about 1 kbar is small. The half-life for the pressure runs in this study ranged from $2{\cdot}5\times10^{-2}$ to 5×10^{-3} sec corresponding to initial rates of 10^4 to 5×10^4 °C/sec. It has been shown[1] that such a variation in quench rate for quenches below 600°C does not markedly affect the total quenched-in resistance of gold.

The measurement procedure followed throughout most of the work reported herein was as follows.

Newly mounted specimens were given at high temperature anneal (temperatures from 800° to 900°C for 1 hr) followed by a gradual cooling to room temperature. Resistivity measurements at room temperature after subsequent anneals indicated no additional resistivity change after the first anneal. The sample holder was then cooled in the pressure vessel to the measuring temperature and, if desired, pressure was applied. Potentiometric measurement of R_S-R_D was made with the balanced bridge circuit previously described. Several series of measurements were made over a period of time to determine whether the equilibrium measuring temperature was reached. Generally about five such consecutive resistance differences, constant to within $\pm1\ \mu\Omega$, established this. The specimen alone was then quickly heated to the quench temperature, held there for about 3–5 sec (sufficient to establish the equilibrium vacancy concentration[19]), and then quenched by turning off the heating current. The value of R_S-R_D was again measured after the system returned to equilibrium as before, once more with the requirement of constancy of readings. The change in the resistance difference from the value obtained before the quench was then interpreted in terms of the excess vacancy concentration characteristic of the particular quench temperature and pressure used.

RESULTS

To determine the validity of the experimental techniques used, the additional defect resistance quenched into several specimens at atmospheric pressure was determined as a function of quenching temperatures. From equation (3) it follows that from the slope of a plot of log $(\Delta R/R)$ against $1/T$, the formation energy for the defect may be obtained. Figure 4 shows the fractional resistance quenched into three specimens in the temperature range from 510° to 890°C. The curves shown are displaced vertically for the sake of clarity. The curves for specimens A and B actually involved the use of the same wire but with a slightly different heat treatment prior to quench. The data from these curves, as well as those for specimen C, actually superimpose, indicating the effectiveness of the annealing procedures. Some curvature is seen in the temperature region above 725°C, indicating that annealing is occurring during quenches from above this temperature. The observed linearity below this temperature supports the assumption that simple defect production predominates. The best fit of the data below 725°C gives formation energies of 0·90, 0·93, and 0·97 eV. The average of these three determinations is 0·93 eV.

The results obtained from quenches made under high pressures are given in Table 1. The quenched-in resistance was corrected to 600°C by use of an Arrhenius type equation using the value of 0·93 eV for the formation energy and the assumption that the change of the derivative of the energy with pressure is temperature independent over the small temperature interval in which the data were obtained.

Table 1. *Data for pressure runs* [$(\Delta R/R)$, *fractional resistance quenched into several specimens at temperature* T_Q; $(\Delta R/R)_{corr}$, *ratios corrected to* 600°C]

Run	p (bars)	T_Q (°C)	$(\Delta R/R)\times10^4$	$(\Delta R/R)_{corr}\times10^4$
1	0	509	1·60	8·53
2	783	592	7·35	8·16
3	2300	612	8·88	7·50
4	2550	590	6·17	7·18
5	3050	598	6·68	6·88
6	3720	570	4·24	6·60
7	3800	584	5·17	6·48
8	4600	579	4·42	6·15
9	5360	591	5·44	6·03
10	6100	581	4·22	5·60

A semilogarithmic plot of the corrected resistivities as functions of pressure is shown in Fig. 5. The slope of the curve of Fig. 5 in equation (4) yields a formation volume of $\Delta V_f = 5{\cdot}45\pm0{\cdot}7$ cm³/mole. The molar volume of gold at 600°C can be estimated from the molar volume at room temperature, the thermal expansion, and the compressibility. The value obtained is 10·45 cm³/mole. The specific volume change per defect is then

$$\frac{5{\cdot}45\ \text{cm}^3/\text{mole}}{10{\cdot}45\ \text{cm}^3/\text{mole}} = 0{\cdot}52\pm0{\cdot}07\ \text{at. vol.}$$

DISCUSSION

Formation energy

The energy for defect formation obtained from

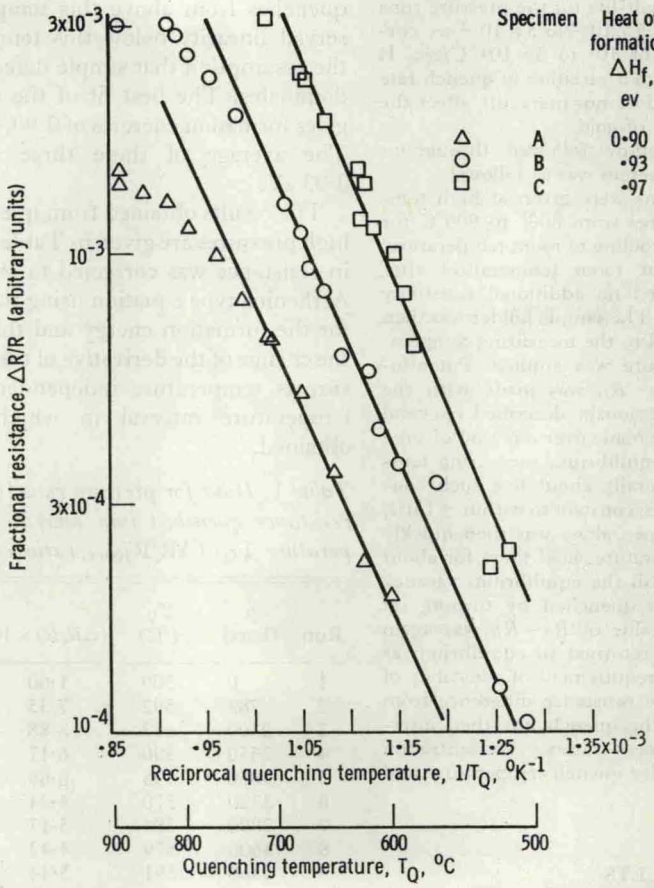

FIG. 4. Semilogarithmic plot of quenched-in resistance as a function of reciprocal of absolute quenching temperature at atmospheric pressure. (Curves for three specimens are displaced vertically for the sake of clarity.)

Fig. 4 is in good agreement with the values, quite generally accepted as the single vacancy formation energy, obtained from atmospheric quenching experiments and from calorimetric, dilatometric and other methods. The best estimates from these measurements range from 0·94 to 0·98 eV.[20] Above about 725°C, deviations from linearity appear in the curves of Fig. 4 possibly indicating annealing during the quenches from above this temperature. This deviation is consistent with the quenching studies of KAUFFMAN and others[1] for the quench rates obtainable at atmospheric pressure in this experiment. The agreement of the formation energy calculated from the lower temperature data with the existing best estimates engenders confidence in these techniques. This confidence is extended to the results from the high pressure quenches, performed at variable but higher quench rates.

Formation volume

The value obtained for the formation volume is in good agreement with the value of 0·53 at. vol. obtained by HUEBENER and HOMAN[9] by high-pressure quenching. It is also in agreement with the value of 0·57 at. vol. obtained by DESORBO,[11]