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IN QUENCHED GOLD.

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THE EFFECT OF IMPURITIES ON RECOVERY
IN QUENCHED GOLD

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the
Degree Doctor of Philosophy in the Graduate School for
The Ohio State University

By

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* * * * * * *

The Ohio State University

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VITA

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He and his wife Sonja, have two daughters, Karen and Lisa.
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INTRODUCTION

Quenching experiments have primarily been concerned with the central problem of determining the migration energies for particular point defect configurations in high purity f.c.c. metals. The binding energy for certain defect clusters has also been ascertained whenever possible, but many values are only estimates of magnitude. Koehler et al., (1-2) using gold, established the widely accepted quenching method for introducing excess vacancies into a crystal and the method of observing the recovery of quenched-in extra resistivity during annealing to study the kinetics. They assumed that the extra resistivity after quenching is directly related to the behavior of lattice defects, and they were subsequently able to determine values for the energy of formation of vacancies and migration energies for particular defects. Experimental evidence points up the fact that the recovery process is not simple when the initial concentration of single vacancies exceeds some critical value (3-5). Electron transmission studies by Cotterill (6) and Silcox and Hirsch (7) have provided evidence that vacancy clusters play an important role in the recovery kinetics. The possibility exists that elastic strains can be minimized if the vacancies in the lattice are not distributed as single voids but are
clustered into groups of two or more vacancies. These clusters can be likened to polyatomic molecules which have a certain binding energy. The disappearance of these clusters may not be determined by their migration energy, but it may be determined by its dissociation into simpler and more mobile defects.

The bulk of the research has been centered around the problem of vacancy interactions in the pure f.c.c. metals, and the complications associated with vacancy-impurity interactions have not been satisfactorily elucidated. Damask and Dienes (8) and Sosin (9) have treated the general problem by means of analog computer solutions of differential equations governing vacancy decay which are derivable from the following chemical reactions:

\[
C_1 + I \xrightleftharpoons*{K_1 \over K_2} C_x \quad (1)
\]

\[
\xrightarrow{K_3} C_1 \rightarrow \text{sinks} \quad (2)
\]

\(C_1\), \(I\), and \(C_x\) are concentrations of vacancies, free impurities, and vacancy-impurity complexes, respectively, and the \(K\)'s are the appropriate rate constants. The main conclusion that can be drawn from this work is that the activation energy for defect motion will probably range between \(E_{m}^{1}\), the migration energy of a single vacancy, and \(E_{m}^{1} + B_x\) where \(B_x\) is the binding energy of the vacancy-impurity complex. The initial stage of recovery is controlled by the migration
energy of a single vacancy, and the second stage is controlled by the mobility and binding energy of the vacancy-impurity complex.

Cattaneo and Germagnoli (10) have experimentally studied the influence of silver impurities on the annealing kinetics of quenched gold for the condition where $I_0 > C_x$. Their results were, in general, more complicated than that predicted by Damask and Dienes (8). During isothermal recovery the resistivity was observed to go through a maxima after short aging times. This phenomenon was attributed to the clustering of vacancies around impurity atoms, and this characteristic behavior of the resistivity might be indicative of all f.c.c. metals having impurities present. Similar observations were observed by Mori, Meshii, and Kaufman (11) for "pure" gold quenched from temperatures near 600°C. They attributed this to divacancy formation rather than to impurity atoms. Precipitation hardening systems such as the aluminum-10% zinc system studied by Panseri and Federighi (12) and the aluminum-copper system studied by De Sorbo, Treftis and Turnbull (13) when rapidly quenched from a solution heat treatment temperature and subsequently annealed, also exhibit the same characteristic behavior of the resistivity. The level of impurity needed to produce this maxima in the resistivity is not known, but it is probably related to the binding energy of the impurity-vacancy complex in a manner that the amount of impurity required
decreases as the binding energy for the impurity complex increases. The kinetics associated with vacancy-impurity interactions have not been studied extensively, so it is impossible to arrive at any conclusive interpretations about the various stages of recovery. The experiments which have been carried out on the kinetics have been for cases where the vacancy concentration was low in comparison to $I_0$. The recovery process will certainly be more complicated when the kinetics are investigated for high temperature quenches. No satisfactory experiments have been carried out on the annealing kinetics, since Damask and Dienes (8) have pointed out that it is doubtful that isothermal experiments can be used to determine activation energies even though the effective rate constant may appear to follow the Arrhenius equation. Resistivity changes may not be the best physical property to use to follow the kinetics, since it may not be sufficiently sensitive to distinguishing between the different types of defects when impurities are present. The present investigation was undertaken to study the detailed nature of the annealing process of quenched metals using the thermoelectric force method for distinguishing between the different defect configurations.
THEORETICAL

This problem is divided into two basic sections: (1) theoretical and (2) experimental. The purpose of the theoretical section is to provide background for the interpretation of the experimental data. The theoretical section consists of two parts: (1) An analysis of the athermal loss of vacancies caused by impurity atoms and (2) the annealing behavior of quenched gold as described by isochronal (tempering) anneals. The calculations were made on an IBM 7094 computer using numerical values for $E_m^1$, $E_m^2$, $B_2$, that have been determined for gold (1-2). $E_m^1$, $E_m^2$ are the activation energies for monovacancies and divacancies, respectively, and $B_2$ is the binding energy of a divacancy. $E_m^c$, the migration energy of a vacancy-impurity complex, and $B_X$, the binding energy of the vacancy-impurity complex, were determined from the experimental results of this work. $B_X$ was considered a variable in the tempering studies to show the effect of binding energy on the recovery process. $B_3$, the binding energy of a trivacancy, has not been determined by any experiment. However, if the equilibrium configurations of the trivacancy is assumed to be that of an equilateral triangle, then it is reasonable to assume that $B_3$ is approximately equal to $3B_2$ (14).
Taking $B_2$ to be equal to 0.07 eV, $B_3$ is then equal to 0.21 eV. It will be shown from the experimental results that $B_3$ is equal to about 0.23 eV.

