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TITLE **HYDROGEN ISOTOPIC EXCHANGE OVER PALLADIUM METAL**

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HYDROGEN ISOTOPIC EXCHANGE OVER PALLADIUM METAL

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SUMMARY

We have recently developed the laser-Raman technique as a means of unambiguously measuring the partial pressures of all possible hydrogen isotopes in the gas phase. Using this technique we have investigated the hydrogen-deuterium exchange in a number of metals. This report presents detailed data for isotopic exchange in the palladium hydride system over the temperature range 26°C to -100°C at a pressure of 7 atm. First order kinetic rate constants and activation energies are summarized for the forward (hydride to deuteride) and reverse (deuteride to hydride) exchange processes. In addition, we have found that small amounts (100 ppm) of impurities in the exchange gases considerably slow the exchange kinetics with the effect increasing down the series CH_4, CO_2, H_2O, and CO.

INTRODUCTION

Hydrides of metals and alloys often show isotopic exchange at temperatures at which they display an appreciable hydrogen equilibrium overpressure [1]. The exchange process offers a convenient method of preparing bulk amounts of pure mixed-isotope materials [2] and has also been used to prepare laser fusion targets [3] containing deuterium and tritium. Recently metal exchange has been proposed as a means of purifying isotopic mixtures of hydrogen gases [4]. In addition, it provides a technique for probing and studying the interactions, both on the surface and in the bulk, between hydrogen and its isotopes and hydride forming metals. Palladium is particularly amenable to such studies since it can readily be activated to allow rapid reactions. As such, it has been widely studied.

Laser-Raman spectroscopy is a convenient and accurate method for analyzing mixtures of hydrogen, deuterium, and tritium gas mixtures [1,5,6,7]. The technique has a number of advantages: it is rapid and can continuously monitor gas streams at rates of up to 10 measurements per second [1,7]; it is quantitative since line intensities are directly proportional to the partial pressures of the species involved [6,7]; and, the method is completely non-destructive [7].

We have developed this method for studying rates of isotopic exchange between hydrogen and deuterium over metal hydrides. Our intent is to use this approach for studying hydrogen-metal interactions, hydrogen diffusion rates in metals, as well as impurity effects on kinetics.

In this paper, we include data for the hydrogen-deuterium exchange over palladium metal powder. At room temperature the exchange occurs rapidly and continues in the absence of impurities down to temperatures below $-100^{\circ}C$. Effects of four impurities (CH_4, CO_2, H_2O, and CO) were also investigated. These experiments indicated that small amounts of impurities can drastically effect the exchange rate. Even though steps were taken to clean up the exchange gases, the results with purified gases were not completely reproducible. Because of this, the data is considered only preliminary.

EXPERIMENTAL DETAILS

The experimental apparatus has been discussed previously in more detail [1,5,6,8]. Briefly, a 4-g sample of fine palladium powder (Englehardt, 0.5 micron diameter) was constrained by frits in a stainless steel holder. It was then hydrided under constant hydrogen flow at $150^{\circ}C$. As it hydrided, it expanded giving a mechanically sound compact. After cooling to lower temperatures, the hydride was exposed successively to deuterium or hydrogen (flow rates of 2 l/min) to initiate a complete exchange. Pressures inside the compact were kept at about 7 atm during all the runs. During the exchange, the gas coming from the sample was monitored by passing it through a laser excitation cell. The scattered Raman light was then used to measure the gas composition of the exchange gas. We maintained the temperature of the compact by thermostatically controlling a flow of gas from liquid nitrogen gas over the holder. The latter was surrounded by a foam insulator and three thermocouples (one inside the compact) measured temperatures. We also performed experiments in the reverse direction (deuteride to hydride) at each temperature.

At room temperature, the exchange process was rapid, taking only a few seconds. As the temperature dropped, however, it was much slower. Because of the heats of exchange, the temperature of the compact increased for the forward (H to D) and decreased for the reverse (D to H) reactions. The magnitude of the change was on the order of 5°C. In the discussions, the temperature of the sample is taken as the initial temperature, ignoring this change.

