363. *The Kinetics of the Decomposition of Nickel Formate.*

By L. L. Bircumshaw and Joseph Edwards.

Accurate analysis of the gases evolved when anhydrous nickel formate is heated *in vacuo* at 165—180° indicates that the reaction is represented mainly by the equation :

$$2(H{\cdot}CO_2)_2Ni \longrightarrow 2Ni + 3CO_2 + CO + H_2 + H_2O$$

The rate of the thermal decomposition of this salt has been investigated in this temperature range, as well as the influence on the decomposition of (1) spreading the material, (2) allowing the gaseous products to accumulate, (3) preliminary grinding of the salt, (4) mixing the salt with the solid residue, and (5) interrupting the reaction.

The decomposition follows the Prout–Tompkins relationship, $\log (p/p_f - p) = kt +$ constant, if the salt is "spread." The solid product catalyses the reaction, and the gaseous products have a considerable inhibiting effect. Water vapour is particularly important in this respect, especially in connection with the induction period and the initial stages of the reaction.

In spite of the importance of nickel formate as a source of active nickel for use in a number of catalytic processes, little appears to be known of the manner in which it decomposes. Caujolle (*Compt. rend.*, 1939, **204**, 445) heated its dihydrate in a vacuum, raising the temperature gradually to 300°. The gaseous products evolved were collected in two fractions between 100° and 200° and 200° and 300° and analysed separately. The greater part of the gas was evolved between 200° and 300° but the compositions of both fractions were similar. The residue was entirely metallic nickel and a certain amount of methane appeared if the decomposition was carried out at higher temperatures. Balandin, Gregorian, and Janischeva (*J. Gen. Chem. Russia*, 1940, **10**, 1031) from a study of the decomposition between 215° and 270° considered that the two reactions

$$(H{\cdot}CO_2)_2Ni \longrightarrow \begin{cases} Ni + H_2 + 2CO_2 & (a) \\ Ni + H_2O + CO + CO_2 & (b) \end{cases}$$

proceed simultaneously until 40—50% has decomposed, after which only reaction (*a*) persists. The decomposition was carried out in air, in nitrogen, and in oil. The nickel residue obtained in air or nitrogen was almost completely catalytically inactive, but that obtained in oil was extremely active. If the gaseous products were left in contact with the residue a slow contraction (about 5%) took place, owing to the catalytic formation of methane from the carbon monoxide and hydrogen. Dobytshin and Zelmskaja (*Bull. Inst. Chem. Phys.*, 1938; but see also Roginsky, *Trans. Faraday Soc.*, 1938, **34**, 959) believed the decomposition to proceed according to equation (*a*). Unfortunately, we do not know the exact conditions under which their experiments were carried out, as their paper could not be obtained. Clearly, the course of the thermal decomposition of nickel formate had to be clarified as an essential preliminary to any work on the kinetics.

Analyses of the gases produced at four different temperatures (105—180°) were carried out. The effect of varying the rate at which gas is pumped off from the decomposing solid was investigated—also that of leaving the gas in contact with the solid residue for varying periods of time. Since even the most rapid rate of pumping with a Toepler pump does not compare with that of the pumping unit in the kinetics experiments the effect of removing carbon dioxide and water by means of a liquid-oxygen trap while pumping (with the Toepler pump) as quickly as possible was also tested. The weight and appearance of the residue were noted in each experiment.

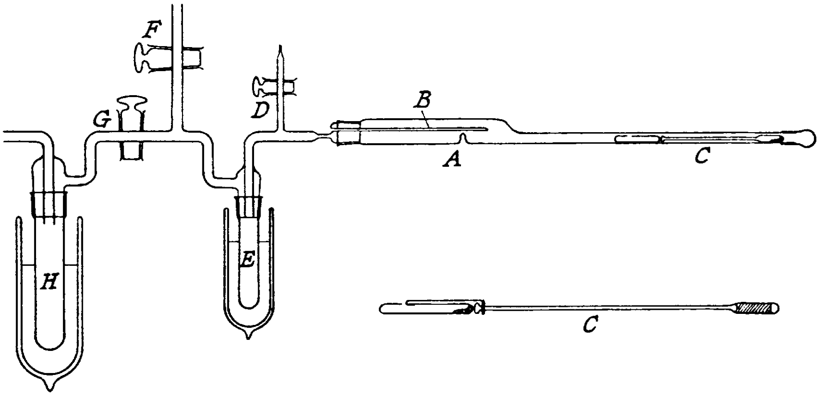
Experimental.