**Differential equations governing the loss of vacancies**

Koehler, Seitz, and Bauerle (2) and de Jong and Koehler (3) have described the loss of vacancies in pure gold. In this work some of their basic ideas are extended to include the effects of impurity atoms on the life history of vacancies in gold.

The general set of chemical reactions describing the behavior of point defects are given in Table 1. The configurations assumed for the trivacancies and tetravacancy were that of a defect having $60^\circ$ angles between bonds (3).
TABLE 1
CHEMICAL REACTIONS AND RATE CONSTANTS

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<th>Reaction</th>
<th>Rate Constant</th>
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<tr>
<td>(1) $C_1 + C_1 \xrightarrow{K_1} C_2$</td>
<td>$K_1 = 84 \nu_1 \exp^{-E_m^1/kT}$</td>
</tr>
<tr>
<td>(2) $C_1 + C_2 \xrightarrow{K_2} C_3$</td>
<td>$K_2 = 20 \nu_1 \exp^{-E_m^1/kT}$</td>
</tr>
<tr>
<td>(3) $C_1 + C_2 \xrightarrow{K_3} C_3$</td>
<td>$K_3 = 20 \nu_2 \exp^{-E_m^2/kT}$</td>
</tr>
<tr>
<td>(4) $C_1 + C_3 \xrightarrow{K_4} C_4$</td>
<td>$K_4 = 12 \nu_1 \exp^{-E_m^1/kT}$</td>
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<tr>
<td>(5) $C_1 + I \xrightarrow{K_5} C_x$</td>
<td>$K_5 = 42 \nu_1 \exp^{-E_m^1/kT}$</td>
</tr>
<tr>
<td>(6) $C_1 \xrightarrow{K_6} \text{Sinks}$</td>
<td>$K_6 = \alpha \nu_1 \lambda \exp^{-E_m^1/kT}$</td>
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<tr>
<td>(7) $C_2 \xrightarrow{K_7} \text{Sinks}$</td>
<td>$K_7 = \alpha \nu_2 \lambda \exp^{-E_m^2/kT}$</td>
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<td>(8) $C_x \xrightarrow{K_8} \text{Sinks}$</td>
<td>$K_8 = \alpha \nu_x \lambda \exp^{-E_m^c/kT}$</td>
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<td>(9) $C_x \xrightarrow{K_9} \text{Variable Sinks} + C_1$</td>
<td>$K_9 = \frac{\lambda}{2} \exp^{-E_m^c/kT}$</td>
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<tr>
<td>(10) $C_2 \xrightarrow{K_{10}} 2C_1$</td>
<td>$K_{10} = 14 \nu_1 \exp^{-E_m^1+B_2}/kT$</td>
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<tr>
<td>(11) $C_3 \xrightarrow{K_{11}} C_2 + C_1$</td>
<td>$K_{11} = \nu_2 \exp^{-E_m^1+B_3}/kT$</td>
</tr>
<tr>
<td>(12) $C_3 \xrightarrow{K_{12}} C_2 + C_1$</td>
<td>$K_{12} = 15 \nu_1 \exp^{-E_m^1+B_3}/kT$</td>
</tr>
<tr>
<td>(13) $C_x \xrightarrow{K_{13}} C_1 + I$</td>
<td>$K_{13} = 7 \nu_1 \exp^{-E_m^1+B_x}/kT$</td>
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$C_1$, $C_2$, $C_3$, $C_4$ and $C_x$ are the concentrations (mole fractions) of mono-, di-, tri-, tetravacancies and vacancy-impurity complexes respectively. The $K$'s are the appropriate rate constants, and $\nu_1$, $\nu_2$, $\nu_3$, and $\nu_x$ are the frequencies of vibration of an atom next to a vacancy, a common neighbor of both members of a divacancy, and a common neighbor of both of the members of a vacancy-impurity pair, respectively; $E_{m}^1$, $E_{m}^2$, and $E_{m}^c$ are the corresponding energies of migration. $B_2$, $B_3$ and $B_x$ are the association energies.
of a divacancy, trivacancy, vacancy-impurity complexes, respectively. $\lambda$ is the concentration of dislocation sinks taken equal to $10^{10}$; $\lambda^2$ is the square of the effective jump distance taken equal to $10^{-15}$ cm$^2$; $N_s$ is the concentration of variables sink nuclei that are assumed to form during the cooling period. The term sink is construed to mean a fixed sink (dislocations) whose concentration does not change with time.

The differential equations that correspond to the chemical reactions listed in Table 1 are:

$$\frac{dc_1}{dt} = -c_1^2 K_1 + c_2^2 K_13 - c_1 K_6 + 2c_2 K_{10} - c_1 c_2 K_2 + c_4 K_{12} - c_1 c_2 K_3 + c_3 K_{11} - c_1 c_3 K_4 - c_1 I K_5 + c_x K_9$$

(3)

$$\frac{dc_2}{dt} = c_1^2 K_1 - c_2^2 K_{10} - c_1 c_2 K_2 + c_3 K_{12} - c_2 K_7 - c_1 c_2 K_3 + c_3 K_{11}$$

(4)

$$\frac{dc_3}{dt} = c_1 c_2 K_2 - c_3 K_{12} + c_1 c_2 K_3 - c_3 K_{11} - c_1 c_3 K_4$$

(5)

$$\frac{dc_4}{dt} = c_1 c_3 K_4$$

(6)

$$\frac{dc_x}{dt} = -c_x K_{13} - c_x K_8 - c_x K_9 + c_1 I K_5$$

(7)

$$\frac{dN}{dt} = d(c_1 + 2c_2 + 3c_3 + c_x)/dt = -c_1^2 K_1 - c_1 K_6 - c_x K_8$$

(8)

$$\frac{dI_t}{dt} = c_1 I K_5$$

(9)

This coupled set of nonlinear differential equations has been simplified to include only the combination numbers for the equilibrium configurations of the defects. The method for arriving at the appropriate combination numbers
is given in the book by Damask and Dienes (8).

