

## Point Defects in Platinum†

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### ABSTRACT

An investigation was made of the mobility and types of point defect introduced in platinum by deformation in liquid nitrogen, quenching into water from 1600°C, or reactor irradiation at 50°C. In all cases the activation energy for motion of the defect was determined from measurements of electrical resistivity. Measurements of density, hardness, and x-ray line broadening were also made where applicable.

These experiments indicated that the principal defects remaining in platinum after irradiation were single vacant lattice sites and after quenching were pairs of vacant lattice sites. Those present after deformation in liquid nitrogen were single vacant lattice sites and another type of defect, perhaps interstitial atoms.

### § 1. INTRODUCTION

ALTHOUGH an equilibrium number of the point defects, vacancies and interstitial atoms are present in a metal, a larger concentration is thought to be introduced by cold working, quenching, or irradiating. The concentration, distribution and type of the extra defects retained in the sample will depend on the temperature and method of production. If the defects are mobile at the temperature of production, they will move about the lattice until they reach a position of lower energy where they are trapped or annihilated. Foreign atoms are expected to act as trapping centres, while grain boundaries, voids, free surfaces, and perhaps dislocations will act as annihilation centres or sinks. An interesting review on the effect of lattice defects on some physical properties of metals was recently given by Broom and Ham (1958).

Many different physical properties have been measured to detect vacancies and interstitial atoms. Electrical resistivity, which is very sensitive to their presence, is often used to measure their mobility. From this the activation energy required for one atomic jump of the defect can be calculated and the type of defect can be inferred. Also, the number of jumps required by the defect to reach the sink can be determined, from which the type of sink can be inferred. Unfortunately, all point defects increase the resistivity so that changes in other physical

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† Communicated by the Author.

properties are necessary to determine exactly what type of defect is present. Changes in density and lattice parameter should discriminate between vacancies and interstitial atoms. The x-ray line width is unchanged by point defects but indicates the amount of lattice strain produced by dislocations in deformed samples.

In the present experiments the point defects were introduced by cold work at  $-196^{\circ}\text{C}$ , by quenching from above  $1600^{\circ}\text{C}$ , and by fast neutron irradiation at  $50^{\circ}\text{C}$ . The electrical resistivity, density, lattice parameter, hardness, and x-ray line width were measured before and after the defects were introduced into the sample. In addition, the mobility of the defects was determined from changes of electrical resistivity due to heat treatment.

## § 2. CHOICE OF MATERIAL

The choice of sample material for these experiments was mainly determined by the irradiation conditions. The sample should have a high melting point in order to retain a maximum amount of radiation damage at  $50^{\circ}\text{C}$ , the temperature of irradiation. In addition it should have a low gamma activity after irradiation. These two conditions, combined with the usual requirements of simple crystal structure, high purity, and good surface properties, made platinum the obvious choice.

The platinum used was Johnson Matthey and Mallory thermocouple grade (99.99%), so that direct comparison could be made with the platinum self-diffusion experiments of Kidson and Ross (1957), which were made on similar material.

## § 3. METHODS FOR INTRODUCING DEFECTS INTO PLATINUM

### 3.1. *Deformation*

The 0.010 in. diameter platinum wires were annealed in air at  $900^{\circ}\text{C}$ . for 30 min, and then extended 8% in liquid nitrogen. They were removed from the extension apparatus while immersed in liquid nitrogen. Since the potential leads were silver-soldered to the sample before the extension, the resistivity could be measured after any recovery anneal above  $-196^{\circ}\text{C}$ .

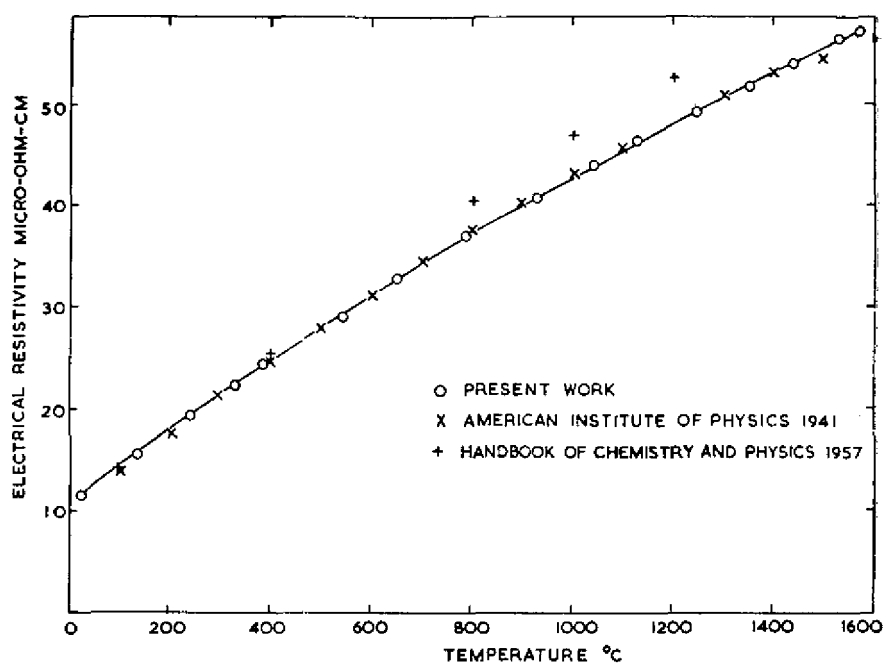
The hardness samples were 0.1 in. thick platinum flats rolled to 8% reduction with the sample immersed in liquid nitrogen between each pass.

### 3.2. *Quenching*

An electric current was used to heat a 4 in. long 0.010 in. diameter platinum wire. The potential leads of 0.003 in. diameter platinum wire were spot-welded one inch from the ends of the sample. The temperature of the heated sample was determined from its resistance. The calibration curve for resistance against temperature is shown in fig. 1.

The sample was cooled rapidly (quenched) by sudden immersion into cold water. To reduce the deformation during this quench, the axis of the wire sample was perpendicular to the surface of the water. The time taken to cool the sample was measured by retaining the heating current and recording the voltage across the sample on an oscillograph. A typical quench, shown in fig. 2 (Pl. 25), gives a time of 0.02 sec to cool from 1600°C to 20°C.

Fig. 1



Electrical resistivity of thermocouple grade platinum. No correction was made for the change in sample dimensions with temperature.