As nickel formate dihydrate is almost equally soluble in hot and in cold water, it was necessary to obtain the substance by careful evaporation of a solution. "AnalaR" Nickel carbonate (20 g.) was added, in small portions, to a solution (500 ml.) containing an excess of formic acid (if sufficient formic acid is not present a formo-carbonate may be produced). The resulting solution was filtered and then evaporated slowly to about one-third of its bulk. After the mixture had been cooled and kept overnight the dihydrate was filtered off and washed with distilled water until no smell of formic acid could be detected. The salt was then recrystallised twice in the same way, dried in a vacuum desiccator, and stored in a desiccator containing no drying agent. Thus prepared the dihydrate was a very fine green powder which was seen under a microscope to consist of very small crystals. The nickel content (Found: Ni, 31·6. Calc. for $C_2H_2O_4N,2H_2O$: Ni, 31·8%) was determined by the dimethylglyoxime method.

The gases were usually collected by use of a decomposition tube of the type shown (Fig. 1), which was used for the kinetic experiments. A constriction on the tube ensures that the salt is always in the same position relatively to the thermocouple in *B*. The formate was introduced by means of a permanent magnet and a glass rod attached to a tube containing a small piece of iron (*C*). The enlarged view of *C* shows the arrangement for interrupting the decomposition: a platinum wire attached to the glass rod by a wire collar engages the hole in the small tube making it possible to withdraw it by means of the magnet. With this arrangement part of the rod must remain in the furnace during the decomposition. It was found, however, to have no great effect on the course of the reaction though it did take slightly longer to attain a constant temperature. The water formed is condensed in *E*, surrounded by solid carbon dioxide and alcohol. The apparatus is evacuated through *I* which is connected to a mercury trap, a two-stage mercury-vapour pump, and a Cenco oil pump. A liquid-oxygen trap *H* is included and the whole apparatus is made of wide-bore Pyrex tubing to ensure rapid evacuation. The rate of decomposition is measured by cutting off the pumps (*i.e.*, closing tap *G*) at fixed intervals, allowing the pressure to rise for 30 seconds, and measuring it in a McLeod gauge connected through *F*. *D* is a leak tap. The gas collected over the Toepler pump was analysed in an Ambler gas-analysis apparatus.

In the few experiments in which the products were allowed to accumulate the volume of the apparatus was increased by attaching bulbs of various sizes to the end of the decomposition tube.

FIG. 1.



After a few preliminary experiments had been made on the kinetics of the decomposition it became important to discover the precise effect of variations of temperature, rate of pumping, etc., and a more thorough investigation was carried out.

Decomposition was carried out at the four temperatures used in the kinetical work, *viz.*, 165°, 170,° 175°, and 180°. With a " normal " rate of pumping—one stroke of the Toepler pump per minute—the compositions of the gases at the four temperatures were compared. Then at 180° experiments were made to test the effect of pumping at two strokes per minute. Since this rate of removal of the product gases did not compare with that in the kinetical experiments, a run was performed with liquid oxygen around the trap *E* instead of solid carbon dioxide and alcohol. This, of course, removed the carbon dioxide as well as the water. When decomposition was complete the liquid oxygen was replaced by carbon dioxide–alcohol, the remaining gas was pumped off, and the total gas analysed.

The effect of leaving the gases produced in contact with the nickel residue was next investigated. Since the volume of the apparatus was comparatively small, the final pressure attained was considerable, and any reaction caused catalytically by the nickel should certainly be apparent. To decide whether the reaction is the same over the whole course of the decomposition, the gases produced in one run were collected in fractions corresponding roughly to the first and the second half of the decomposition.

The most important point emerging from these experiments is that the variations in composition of the gases under the different conditions are very small indeed. No methane was detected in any of the samples but this is not surprising in view of the low temperature.

The mean result (excluding those of the incomplete accumulated-pressure run and the broken run) is :

	Ml. from 40 mg.	%.	Litres/g.-mol.
CO_2	7·28 (7·28)	60·9 (60·0)	33·6 (33·6)
CO	2·29 (2·42)	19·2 (20·0)	10·6 (11·2)
H_2	2·38 (2·42)	19·9 (20·0)	11·0 (11·2)
Total	11·95 (12·12)	100·0 (100·0)	55·2 (56·0)

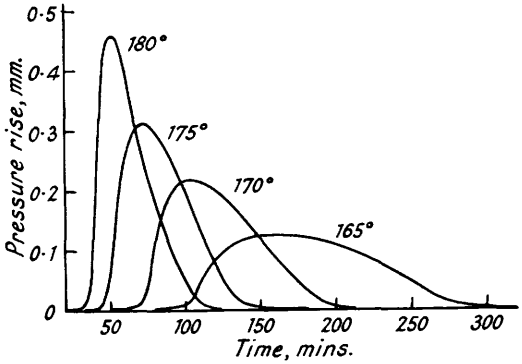
(Mean wt. of residue = 0·0128 g.)