The model for writing the chemical reactions was based on the assumption that each mobile defect configuration executes a sequence of jumps from one position to another until it encounters a trap or a sink. Entities which are known to function as traps and sinks are external and internal boundary structures, dislocations, impurity atoms, and other point defect configurations. In this model, the general annealing process consists of permanent defect loss at sinks and thermally activated release processes at traps, vacancy clusters, and vacancy-impurity complex formations. Vacancies and divacancies are generally referred to as being point defects. However, both experiment and theory indicate that they should be thought of as small regions with imperfect structure. Diffusion theory does not in general take into account the effects of long range strain field interactions of the various point defect configurations. Assuming a first-neighbor interaction range between point defects, Beeler (15) has shown that the initial vacancy clustering rate is greater than that given by the chemical rate approach. Long range strain field interactions serve to enhance concentration fluctuations and promote clustering. However, the rate of vacancy decay computed by the average chemical approach agrees well with the Monte Carlo approach having built-in concentration fluctuations after an initial transient. The solution of the set of nonlinear coupled differential
equations will give the generalized behavior of a vacancy in gold. In solving the equations, it is assumed that both the initial concentrations of vacancies, impurity atoms, and dislocation sinks are randomly distributed.

**Athermal trapping of vacancies**

Athermal trapping of vacancies is the disappearance of vacancies to sinks during the process of quenching from a high temperature where single vacancies are abundant to a very low temperature where the mobility of point defects is low. When the cooling period is of appreciable length, vacancies make a sufficient number of jumps to have enabled them to have encountered many traps during the cooling period. Thus when the concentration of trapping centers is appreciable many vacancies will be lost. The "freeze-in" factors are dislocation density, initial vacancy concentration, defect diffusivity, the mechanism of heat transfer from the wire, impurity level, etc.

The influence of quenching rate on the energy of formation of vacancies, $E_f$, has been observed for some time. Kauffman and Koehler (1) quenched gold in a helium blast; Bauerle, Seitz, and Koehler (2) quenched gold in water. The energy of formation of vacancies was larger for the specimens quenched by the helium blast than for those quenched in water. This effect can in part be explained by the difference in quenching mechanisms of the two mediums.
Water will form a vapor blanket around the wire which tends to insulate it from the bulk water whereas the moving helium gas blast would tend to minimize this insulating effect and the time spent at the high temperature region would be less.

Mori, Meshii, and Kauffman (16) investigated the effects of quenching speed on the quenched-in resistivity over a limited range of quenching speeds and temperatures. They observed the initial value of the quenched-in resistivity to increase with both quenching rate and quench temperature.

More recently, Flynn, Bass, and Lazarus (17) studied the quenching rate variable and showed that the energy of formation of vacancies cannot be determined from experiments which make use of a single quenching speed because of the loss of vacancies during the quench. They assumed that vacancies lost during the cooling period disappear at fixed sinks (dislocations, surfaces). However, their results suggested that the sinks did not have the character of a surface. Gerstriken et al. (18) made similar observations on silver and platinum when they investigated the effect of wire diameter on the annealing behavior of these metals. Changing the specimen diameter did not alter the annealing behavior, but, rather, their investigations showed that internal sinks were the important trapping centers.

The possibility of impurity atoms as important trapping centers for vacancies will be considered and the influence
of them on the determination of the energy of formation of vacancies will be discussed. The set of simultaneous nonlinear differential equations describing the change in the concentration of vacancies are solved using numerical values for the parameters on an IBM 7094 computer.

The migration energy of the vacancy-impurity complex, $E_m^C$, and the binding energy of the complex, $B_x$, was assumed to be 0.7 eV and 0.15 eV respectively. These values are only slightly larger than the migration energy of the divacancy in gold (0.66 eV) and the binding energy of a gold divacancy (0.07 - 0.10 eV). The binding energy is the most important parameter, since it controls the number of complexes that form in excess of the random number when the binding energy is equal to zero. The initial concentration of mobile defects, $Z_0$, was taken to be equal to $3 \times 10^{-4}$ atom fraction at time $t = 0$.

Experimental cooling curves obtained by measuring the change in electrical resistivity as a function of time on an oscilloscope was used to describe the rate of change of temperature. The actual curve was approximated by a series of piecewise segments and programmed into the computer. The diameter of the gold wire used for the determination of the cooling curve was 0.025 cm., and the quenching temperature was 1273°K. Water and mineral oil were the quenchants, and the respective average cooling rates were $2 \times 10^7$°C/sec and $3 \times 10^4$°C/sec. The oscilloscope curves are shown in Figure 1.
Quenching Rate Curves For Gold Wires.

Figure 1
Cooling Curves
The effect of cooling rate on the athermal loss of single vacancies is presented in Figure 2 where the change, \( \Delta C_1 \), in the concentration of vacancies is given as a function of time for the two cooling rates. The change in vacancy concentration, \( \Delta C_1 \), is defined as \( C_1 - C_t \) where \( C_1 \) is the initial concentration of vacancies taken equal to \( 3 \times 10^{-4} \) atom fraction and \( C_t \) is the concentration of vacancies taken at any time \( t \). A comparison of the curves in Figure 2 shows that an insignificant number of vacancies is lost during the cooling period of the fast quench. The fractional loss of vacancies amounted to only \( 4.33 \times 10^{-4}% \), but for the slow quench, the fractional loss of vacancies was \( 14.4 \times 10^{-2}% \). The fractional change of vacancies that occurred for the slow quench is negligible, and the loss of vacancies to dislocations alone is not sufficient to account for all of the vacancies lost. In fact, if one assumes that the dislocation density is \( 10^{10} \), then the length of a dislocation line in a computational cell containing 1000 atomic sites would only be about two atomic spacings long. Thus the number of trapping sites on dislocations is negligible when compared to the total number of lattice sites. Figure 3 shows the increase in the concentration of divacancies as a function of time for the two cooling periods. Again, a comparison of the two curves shows that a significant number of divacancies was formed during the cooling period of the slow quench. In fact, isothermal annealing was observed
Figure 2
The Effect Of Cooling Rate On The Athermal Loss Of Vacancies
Figure 3
Concentration of Divacancies as a Function of Time for Two Cooling Periods