During these experiments we found that there was an impurity (probably water) in the cylinder gases which greatly impeded the rate of exchange. An analysis of one cylinder gave about 20 ppm water with no other detected impurities. For most of these experiments commercial purifiers (a De-Oxo unit followed by a dryer) were used to clean up the gases. To check impurity effects, cylinders of hydrogen containing 100 ppm of the four impurities were used without further purification.

As mentioned, from the scattered Raman light, we could directly calculate the composition of the three isotopic species (H_2, HD, and D_2) coming from the sample. From these compositions, the pressure, and the flow rate, it was easy to calculate an exchange function, H/M, as a function of time. This is defined as, for the forward reaction, the amount of hydrogen coming out of the compact or deuterium going into the compact. For the D to H case, it obviously is reversed. This calculation process is also discussed in ref [8]. Scatter in this data was on the order of 10%, primarily because of overlap between the laser-Raman bands used to calculate compositions.

Plots of ln (H/M) versus time appeared linear throughout the strongly rising parts of the experimental graphs, suggesting first order kinetics were appropriate. From these plots first-order rate constants (k) were measured.

RESULTS AND DISCUSSION

Kinetic first-order rate constants, plotted as a function of temperature (ln k versus 1/T plots), are shown in Figure 1 (for the hydrogen to deuterium exchanges) and Figure 2 (for the deuterium to hydrogen exchanges). The solid lines and solid circles display the best data (fastest exchange) made under ideal conditions--gases purified with new purifiers in place. The dashed lines and open diamonds indicate results found for cylinder gas with no purification. In several runs, even with the purifiers in place, we were unable to reproduce the ideal conditions, undoubtedly because of small amounts of residual water. These data points, which fall intermediate between the two extremes, are represented by open squares in the figures.

At higher temperatures the exchange in either direction is limited by flow. Essentially, the gas is exchanging as fast as it is getting to the metal. Thus, the leveling off to the left of the plots. This effect was seen in all cases and all experiments.

As mentioned in the previous section, we did a number of runs with various impurity gases (CH_4, CO_2, H_2O, and CO). In these cases, the deuterium was used with the purifiers in place and the contaminated hydrogen gases were used from the cylinders without purification. Plots for the impurities are shown in Figure 3 (hydrogen to deuterium) and Figure 4 (deuterium to hydrogen). In Table 1 we list the activation energies for all the plots shown in Figs. 1-4.

CONCLUSIONS

We have measured the hydrogen to deuterium exchange over palladium for pure gases and gases containing four common impurities. The deuterium to hydrogen exchange proceeds much more rapidly than the hydrogen to deuterium as expected from the differences in stabilities (the hydride has a lower equilibrium pressure [9] and is thus more stable that the deuteride).

We believe cylinder gas has an impurity which greatly slows down the exchange process. From the activation energies and the gas analysis, this is probably a few ppm of H_2O. As can be seen from the table and figures the effect of the impurity gases increases down the above series with CH_4 having virtually no effect and CO having a very strong effect.

ACKNOWLEDGMENTS

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TABLE 1

ACTIVATION ENERGIES (kcal/mole) FOR EXCHANGE OVER PALLADIUM METAL

(numbers in parenthesis are standard deviation of fit)

Contaminant	H to D Exchange	D to H Exchange
none	-2.1 (0.1)	-2.8 (0.3)
CH_4	-2.0 (0.1)	-2.0 (0.4)
CO_2	-4.2 (0.2)	-5.2 (0.4)
H_2O	-8.0 (0.8)	-5.6 (1.2)
CO	-23 (3)	-23 (4)

FIGURE CAPTIONS

1. Plot of ln k versus 1/T for the H to D exchange over palladium metal. See text for details.

2. Plot of ln k versus 1/T for the D to H exchange over palladium metal. See text for details.

3. Plot of ln k versus 1/T for the H to D exchange over palladium metal in the presence of 100 ppm of CH_4 (solid line and circles), CO_2 (dashed line and open squares), H_2O (dotted line and open diamonds), and CO (dot-dashed line and solid triangles).

