The Thermodynamic Properties of Pure Palladium and its Alloys with Hydrogen between 30 and 300°K.[1]

BY PAUL MITACEK, JR., AND JOHN G. ASTON

The heat capacities of palladium and its alloys (H/Pd: 0.125, 0.25, 0.50 and 0.75) have been determined between 30°K. and room temperature. Slow irreversible processes in the alloys have been studied and a method developed to obtain activation energies from the resulting warm drifts. The functional relation of the heat capacities to the temperature together with the energies of activation have been used to develop a detailed model for the structure of the alloys.

Introduction

In a previous investigation of the thermodynamic properties of hydrogen in palladium an anomaly was found in the heat capacity curve at 55°K.[2] The investigation was carried out on a very active palladium black sample with a hydrogen atom to palladium ratio of 0.50.

In the present investigation the effect of the concentration of the hydrogen in palladium on the anomaly was studied by measuring the heat capacity of hydrogen in palladium for ratios of 0.125, 0.25, and 0.75 H/Pd atoms. The measurements were made using block palladium to avoid possible surface effects. For comparison the 0.50 H/Pd ratio had of course to be reinvestigated in the same block sample.

During the course of the heat capacity measurements, temperature-dependent exothermic rate processes occurred in the calorimeter for certain concentrations of hydrogen. Activation energies were calculated for these rate processes in a manner to be discussed in the Experimental section.

Quite evidently, with little extra trouble, it was possible to measure the heat capacity of pure palladium over the temperature range of 30 to 290°K., and it turns out that the precision is somewhat greater than that of the previous measurements of Clusius and Schachinger.[3] It therefore is desirable to report these results.

Experimental

Materials.—The sample consisted of 30 disks of high purity palladium, 1 mm. thick, which were palladium welded to three palladium wires to form a cage 7 cm. long and 3 cm. in diameter. The total weight of the palladium sample was 286.05 g. The hydrogen gas used to make the various hydrogen to palladium ratios was made in the laboratory by electrolyzing distilled water. The collected gas was liquefied and the vaporized liquid compressed into a storage cylinder. Prior to adding the gas to the palladium sample, the gas was passed through an activated charcoal trap immersed in liquid nitrogen.

Apparatus.—The palladium sample was placed inside the gold calorimeter which had a stainless steel filling tube as an inlet for the hydrogen gas. The amount of hydrogen gas added to the palladium was measured by the system described by Giauque and Johnston.[4] The gas pressure was measured by a Gaertner Scientific Corporation M901 cathetometer using two telescopes with micrometer eye pieces and a calibrated stainless steel meter bar. The hydrogen gas thus measured was liquefied in a brass cylinder immersed in a liquid hydrogen bath. The calorimeter and brass cylinder could be isolated by specially designed stainless steel needle valves.[5] After isolating the system, the liquid was vaporized. When the gas pressure increased to ten atmospheres the gas was admitted to the calorimeter containing the sample of palladium which was held at a temperature of 300°. At this temperature and pressure the absorption was rapid.

The heat capacity measurements were carried out using gold calorimeter J as part of an adiabatic system. The basic design

of the adiabatic calorimeter has been previously described.[5a,6b,7] Details are given in a thesis.[5] A strain-free platinum resistance thermometer designated Pt-G-5 was used for all temperature measurements. The calibration of this thermometer has been previously described.[2] Following the completion of all measurements the calorimeter was filled with purified liquid oxygen and the vapor pressure measured with the hydrogen gas manometer system. The temperature measured by the vapor pressure referred to the last calibration and by the resistance thermometer differed by 0.003°K.

Heat capacities were calculated by dividing the energy input by the temperature rise for each heating. The correction for curvature was negligible. The dead space volume of the calorimeter was 42 cc. No correction terms were used for the heat of desorption or for the heat capacity of desorbed gas in the dead space volume, since these terms were below the precision of the measurements.

The rate of certain diffusion processes was studied by rapidly chilling the calorimeter and thermally isolating it.

Activation energies were calculated by means of

$$d \ln \dot{q}/dT = E_A/RT^2 \tag{1}$$

where E_A is the activation energy, R is the gas constant in calories, T is the temperature in degrees Kelvin and $\dot{q}$ is the energy envolved in calories per minute due to the exothermic process in the adiabatic calorimeter.