If the two processes (*a*) and (*b*) (p. 1800) play an equal part in the reaction the theoretical values should be those shown in parentheses above The conclusion can be drawn that nickel formate decomposes at 165—180° according to the reaction $2(H\cdot CO_2)_2Ni \longrightarrow 2Ni + 3CO_2 + CO + H_2 + H_2O$, and that variation in the rate of removal of the gas from the salt or leaving the product gases in contact with the residual nickel has little effect.

The Kinetics of the Decomposition.—The current in the furnace winding was increased for a minute or two before introduction of the salt into the furnace. After a little practice it was possible, in this way, to raise the salt to the temperature required in a very short time. In all experiments the same amount of salt (40 mg. of the dihydrate) was used. Before an experiment was begun, the apparatus was evacuated for one hour and tested for leaks. As the tube was pushed into the furnace by means of a magnet a stop-watch was started. At intervals of 5 minutes (or 2½ minutes where the rate was changing very rapidly) the pumps were cut off and the pressure inside the apparatus was allowed to rise for 30 seconds. The pressure was then read on a McLeod gauge. This pressure is a measure of the rate at which the decomposition is proceeding, the actual value depending of course on the volume of the apparatus and the amount of salt taken. Twice this value was taken as dp/dt, the pressure rise in unit time (1 minute).

FIG. 2.

30-Sec. rise in pressure for unspread formate.



In the runs with the " unspread " formate the salt was shaken into a small heap at the end of the tube but was not allowed to block the whole width of the tube. If it did so, it tended to be blown along the tube as the decomposition proceeded. The best method for the preliminary dehydration was heating in air at 130—135°, and this method was adopted for all the work.

Typical rate–time curves are shown in Fig. 2. In every case there is an induction period which is greater at the lower temperatures. The maximum rate is about 0·46 (in these arbitrary units) after 50 minutes at 180° and 0·125 after 155 minutes at 165°. The curves are typical of a number of solid decompositions in which the rate, after an induction period, accelerates to a maximum and finally falls to zero. The curve in this case is not symmetrical, the rise to the maximum being steeper than the fall to zero.

The total pressure at any time, *i.e.*, the pressure which would have been obtained had the pumps been permanently cut out and the pressure allowed to rise, is proportional to the amount of nickel formate decomposed and can be evaluated by square counting : the area enclosed by the curve and the time axis represents the amount of decomposition which has taken place and is proportional to the total pressure at that time. It is possible, of course, to make direct measurements of p and this was done later. The present method, however, eliminates the retarding effect (if any) of increasing pressure of product gases. Two of the rate–time curves at each of the four temperatures were plotted and integrated by the method of square counting, so that the values of p at each interval were obtained. The pressure–time curves plotted in Fig. 3 have the well-known sigmoid shape. At all four temperatures the maximum rate occurs when the decomposition is about one-third completed.

With the values for dp/dt and the corresponding values for p at the various temperatures we can test the applicability of various equations which have been put forward to account for the course of solid decompositions. We have first

$$dp/dt = kt^m \quad \text{. . . . .} \quad (1)$$

$$dp/dt = kp^{2/3} \quad \text{. . . . .} \quad (2)$$

Both these equations are deduced on the assumption that the reaction spreads spherically into the body of the decomposing solid. Garner has shown that the maximum value of m should be 3·0. Equation (2) involves the assumptions of the simple interface theory. In addition we have the well-known equations derived from the branching theory :

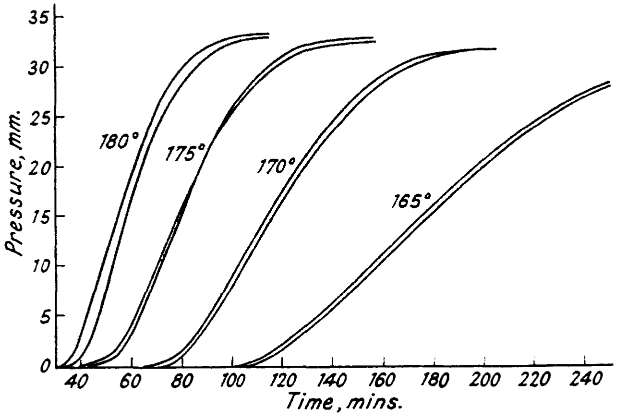
$$\ln p = k_2 t + \text{constant} \quad \text{. . . . .} \quad (3)$$

$$\ln dp/dt = k_3 t + \text{constant} \quad \text{. . . . .} \quad (4)$$

A plot of log (dp/dt) against log p does not give a straight line. This being so, and as m always exceeds 3·0, it appears that the simple interface theory does not apply in the normal decomposition.