4. Plot of ln k versus 1/T for the D to H exchange over palladium metal in the presence of 100 ppm of CH_4 (solid line and circles), CO_2 (dashed line and open squares), H_2O (dotted line and open diamonds), and CO (dot-dashed line and solid triangles).

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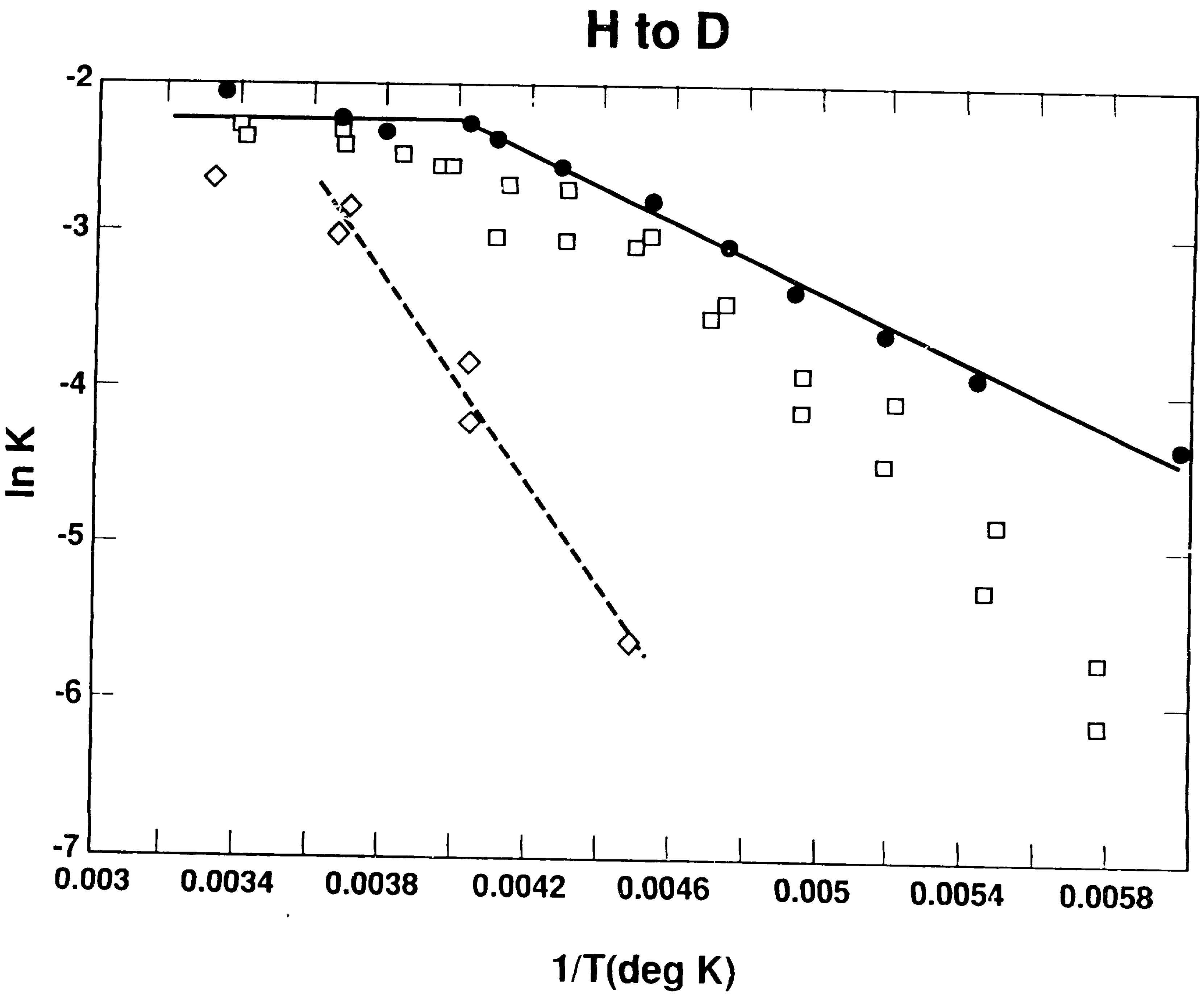