This relationship can be arrived at from the following considerations. For a process

$$A \longrightarrow B - \Delta H$$
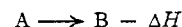
where ΔH is the change in enthalpy, the rate of formation of B will be proportional to the rate of heat evolution, $\dot{q}$. If the rate of the reverse reaction is small, then

$$dC_A/dT = - kC_A^n \tag{2}$$

applies.

Term C_A is the concentration of supercooled species. If the amount transformed is small, C_A is constant and

$$dC_A/dT \; \alpha \; k \tag{3}$$

but

$$dC_A/dT \; \alpha \; d\dot{q}/dT = \dot{q} \tag{4}$$

thus

$$\dot{q} \; \alpha \; k \tag{5}$$

and

$$d \ln \dot{q}/dT = d \ln k/dT = E_A/RT^2 \tag{6}$$

Results

Heat Capacities.—The heat capacity of pure palladium was obtained by subtracting the heat capacity of the calorimeter from the heat capacity of the palladium and calorimeter. The results of the heat capacity measurements are presented on a gram atomic basis in Table I. The values at rounded temperatures are given in Table II. The third column of Table I gives the difference between the experimental values and the best curve through the points. From an inspection of Table I it is evident that our average precision is better than 0.05%. The maximum deviation of the best curve through our points from that through the results of Clusius and Schachinger is about 0.3%. Since the results of Clusius and Scha-

(1) This investigation was supported by the National Science Foundation.

(2) D. M. Nace and J. G. Aston, *J. Am. Chem. Soc.*, **79**, 3627 (1957).

(3) K. Clusius and L. Schachinger, *Z. Naturforsh.*, **2A**, 90 (1947).

(4) W. F. Giauque and H. L. Johnston, *J. Am. Chem. Soc.*, **51**, 2300 (1929).

(5) Paul Mitacek, Jr., Ph.D. Dissertion, Penn. State Univ., University Park, Pa., 1962.

(6) (a) J. G. Aston and G. J. Szasz, *J. Am. Chem. Soc.*, **69**, 3108 (1947); (b) J. A. Morrison and G. J. Szasz, *J. Chem. Phys.*, **16**, 280 (1948).

(7) J. G. Aston, H. L. Fink, G. J. Janz and K. E. Russell, *J. Am. Chem. Soc.*, **73**, 1939 (1951).

chinger[3] above 60°K. are uniformly higher than our values it would appear that there is a fundamental difference in the system of energy measurement. Furthermore, the scatter of the points of the two sets of measurements indicate that the precision of this investigation is better by a factor of at least three. However, the interpretation of their data by Clusius and Schachinger is unaffected by differences such as those just pointed out. Thus the present results can be taken as a complete confirmation of their data.

Heat capacities of the hydrogen dissolved in palladium were obtained by subtracting the heat capacities of the calorimeter and sample without hydrogen in the sample from the heat capacities of the calorimeter with various amounts of hydrogen in the palladium. The results per mole of hydrogen are given at rounded temperatures in Table III.

TABLE I
EXPERIMENTAL GRAM ATOMIC HEAT CAPACITIES OF PALLADIUM AND DEVIATION FROM SMOOTH CURVE

0°C. = 273.16°K., 1 cal. = 4.1833 international joules, atomic weight = 106.7

Temp., °K.	C_p, cal. deg.$^{-1}$ g. atom^{-1}	ΔC_p, cal. deg.$^{-1}$ atom^{-1}	Temp., °K.	C_p, cal. deg.$^{-1}$ g. atom^{-1}	ΔC_p, cal. deg.$^{-1}$ atom^{-1}
30.43	0.7158	0.000	132.85	4.979	0.000
36.55	1.0776	.000	140.34	5.119	.000
41.87	1.4074	.000	148.82	5.238	.000
46.58	1.7082	− .001	157.88	5.357	+ .001
51.20	2.0460	− .001	166.75	5.443	− .001
55.73	2.2870	− .002	175.49	5.541	.000
60.25	2.569	.000	184.09	5.614	.000
64.78	2.821	.000	192.55	5.703	+ .003
69.90	3.080	.001	200.85	5.732	.000
74.45	3.298	− .001	207.12	5.765	− .001
78.75	3.491	.000	216.55	5.832	− .001
82.38	3.662	+ .002	225.88	5.875	− .002
88.60	3.871	− .001	235.12	5.932	.000
94.53	4.100	+ .001	244.27	5.990	+ .001
100.64	4.308	+ .004	253.40	6.003	− .002
107.42	4.451	.000	262.36	6.076	+ .001
114.42	4.621	.000	271.28	6.110	+ .001
125.57	4.869	+ .001	277.59	6.103	− .001

