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THE ENERGY OF FORMATION AND MIGRATION OF VACANCIES IN GOLD AND PLATINUM

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Values of $19 \pm 0.5 \times 10^3$ cal/mole and $27 \pm 0.5 \times 10^3$ cal/mole respectively were obtained for the energies of formation of a vacancy in gold and platinum. The activation energy for migration was found to be $20 \pm 1 \times 10^3$ and $25 \pm 1 \times 10^3$ cal/mole. These results were derived from data on the change of electrical resistance of the metals produced by quenching-in vacancies.

THERE is nowadays an increasing amount of work being devoted to the study of the diffusion mechanism in solids. By different experiments one obtains information on the basic characteristics of the diffusion phenomenon, the energy of formation of a vacancy, Q_1, and the activation energy for migration, Q_2. According to our present ideas, the sum of these two quantities gives the activation energy for self-diffusion: $Q = Q_1 + Q_2$. Q can be determined directly from measurement of the coefficient of self-diffusion, using the relation:

$$D = D_0 \exp\{-Q/RT\}.$$

One of the most direct means of measuring Q_1 and Q_2, and thus also Q, is based on the fact that the electrical resistance of a metal is increased by the presence of quenched-in vacancies, the increases being proportional to the vacancy concentration. This method is being more and more used, and in a previous communication[1] we gave some preliminary results obtained in this way on the self-diffusion of gold and platinum. In the present paper we describe the further development of this work.

EXPERIMENTAL PROCEDURE

Measurements were made on gold and platinum in the form of 0.05 and 0.1 mm diameter wires. These metals are convenient both because of their face-centered cubic lattices (one of the simplest structures) and because, as noble metals, they are easy to handle and can be heated in air.

We had available sufficiently pure metals — not less than 99.99% pure by chemical analysis — with resistance ratios (the ratio of the resistance at 4.2°K to that at room temperature) of 3.5×10^{-3} for gold and 2×10^{-3} for platinum in well-annealed samples.

The specimens were 50 to 70 mm long and current and potential leads of the same material were welded on in a hydrogen flame. After they had been mounted on their supports (quartz or glass) the specimens were thoroughly annealed by passing a current through them. This annealing current passed through leads long enough to ensure uniform heating of the working part of the specimen. The annealing temperature was determined from the resistance, the variation of which with temperature had been determined by heating in a furnace together with a standard platinum-platinum rhodium thermocouple. Before quenching, the specimens were kept at the appropriate temperature long enough for the equilibrium number of vacancies to be produced. The quenching was achieved either by simple cooling in air after switching off the current or, to increase the rate, by immersion in distilled water at room temperature, followed by switching off the current. Separate experiments on annealed specimens showed that the process of rapid immersion itself had negligible effect on the residual resistance (within the experimental uncertainties). Not more than one minute elapsed between quenching and immersion in liquid helium. The resistance of a specimen was measured in the annealed state, then with the quenched-in vacancies and, finally, after annealing again. The increase in resistance, ΔR, is then a measure of the concentration of vacancies at the high temperature. These operations were repeated many times for each temperature.

The temperature range was ~600 to ~1000°C for experiments on gold, and ~800 to ~1500°C for platinum.

Most of the determinations of the increase in resistance were made from measurements at liquid helium temperature, where the increase is appre-

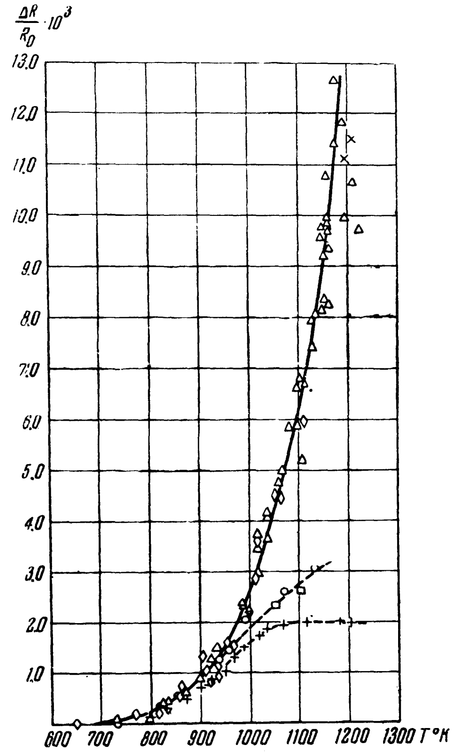

FIG. 1. The dependence of the resistance increase on the temperature, for quenching in vacancies in gold. Δ, +, ×) 0.1-mm diameter specimens; ◊, o, □) 0.05-mm diameter specimens. The full curve is for quenching in water, the dashed curve for quenching in air. All the data are obtained from resistance measurements at 4.2°K, except for the points marked ×, which refer to liquid nitrogen temperature.

ciable in comparison with the resistance of an annealed specimen. Some measurements were also made of the change at liquid-hydrogen and liquid-nitrogen temperatures.