### 3.3. Fast Neutron Radiation

The 0.010 in. diameter platinum wire was annealed in air at 900°C for 30 min and then irradiated at 50°C inside a uranium tube in the NRX reactor (Cook and Cushing 1953). Half the fast neutrons hitting the sample were from the uranium tube and had a fission energy spectrum. The other half from neighbouring fuel rods had the usual  $E^{-1}$  spectrum. The definition of fast neutrons used in this report is neutrons with energy above 1200 eV. This is the minimum energy neutron capable of knocking a platinum atom from its lattice site.

After irradiation, the platinum wires were decontaminated and platinum potential leads spot-welded on.

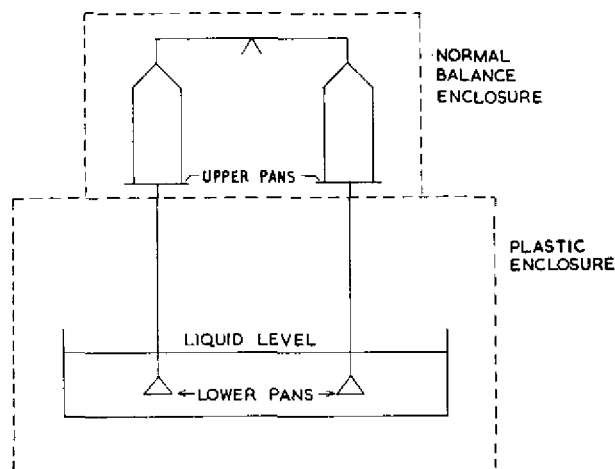
## § 4. METHODS FOR DETECTING DEFECTS IN PLATINUM

4.1. *Electrical Resistivity*

Potential leads were spot-welded to the wire samples, which were 0.010 in. in diameter, and the electrical resistances measured in liquid nitrogen. The values obtained were corrected to a constant nitrogen bath temperature by measuring the resistance of an annealed sample in the same bath. The electrical circuit was made completely of copper with low thermal e.m.f. solder at all joints. A 100 mA current was used with the bath vigorously stirred to prevent temperature fluctuations due to gas bubbles forming on the sample. The potential was read to 0.1 microvolt. By reversing the sample current and potentiometer battery to eliminate stray e.m.f.'s, the resistance values were reproducible to one part in thirty thousand.

The samples were annealed in silicone oil up to 250°C and in molten salt between 250° and 900°C.

Fig. 3



Schematic diagram showing the balance assembly for density measurements.

4.2. *X-ray Line Width*

A long 0.010 in. diameter platinum wire was extended 8% in liquid nitrogen. Sections of it were spot-welded side by side on a platinum frame to fit the diffractometer. The half widths of the (331), (420) and (422) x-ray lines were then measured after annealing the wire sample assembly at successively higher temperatures.

4.3. *Density*

The density of platinum was determined by weighing a 13 g sample in air and water with a weight sensitivity of 0.01 milligrams. The density of the sample was directly compared with an annealed reference sample of

the same size using the system shown in fig. 3. The sample was put in the upper left pan and the reference sample in the upper right pan to obtain the difference between their weights in air. The sample was then placed under the liquid in the lower left pan and the standard in the lower right pan, to obtain the difference between their weights in liquid. The calculations for this method of density determination are given elsewhere (Piercy 1958). This is a very sensitive method for measuring changes in density since the measurements are not strongly dependent on the liquid density, air density, or temperature. Of course, the absolute value depends on the accuracy of the density taken for the reference sample.

Distilled water with the air removed was used for the density measurements. However, hysteresis in the contact angle between water and the 0.003 in. tantalum wire, caused the measured weight to depend on the direction of vertical motion of the balance pan. This effect was markedly reduced by using a solution of 0.08% wetting agent (Kodak Photoflo) in distilled water, which resulted in a density reproducibility of 0.005% for a 13 g platinum sample. The addition of the wetting agent did not affect the absolute value within this limit of error.

#### 4.4. Reaction Kinetics

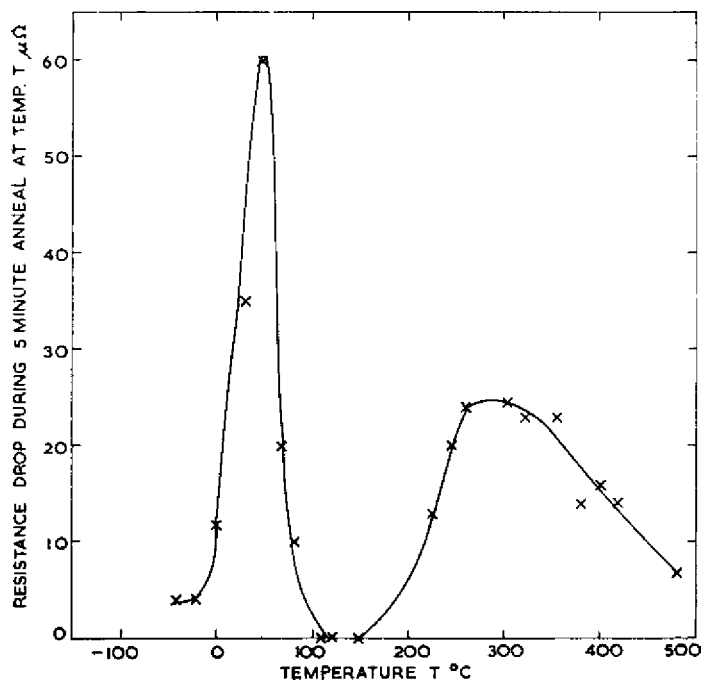
Once the excess point defects were introduced into the sample, the preliminary investigation of measuring the drop in resistivity due to annealing the sample for equal times at successively higher temperatures (an isochronal anneal) determined the minimum temperatures at which these defects were mobile. The decrease in resistance for each 5 min anneal was plotted as a function of the annealing temperature, a typical result for deformed platinum being shown in fig. 4. Once the temperature range for recovery was known, the activation energy was found by measuring the change in slope of the isothermal resistivity-time curve when the temperature was raised by 10°C. The value for the activation energy  $\Delta H_2$  was calculated from the usual equation

$$\Delta H_2 = \frac{T_1 T_2}{T_2 - T_1} K \log_e (S_2/S_1) \quad . . . . . (1)$$

where  $K$  is Boltzmann's constant,  $S_1$  is the final slope of the resistivity-time curve at absolute temperature  $T_1$  and  $S_2$  is the initial slope after raising the temperature from  $T_1$  to  $T_2$ . This process was repeated until there was no further drop in resistivity. A typical set of curves for irradiated platinum is shown in fig. 5.