Influence of Quenching Rate on Divacancy Formation in Gold
Initial vacancy conc. = 3 x 10^{-4}
Initial impurity level = 2 x 10^{-5}

\[
\frac{dT}{dt} = 3 \times 10^4 \text{C/sec.}
\]

\[
\frac{dT}{dt} = 2 \times 10^7 \text{C/sec.}
\]
at the end of the cooling period as evidenced by the increased rate in the formation of divacancies. In summary, 24 times as many divacancies formed during the cooling period of the slow quench than formed during the cooling period of the fast quench. This is a significant number, since the jump frequency of a divacancy is about 300 times that of a single vacancy. Consequently, a small increase in the divacancy concentration will influence the initial annealing kinetics.

Impurity atoms may play a more important role than dislocations in the disappearance of vacancies during the cooling period. The calculations were repeated and the initial concentration of impurity atoms, \( I_0 \), was varied for each computer run. Only one cooling rate was used for these calculations. The values for \( I_0 \) were \( 3 \times 10^{-10} \), \( 10^{-6} \), \( 2 \times 10^{-5} \), and \( 3 \times 10^{-4} \). It is interesting to note that the impurity level of commercially available 99.999% gold may contain between \( 10^{-4} \) to \( 10^{-5} \) atom fraction of impurity atoms. If one desires to do better than that which is commercially available, he must subsequently zone refine the material. Most of the quenching experiments reported in the literature have been performed with the 99.999% commercially pure gold.

The effect of impurity atoms on the loss of vacancies during the cooling period is presented in Figure 4. The significant feature of these curves is that when \( I_0 \) is greater than \( 10^{-6} \) atom fraction the rate of trapping vacant-
Figure 4
The Effect Of Impurity Atoms On The Athermal Loss Of Vacancies

\[ t = 10^4 \]
\[ a = 10^4 \]
\[ Z_a = 3 \times 10^{-4} \]
\[ \frac{dT}{dt} = 2 \times 10^{10} \text{C/sec.} \]
\[ E_H^0 = 0.82 \text{ eV} \]
\[ E_H^2 = 0.66 \text{ eV} \]
\[ E_H^0 = 0.70 \text{ eV} \]
\[ B_X = 0.15 \text{ eV} \]
\[ B_3 = 0.30 \text{ eV} \]

Impurity Trapping Of Vacancies
During The Cooling Period Of A Fast Quench
cies increases very rapidly. The significance of the impurity trapping effect is that the annealing kinetics can either be enhanced or retarded depending in part on the mobility of the complex and in part on the binding energy of the complex.

The effect of impurity concentration on vacancy trapping can be explained by considering the total number of jumps possible by a vacancy during the cooling period of the fast quench and then by considering the number of sites visited by a vacancy prior to being captured by the impurity atom. The average number of jumps possible by a single vacancy during a cooling period according to diffusion theory is:

\[ N = \int_{T_q}^{T_b} Z W \, dt \]  

(10)

where \( Z \) is the coordination number equal to 12 for gold; \( W \) is the jump frequency of a vacancy; \( t \) is the cooling period of the quench; \( T_q \) is the quench temperature taken equal to 1273\(^o\)K and \( T_b \) is the bath temperature taken equal to 273\(^o\)K. Eqn. (10) can be written as:

\[ N = -Z \frac{V_i}{\beta} \int_{T_q}^{T_b} \exp\left(-\frac{E_m}{kT}\right) \, dT \]  

(11)

if a linear relationship \( T = T_q - \beta t \) is assumed for the temperature where \( \beta \) is the cooling rate. This is a reasonable approximation to make, since a considerable portion of
the cooling curve is linear. By substituting $\phi = E_m/kT$
eqn. (11) becomes:

$$N = -Z \frac{\nu_1 E_m^1}{k} \int_{\phi_1}^{\phi_2} \exp -\phi d\phi$$  \hspace{1cm} (12)

Flinn (19) has shown that this eqn. can be integrated if $\phi_2$ is set equal to $\infty$; i.e., $T_D = 0^\circ K$. The number of jumps made from room temperature and $0^\circ K$ is negligible thus producing only an insignificant error in $N$. The approximate expression for $N$ becomes:

$$N = -Z \frac{\nu_1 E_m^1}{k} \left[ \frac{E_m^1/k T_d}{(E_m^1/k T_d)^2} \right]$$  \hspace{1cm} (13)

Taking $E_m^1$ to be equal to 0.82% ev and $\nu_1$ to be equal to $10^{13}$/sec a vacancy can make approximately $7 \times 10^{10}$ jumps during the entire quench period of the fast quench.

The rate at which vacancies are trapped at impurity atoms is proportional to the rate at which they encounter fresh sites that have not been previously visited. It has been shown (20) that the average number of distinct sites visited in $n$ jumps by a migrating vacancy prior to annihilation is given by:

$$S(n) = a + bn$$  \hspace{1cm} (14)

and for $n$ approaching infinity (15):

$$S(n) = bn$$  \hspace{1cm} (15)
The value of \( b \) for f.c.c. lattices is equal to \( .7437 \). Let \( I_0 \) be the concentration of impurity atoms in the system, then the rate of vacancy trapping by impurities is given by (21):

\[
\int_1^\infty n(-dP) = \int_0^\infty bI_0 n \exp(-bPn)dn = 1.345/I_0 (16)
\]

where \( P = \exp(-bI_0 N) \) is the probability of a jump to a new site, and \( I_0 \) is the probability that an impurity atom will be there. The average number of jumps until trapping ranged from \( .45 \times 10^4 \leq N \leq .45 \times 10^{10} \) assuming that only impurity atoms were the trapping centers. The conclusion is that every vacancy will encounter a large number of impurity atoms during the cooling period, and many of them will react to become vacancy-impurity complexes. It can further be concluded that when the binding energy of a vacancy-impurity complex is at least 0.15 eV zone refined material must be used in order to avoid complications in determining the energy of formation of vacancies, \( E_f \), the energy of migration of vacancies, \( E^1_m \), and the migration of a divacancy, \( E^2_m \).