TABLE II
ROUNDED VALUES OF THE GRAM ATOMIC HEAT CAPACITY OF PALLADIUM

0°C. = 273.16°K., 1 cal. = 4.1833 international joules, atomic weight = 106.7

Temp., °K.	C_p, cal. deg.$^{-1}$ mole^{-1}	Temp., °K.	C_p, cal. deg.$^{-1}$ mole^{-1}
30	0.688	180	5.574
40	1.298	190	5.654
50	1.943	200	5.729
60	2.562	210	5.793
70	3.096	220	5.863
80	3.551	230	5.918
90	3.930	240	5.958
100	4.250	250	6.008
110	4.519	260	6.053
120	4.754	270	6.088
130	4.949	280	6.113
140	5.114	290	6.133
150	5.254		
160	5.374		
170	5.479		

Figure 1A presents the results for the 0.50 H/Pd ratio both in the block sample and the powder sample, 1B presents the results for the 0.75 H/Pd ratio in block palladium, 1C presents the 0.25 H/Pd ratio in the block sample, and 1D presents the 0.125 H/Pd ratio

TABLE III
MOLAL HEAT CAPACITY OF HYDROGEN ADSORBED IN PALLADIUM AT CERTAIN MOLAL RATIOS

0°C. = 273.16°K., 1 cal. = 4.1833 international joules (units cal. deg.$^{-1}$ mole^{-1})

Temp., °K.	H/Pd ratio 0.125 C_p	0.25 C_p	0.50 C_p	0.75 C_p
30	0.00	0.00	0.00	0.00
35	.00	.00	.20	.00
40	.60	.00	.50	.10
45	1.50	.20	.80	.65
50	2.90	2.00	2.00	1.40
55	2.95	3.00	2.80	2.70
60	2.60	2.45	2.10	2.40
65	1.85	1.90	1.70	2.10
70	1.70	1.60	1.40	1.70
75	1.65	1.50	1.35	1.50
80	1.60	1.40	1.30	1.45
85	1.55	1.35	1.25	1.35
90	1.55	1.35	1.20	1.35
95	1.55	1.30	1.20	1.30
100	1.50	1.30	1.20	1.30
105	1.50	1.30	1.20	1.30
110	1.50	1.35	1.25	1.35
115	1.50	1.35	1.30	1.40
120	1.55	1.40	1.35	1.45
130			1.55	1.60
140			1.80	1.95
150			2.00	2.10
160			2.25	2.40
170			2.50	2.60
180			2.80	2.85
190			3.10	3.10
200			3.30	3.30
210			3.50	
220			3.75	
230			4.00	
240			4.35	
250			4.60	
260			5.00	
270			5.35	

in the block sample. In all the graphs the value plotted is the heat capacity per mole of hydrogen in excess of that due to the palladium, i.e.

$$\bar{C}_{p\,H_2} = (C_{p_{total}} - C_{p_{cal}} - n_{Pd}\bar{C}_{p_{Pd}})/n_{H_2}$$

where $\bar{C}_{pH_2}$ is the molar heat capacity of the hydrogen, $C_{p_{total}}$ is the heat capacity of the total system, $C_{p_{cal}}$ is the heat capacity of the calorimeter, $\bar{C}_{p_{Pd}}$ is the molar heat capacity of the palladium and n_{H_2} and n_{Pd} are the number of moles of hydrogen and palladium, respectively.