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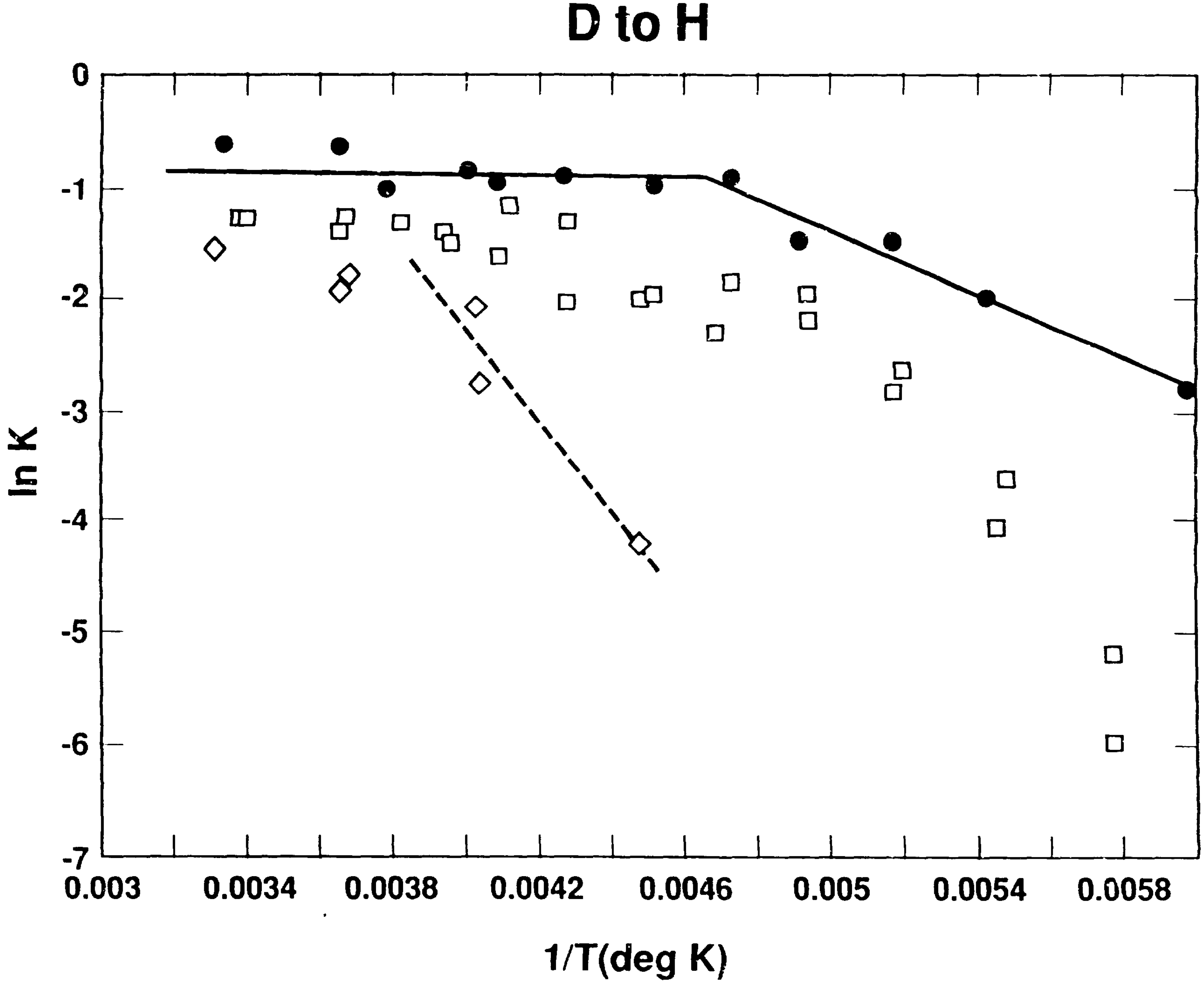