FIG. 3.

Total pressure–time curves by integration of rate–time curves for unspread formate.



It is often found in solid decompositions which occur with evolution of a gas that the pressure increases exponentially with time. The decomposition of anhydrous nickel formate is no exception. As can be seen from Fig. 4, equation (3) is obeyed practically up to the time of maximum rate. The values of the constants k_2 are :

Temp.	165°	170°	175°	180°
k_2	0·079	0·107	0·162	0·208

The branching-chain equation (4) has been found to apply in many cases where the exponential equation holds. Plotting log dp/dt against t gives straight lines for the initial part of the decomposition at all four temperatures but the relation breaks down before the maximum rate of decomposition is reached, k_3 being :

Temp.	165°	170°	175°	180°
k_3	0·0863	0·128	0·169	0·265

It should be noted that equations (3) and (4) are, except for the integration constant, identical, *i.e.*, k_2 should be equal to k_3.

The final stages of the decomposition do not follow a first-order law

$$k_4 = [1/(t_2 - t_1)] \ln (p_f - p_{t_1})/(p_f - p_{t_2})$$

where p_f is the total final pressure.

In their work on the thermal decomposition of potassium permanganate (*Trans. Faraday Soc.*, 1944, **40**, 488), Prout and Tompkins concluded that the whole course of the decomposition could be expressed by the equation log $p/(p_f - p) = kt +$ constant, where k has two different values before and after the time of maximum rate. This has been found to apply in a number of other decompositions and has been tested with the present results. The agreement with the equation is only moderate. The graphs are continuous curves which only approximate to straight lines. In other decompositions, for which this relation holds approximately, a departure often occurs towards the end of the decomposition. In this case the departure is particularly marked and the values appear to lie in a third straight line. It is pointless to speculate on the cause of this and, as will be seen later, the effect disappears when the salt is spread. The intersection of the lines corresponding to the acceleration and the decay of the reaction is seen in each case to occur slightly before the time of maximum rate.

FIG. 4.

log p–t *for unspread formate.*

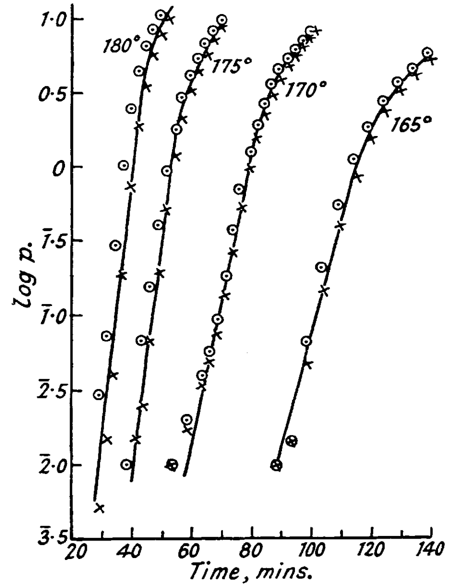


FIG. 5.

Total pressure–time for unspread formate.

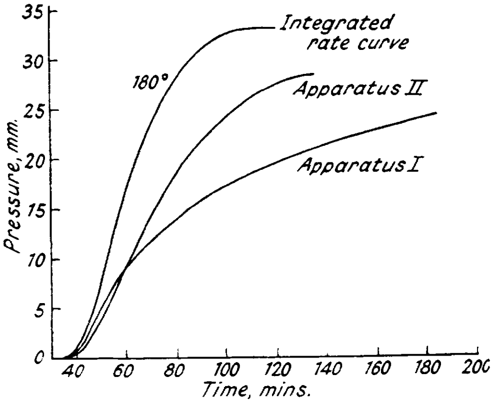
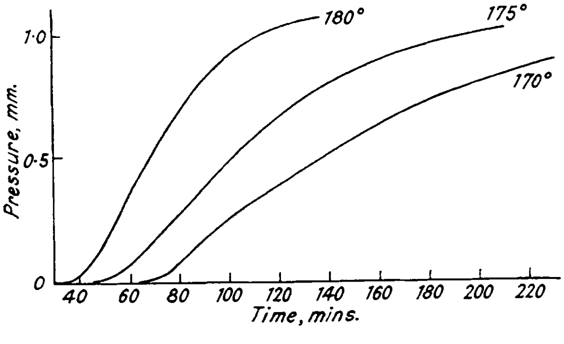


FIG. 6.

