FIG. 3. The ortho concentration plotted as $1/c$ versus the time after cooling to 4.2°K for relative densities of 1.00 and 1.55. The relative density $\rho/\rho_0 = 1.55$ was produced 50 min after the cryostat had reached 4.2°K.

An experiment was always started with the room-temperature ortho concentration in each gas. During the experiment there was, as mentioned before, a sizable ortho-para conversion for H_2 and it was important to know the concentration at any moment. The first concern was therefore to obtain a reliable determination of the conversion rate. A measurement of the ortho concentration by the thermal-conductivity method[38] before and after an experiment could not be carried out because the potassium washer on the piston was not tight to gas and after warming up the cavity above 4°K the gas could not be recovered. The conversion rate was found by measuring the area under the resonance curve as a function of time for various densities. This area is known to be proportional to the ortho concentration. For this purpose, the derivative of the line had to be twice integrated graphically. At the same time this experiment could give a determination of the linewidth and second moment for various ortho concentrations at a given density. All the linewidth measurements were made at 4.2°K as this temperature was found to be
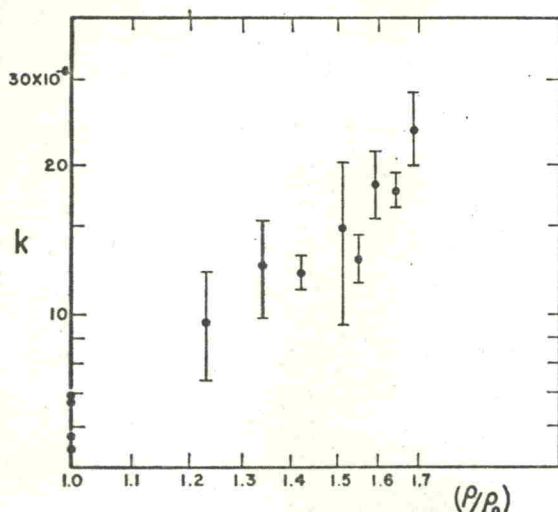

FIG. 4. The ortho-para conversion constant k in $(\%/min)^{-1}$ versus the relative density.

[38] E. R. Grilly, Rev. Sci. Instr. 24, 72 (1952).

above T_λ for all the densities used. For D_2, where the conversion rate is negligible, the recordings of the derivative were taken as a function of density by increasing the pressure step by step at constant temperature between 1.6 and 4.2°K.

For determinations of the T_λ in H_2, the initial pressure-cycling procedure was done as before at 4.2°K. The pressure was then set to a certain value and the temperature of the helium bath was slowly reduced. Eventually the transition temperature was passed. As it was difficult to see the satellites appear at T_λ, the method used by McCormick[15] was adopted. This technique consisted of taking tracings of the line at different temperatures below T_λ. Then a plot of the ratio of the satellite height to that of the central line was made versus temperature.[39] A straight line was fitted to these points and the temperature of zero intercept was taken as T_λ. Ten lines were taken on the average for each transition point. As the lines were covered in about 30 min, the change in ortho concentration would not seriously affect the results. The lines were taken over a spread of about 1°K. This gave a good range in the value of the ratio and made the T_λ determination reasonably accurate. About 30 points were taken at various densities and ortho concentrations.

IV. RESULTS AND DISCUSSION

A. Hydrogen

(a) Ortho-Para Conversion

The ortho-para conversion was measured at 4.2°K, as this is the most convenient temperature. The ortho concentration was measured in arbitrary units as described before and was normalized to 75% at the beginning of the experiment ($t=0$). As expected, c was found to decrease faster with time as the density was higher. (See Fig. 3.) The increased scatter at high densities is due to the difficulty in doubly integrating the broadened line. The location of the line extremities becomes more uncertain at high densities. The expected functional relationship between c and t comes from an integration of the relation given by Cremer and Polyani,[40]

$$dc/dt = -kc^2, \qquad (7)$$

where k is the reaction constant, assumed to be independent of c. If there is a possibility of a small O_2 impurity, there is an additional conversion rate[9] equal to Kc. The constant K is a function of the distance from the O_2 to the nearest ortho molecules. When H_2 is solidified, there is initially a rapid conversion of the ortho molecules around the impurity.[9] After some time, of the order of 30 min, the conversion is calculated to

[39] For a typical line derivative below T_λ see for instance Fig. 7 in Ref. 6. The "satellite" lines there are labeled H_s^1 and H_s^{11}.
[40] E. Cremer and M. Polanyi, Z. Physik. Chem. B21, 459 (1936); E. Cremer, ibid. B29, 445 (1938).