The effect of concentration of hydrogen on the transition in the heat capacity is presented in Fig. 2 by plotting the molar heat capacity vs. temperature for all concentrations in the region of the anomaly. One curve for all concentrations can be drawn within the reproducibility of the data. The effect of the palladium sample size is evident from Fig. 1A. We hasten to add that the reproducibility is of a lower order than the precision of the points. Beyond the transition the hydrogen heat capacity in the powder is larger than in the block sample.

Warm Drifts and Activation Energies.—Using eq. 1, activation energies were obtained from the warm drifts in the hydrogen and palladium samples. Figure 4 presents plots of the natural logarithm of the heat leak vs. the reciprocal temperature. The warm drifts were related to the concentration of the hydrogen in the palladium sample. Table IV gives the values of the activation energies obtained. It also

gives the temperature region and the concentration for the occurrence of the drifts.

Discussion of Results.—From Fig. 2 it is evident that the nature of the species which is responsible for the transition in the heat capacity curve is concentration independent. That the amount of the species
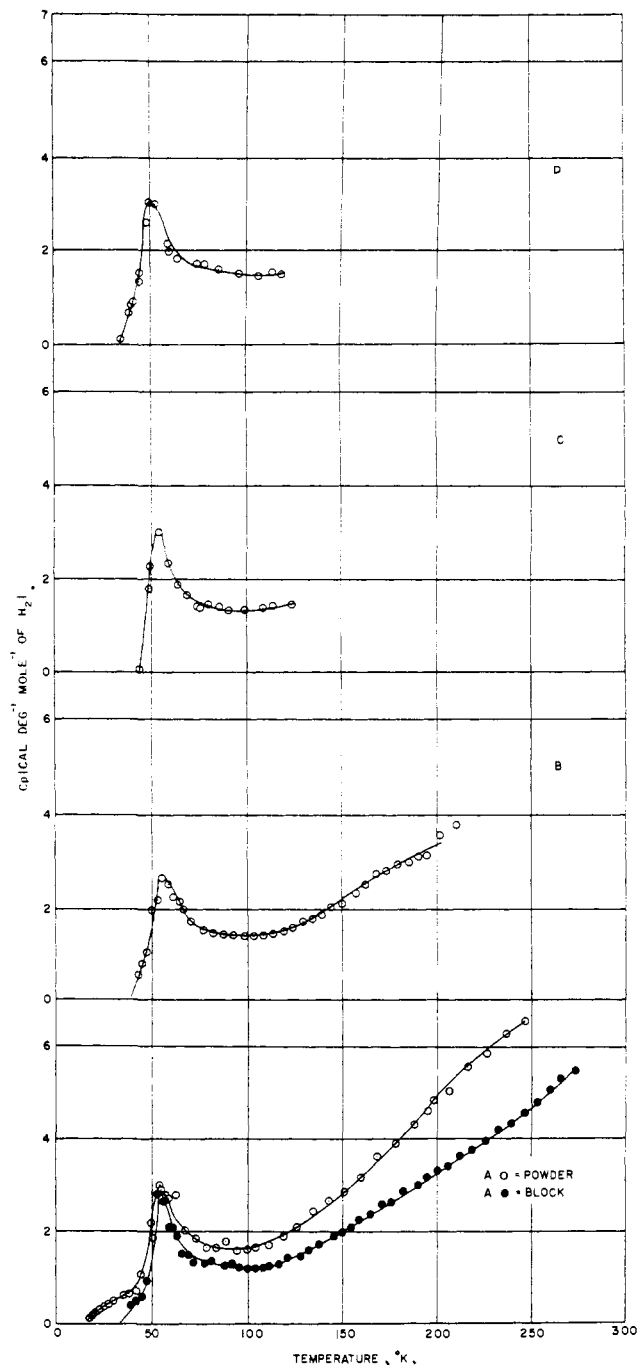

Fig. 2.—C_p of a mole of H_2 in block palladium samples of ratio 0.75, 0.50, 0.25 and 0.125 H/Pd and palladium powder sample of 0.50 H/Pd ratio between 35 and 85°K.

depends somewhat on the nature of the palladium sample.

From experimental results reported here together with those of other investigators, a model of the hydrogen–palladium system immediately suggests itself which is consistent with all the diverse experimental results available.