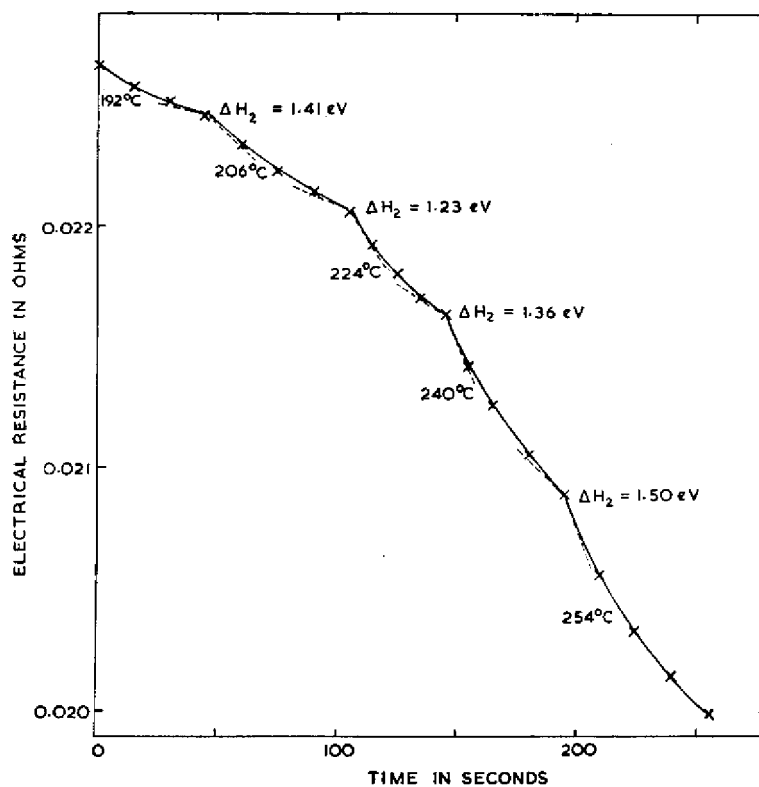
The slope at the end of each curve was determined in the following manner: the slope at the midpoint of a curve between two experimental points A and B was assumed equal to that of the straight line joining A and B. Therefore by measuring seven experimental points on the isothermal

Fig. 4



Isochronal recovery of platinum after deformation in liquid nitrogen. The drop in sample resistance for successive anneals of 5 min at temperature  $T$  is plotted against annealing temperature.

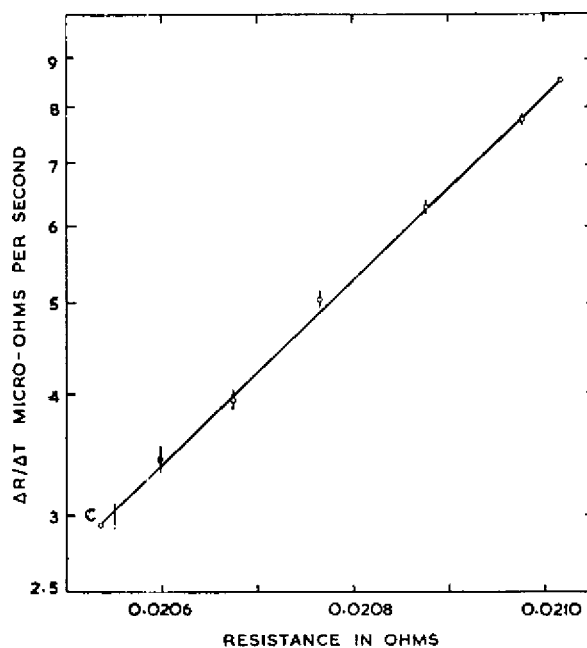
Fig. 5



A typical set of curves to determine the activation energy required for recovery of irradiated platinum.

anneal, the values for the slope of the curve at the six intermediate points were determined. Then, by plotting the curve for these values of slope against the resistivity at these intermediate points and extrapolating the curve a short distance, the value for the slope at the end of the curve was obtained. The logarithm of the slope against the resistance at the intermediate points was usually plotted in order to have a straighter line to extrapolate. A typical example for irradiated platinum is shown in fig. 6. This is one of the few methods that determines the slope using all the experimental points equally.

Fig. 6



Determination of slope at the end of an isothermal annealing curve. The log of the slope found at a point midway between two experimental points is plotted against the electrical resistance at that point. The line is extrapolated to point C to obtain the slope at the end of the isothermal curve.

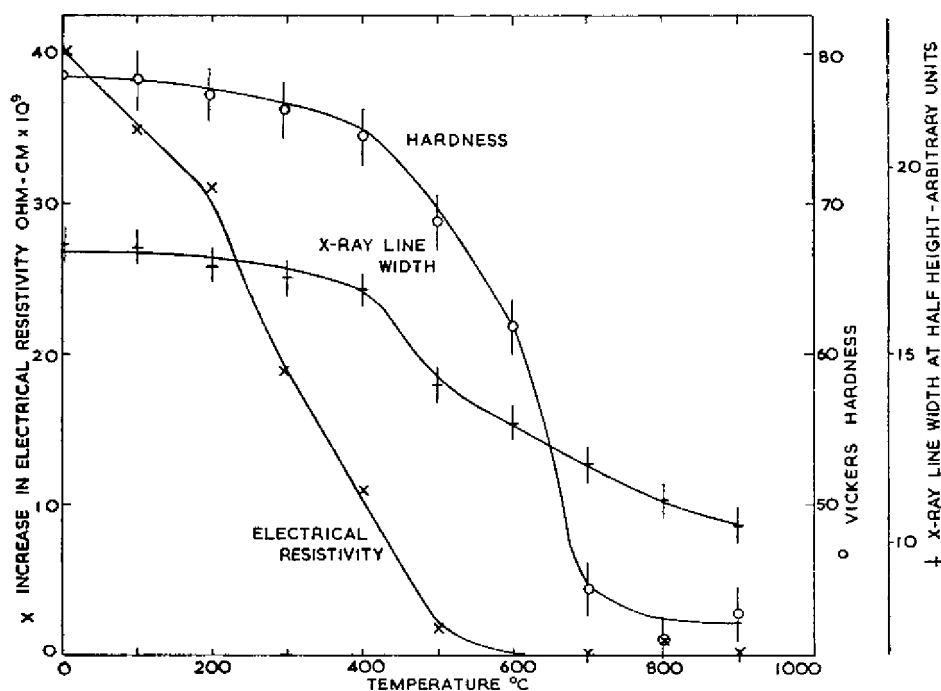
When the activation energy was known, the number of jumps required by the defect to reach the sink was determined from the slope of the curve obtained by plotting the logarithm of the fraction of resistivity increase remaining against the time at constant annealing temperature and applying eqn. (9) of the Appendix. The order of reaction was found from the same isothermal anneal using the method of Meehan and Brinkman (1956).