Total pressure–time curves by direct measurement—Apparatus II, unspread formate.

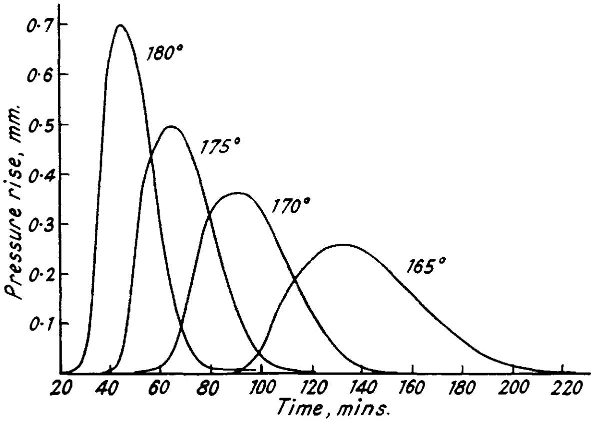


The Effect of Allowing the Products of Decomposition to Accumulate in the Apparatus.—This effect has been studied by making a number of experiments in which the pumps were cut off permanently and the pressure allowed to rise in the apparatus. It was advisable to retain the same quantity of material and hence to ensure that the pressures developed could be measured on the McLeod gauge the volume of the apparatus had to be increased. This was done in the first case (apparatus I) by attaching a 1-litre bulb, through a tap and Quickfit joint, to the end of the decomposition tube. The ratio of the volumes, with and without the bulb, was measured by allowing a little air to enter the evacuated apparatus and reading the pressure. The tap connecting with the bulb was then opened and the pressure read again. The ratio of the former to the latter pressure gave the conversion factor. A plot of the results obtained, corrected for the volume increase at 180°, is seen in Fig. 5. It will be noticed that the pressure produced has a strong retarding effect on the reaction, so much so that the complete decomposition even at 180° takes more than 4 hours. Experiments were also made on an apparatus with a volume further increased. Six 1-litre bulbs were added in this case, and experiments were made at 180°, 175°, and 170°.

The results are shown graphically in Fig. 6. It will be noticed in Fig. 5 that there is a difference in final pressure between apparatus I (28·12 mm.), apparatus II (28·50 mm.) and the integrated rate curve (33·13 mm.). This is due to the presence of water vapour in the products of decomposition. The magnitude of the difference indicates that even when a carbon dioxide–alcohol trap is included in the system the rate of condensation of water is much slower than its rate of production, so that part of the pressure recorded is due to some water vapour. The final pressure reading in the direct p–t measurement does not of course include any water vapour. According to the equation deduced for the reactions, the volume of water vapour should be one-fifth of the sum of the other gases, and the difference in the final pressure (integrated) is about one-sixth of the " accumulated " pressures (no water). Thus it appears that in the 30 seconds only a small fraction of the water vapour is condensed in the trap. If we make the highly probable assumption that the rate of condensation at any moment is proportional to the pressure of water vapour present (during the 30-second intervals), at least over the range investigated, then the integrated p's are still proportional to the actual rate of decomposition of the nickel formate. The rates of production of water vapour are widely different at the different temperatures, yet the fractional differences between final pressures (integrated and " accumulated " pressures) remain sensibly the same.

FIG. 7.

30-Sec. rise in pressure for spread formate.



Effect of Spreading the Nickel Formate.—In connection with the work described in the last section (direct total pressure measurements) it was decided to make experiments, in the same apparatus, with smaller quantities of formate. In an exploratory run, however, small decomposed much more rapidly than larger quantities. This raised the question of the effect of spreading on the rate of decomposition, since the increase in rate with smaller quantities may be due to the diminished resistance offered to the escape of gases by the solid product. The rate of decomposition of the spread salt was, in fact, found to be considerably greater than that of the unspread. The rates were therefore investigated at the four temperatures, the formate being spread out along the whole length (about 4 cm.) of the small tube. The rate–time curves are given in Fig. 7. The increase in maximum rate over the unspread salt varies between 50 and 100% and is greatest at the lowest temperature. The total pressures were evaluated by graphical integration and the pressure–time curves for the four temperatures are shown in Fig. 8.

As with the unspread salt, the value of m derived from the equation (1) exceeded 3·0, and a plot of log dp/dt against log p did not give a straight line, so the simple interface theory does not apply. Both the exponential and the branching-chain equations hold over the first part of the decompositions (Fig. 9). The constants k_2 and k_3 are given below, agreement being excellent.

Temp.	165°	170°	175°	180°
k_2	0·102	0·132	0·189	0·249
k_3	0·098	0·125	0·190	0·246

FIG. 8.