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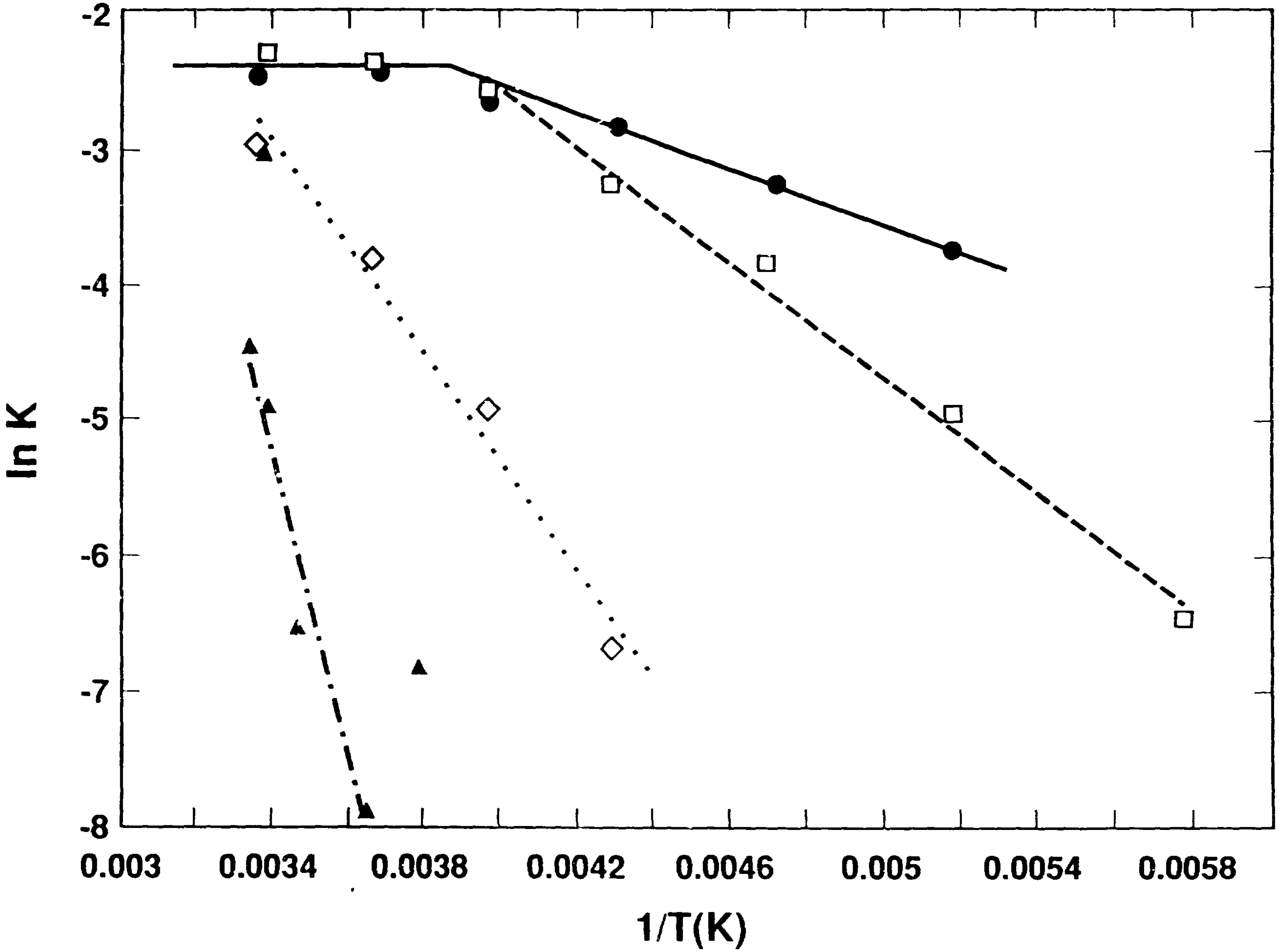

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