The results of these calculations are summarized in Table 2.
TABLE 2

INFLUENCE OF IMPURITY ATOMS
ON THE LOSS OF VACANCIES DURING THE
QUenchING PERIOD

<table>
<thead>
<tr>
<th>$I_o$</th>
<th>$C_2$</th>
<th>$C_x$</th>
<th>$I_o/C_x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3 \times 10^{-10}$</td>
<td>$9 \times 10^{-14}$</td>
<td>$9 \times 10^{-14}$</td>
<td>$1/3 \times 10^4$</td>
</tr>
<tr>
<td>$1 \times 10^{-6}$</td>
<td>$9 \times 10^{-14}$</td>
<td>$3 \times 10^{-10}$</td>
<td>$1/3 \times 10^4$</td>
</tr>
<tr>
<td>$2 \times 10^{-5}$</td>
<td>$9 \times 10^{-14}$</td>
<td>$6 \times 10^{-9}$</td>
<td>$1/3 \times 10^4$</td>
</tr>
<tr>
<td>$3 \times 10^{-4}$</td>
<td>$9 \times 10^{-4}$</td>
<td>$8 \times 10^{-8}$</td>
<td>$3/8 \times 10^4$</td>
</tr>
</tbody>
</table>

The values reported in the table represent the concentrations of the particular point defect at the end of the quenching period. It can be observed that the concentration of divacancies remains constant in spite of the fact that the impurity level is increasing. The ratio $I_o/C_x$ remains constant with increasing impurity concentration up to $3 \times 10^{-4}$ atom fraction. When the concentration of vacancy-impurity complexes ceases to be a linear function of the impurity content, the quenching experiments cannot be interpreted in terms of a pure metal.

Impurity atoms will have a strong influence on the effective energy of vacancy formation when the binding energy of the vacancy-impurity complex is 0.15 eV or greater because of the impurity effect on the athermal loss of vacancies. Metals that have an impurity level of $10^{-5}$ to $10^{-4}$ atom fraction will have a probable error in the energy of forma-
tion of vacancies which is a considerable fraction of the unknown binding energy.

Isochronal annealing of gold

The isochronal recovery curves of metals containing excess point defects provide a qualitative map of the annealing characteristics. By increasing the heating rate in a linear fashion the concentration of point defects is obtained as a function of temperature. Sosin (9) was the first to demonstrate the usefulness of this type of annealing curve. When these curves are calculated using the appropriate values for the migration and binding energies for gold and when a constant heating rate experiment is simultaneously run, the calculated curves can be used to evaluate the experimental results. In order to ascertain fundamental information about the various clusters from these experiments, the value for \( E_m^3 \) must be known very accurately. The value reported by de Jong and Koehler (2) of 0.82 ± 0.03 eV appears to be the best value reported in the literature. The heating rate is an important variable in these experiments from a practical point of view. When the linear heating rate is sufficiently fast only the most mobile species will have sufficient energy to permit them to jump and react to form higher order clusters or to annihilate at sinks. Experimentally, it is an advantage to be able to avoid forming clusters of sizes larger than a trivacancy, for the annealing curve will not be as
complicated as it might be and only those activation energies for migration and dissociation of the basic defects will be detected. Chemical rate equations cannot be written that will adequately describe the segregation of impurities and their breakup, since there is no way to estimate the binding energy of the impurity clusters which tend to increase with cluster size. There will be a distribution of impurity segregate sizes that will decompose over the entire temperature range producing activation energies that are greater than one electron volt. Cattaneo and Germagnoli (10) observed an activation energy greater than 1.0 eV which they could not explain. Isochronal annealing curves were calculated for a heating rate equal to 0.416K/sec. The effect of $E_g$ and $Z_0$ on the recovery curve was made to assist in evaluating the experimental results.

In the calculations by Sosin (9) and Damask and Dienes (8), they assumed that the vacancy impurity complex was immobile or that it diffuses more slowly than the single vacancy. The experimental results for the migration of the copper-vacancy complex in gold suggested that the activation energy for motion of this complex is about 0.56 ± .03 eV. This suggests that the copper-vacancy complex migrates faster than either the single vacancy or the divacancy. The latter occurs when the vacancy interchanges atomic positions both with the adjacent impurity and with a lattice atom adjacent to both of them faster than with a normal lattice atom (8).
This behavior may be reasonable for the case of the copper-vacancy complex in gold, since a copper atom is slightly smaller than a gold atom and the strain energy associated with the interchange of a normal lattice atom. When the vacancy-impurity complex migrates faster than a monovacancy the process of vacancy-impurity complex annihilation leads to impurity segregation. A process for impurity segregation is described by the following chemical reactions:

\[ C_x \rightarrow \text{Sinks} + I_t \quad (17) \]
\[ C_x \rightarrow \text{Variable Sinks} + I_t + C_1 \quad (18) \]

where \( I_t \) is the fraction of trapped impurity atoms.