Total pressure–time curves by integration of rate–time curves for spread formate.

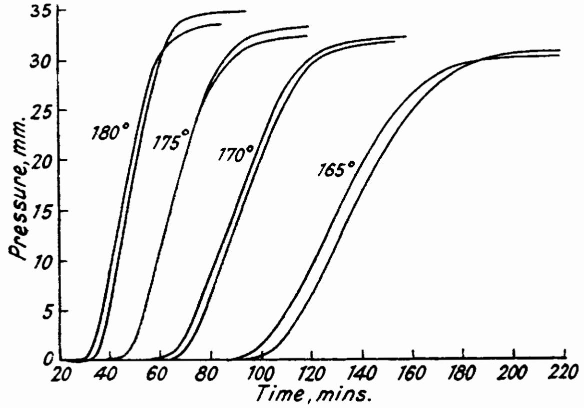


FIG. 9.

log p–t *for spread formate.*

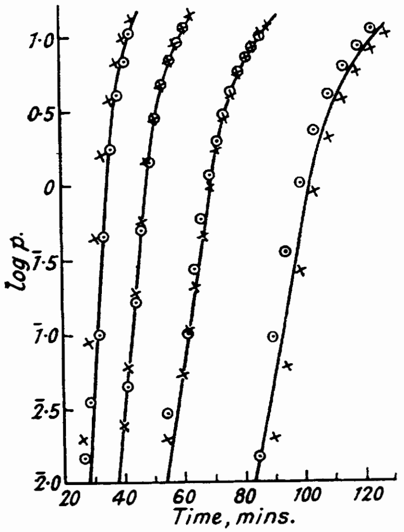
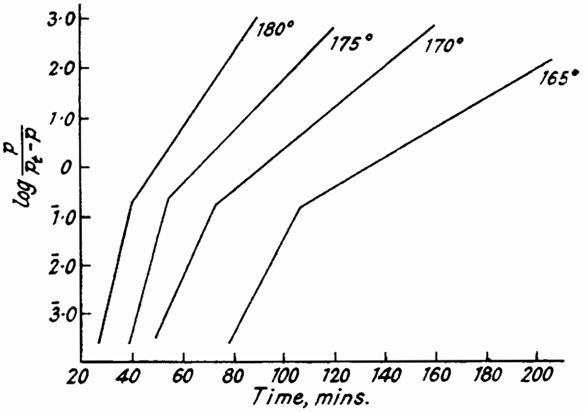


FIG. 10.

$\log \frac{p}{p_t - p}$–t *for spread formate B.*



Very good agreement is also obtained with the Prout–Tompkins equation. Two straight lines account for the whole course of the reaction at all temperatures (see Fig. 10). The intersection of these lines is still, however, as with the unspread salt, before the time of maximum rate. The mean constants k_a and k_b are :

Temp.	165°	170°	175°	180°
k_a	0·093	0·122	0·173	0·2215
k_b	0·030	0·042	0·056	0·0747

The plot of log k in each case against $1/T$ is shown in Fig. 11, and E calculated from the four slopes is: k_2 22,900, k_3 20,100, k_a 23,800, and k_b 24,100 cals. (mean 22,700). This may be compared with the value (26,400 cals.) for E for the unspread salt.

The Effect of Grinding the Formate before Decomposition.—The preliminary grinding of solids before decomposition generally modifies the rate of reaction (by reducing the particle size) and almost eliminates any induction period (by increasing the rate of nucleation). The particle size of anhydrous nickel formate is already very small, and it seemed possible that the rate of decomposition would not be greatly altered by grinding. This was tested experimentally. Ordinary dry grinding was found to be most unsatisfactory. The formate was compressed into lumps which decomposed very irregularly. Grinding was therefore carried out with an agate pestle and mortar under carefully dried carbon tetrachloride (1) before dehydration and (2) after dehydration, and also (3) one sample of the salt was treated with carbon tetrachloride without grinding. In no case was any noticeable effect on the rate observed, nor was the induction period removed.