DETERMINATION OF THE ENERGY OF FORMATION OF VACANCIES

Figure 1 shows the results of measurements of the increase in resistance on quenching in vacancies, as a function of the temperature from which the quenching was carried out. The increase is plotted relative to the resistance at 20°C (R_0) to eliminate the influence of the dimensions of the great number of specimens measured.

For the results to be reliable one must ensure that all the vacancies are preserved during quenching. The quenching rate in air is sufficient for 0.1 mm diameter specimens at temperatures up to ~ 900°K and for 0.05 mm specimens up to ~ 950°K. This can be deduced from the agreement between the dotted and solid curves up to these temperatures. The solid curve follows an exponential variation over the whole temperature range, as can be seen from Fig. 2, where $\ln(\Delta R/R_0)$ is plotted against $1/T$. The results fall on a straight line very well, so that one can be very certain that the mechanism of the resistance increase is the same throughout this temperature interval.

The rate of cooling in air was determined from an oscillograph record of the fall in temperature with time. It was found, for example, that a 0.1-mm specimen cooled from 900°K to 500°K in 0.14 sec. Cooling in water reduced this time by several factors of ten and preserved the vacancy concentration on quenching from all temperatures up to the melting point.

The slope (Q_1/R) of the straight line in Fig. 2 gives us the value of the energy of formation of vacancies in gold as $Q_1 = 19.0 \times 10^3$ cal/mole (0.82 ev). From the relatively small scatter of points the uncertainty in Q_1 is not more than 3%, i.e., 0.5×10^3 cal/mole. Within the limits of experimental errors this value of Q_1 agrees with the value given in the previous paper.[1]

The large number of points shown on the graph, obtained with a variety of specimens, were taken because during the course of this work values of Q_1 were published which were considerably different from our value.

Without knowing the exact conditions in other experiments it is difficult to find reasons for the discrepancies between the results. However, it can be said, for example, that the accuracy in determining Q_1 is evidently overestimated in the work of Koehler et al.[2] In one case they give a value 1.28 ± 0.03 ev and in the other 1.02 ± 0.06 ev; the 25% discrepancy is completely outside the estimated experimental error.

To approximate the experimental conditions used by these authors, we measured the increase

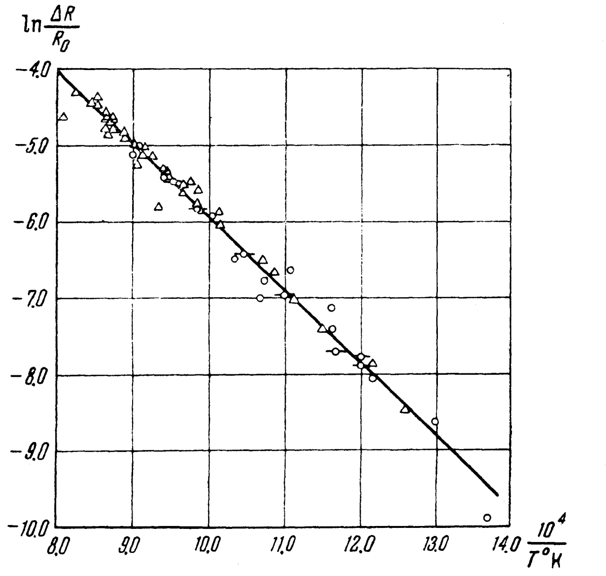

FIG. 2. The dependence of $\ln(\Delta R/R_0)$ on $1/T$, for gold.

in resistance, ΔR, not only at helium temperatures, but also at liquid-nitrogen temperature and, as shown above, the results agreed. The uncertainty in ΔR is considerable at nitrogen temperature, as the resistance of the specimen is tens of times larger than ΔR, while at helium temperature ΔR is measured as an increase in the residual resistance, which is itself smaller than the increase produced.