## § 5. RESULTS AND OBSERVATIONS

5.1. *Changes in Physical Properties*

The electrical resistivity isochronal recovery curve for platinum extended 8% in liquid nitrogen (fig. 4) has two distinct recovery stages; one below 100°C in which 0.004 micro-ohm-cm recovers, and one between 100°C and 600°C in which 0.024 micro-ohm-cm recovers. For comparison,

Fig. 7



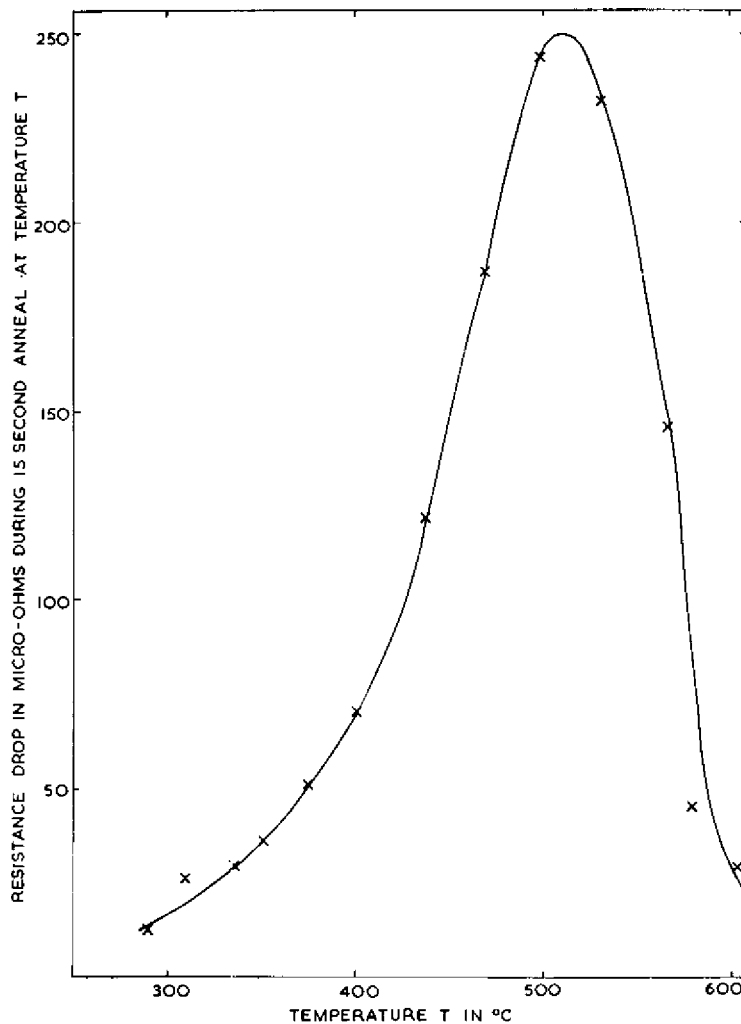
Recovery of electrical resistivity, hardness and x-ray line width of platinum samples deformed 8% in liquid nitrogen. Successive anneals for 30 min every 100°C were used.

the electrical resistivity of platinum in liquid nitrogen is 1.85 micro-ohm-cm. There was no appreciable recovery below -50°C which is contrary to the experiments of Manintveld (1954). The recovery of x-ray line width, electrical resistivity and hardness for platinum deformed 8% in liquid nitrogen are shown together in fig. 7. Because the temperature intervals are larger, this curve for the recovery of electrical resistivity does not resolve the two peaks shown in fig. 4. The x-ray line width does not change until nearly all the increase in electrical resistivity has recovered, indicating that both stages in the recovery of electrical resistivity shown in fig. 4 are mainly due to point defects, rather than to annihilation or redistribution of dislocations. However, some annihilation of dislocations



may be occurring at the very end of the recovery of electrical resistivity. The recovery of the hardness and x-ray line width above 400°C is probably due to recrystallization.