The isochronal recovery curves presented are those which best describe the experimental results for the quenched gold wires. The 800°C curve is presented in Figure 5. The initial impurity level was \( 3 \times 10^{-4} \) and \( B_x \) was 0.15 eV. The entire annealing process for the heating rate of 0.416°C/sec is described by the concentration plot as a function of temperature. The initial part of the curve shows an increase in the concentration of divacancies, trivacancies, and vacancy-impurity complexes at the expense of the excess vacancies. There is no apparent effect due to fixed sinks. The concentration of the different clusters increases to a maximum and then it finally decays towards zero concentration. In the same temperature range the excess vacancy concentration decreases towards equilibrium value very rapidly in spite of
Figure 5
Isochronal Annealing Curve For An 800°C Quenching Temperature
the fact that the decomposition of the clusters are feeding free vacancies back into the system. The decomposition of the clusters is a result of the shift in the ratios of the appropriate rate constants with increasing temperature. The position of the peaks of the cluster concentration with respect to the temperature scale is dependent on the value assigned to $B_2$, $B_3$ and $B_x$. Figure 6 illustrates the influence of $B_x$ on the maximum for the vacancy-impurity complex concentration. Increasing $B_x$ causes the concentration of $C_x$ to increase and the maximum of $C_x$ to shift to higher temperatures. The activation energy of motion of the vacancy-impurity pair has an additional effect on the position of the concentration maximum with respect to temperature. When $E_{cm}$ is increased to values greater than that for $E_{cm}$ the peak becomes broader and shifts to a higher temperature. The loss of vacancy-impurity complexes to sinks is virtually eliminated, since they are now relatively immobile. The effect of increasing $E_{cm}$ from 0.56 eV to 1.2 eV is illustrated in Figure 7.

When $E_{cm}$ was increased to 1.2 eV the vacancy concentration decreases to a minimum value and then increased asymptotically to the initial concentration of vacancies. The vacancy-impurity complex increased to a maximum and subsequently decayed slowly. This behavior of $C_x$ is quite different from the case where $E_{cm}$ was equal to 0.56 eV. The difference in behavior is probably due to the fact that when
Figure 6
The Effect Of Bx On The Position Of The Vacancy-Impurity Pair Maximum
The Effect of Sm on the Cx Maximum

Figure 7

Log Concentration vs. Temperature

Z_0 = 2.7 x 10^{-5}
I_0 = 3 x 10^{-4}
E_{A1} = 1.2 eV
E_{A2} = 0.82 eV
E_{A3} = 0.66 eV
\theta_1 = 0.15 eV
\theta_2 = 0.07 eV
\theta_3 = 0.21 eV
\beta = 0.416 K/sec.

Monovacancies

Vacancy-Impurity Complexes

Duvacancies
$E_m^C$ is high, $C_x$ is immobile and it does not become trapped by sinks. $C_1$ and $C_2$ do not decay as rapidly as when $E_m^C$ is 0.56 eV. $C_1$ increases as $C_x$ decreases due to the increase in the relative number of free vacancies that are in equilibrium with clusters in the absence of sinks previously encountered. $C_2$ and $C_3$ do not decrease rapidly because their concentration is a strong function of $C_1$.

The tempering curves for $700^\circ C$ and $600^\circ C$ are similar to the $800^\circ C$ curve. The basic difference lies in the concentration of the clusters that formed during tempering. The concentration of di- and trivacancies and vacancy-impurity complexes increases with higher values for the initial concentration of monovacancies, and this difference in concentration has a strong effect on the activation energy spectra of the real specimens through its influence on the effective diffusivity. The concentrations of divacancies and trivacancies are equal for the $800^\circ C$ quenching temperature when the maximum value for the divacancies and trivacancies is reached at their respective temperatures for the calculated $800^\circ C$ curves. The curves are presented in Figure 8. The quenching temperature of $800^\circ C$ appears to be a critical temperature for gold that is contaminated with $3 \times 10^{-4}$ atom fraction of impurity atoms. $800^\circ C$ was a critical quenching temperature for Koehler et al. (2). It was observed that if gold wires were quenched from $800^\circ C$ or above and subsequently annealed in the neighborhood of room tempera-
ture, the annealing curve was not exponential. Rather, the curve had an S-shape. Koehler, Seitz, and Bauerle (2) attributed the S-shape to the clustering of vacancies to form additional sinks. Silcox and Hirsch (7) and Cotterill (6) observed by electron transmission investigations that stacking fault tetrahedra are formed in gold quenched from 850°C and above. de Jong and Koehler (3) looked at the residual resistivity of gold specimens after an infinite anneal in the vicinity of 100°C and observed it to be very small. They subsequently concluded that clustering was negligible. For $I_0$ equal to $3 \times 10^{-4}$, the tempering curve calculations revealed that 800°C is indeed a critical quenching temperature for the formation of equal concentrations of divacancies and trivacancies. This finding supports the suggestion made by Seitz et al. that vacancy cluster formation is responsible for the S-shaped resistivity recovery curves. The critical quenching temperature for clustering depends on the concentration of impurity atoms in the specimen, since the number of jumps necessary to trap a vacancy by an impurity atom is equal to $1/b I_0$. Thus when $I_0$ is increased the critical quenching temperature for clustering is raised and, in a similar way, the recovery processes associated with vacancy clusters will be shifted to higher temperatures. The shift in the recovery processes to higher temperatures due to an increasing amount of impurity atoms will be illustrated when the experimental results are
discussed. The recovery processes are shifted to higher temperatures because of the same factors that are responsible for the S-shaped resistivity recovery curves. Namely, the sensitivity of vacancy cluster formation to the concentration of free vacancies in the metal lattice. That the free vacancy concentration effect is responsible for the shift to higher temperatures is illustrated by the fact that de Jong could normalize all of the recovery curves of gold specimens quenched in the range of 845°-950°C by dividing the annealing times by the time necessary to recover 50% of the quenched-in resistivity.

The effect of decreasing $I_0$ to $10^{-10}$ is to reduce the number of point sinks considerably. Decreasing the number of point sinks influences $C_1$ and $C_2$ in the same manner increasing $E_m$ to a value that made the complex immobile. There is an obvious earlier removal of vacancies when $I_0$ is approximately $10^{-4}$. Figure 9 illustrates the case of $I_0 = 10^{-10}$ where the point sinks in the metal have been reduced by a factor of $10^+6$. When dislocation sinks are neglected the vacancy concentration in equilibrium is approximately (9):

$$C_1 = \left[ \frac{K_{13}}{K_5 I_0 + K_{13}} \right] Z_0$$

(19)

Since $K_{13}$ increases more rapidly than $K_5 I_0$ at increasing temperatures, the rise in vacancy concentration approaches the initial value of $Z_0$ at high temperatures.
Figure 9
Tempering Curve For $I_0$ Equal To $10^{-10}$ And The Quenching Temperature Equal To 800°C
The tempering curves suggest that the decay of excess vacancies in the presence of impurity atoms involves several distinct resolvable stages which are a function of the physical parameters of the system. It is clear that all of the physical parameters interact to govern the many rate-determining mechanisms of recovery. Presumably, the best way to attempt to determine some of the physical parameters is to study a situation where the concentration of one defect is considerably greater than any other defect. The set of differential equations used for these calculations are a simplified set and they do not adequately describe the real situation. However, by choosing the heating rate to be very fast, the number of jumps made by a defect are limited, and the simplified differential equations adequately approximate the real situation. Thus the problems associated with describing impurity segregation are avoided.