The uncertainty in the work of Bradshaw and Pearson[3] is 10%, because of the few experimental points, and the value of Q_1 is 0.95 ± 0.1 ev. With this uncertainty, their result is close to ours.

It is appropriate here to consider methods[4,5] of determining Q_1 which depend on the temperature variation of the resistance of gold at high temperatures. These methods make use of the well established relation for the temperature variation of the resistance of gold,[6] $R = R_0 + AT + BT^2$, which holds for not too high temperatures. This relation fits the behavior up to 500 or 600°C, but the experimental curve lies above the curve given by this expression at higher temperatures. The authors ascribe this discrepancy to the effect of vacancies and determine ΔR from the difference between the two curves. From the temperature variation of ΔR, values of $Q_1 = 0.67$ ev[4] and $Q_1 = 0.69$ ev[5] were deduced.

We have also measured the R-T relation from rom temperature up to 950°C, and the results agree closely with those of Meechan and Eggleston.[4] This method of determining Q_1 is open to some doubt, as there is little justification for the extrapolation of the R-T curve up to the melting point.[7] The value of ΔR derived in this way and ascribed to vacancies is one order of magnitude larger than the ΔR obtained from quenching. It is hardly likely that this great difference can be due to departures from Matthiesen's rule at high temperatures, when it applies between 4.2 and 273°K. In any case, the resistance variation over the whole temperature range (up to 900°C) can be well described by the inclusion of a term in T^3 in the previous equation.

An expression for the dependence of extra resistivity on vacancy concentration can be derived from Fig. 2:

$$\Delta\rho = (\Delta R / R_0)\rho = 7.7 \cdot 10^{-5} \exp(-Q_1 / RT) \text{ ohm-cm}.$$

It is customary to refer to the increase in resistivity for one atom-% of vacancies, and to obtain this we must divide by the vacancy concentration, i.e., by $C = A \exp(-Q_1/RT)$. Unfortunately, the constant A is only known roughly. If we take A = 1 then increase in resistivity for one atom-% of vacancies in gold is 0.77×10^{-6} ohm-cm/atom-%. Theoretical values range from 0.4×10^{-6} (reference 8) to 1.5×10^{-6} (reference 9) ohm-cm/atom-%. It is possible that this difference by a factor of nearly two indicates that the constant A should be ~ 0.5. We may note that the change in resistance due to vacancies is very close to the change produced by one atom-% of elements similar to gold (e.g., 0.68×10^{-6} ohm-cm/atom-% for silver and 0.48×10^{-6} ohm-cm/atom-% for copper). From a rough calculation based on this data we can conclude that A should lie between 0.5 and 2.

We carried out similar experiments on platinum and obtained $Q_1 = 27.0 \pm 0.5 \times 10^3$ cal/mole. This is in satisfactory agreement with the value of 1.4 ev obtained by Bradshaw and Pearson,[10] especially if one takes into account their large experimental scatter.

Assuming that A = 1, the resistivity increase, $\Delta\rho = 12 \times 10^5 \exp(-Q_1/RT)$ ohm-cm, leads to the value 1.2×10^{-6} ohm-cm for the resistivity due to 1 atom-% of vacancies in platinum.

It is interesting to note that these results confirm LeClaire's calculation[11] of the ratio of the heat of formation of vacancies to the heat of vaporization. According to LeClaire, this ratio should be 0.22 for a face-centered metal, and from our results the values are 0.22 for gold and 0.23 for platinum.

DETERMINATION OF THE ACTIVATION ENERGY FOR VACANCY MIGRATION

In our preliminary communication we also derived the activation energy for migration of vacancies. This was 12×10^3 cal/mole for gold and 25×10^3 cal/mole for platinum. The value of Q_2 is obtained from curves of the reduction of the resistance increase, ΔR, during isothermal annealing.

The dependence of $\ln(\Delta R/\Delta R_0)$ on time for a 0.1-mm diameter gold wire is shown in Fig. 3 (ΔR_0 is the initial increase in resistance on quenching). The curves shown refer to one tem-

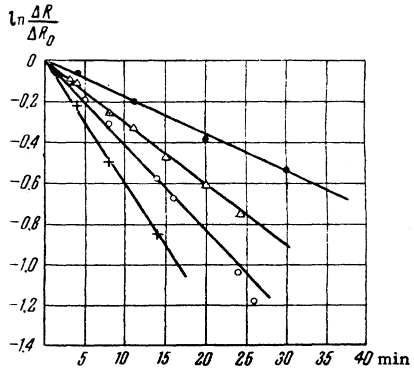

FIG. 3. Curves of the reduction of the resistance increment with annealing time.