Fig. 8

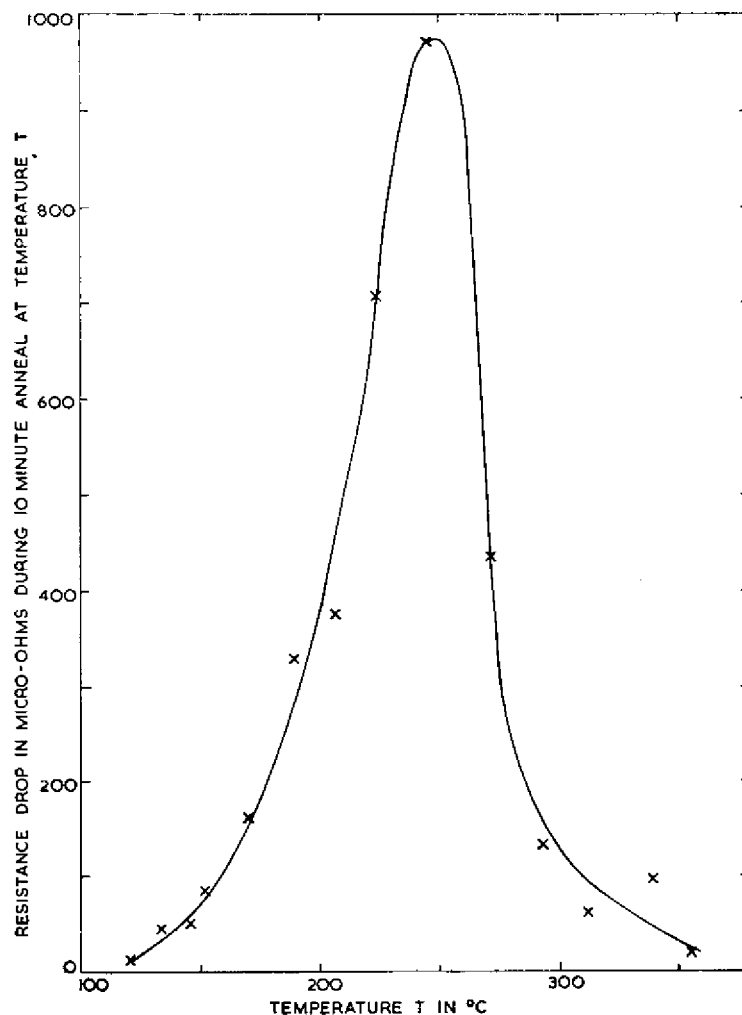


Isochronal recovery of quenched platinum showing the drop in sample resistance for successive anneals of 15 sec at temperature  $T$ .

The isochronal recovery of quenched platinum shown in fig. 8 has one recovery stage in the region 300 to 600°C, during which a resistivity drop of 0.12 micro-ohm-cm occurs. There was no further recovery on annealing up to 800°C. The isochronal anneal of irradiated platinum shown in fig. 9 also has only one recovery state and this occurs in the region 130-350°C. However, the large decrease of 0.48 micro-ohm-cm occurs here. There was no further recovery on annealing up to 900°C.

The recovery of the density and yield stress of irradiated platinum was examined to determine whether these recovered at the same rate as the electrical resistance. The results shown in table 1 indicate that both the density and the yield stress recover at the same rate as the electrical resistance and, therefore, are probably due to the same defect. Since the

Fig. 9



Isochronal recovery of irradiated platinum showing the drop in sample resistance for successive anneals of 10 min at temperature  $T$ .

density decrease is 0.07% due to irradiation, while the lattice parameter change for the same irradiation is less than 0.005% (Tuxworth 1958 unpublished data), the defects remaining in the sample are probably single, double, or clusters of vacancies.

Table 1. The Recovery of Electrical Resistivity, Density, and Mechanical Properties of Irradiated Platinum

Treatment	Electrical resistivity in liq. N <sub>2</sub> μΩ cm ± 0.0001 μΩ cm	% resistivity increase remaining	Density at 22.2°C g/cm <sup>3</sup> ± 0.001 g/cm <sup>3</sup>	% density decrease remaining	Ultimate tensile strength p.s.i. ± 1000 p.s.i.	% Ultimate strength increase remaining	Proportional limit p.s.i. ± 1000 p.s.i.	% Proportional limit increase remaining
Annealed prior to irradiation	1.850	—	21.4413	—	19000	—	8000	—
Irradiated with $2 \times 10^{20}$ fast n/sq. cm	2.52	100	21.4255	100	26300	100	15000	100
Irradiated plus 50 min 200°C	2.22	55	21.4335	49	23000	54	10800	40
Irradiated plus 180 hr 200°C	1.94	13	21.4396	11	20200	—	8200	—

From the results shown in table 1, the ratio of the resistivity change to fractional volume change due to irradiation is  $9 \times 10^{-4}$  ohm-cm. Since this is comparable with the value  $3 \times 10^{-4}$  ohm-cm found in gold wire that was quenched from  $900^\circ\text{C}$  (Bauerle and Koehler 1957), the defects in irradiated platinum are probably similar to those in quenched gold, i.e. isolated or small grouping of vacancies rather than large clusters. If one vacancy in the irradiated platinum produces an effective volume change of 0.5 atomic volumes (the number will be less than 1.0 due to relaxation about the vacancy), then the resistivity per atomic per cent vacancies when calculated from the ratio of resistivity change to fractional volume change is 4.5 micro-ohm-cm. This value, which is about three times that predicted for copper (Overhauser and Gorman 1956) is a reasonable resistivity for vacancies in platinum and will be used for later calculations of defect concentrations produced in platinum by other means. The concentration of vacancies determined for the irradiated sample by using this value is  $1.2 \times 10^{-3}$ .

The defect concentration produced by fast neutrons can be calculated from the theory of Seitz and Koehler (1956), and also the theory of Brinkman (1956). Taking the total elastic scattering cross section for fast neutrons to be 5.5 barns (Langsdorf *et al.* 1957), the concentration of defects produced in platinum which is irradiated with  $2 \times 10^{20}$  fast neutrons per square centimetre in NRX is 0.30 when calculated from the theory of Seitz and Koehler. On the other hand, Brinkman's estimate for the concentration of defects remaining in a displacement spike is only about 0.001 (Brinkman 1954). Therefore, this should be the limiting value when all the atoms of the sample have been in at least one displacement spike, as would probably occur with the high integrated flux used here. The concentration of defects measured in this experiment, however, is expected to be much lower than the actual numbers produced, due to annihilation of the vacancies by interstitial atoms that are mobile during irradiation. Therefore, the experimental value of 0.0012 deduced from the density and resistivity change indicates that Brinkman's estimate of 0.001 for the concentration of defects remaining in a displacement spike is much too low if the displacement spike concept is applicable to platinum.

### 5.2. Reaction Kinetics

The results for the activation energy measurements on extended, quenched and irradiated platinum are given in table 2. They were all measured by the change in slope of an isothermal recovery curve when the temperature was raised.

A lattice distortion or strain will alter the distance between atoms and hence may alter the activation energy required for the atomic jump process. Since a comparison between the activation energy of recovery after cold working, quenching, and irradiating is required, and these do not produce the same lattice strain in the metal, the possible change in

activation energy with lattice strain was investigated using an irradiated sample. A load equal to half the proportional limit of platinum at 400°C was hung from an irradiated sample during recovery. Although this increased the rate of recovery by a factor of two, the activation energy was still the same within experimental error.

Table 2. Activation Energy for the Recovery of Platinum after Deformation, Quenching or Irradiation

Treatment	Temperature range °C	Activation energy eV	Number of determinations
Extended 8-10% in liquid nitrogen	38 to 135	$0.73 \pm 0.06$ †	5
Extended 8-10% in liquid nitrogen and annealed to remove lower recovery stage	230 to 360	$1.43 \pm 0.09$	7
Quenched from above 1600°C to 20°C in less than 0.04 sec	240 to 370	$1.13 \pm 0.11$	14
Irradiated at 50°C with $6 \times 10^{19}$ fast neutrons per square centimetre	190 to 280	$1.40 \pm 0.11$	11

† The limits given are the standard deviations of all measurements taken.