FIG. 11.

log k–1/T *for spread formate.*

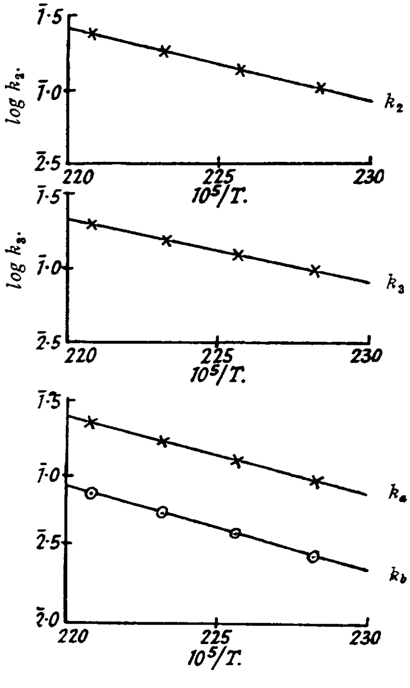
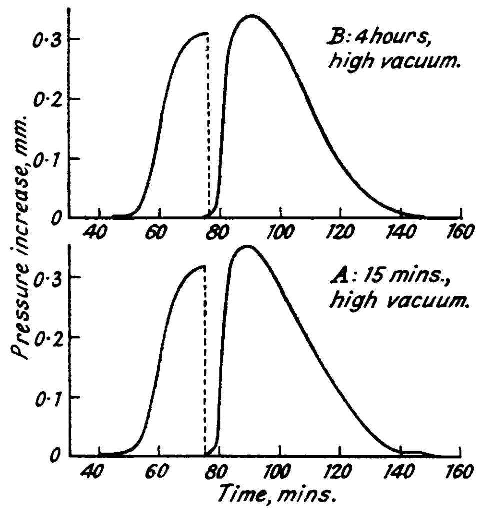


FIG. 12.

Interrupted runs, unspread formate at 175°.



The Effect of the Nickel Residue on the Decomposition.—In a number of solid decompositions, the reaction, after the time of maximum rate, follows a first-order law. In others, however, the solid product catalyses the reaction. In their study of the decomposition of potassium permanganate Prout and Tompkins assume this to be so when deriving their equation. Since the Prout–Tompkins equation holds for the decomposition of the present substance, it seemed likely that the nickel residue was capable of catalysing the reaction. Direct observation of partially decomposed material in which decomposition was seen to have occurred in patches confirmed this.

Direct experiment with the usual quantity of dehydrated salt mixed with the entire residue from a previous run showed that the decomposition followed a normal course for about 20 minutes and then suddenly accelerated, reaching a maximum rate higher than that of a normal run. The rate then dropped rapidly but the final stages of the decomposition appeared to be slower than usual. The induction period remained practically unchanged. However, the mixing may be uneven, and simple contact may not be sufficient for pronounced catalysis; also the bulk of the material is almost doubled, so it is difficult to compare the extent to which the formate itself is spread, and the gases produced must escape through a solid layer containing a higher proportion of residue.

Interruption of the Reaction.—It was obviously valueless to interrupt the reaction at a point where the rate was changing rapidly, so the decomposing salt was in each case withdrawn from the furnace as nearly as possible at the time of maximum rate. The solid was allowed to cool in a high vacuum or in air for various times. In view of the influence of water vapour on the induction period (see next section) experiments were also made in which the solid was allowed to cool in (1) dry air and (2) water vapour. In the latter case, after withdrawal of the solid, the pumps were cut off and the liquid oxygen was removed from a trap in the system which contained a little water. Before continuing the decomposition, of course, the apparatus was completely evacuated. All the experiments were made at 175° and results are given in Figs. 12 13 and 14.

FIG. 13.

Interrupted runs, unspread formate at 175°.

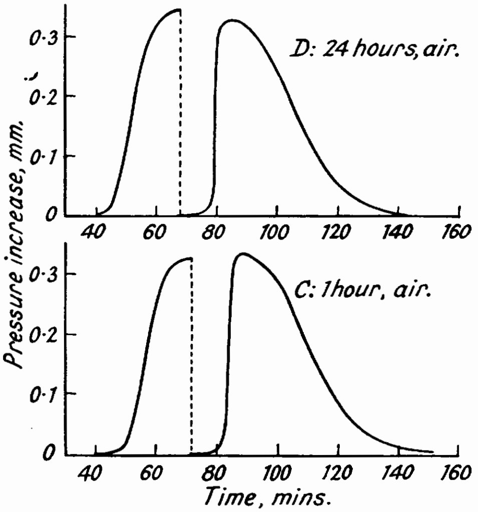
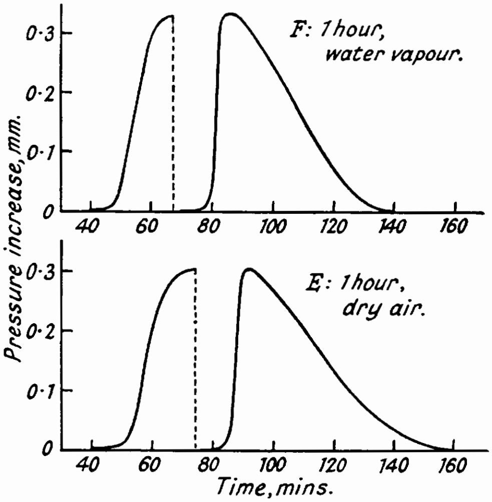


FIG. 14.

