might be to take the ratio of the increase per cent. of pauperism to the increase per cent. of unemployment as the measure of the effect of one upon the other. The ratio of the increase per cent. of coal or oil consumed in a ship to the increase per cent. in the number of knots attained by the vessel might be used with advantage in comparing the merits of coal and oil.

[*June* 15.—The referees of this paper have asked the author to discuss, with reference to the law here advocated, the experiments of TRAUTZ and VOLKMANN "On the Saponification of Esters," 'Zeit. Phys. Chem.,' 1908, 64, pp. 53–88; 1909, 66, p. 496; 67, p. 93; 68, p. 295.*

TRAUTZ calls the ratio $n = k_{t+10}/k_t$ the temperature coefficient of the rate of chemical change; and he discusses the effect of temperature on the value of n, which is a constant when the rate increases in geometrical progression as the temperature increases in arithmetical progression. This relation has been often used since its first use by BERTHELOT in 1862. In most experiments n has been found to decrease with temperature, but in the cases of saponification of esters it first increases and then decreases, having a maximum value between 10° C. and 20° C. TRAUTZ connects this with a similar maximum of viscosity in the medium in which the chemical action is taking place.

The value of $m = (k^{-1}\,dk)/(\mathrm{T}^{-1}\,d\mathrm{T})$ also shows a maximum value at the same point. The following table exhibits the values of m and n in the experiments with methyl acetate, vol. 64, p. 83:—

t.	m.	n.	$\frac{m = 20}{n}$.
0	—	—	—
10	17·9	1·85	2·05
20	23·5	2·26	2·00
30	19·0	1·87	1·96
40	18·2	1·81	1·91
50	17·7	1·75	1·87

[* It appears from the results of several experimentalists that the saponification of esters at different temperatures does not give, for the change of rate with temperature, interpretable results. This may be owing to a complication in the reaction or a liability to error in the subsequent analysis. VOLKMANN does not describe his *modus operandi* fully enough for any judgment to be formed. Nor does he interpret his results. See p. 88.

Both he and TRAUTZ, who is the sole author of the three subsequent papers in vols. 66, 67, and 68 of the 'Zeitschrift für Phys. Chem.' (in which there is no experimental work), give lists of the literature of the subject which do not include ESSON'S and my papers. Our formula is given, vol. 64, p. 57, but is not referred to elsewhere or discussed. Nothing in VOLKMANN and TRAUTZ'S papers leads me to doubt of anything we have written.—A. V. H.]

When m has the constant value 20, the values of n in the fourth column of the table diminish regularly.

The conditions of these experiments are such that no definite measure of the effect of heat energy upon chemical energy can be deduced from them.

In the next paper, vol. 66, pp. 496–510, TRAUTZ obtains a formula for n of a complicated character based on thermodynamical principles and containing expressions involving atomic heat, vapour pressure, and molecular heat of combination. The fundamental theorem of the investigation is open to criticism, and has been shown to be erroneous by SACKUR in a paper in 'Zeit. für Electrochemie,' Nov. 15, 1909, 15, 22, p. 865. TRAUTZ uses his expression to calculate the values of k in several experiments, but the values found and calculated do not agree sufficiently to render the expression probable.

In any experiments upon the effect of temperature on chemical change which are affected by the variation of the side effects of temperature enumerated above, the main effect is inevitably masked, because more than one condition is varied at the same time. In the experiments by HARCOURT and the author, recorded in the Bakerian Lecture, 1895, and in the experiments by HARCOURT set forth in the present paper, 1912, these complications have been avoided and the true relation between temperature and chemical change has been established.]