TABLE IV

ACTIVATION ENERGIES FOR DIFFUSION IN PdH$_x$

Region of drift X =	0.125	0.25	0.50	0.75
150°K.–200°K.	2.9 kcal.	2.9 kcal.	No drift	No drift
200°K.–250°K.	6.4 kcal.	6.4 kcal.	No drift	5.5 kcal.

From the neutron diffraction work of Shull and collaborators[8] at room temperatures the position of the hydrogen atoms in the palladium lattice has been fixed in the octahedral positions of the palladium lattice forming an NaCl type crystal with a hydrogen deficiency. This work has been extended down to 20°K. by Schindler[9] who found that the positions of the hydrogen atoms remain the same as at room temperature except in the immediate neighborhood of the heat capacity peak at 55°K. This work excludes the possibility that the transition in the heat capacity curve at 55°K. is the result of an order–disorder mechanism accompanying a change in the crystal structure.

Resistivity measurements by Schindler[10] for various compositions are presented in Fig. 3 along with heat capacity data on the black.[2] A marked change

Fig. 1.—A, C_p of a mole of H_2 in powder and block samples of 0.50 H/Pd ratio; B, C_p of a mole of H_2 in block palladium sample of 0.75 H/Pd ratio; C, C_p of a mole of H_2 in block palladium sample of 0.25 H/Pd ratio; D, C_p of a mole of H_2 in block palladium sample of 0.125 H/Pd ratio.

formed is directly proportional to the amount of hydrogen in the sample follows from the fact that the molal heat capacity is concentration independent. Beyond the transition region in the heat capacity curve effects of concentration become evident in the occurrence of slow exothermic processes. Likewise the part of the heat capacity due to the hydrogen
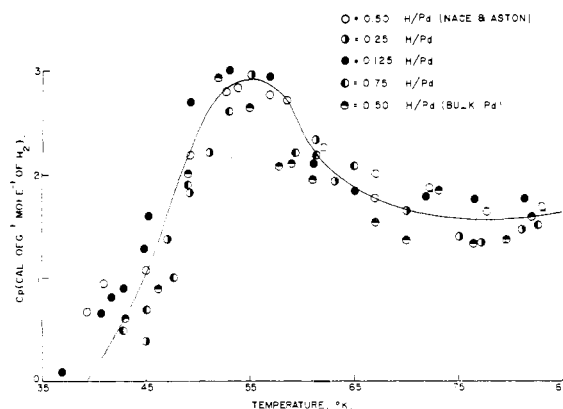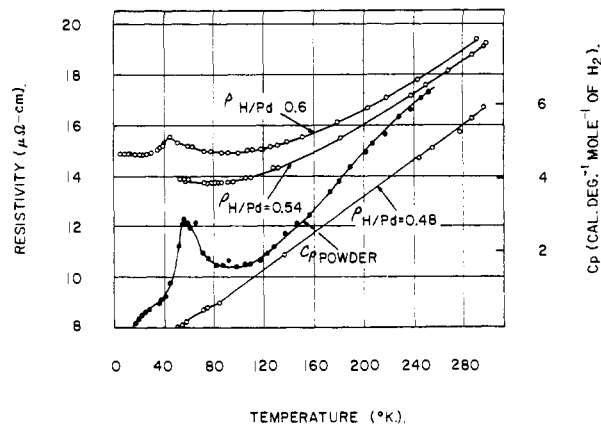

Fig. 3.—Mole heat capacity and resistivity of hydrogen $vs.$ temperature (O, resistivity; ●, C_p).

(8) J. E. Warsham, Jr., M. K. Wilkinson and C. G. Shull, $J.$ $Phys.$ $Chem.$ $Solids,$ $\mathbf{3},$ 303 (1957).

(9) A. I. Schindler, unpublished work.