The average values of activation energy from table 2 were used to calculate the order of reaction and the number of jumps required by the defect to reach the sink. These, together with the concentration of defects (based on recovery of electrical resistivity, assuming 4.5 micro-ohm-cm per atomic percent defects) are shown in table 3. The activation energy for the recovery of irradiated platinum, the only case for which two identical samples were available, was also measured by the technique of Meehan and Brinkman (1956). The result shown in fig. 10 and given in table 3 is within the limit of error of the slope change method.

## § 6. DISCUSSION

A comparison between the present results for the reaction kinetics and other investigators are given in table 4. The values for activation energy do not agree except for quenched platinum. Since the purity of Manintveld's extended platinum was not reported, the difference in results may be due to an impurity effect. Unfortunately, his annealing experiments were not taken above 90°C. Dugdale's results on platinum irradiated or extended at room temperature (Dugdale 1952) are both the same

Table 3. Summary of Parameters for the Motion of Defects in Platinum

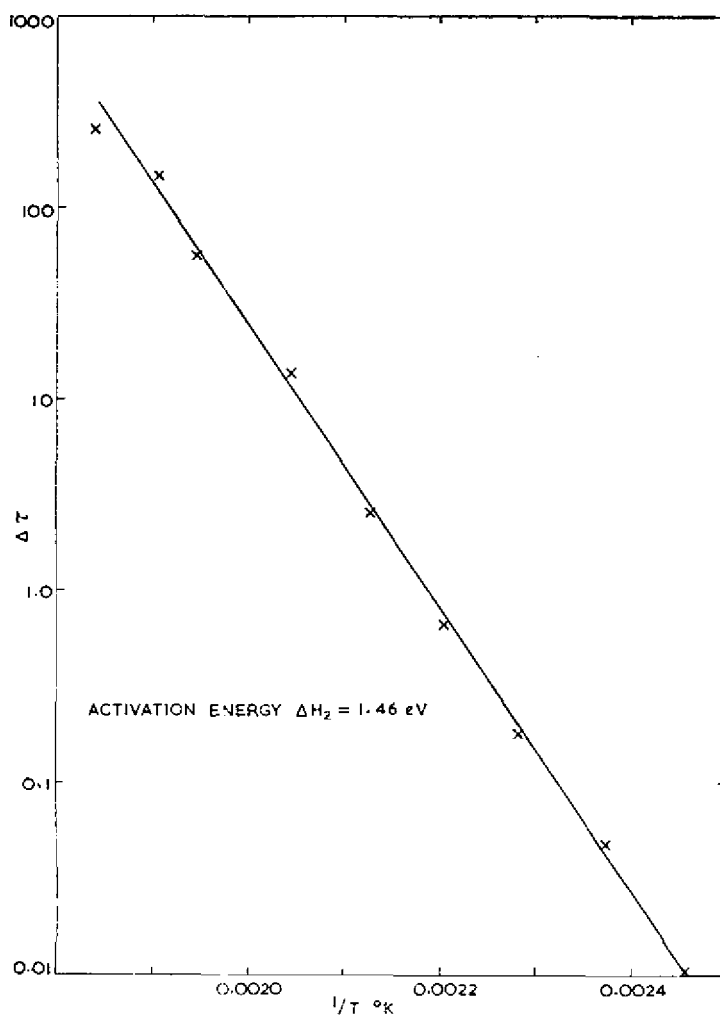
Treatment	Temperature range of recovery °C	Activation energy eV	Order of reaction	Number of jumps to sink† for given amount of recovery remaining	Concentration of defects‡
8-10% extension in liquid nitrogen	0 to 100	$0.73 \pm 0.06$	1.8 to 2.2	$7 \times 10^6$ for 50% remaining $2 \times 10^7$ for 25% remaining	$1 \times 10^{-5}$
	200 to 400	$1.43 \pm 0.09$	5.05	$3 \times 10^4$ for 75% remaining $1 \times 10^5$ for 50% remaining $7 \times 10^6$ for 25% remaining	$6 \times 10^{-5}$
Quenched from above 1600°C to 20°C in 0.03 sec	300 to 500	$1.13 \pm 0.12$	1.46	$6 \times 10^8$ for 75% remaining $8 \times 10^8$ for 50% remaining $1 \times 10^9$ for 25% remaining	$3 \times 10^{-4}$
Irradiated with $6 \times 10^{19}$ fast n/sq. cm at 50°C	150 to 400	$1.40 \pm 0.11$ $1.46 \pm 0.05$ §	2.8	$1 \times 10^3$ for 75% remaining $2 \times 10^3$ for 50% remaining $7 \times 10^3$ for 25% remaining	$1.2 \times 10^{-3}$

† Number of jumps calculated with eqn. (9) of the Appendix.

‡ The concentration is calculated from electrical resistivity measurements assuming 4.5 micro-ohm-centimetres per atom percent defects.

§ By the method of Meechan and Brinkman (Meechan 1956)—all others by the slope-change method from table 2.

Fig. 10



Activation energy for the recovery of irradiated platinum determined by the method of Meechan and Brinkman (Meechan 1956). The time  $\Delta\tau$  required at  $196^{\circ}\text{C}$  for the same recovery occurring 10 min at temperature  $T$  of the isochronal anneal is plotted against  $1/T$ . The slope of the line gives an activation energy of 1.46 eV for the whole recovery process.

but are significantly below those reported here. However, he made only three activation energy measurements and all were taken after about 8% recovery. Once again, the difference may be due to sample impurity since his is unspecified. Because of these discrepancies, no single model can explain all the past results. Therefore a model will be proposed to explain the results of the present experiments in which point defects were produced by three methods and in which all measurements were made under the same conditions.

Since the density of platinum decreased after irradiation while the lattice parameter showed no significant change, the defects remaining after a room temperature irradiation are probably vacancies, divacancies or vacancy clusters. Because the changes in density and electrical resistance recover at the same rate after irradiation, they are probably caused by the same point defect. Therefore, the recovery of electrical resistivity in irradiated platinum that requires an activation energy of 1.43 eV is probably due to vacancies, divacancies, or vacancy clusters.