Thermal stresses in a quenched gold wire

When a hot wire is immersed into a liquid, thermal stresses will be set up in the wire due to the temperature gradient between the surface of the wire and the center. There exists a critical quenching speed that will cause plastic deformation to take place. The critical quenching speed occurs when classical Newtonian cooling no longer occurs, i.e., when the temperature at the center of the wire no longer changes at the same rate as that of the surface. Care must be
taken not to exceed the critical quenching speed, since plastic deformation will cause dislocations to be generated.

Thermal stresses introduced into the wire by quenching can be computed by thermal-elastic theory provided the temperature distribution in the wire is known.

Formulas (22) for the radial and tangential stresses caused by a temperature gradient between the surface and the core of the wire are:

\[
\sigma_r = \frac{\varepsilon}{(1-\mu)} \left[ -\frac{1}{r^2} \int_0^r T(r,t) r \, dr + \frac{1}{a^2} \int_0^a T(r,t) r \, dr \right] \tag{20}
\]

\[
\sigma_\tau = \frac{\varepsilon}{(1-\mu)} \frac{1}{r^2} \int_0^r T(r,t) r \, dr + \frac{1}{a^2} \int_0^a T(r,t) r \, dr - \delta T(r,t) \tag{21}
\]

where \(\delta\) is the thermal expansion coefficient, \(a\) is the radius of the wire; \(T(r,t)\) is the temperature distribution; \(E\) is the modulus of elasticity; and \(u\) is Poisson's ratio. The maximum sheer stress in the wire is given by:

\[
\tau_{\text{max}} = \frac{\sigma_\tau - \sigma_r}{2} \tag{22}
\]

If the distribution of temperature over the radius of the wire is known, the integrals in the expression for \(\sigma_\tau\) and \(\sigma_r\) can be evaluated for each case. The temperature distribution for gold wire specimens was determined by an analog computer solution of the following partial differential equation for heat diffusion in an infinitely long cylinder:

\[
\frac{\partial T(r,t)}{\partial t} = D \frac{\partial^2 T(r,t)}{\partial r^2} + \frac{D}{r} \frac{\partial T(r,t)}{\partial r} \tag{23}
\]
D is the thermal diffusivity for gold and it is assumed to be constant with temperature. During the process of solving eqn. (23) on the analog computer, a number of different quenching rates were used. No temperature differential between the surface and the core of the wire whose diameter was 0.25 mm could be calculated until the quenching speed exceeded $10^6^\circ$C/sec. Thus, the critical quenching speed for the 0.25 mm gold wires used in the experiments is approximately $10^6^\circ$C/sec.

The temperature distribution, $T(r,t)$ for a wire quenched at approximately $2 \times 10^7^\circ$C/sec is presented in Figure 10, and the values for $\int T(r,t)rdr$ as a function of $r$ are presented in Figure 11. The maximum shear stress, $T_{\text{max}}$, was calculated for a constant $Dt$ value where the largest temperature difference existed between the surface and the core. $T_{\text{max}}$ as a function of $r$ is presented in Figure 12. The maximum value for $T_{\text{max}}$ was calculated to be approximately $7 \text{ Kg/M}^2 \times 10^6$. Since the yield strength of gold should be approximately $10^{-3}E$ ($E = 8.17 \times 10^7 \text{ Kg/M}^2$), the calculated maximum value for $T_{\text{max}}$ approaches the value necessary to cause plastic flow.

The conclusion to be drawn from this calculation is that thermal stresses are not an important factor in the interpretation of the quenching experiments when gold is the metal being studied, for the actual quenching rates cited in the literature never exceed $10^5^\circ$C/sec. (2)(3)(4)(6).
Figure 10
Temperature Distribution In A Wire Quenched
At A Rate Of Approximately $2 \times 10^7^\circ$C/sec.
Figure 11

Values for $\int T(r,t) \, rdr$ as a function of $r$.
Figure 12
Calculated Values for $\tau_{max}$ as a Function of $r$ for Gold Wires
EXPERIMENTAL METHOD

Quenched gold anneals by a series of successive reactions which in turn generate another (1-2). A physical property which is capable of distinguishing between the different recovery stages must be used to study the kinetics of the process, if all of the recovery processes are to be observed. Since this investigation is concerned with the influence of impurity atoms on the annealing kinetics of quenched gold, the physical property must be capable of quantitatively distinguishing between vacancies, vacancy clusters, vacancy-impurity complexes, and free impurity atoms. The experimental method, i.e., the manner which the annealing temperature is changed, is determined by the behavior of the effective rate constant, \( K_e \), with respect to \( I_0 \) and temperature.