(10) A. I. Schindler, R. J. Smith and W. Kammer, Commission 1, Internat'l Ints. for Refrigeration, Copenhaven, Aug., 1959.
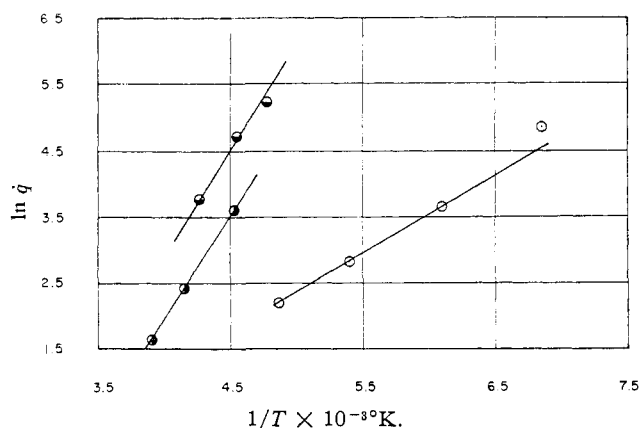
Fig. 4.—Natural logarithm of the heat leak *vs.* the reciprocal temperature to give activation energies for the three samples: ○, 0.125 H/Pd from 150 to 200°K.; ◐, 0.125 H/Pd from 200 to 250°K.; ◑, 0.75 H/Pd from 200 to 250°K.
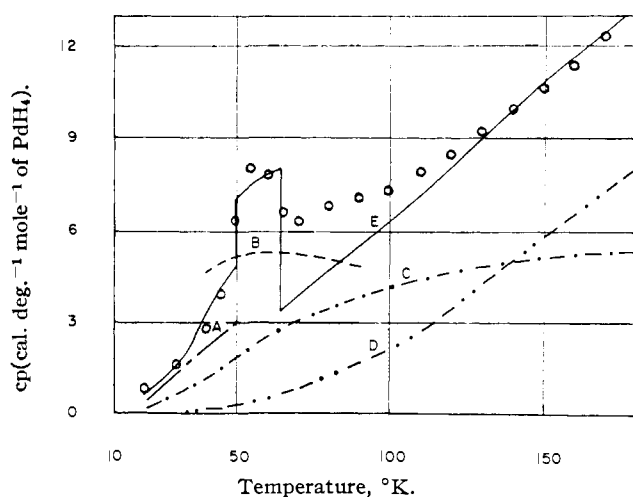

Fig. 5.—Experimental and calculated C_p for PdH₄ from 10 to 180°K.

drogen present. For compositions of H/Pd = 0.5 and below the transition point in the heat capacity curve, the four hydrogen atoms in a plane cluster about the center palladium atom to form a square planar PdH₄ molecule. Hydrogen bonding between the neighboring palladium atoms forms, at low temperatures, a regular network which must be stabilized by resonance effects in the plane to explain the data. The hydrogen atoms begin to librate in the network as the temperature increases. This decreases resonance stabilization and allows the atoms to move to equivalent positions by means of a ring diffusion mechanism involving four hydrogen atoms equivalent to a rotation of the PdH₄ square plannar molecule about an axis perpendicular to the plane. This would produce the sort of heat capacity effect noted in the measurements. The same effect is apparent in the resistivity measurements when the hydrogen concentration is large enough to fill the face-centered planes.
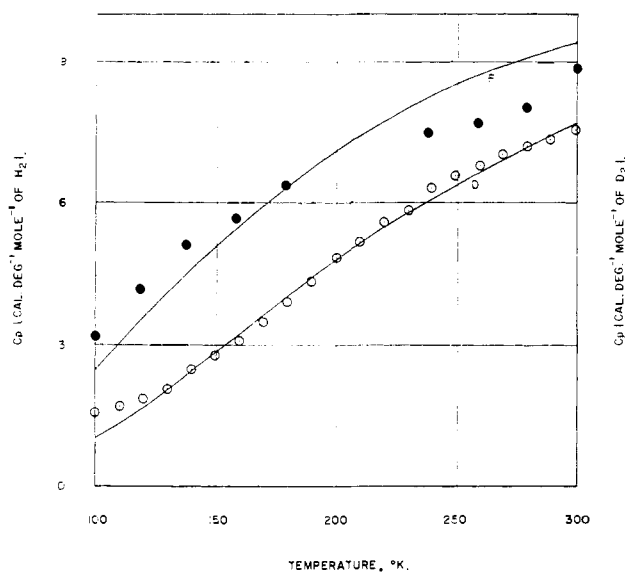

Fig. 6.—Experimental and calculated C_p for hydrogen and deuterium in palladium from 100 to 300°K.

in the magnitude of the values and the character of the curve is noted upon changing the concentration from 0.48H/Pd ratio to 0.54H/Pd ratio. By adding hydrogen atoms between the corner palladium atoms compositions of H/Pd ratio up to 0.50 can be formed. The face-centered atoms form a hydrogen-free plane between the two planes that have hydrogen in them. These latter planes extend throughout the lattice randomly changing direction by $\pi/2$. The randomness of the changing directions of the planes is limited only by the condition that the planes cannot intersect. To form ratios above 0.50H/Pd, hydrogen has to enter the plane formed by the face-centered atoms between the planes of hydrogen atoms characteristic of all compositions below H/Pd = 0.5.