There are several arguments that strongly suggest the defects in irradiated platinum are isolated or small groups of vacancies rather than large clusters. The first, mentioned previously, is the agreement between the

Table 4. A Summary of Activation Energies Measured for the Recovery of Platinum

Method of introducing defects	Recovery temperature range examined °C	Activation energy eV	Reference
Extended at -196°C	-150 to -70	0.22	Manintveld 1954
Extended at 20°C	-10 to 70	0.99	" "
Extended at -196°C	70 to 100	1.19	Dugdale 1952
	0 to 100	0.73	Present work
	200 to 400	1.43	" "
Quenching from above 1600°C	—	1.1	Lazarev and Ovcharenko 1955
	300 to 500	1.10	Bradshaw and Pearson 1956
	300 to 500	1.13	Present work
Quenching from 1100°C to 1400°C	450 to 580	1.42	Ascoli <i>et al.</i> 1958
	—	1.48	Bacchella <i>et al.</i> 1959
Reactor irradiation at 50°C	70 to 90	1.19	Dugdale 1952
	100 to 300	1.43	Present work

ratio of density decrease to resistivity increase in irradiated platinum with that found in quenched gold. The second, is the excellent agreement between the migration energy for defects produced by irradiation (1.43 eV) with those produced by quenching platinum from temperatures substantially below the melting point, 1.42 eV (Ascoli *et al.* 1958). A quench from these temperatures is expected to leave single vacancies while a quench from near the melting point may leave double vacancies (Koehler *et al.* 1957). The lower values of 1.1 eV required for defect migration after quenching from near the melting point as shown in table 4 are probably due to double vacancies.



The third argument that suggests the defects produced by irradiation are single vacancies, is the qualitative agreement between the measured migration energy of  $1.43 \pm 0.1$  eV and the calculated migration energy of  $1.65 \pm 0.15$  eV from the energy of self-diffusion in platinum of  $2.96 \pm 0.06$  eV (Kidson and Ross 1957) less the formation energy of vacancies in platinum  $1.30 \pm 0.1$  eV (Bradshaw and Pearson 1956, Ascoli *et al.* 1958, Bacchella *et al.* 1959).

The activation energy required for recovery of the electrical resistivity after 8% extension in liquid nitrogen was 0.73 and 1.43 eV. The higher value has already been attributed to the migration of single vacancies and the lower one is perhaps due to the release of interstitial atoms from trapping sites. Both vacancies and interstitial atoms may be produced by the crossing of screw dislocations during deformation.

The order of reaction is a measure of the rate of change of the number of jumps required by a defect to reach the sink during the recovery process. Once it rises above the value two, its interpretation becomes vague and in many cases may be caused by a nonrandom initial distribution of defects. This nonrandom distribution of defects is one possible explanation for the high order of reaction and the low number of jumps required for the recovery of irradiated platinum. If the damage from a fast neutron is concentrated in one small volume the local concentration of defects may be very high. Therefore the vacancies would require only a small number of jumps before combining with another vacancy, after which they could move more rapidly. Also, if the damage from fast neutrons is concentrated in a small volume, there may be other traps for vacancies such as dislocation rings or clusters of interstitial atoms that are produced by the same neutron. Therefore the vacancies would again require only a small number of jumps before reaching these sinks.

From the number of jumps required for the defect to reach a sink in the recovery of quenched and deformed platinum, an interpretation of the type of sink can be made. In the quenched sample with a defect concentration of  $3 \times 10^{-4}$ , the number of jumps ( $8 \times 10^8$ ) is much too high for recombination of defects. The low order of reaction 1.46 also discourages this interpretation. However, if the defects are going to dislocations, an argument which agrees with the observed number of jumps, an order of reaction equal to 1.0 might be expected. The higher order of reaction observed (1.46) may be caused by the change in dislocation network due to extensive climb of dislocations which absorb defects. Thus, the last defects will migrate to a much different distribution and perhaps even different type of dislocation network than was initially present.

The eight per cent extension of platinum is expected to increase the dislocation density from  $10^8$  to about  $10^{10}$  lines per square centimetre. Therefore, the number of jumps required by the defect to reach a dislocation will be reduced from  $10^7$  to  $10^5$  (Lomer and Cottrell 1955) which is similar to the number of jumps required for the defects to combine. The recovery of extended platinum at 60°C appears to be by defects

combining since the order of reaction is close to two. However, the high order of reaction (5.05) for the recovery of deformed platinum at 300°C, which is reflected in the large increase in number of jumps during recovery, indicates the defects are diffusing to several different types of exhaustible sinks or the sink concentration is decreasing during the recovery. The latter view is perhaps more favourable, since the experiment on the recovery of x-ray line broadening shown in fig. 7 indicated that some reduction in the dislocation density may occur during the recovery of the electrical resistivity. However, because of the unique activation energy and the large drop in line broadening on annealing at higher temperatures, the main recovery of electrical resistivity in the region of 300°C is thought to be due to vacancies rather than to dislocations.

### § 7. CONCLUSIONS

An interpretation of the point defects in platinum consistent with all our experimental results is the following:

(1) The principal lattice defects remaining in platinum after fast neutron irradiation are single vacancies with an activation energy for migration of 1.43 eV.

(2) The principal lattice defects remaining in platinum after quenching from above 1600°C are divacancies with an activation energy for migration of 1.13 eV.

(3) The two principal lattice defects remaining in platinum after an extension of 8% in liquid nitrogen are an unknown defect, perhaps interstitial atoms, with an activation energy for migration of 0.73 eV, and single vacancies with an activation energy for migration of 1.43 eV.

### ACKNOWLEDGMENTS

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### APPENDIX

#### NUMBER OF JUMPS REQUIRED BY DEFECT TO REACH SINK

The average number of jumps required by defects to reach a sink can be calculated from the recovery of electrical resistivity at constant temperature  $T$ . If the defect concentration is assumed proportional to the additional resistivity  $R$  above that for the fully recovered sample, the recovery rate depends on three factors

$$dR/dt = -R\Gamma p \quad \dots \dots \dots (1)$$

where  $t$  is the time,  $\Gamma$  the defect jump frequency, and  $p$  the probability per jump that a defect reaches a sink.