Interrupted runs, unspread formate at 175°.



They fall into two groups : (1) those with cooling in a high vacuum, and (2) the remainder. In the first, the reaction continues immediately after the interruption, as before, if we allow for the short time it takes the sample to become heated. The maximum rate attained after interruption is slightly higher than usual. This is probably due to a slight spreading due to moving the tube in and out of the furnace. In the other four experiments there is an induction period of about ten minutes before the reaction begins again. The rate then rises rapidly to the maximum—more rapidly than before, since in this case the sample will, during the induction period, have attained the temperature of the furnace. The maximum attained is the same as the original maximum.

The temporary inhibition of the reaction in the presence of adsorbed water vapour is important. Apparently, the interface is completely poisoned by adsorbed gas and the reaction can only proceed when the gas has been removed. There is a possibility that the effect is produced by water vapour; under the conditions of the experiment, the dried air might contain a trace of water vapour, enough to inhibit the decomposition.

The Induction Period.—The induction period becomes shorter with rise of temperature. The values of t_0, the induction period, and log $1/t_0$ for the various temperatures are given below :

		165°	170°	175°	180°
Temp.		165°	170°	175°	180°
Unspread	t_0	80	52·5	35	25
	log $1/t_0$	$\bar{2}$·097	$\bar{2}$·280	$\bar{2}$·456	$\bar{2}$·602
Spread	t_0	70	45	30	20
	log $1/t_0$	$\bar{2}$·155	$\bar{2}$·347	$\bar{2}$·522	$\bar{2}$·699

The values are plotted along with the corresponding values of k_b—probably the most reliable of the rate constants. The points lie quite close to a straight line in each case, and it will be seen that the slope and therefore the activation energy of the induction process is of the same order as that of the decomposition itself (Fig. 15).

Some experiments were made to test the effect of interrupting the induction period. Samples of unspread formate were heated *in vacuo* at 165° for 60 minutes, withdrawn from the furnace, allowed to cool for a time, and then returned to the furnace, and the length of the induction period was measured. This period was found to depend on the conditions of cooling:

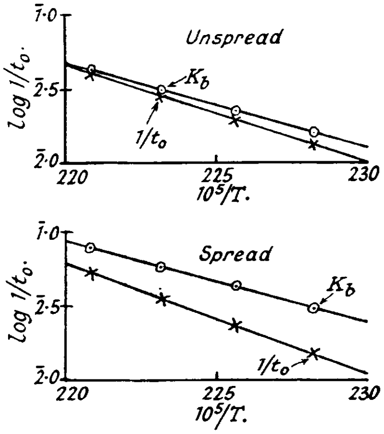
	(1)	(2)	(3)	(4)	(5)
Conditions of cooling	1 hour, high vac.	5 hours, high vac.	24 hours, high vac.	1 hour, air	24 hours, air
t_0 after interruption	25	25	35	80	80
	(6)	(7)	(8)	(9)	
Conditions of cooling	1 hour, water vap.	24 hours, water vap.	1 hour, dry air	5 hours, dry air	
t_0 after interruption	80	80	30	40	

These results appear to show that whatever occurs during the induction period persists through an interruption if it takes place in the absence of water vapour. When the latter is present, however, the complete induction period is restored. Small amounts of water vapour are undoubtedly responsible for the slight increase of t_0 in (3) and (9).

It might seem that the induction period is simply a period of desiccation necessary before any decomposition can take place. It must be remembered, however, that water is one of the products of the decomposition and hence complete desiccation at a temperature at which decomposition can take place is not possible. Further, the length of time a sample is left in the drying oven (at 130°) or in the evacuated apparatus (at room temperatures) before decomposition has no effect on t_0. Hence, the induction period is not the consequence of water originally present in the salt. It is probable that decomposition begins as soon as a sample is introduced into the furnace. Acceleration is slow since the nuclei are small and because gaseous products (probably water is the most important) tend to depress the rate of reaction. If the products are removed more quickly the acceleration is increased. Thus spreading reduces t_0 a little, and the addition of a layer of residue increases it. At time t_0 the rate of decomposition becomes measurable, and shortly afterwards a rapid acceleration occurs, presumably when the nuclei reach a certain size. Since cooling in water vapour restores the full induction period, it must be assumed that a sufficient concentration of water is able to poison completely those nuclei which have already begun to grow.

FIG. 15.

log $1/t_0 - 1/T$.



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