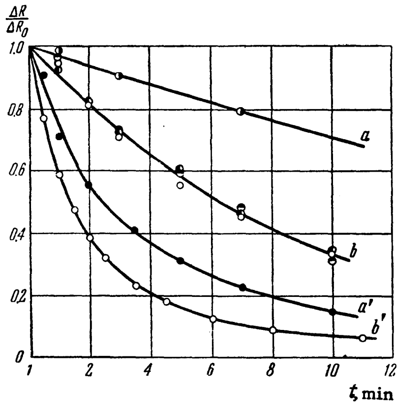

FIG. 4. The influence of wire diameter and concentration of quenched-in vacancies, for gold. Curves a and a′) 0.1-mm diameter wire, Curves b and b′) 0.05-mm diameter wire.

perature (in this case 100°C) and the different points correspond to different concentrations of quenched-in vacancies (i.e., to different initial values of $\Delta R_0/R_0$).

Similar curves were obtained for different annealing temperatures (75, 90, 100, 107 and 127°C) and for initial concentrations varying over a factor of more than 10 ($\Delta R_0/R_0$ from 1×10^{-3} to 12×10^{-3}).

The strong dependence of the kinetics of vacancy annihilation on concentration is noticeable — the curves of resistance removed become steeper with increasing resistance. It appears that the annihilation process is predominantly a diffusion process only for the smallest vacancy concentrations. For the largest concentrations vacancy coagulation plays a very important part. This is borne out by the curves of Fig. 4, which show the results of annealing specimens of two diameters at 120°C. For pure diffusion to the outside, the times for the concentrations to reach the same relative values, for different diameters, should be in the ratio of the squares of the diameters, i.e., 4 in our case. In fact, for small concentrations ($\Delta R_0/R_0 \sim 2 \times 10^{-3}$) the times for two different specimens (curves a and b) differ by a factor 3, so that even for these concentrations the process is not pure diffusion. For larger concentrations (up to $\Delta R_0/R_0 \sim 9 \times 10^{-3}$, curves a′ and b′) the time ratio becomes less than 2.

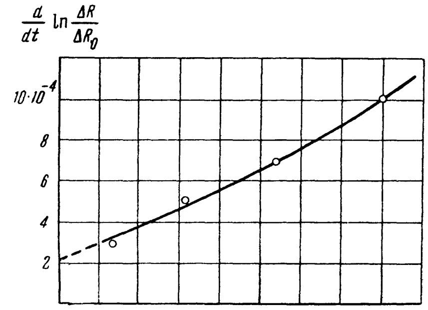

FIG. 5. The variation of slope of the annealing curves with initial vacancy concentration, for gold.

We can understand the fact that we do not have pure diffusion even for the smallest values of $\Delta R_0/R_0$ in a quenched specimen, if we bear in mind that for any measurement of concentration, the vacancy annihilation is taking place at a considerably lower temperature than that from which the quenching was carried out. This means that the vacancy solution is greatly supersaturated and there is inevitably a type of vacancy coagulation in it. Nevertheless, it seems possible to derive sufficiently reliable values for the activation energy of vacancy migration from such measurements. It is assumed that it is sufficient to extrapolate the kinetics curves to the limit of small concentrations. Such an extrapolation is shown carried out in Fig. 5, where the initial slopes of the annealing curves are plotted against the initial vacancy concentrations, ΔR_0.

Curves for each of the annealing temperatures given above were obtained in this way. Extrapolation of these curves gives the value of $d/dT \times \{\ln(\Delta R/\Delta R_0)\}$ for such small concentrations that we can consider the diffusion process to be dominant in vacancy annihilation.

As is well known, the solution of the diffusion problem for a cylinder of radius r, for sufficiently large times, gives a time dependence of concentration in the material in the form

$$\frac{N}{N_0} = \frac{\Delta R}{\Delta R_0} = \frac{4}{5.78}\exp\left\{-\frac{5.78}{r^2}D_v t\right\},$$

from which we obtain

$$\frac{d}{dt}\ln\frac{\Delta R}{\Delta R_0} = -\frac{5.78}{r^2}D_v,$$

where $D_V = D_0 \exp(-Q_2/RT)$ is the coefficient of diffusion of vacancies and Q_2 is the activation energy for their migration.

We should be able to calculate the diffusion coefficient for the whole temperature range of the experiments from these expressions.