In this way the paths of metallic conduction through the lattice are destroyed and the sudden rise in resistivity results. The peaks in the resistivity curves above 0.50H/Pd are then evidently related to the similar peak in the heat capacity curves because electron-phonon scattering is influenced by the hydrogen in planes of the face centered atoms. The hydrogen in the lattice above the ratio H/Pd = 0.5 are in planes at right angles to the planes which have been formed below this composition and since they are between corner palladium atoms affect the heat capacity in the same way.

The addition of more hydrogen forms more of the planes of hydrogen between corner palladium atoms and thus the heat capacity is proportional to the hy-

For concentrations below 0.50 H/Pd ratio small patches of planes and incomplete PdH₄ molecules will occur. At low temperatures these incomplete planes will diffuse into neighboring planes to produce planes which are complete and which have lower energies. This neighboring diffusion produces the low temperature warm drifts noted in the samples. Above 0.50 H/Pd ratio this situation is eliminated and the warm drifts do not occur. The activation energy for this process has been measured by Spalthoff[11] by n.m.r. methods and the two methods give the same value within experimental accuracy.

The activation energy for the higher temperature warm drifts in Table III is of the same order as the activation energy found by Barrer[12] for the diffusion of hydrogen through palladium. The two effects are due to the long range diffusion of hydrogen through the lattice. The warm drifts arise from the fact that hydrogen in a quickly cooled sample is no longer in equilibrium. Hydrogen scattered through the lattice diffuses back into the sheets of planes which are stable at low temperatures. This back diffusion is controlled by the activation energy for long range diffusion. The formation of the sheets of planes is exothermic, thus producing warm drifts. The occurrence of this process

(11) W. Spalthoff, Z. physik. Chem., 29, 258 (1961).
(12) R. M. Barrer, "Diffusion In and Through Solids," Cambridge University Press, New York. N. Y., 1941.

at higher temperatures is substantiated by results from n.m.r. work by Burger, et al.[13]

From the model a heat capacity curve can be calculated and compared with the experimental values. Figure 5 presents the experimental heat capacity for four hydrogen atoms and a palladium atom from the data of Nace and Aston[2] between 10°K. and 180°K. It also presents the calculated curve from the model along with the individual components that make up the calculated values.

Curve A of Fig. 5 gives a graph of the contribution due to three torsional Debye modes with $\theta = 200°K.$ Curve B represents the heat capacity contribution of three hindered rotational degrees of freedom calculated from eq. 7

$$V = V_0(1 - \cos 3\varphi)/2 \qquad (7)$$

where V_0 is arbitrarily picked at 390 cal. mole^{-1} to fit the maximum in the heat capacity curve. Curve C represents the Debye lattice contribution of the motions of the centers of gravity with $\theta = 275°K.$ which is the experimental value for pure palladium. Curve D represents the heat capacity of a Debye lattice containing four hydrogen atoms with $\theta = 950°K.$ The reason for this choice is that these hydrogen atoms form a superlattice of highly hindered translators. Since the lower levels of such a system evidently approximate those of a harmonic oscillator, the whole assembly becomes a Debye sublattice of three degrees of freedom.

The solid curve is made up of curves A and C up to 50°K. From 50 to 65°K. it is curve B and C.

(13) J. P. Burger, N. J. Paulis and W. P. Hass, Physica, del., 27, 514 (1961).

Curves C and D then made up the calculated curve from 65°K on. The resulting curve, E, reproduces the shape and values of the experimental points of Nace and Aston[2] quite well and produces additional evidence that the model presents a correct picture.

