The thermal decomposition of nickel carbonyl may take place, depending on the process parameters (temperature conditions, rate of vapor supply, dimensions of the apparatus), both within the apparatus (heterogeneous decomposition) and on its walls (heterogeneous decomposition).

The kinetics of the heterogeneous decomposition of nickel carbonyl in a flow-type system at temperatures ranging from 70 to 150°C was investigated using the laboratory installation illustrated diagrammatically in Fig. 1. The principal part of the installation was the reaction tube 2 placed within the quartz decomposer 1. The tube was heated along the whole length of the reaction zone with the internal electric heating element 4. Operating in conjunction with the regulator 10, the heating element enabled any desired temperature to be maintained on the tube surface. The temperature was monitored with the millivoltmeter 6. To ensure that no homogeneous decomposition of nickel carbonyl occurred in the reaction zone, the outer wall of the decomposer was maintained at a temperature of 4°C by means of the cooling jacket 3.

The decomposer and reaction tube diameters were 3.0 and 1.4 cm, respectively, giving a 0.8-cm wide gap. The total length of the reactor consisted of two parts, the 3.5-cm long admission part a, in which a uniform, laminar flow of the gas stream was secured, and the reaction part b. In the latter part, which was heated on a length of 5 cm, decomposition of nickel carbonyl took place. To calculate the length of a hydrodynamic zone in which a laminar gas stream attains a constant velocity, use was made of the formula proposed by Boettger [1] for the flow of gas through an annular orifice

$$L = 0.04 \cdot \text{Re} (r_1 - r_2).$$  \hspace{1cm} (1)

In our experiments, the Reynolds numbers ranged from 15 to 50, so that the flow of gas was always laminar. According to Eq. (1), a length of 3.5 cm was entirely sufficient for the complete stabilization of velocities in the gas stream.

Nickel carbonyl was vaporized in a nitrogen stream, the rate of supply of nitrogen being measured with the rotameter 9. To ensure that the desired nickel carbonyl temperature was maintained constant, the vaporizer 7 was placed in the constant-temperature tank 8.

Before each experiment, it was necessary to clean the reaction surface free from nickel deposits. Such a cleaning treatment was essential for securing reproducible results, because freshly deposited nickel strongly affects decomposition rate.

The degree of nickel carbonyl decomposition was determined from the amount of metallic nickel deposited on the reaction surface. The velocity of the gas stream in the course of the experiments ranged from 6 to 10 cm/sec, the residence time of the
Fig. 2. Effect of gas flow rate on fraction of decomposed pure nickel carbonyl at various temperatures.

Fig. 3. Temperature dependence of rate constant of reaction.

gas in the reaction zone being 0.8-1.2 sec. Initially, determinations were made of the nitrogen feed velocities at which the nickel carbonyl concentration in gas was constant for all experiments. For this purpose, a given volume of liquid nickel carbonyl (2 ml) was evaporated in a stream of nitrogen admitted into the vaporizer at a constant rate (10 and 20 liters/h) and a constant nickel carbonyl temperature in the vaporizer (32, 36, and 40°C). Next, curves of nickel carbonyl concentration of gas were plotted against nitrogen feed rate for the three nickel carbonyl temperatures, and with their aid working nitrogen feed rates for evaporation were determined (7, 13, and 18 liters/h). The rate constants of the decomposition reaction were determined at reaction tube surface temperatures of 70, 90, 100, 110, 130 and 150°C.

For each experiment, the fraction of decomposed nickel carbonyl, \( \alpha \), was calculated from the weight of nickel deposited on the reaction surface; the total amount of nickel carbonyl evaporated during an experiment was 2.56 g (2 cm\(^3\) x 1.28 g/cm\(^3\)).

Plotting curves of gas feed rate vs \( \alpha \) (Fig. 2) and extrapolating them to the axis of ordinates gave the value of \( \alpha_0 \) (fraction of decomposed pure nickel carbonyl) for each decomposition temperature.

The rate constant is calculated with the formula:

\[
K = \frac{2.3}{\text{tres}} \cdot \log \frac{P_0}{P_t}.
\]  

(2)

Here \( P_0 \) and \( P_t \) are the nickel carbonyl concentrations at the initial and final instants, respectively, and \( \text{tres} \) is the residence time of gases in the apparatus;

\[
P_0 = \frac{V_{\text{Ni(CO)}_4}}{V_{\text{Ni(CO)}_4} + V_{\text{nit}}},
\]  

(3)

where \( V_{\text{Ni(CO)}_4} \) is the volume of evaporated nickel carbonyl and \( V_{\text{nit}} \) is the volume of nitrogen admitted into the vaporizer (5.7 liters);

\[
P_t = \frac{V_{\text{Ni(CO)}_4}(1 - \alpha_0)}{V_{\text{Ni(CO)}_4}(1 + 3\alpha_0) + V_{\text{nit}}}.
\]  

(4)

(\( \alpha_0 \) is obtained from the graph);

\[
\text{tres} = \frac{V_{\text{app}}}{V_{\text{mean}}}.
\]  

(5)

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