The table gives values for the coefficient of diffusion (D_1) of vacancies in gold wire, taking $r = 5 \times 10^{-3}$ cm, the radius of the wire. For compari-

T °K	$c = \exp(-Q_1/RT)$	D_1 (cm²/sec)	$D_2 = D_a/c$ (cm²/sec)
348	$1.78 \cdot 10^{-12}$	$1.12 \cdot 10^{-10}$	$3.91 \cdot 10^{-15}$
363	$5.75 \cdot 10^{-12}$	$6.89 \cdot 10^{-10}$	$1.29 \cdot 10^{-14}$
373	$1.12 \cdot 10^{-11}$	$9.35 \cdot 10^{-10}$	$2.83 \cdot 10^{-14}$
380	$1.70 \cdot 10^{-11}$	$2.15 \cdot 10^{-9}$	$4.92 \cdot 10^{-14}$
400	$5.88 \cdot 10^{-11}$	$5.60 \cdot 10^{-9}$	$1.91 \cdot 10^{-13}$

son we give the diffusion coefficient derived from data on the self-diffusion of gold atoms obtained with radioactive isotopes.[12]

It can be seen that the value of D_1 is greater than the directly determined D_2 by a factor $\sim 4 \times 10^4$ over the whole temperature range. To explain the much greater value of D_1 one must assume that the diffusion length is not equal to the radius of the wire, but is considerably less and must be 2.5×10^{-5} cm.

We can then believe that vacancy annihilation is accomplished at small concentrations by a diffusion process, and use the results to determine the activation energy for vacancy migration. The dependence of $\ln D_1$ on $1/T$ is given in Fig. 6.

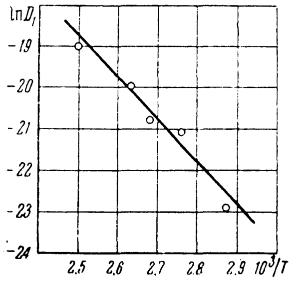

FIG. 6. Variation of ln D_1 with 1/T, for gold.

The slope (Q_2/R) leads to the value $Q_2 = 20 \pm 1 \times 10^3$ cal/mole. This value is considerably different from our preliminary result (12×10^3 cal/mole) when we were unaware of the great dependence of the annealing curves on the quenched-in concentration. This was also neglected in other work,[2,3] and probably accounts for the lower values of Q_2.

The sum $Q_1 + Q_2$ is the activation energy for self diffusion. Our value is $39.0 \pm 1.5 \times 10^3$ cal/mole, which is close to the most recent determinations by direct self-diffusion measurements: 39,360 ± 280 cal/mole,[12] 41,700 ± 300 cal/mole,[13] and 42,900 cal/mole.[14]

Annealing curves were also obtained for a wide concentration range in platinum. There is here a smaller concentration dependence than in gold, and only for large concentrations does the initial slope increase, while for small concentrations the curves coincide. These measurements were made on two specimens at temperatures from 500 to 300°C. There is only a few per cent uncertainty in Q_2, $25 \pm 1 \times 10^3$ cal/mole. The small dependence of the annealing curves on concentration explains the good agreement with our previous work (25×10^3 cal/mole) and with the results of Bradshaw and Pearson (25.3×10^3 cal/mole).

The activation energy for self diffusion in platinum $Q = 52 \pm 1 \times 10^3$ cal/mole. This value is known more accurately for platinum than for gold.

CONCLUSIONS

We can draw some general conclusions from our results.

The heat of formation of vacancies can be determined from the measurement of the increase in resistance on quenching, especially if the resistance change is measured at liquid-helium temperature. The results of the most reliable measurements on gold and silver are, within the limits of experimental error, in good agreement.

There are quite large discrepancies in the values found for the activation energy for vacancy migration in gold. When the concentration dependence of the annihilation process is taken into account, the results described above make it possible to derive a completely reliable value for this too.

The method of quenching-in vacancies can then yield a value for the activation energy for self diffusion with an accuracy as great as that achieved by use of radioactive isotopes.

There is, however, an inconsistency which must be pointed out. As has been noted, in the limit of small concentrations, vacancy annihilation is achieved by a diffusion process over a distance considerably less than the specimen diameter (it is hundreds of times less). We would then expect the cross-sectional dimensions not to matter. However, as can be seen from Fig. 4, there is a noticeable dependence of the annihilation kinetics during annealing on wire diameter, not only at small vacancy concentrations, but right up to the largest concentrations.

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