Figure 6 presents a comparison of the measured and calculated heat capacity contribution of two hydrogen atoms in the range of 100° to 300°K. (curve D). A Debye superlattice of 6 degrees of freedom per H_2 with $\theta = 950°K.$ was of course assumed. Curve F is a curve similar to curve D calculated for deuterium with $\theta = 950°/\sqrt{2} = 750°$ for the torsional modes. The experimental points for deuterium are those of Nace and Aston.[2]

It has previously been found that the zero point entropy of two Pd_2H units in palladium black is 1.18 ± 0.36 cal. deg.$^{-1}$ mole^{-1}.[2] At the composition 0.50 H/Pd, if certain hydrogens on the corner palladium atoms move to adjacent sites, the sheets suffer a sharp bend by $\pi/2$. Since two Pd_2H units contain one corner palladium atom and three face-centered ones, the unit involved in the sheets is PdH_2. Thus, if the bending of the planes by $\pi/2$ is performed at random the situation is numerologically equivalent to that of ice for which the theoretical zero point entropy is 0.82 cal. deg.$^{-1}$mole^{-1}. This is within experimental error of the zero point entropy found.

The Origin of Epoxides in the Liquid Phase Oxidation of Olefins with Molecular Oxygen[1]

BY WILLIAM F. BRILL

In the liquid phase oxidation of cyclohexene and 2,4,4-trimethyl-1-pentene with molecular oxygen, epoxides are formed in addition to hydroperoxides as a primary product of the radical chain reaction. It was demonstrated unequivocally that the non-catalytic reaction of hydroperoxides with olefins is able to produce epoxides. However, oxidation by hydroperoxide is not rapid enough to account for epoxide formed during olefin autoxidation. Attack of alkyl peroxy radical on the double bond is the most likely source of epoxide.

The origin of epoxides in olefin autoxidation products has important implications on olefin oxidation theory and on the potential use of autoxidation as a synthetic method. While the major products reported for the oxidation of olefins are hydroperoxides, aldehydes, ketones and acids, the formation of minor amounts of epoxides was noted by early investigators working with rubber and drying oils. Recently it has been reported that many olefins may be autoxidized by a variety of techniques in the liquid phase to practical synthetic yields of epoxides. Yields of 50% or better may be obtained from the oxidation of 2,4,4-trimethyl-1-pentene,[2] 2-methyl-1-butene[3] and cyclooctene.[4] Even the simplest low molecular weight olefins give epoxides in fair yields—propylene, 26%[5]; butene-2, 38%[6]; butene-1, 30%; and isobutene, 18%.[3] These yields

(1) Presented at the Second Princeton Scientific Community Conference, Princeton, N. J., November 16, 1961.

(2) E. J. Gasson, et al., J. Chem. Soc., 2161 (1954).

(3) W. F. Brill and B. J. Barone, unpublished work.

(4) W. Reppe, O. Schlichting and K. Mueller-Clieman, U. S. Patent 2,769,017 (1956).

(5) J. Gardner and N. Robertson, U. S. Patent 2,780,635 (1957).

(6) A. F. Millidge and W. Webster, U. S. Patent 2,741,623 (1956).

suggested that the importance of epoxide formation had not been fully recognized and a close examination of its role in autoxidation was justified.

Various mechanisms have been proposed to explain epoxide formation, but no specific studies have been reported. It has been proposed that double bonds react with (a) hydroperoxide or (b) peroxy radical or (c) molecular oxygen to yield epoxides as:
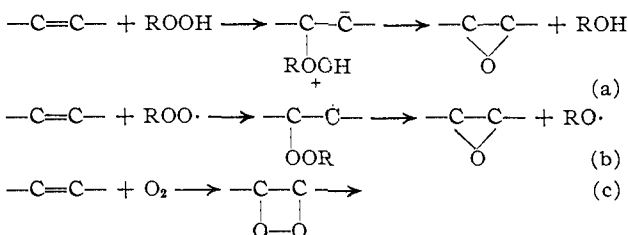
Farmer proposed the reaction of hydroperoxide with oxygen (a), but failed to demonstrate its importance experimentally.[7] He also proposed the reaction of peralkoxy radical with olefin (b), but did not give it further consideration. Closure of the intermediate