The jump frequency  $\Gamma$  also depends on three factors

$$\Gamma = Z(\alpha\nu) \exp(-\Delta F_2/KT) \quad (2)$$

where  $Z$  is the number of adjacent sites to which the defect may go,  $\alpha\nu$  is the frequency of attempts by the defect to move to each adjacent site, and  $\exp(-\Delta F_2/KT)$  is the fraction of time that a defect has sufficient free energy to jump.  $\nu$  is the vibration frequency of the atom, and  $\alpha$  is the fraction of these vibrations in each jump direction. The free energy required by the defect to jump is

$$\Delta F_2 = \Delta H_2 - T\Delta S_2 \quad (3)$$

where  $\Delta H_2$  is the activation energy required to move the defect one jump and  $\Delta S_2$  is the entropy change produced by the defect moving from one site to the saddle point midway between sites.

The probability per jump that a defect reaches a sink is equal to the fraction of lattice sites from which the defect is directly attracted to the sink. This depends on the concentration of sink sites, their distribution, and the maximum distance of attraction between the defect and sink. Therefore

$$p = j^{-1} = \beta C_s \quad (4)$$

where  $j$  is the average number of jumps required by the defect to reach the sink,  $C_s$  is the concentration of sink sites and  $\beta$  is a term depending on the sink distribution and the maximum distance of attraction between defect and sink. The term  $\beta C_s$  could well be called the 'effective sink concentration'.

Putting eqns. (2), (3), (4) into eqn. (1) gives:

$$S = -\frac{1}{R} \frac{dR}{dt} = -\frac{d(\ln R)}{dt} = Z\alpha\nu j^{-1} \exp(\Delta S_2/K) \exp(-\Delta H_2/KT) \quad (5)$$

where  $S$  is the slope of the graph  $\ln R$  vs. time. Solving for  $j$  gives:

$$j = Z\alpha\nu S^{-1} \exp(\Delta S_2/K) \exp(-\Delta H_2/KT) \quad (6)$$

$\Delta H_2$  is calculated from other experiments using eqn. (1) of the main text. Unfortunately the frequency factor  $Z\alpha\nu \exp(\Delta S_2/K)$  has not been measured directly, but each factor can be estimated. Because the total vibrational energy is considered in the  $\Delta H_2$  term in eqn. (6),  $\nu$  must be the frequency of the resultant vibration containing the total vibrational energy of the atom making the jump and  $\alpha$  is the fraction of these resultant vibrations in each jump direction. The Debye frequency is usually used for  $\nu$ . Bradshaw and Pearson (1956) and LeClaire (1953) take  $\alpha=1$  but the value  $\alpha=Z^{-1}$  assumed by Jost (1952) seems more reasonable for vacancy diffusion since only the resultant vibration is considered. Because there are  $Z$  possible jump directions, the fraction of the resultant vibrations in any one jump direction will be about  $Z^{-1}$ . If the resultant vibration of an atom adjacent

to a vacancy is always in the direction of the vacancy, then  $\alpha = 1$ . This is unlikely, however, because each atom vibrates in phase with its nearest neighbours and the wavelength of vibration is usually greater than three to four atoms. The remaining factor,  $\exp(\Delta S_2/K)$ , was assumed by Bradshaw and Pearson (1956) to lie between one and ten.

Because of uncertainty in the choice of these parameters for the frequency factor, a more direct value was taken from the self diffusion measurements of Kidson and Ross (1957). Their measured value for  $D_0$  was  $0.33 \text{ cm}^2 \text{ sec}^{-1}$  which gives (LeClaire 1953)

$$\alpha \nu \exp[(\Delta S_1 + \Delta S_2)/K] = D_0/a^2 = 2.2 \times 10^{14} \quad (7)$$

where  $a = 3.9 \times 10^{-8} \text{ cm}$  is the lattice parameter and  $\Delta S_1$  is the vibrational entropy due to a vacancy at a lattice site. The left side of eqn. (7) is similar to the frequency factor in eqn. (6) except for the added  $\Delta S_1$  term. However, from calculations on the relative values of  $\Delta S_1$  and  $\Delta S_2$  (Huntington *et al.* 1955)

$$\exp(\Delta S_2/K) = 0.24 \exp[(\Delta S_1 + \Delta S_2)/K]. \quad (8)$$

Therefore by combining eqns. (7) and (8) with (6) and taking  $Z = 12$  for f.c.c. lattices,  $j$  becomes

$$j = 6.3 \times 10^{14} S^{-1} \exp(-\Delta H_2/KT) \quad (9)$$

where  $S$  is the slope of  $\ln R$  vs. time and  $\Delta H_2$  is the activation energy for recovery at temperature  $T$ . This equation was used to calculate the number of jumps required by the defect to reach the sink for all recovery stages investigated. The frequency factor may be incorrect if recovery other than vacancy diffusion occurs. This frequency factor is the same as that of Bradshaw and Pearson's (1956) using their assumptions ( $B = \exp(\Delta S_2/K) = 5$ ,  $\alpha = 1$ ,  $\nu = 10^{13}$ ) and including the extra  $Z$  term discussed in his later paper (Bradshaw and Pearson 1957).

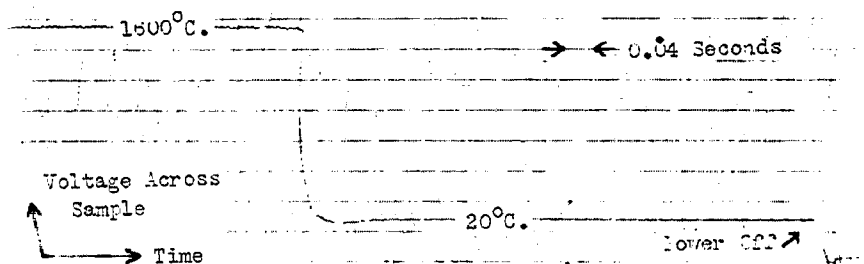
An estimate of  $B = \exp(\Delta S_2/K)$  can be made from eqns. (7) and (8). If  $\alpha = Z^{-1}$ , which seems reasonable for vacancy diffusion, and  $\nu = 5 \times 10^{12}$ , the Debye frequency for platinum (Seitz 1940); then a value for  $B$  of 125 is required to match the diffusion results.

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Fig. 2



Relative temperature of platinum wire *vs* time when quenched into water. The temperature is measured by the resistance of the sample which is proportional to the voltage if the heating current is left on during the quench.