Damask and Dienes (8) discussed the behavior of \( K_e \) in their general treatment of vacancy decay, and showed that \( K_e \) was not a characteristic rate constant which describes the decay of a concentration of reaction processes. The solution of the differential equations for the chemical reactions given by expressions (1) and (2) show that there is an initial transient which lasts for only a short time when the vacancies come into equilibrium with the vacancy-impurity complexes. After the initial transient is terminated, the
vacancies decay exponentially. The differential equations can be solved for a steady state on \( C_x \). The equations are:

\[
\frac{dC_x}{dt} = K_1 I_0 C_1 - K_2 C_x \tag{24}
\]

\[
\frac{dC_1}{dt} = K_1 I_0 C_1 + K_2 C_x - K_3 C_1 \tag{25}
\]

\( I_0 = I_0 - C_x \) was used for the concentration of free impurity atoms in the above equations. The extent of the annealing process is given by the next differential equation:

\[
\frac{dN}{dt} = \frac{d(C_1 + C_x)}{dt} = -C_1 K_3 \tag{26}
\]

Using the law of mass action for expression (1), \( C_x \) can be written as:

\[
C_x = \frac{K_1}{K_2} \frac{(I_0 C_1)/(1 + K_1 C_1)}{C_1} \tag{27}
\]

The substitution of eqn. (27) into eqn. (26) followed by an integration gives the result:

\[
\ln \frac{C_1 + K I_0}{K I_0} - \frac{K I_0}{1 + K C_1} \ln(1 + K C_1)/C_1 + A = -K_3 t \tag{28}
\]

where \( A \) is a constant of integration. Since we can assume \( I_0 \gg C_x \) eqn. (26) can be simplified to:

\[
\frac{C_x}{C_1 I_0} = \frac{K_1}{K_2} = K \tag{29}
\]
Integration after the substitution of eqn. (29) into eqn. (26) gives:

\[ \ln \frac{c_1}{c_1^0} = -K_e t \]  \hspace{1cm} (30)

where \( K_e \) is equal to \( K_3/1 + K_{10} \) and \( c_1^0 \) is the concentration of vacancies just after the initial transient. \( K_e \) does not in general follow the Arrhenius equation even though such relationships have been observed experimentally by Cattaneo and Germagnoli (10). \( K_e \) is an effective rate constant that contains the ratio of two temperature dependent rate constants multiplied by the concentration of impurity atoms. Damask and Dienes (8) have shown both linear and nonlinear behavior for Arrhenius plots of \( K_e \), and they have concluded that the change of slope technique (14) and other isothermal techniques can not be used to determine meaningful activation energies. This is particularly true when the activation energies are not widely separated. An alternate experimental technique must be used for the determination of the activation energy of a particular recovery process.

Sosin (9) has shown by analog computer solutions of chemical reactions (1) and (2) that the entire annealing process can be studied in complete detail by continuously heating the quenched specimens. Electrical resistivity measurements are not suitable for this type of experiment, because the measurement must be made at liquid helium temperature.

Electrical resistivity measurements are sensitive to the
different defects (Mathiessen's rule) in that the scattering of electrons by an impurity and all other electron scattering events in the crystal are independent of each other, but thermal scattering of electrons will dominate the other scattering events at temperatures above 4.2°.

Another possible method for studying the annealing process is a measurement of the change of absolute thermoelectric power due to defects and impurities, since the thermoelectric power depends on the way in which the mean free path and the effective mass of the electrons, which determine \( \sigma(E) \), vary with energy.

The thermoelectric power of a metal is due to two mechanisms (23). The first mechanism is referred to as the electronic component of the absolute thermoelectric power and the second mechanism is called the phonon-drag component. The electronic portion of the absolute thermoelectric power for a pure metal is given by the expression (24):

\[
S_e = \frac{\pi^2 k^2 T}{3eE_f} \left[ \frac{\partial \ln \sigma(E)}{\partial \ln E} \right]_{E_f} \tag{31}
\]

where \( \sigma(E) \) is the conductivity of electrons of energy \( E \), \( E_f \) is the Fermi energy, \( k \) is Boltzmann's constant, \( T \) is the absolute temperature, and \( e \) is the absolute value of the elementary charge. The conductivity of a metal has the form (25):

\[
\sigma = \frac{e^2 LA}{\pi^3 \hbar} \tag{32}
\]
where $A$ is the area of the Fermi surface and $L$ is the mean free path between electrons of energy $E_F$. $L$ is characteristic of the interactions of conduction electrons with lattice imperfections (phonons, vacancies, impurities, etc.). In accordance with eqn. (31), the electronic thermoelectric power, $S_e$, is related to the energy dependence of $L$ and $A$ at the Fermi energy. The result is that $S_e$ is more sensitive to lattice defects than electrical resistivity.

The phonon-drag portion of the thermoelectric power undergoes changes due to impurities and defects which manifest itself through the effect of imperfections on reducing the phonon-phonon relaxation time (26). The phonon scattering mechanisms as determined by Huebener (27) for point defects (vacancy clusters, vacancy-impurity pairs, etc.). Since each particular defect has its own peculiar strain pattern, it is possible to detect annealing stages associated with each defect. Also in this respect the thermoelectric power is more sensitive to lattice defects than electrical resistivity. Changes in the absolute thermoelectric power caused by point defects seem to provide a more sensitive method for elucidating the decay of vacancies in the presence of free impurity atoms. The change in the absolute thermoelectric power, $\Delta S$, can be determined by measuring the thermoelectric force developed between an annealed metal and a quenched metal of the same purity.

According to Mayer and Mayer (28), the thermoelectric...
force developed between metals A and B having junction temperatures at \( T_1 \) and \( T_2 \) is:

\[
\theta_A - \theta_B = \frac{\pi^2 k^2}{3eE_f} \int_{T_1}^{T_2} \left[ \frac{1}{E_A} \left( 1 + \frac{L_A^1 L_A}{L_A} \right) - \frac{1}{E_B} \left( 1 + \frac{L_B^1 L_B}{L_B} \right) \right] dT \tag{33}
\]

where \( E_A \) and \( E_B \) are the energies of the conduction electrons near the Fermi energy; where \( L_A^1 \) and \( L_B^1 \) are equal to \((\partial L_A/\partial E)_{E_f}\) and \((\partial L_B/\partial E)_{E_f}\) for metals A and B respectively. Let A represent the quenched metal and let B represent the annealed metal. Since metal A and metal B have the same chemical composition and differ only in the concentration of point defects, \( E_A \) can be assumed to be equal to \( E_B \). Thus eqn. (33) can be simplified to read:

\[
\theta_A - \theta_B = \frac{\pi^2 k^2}{3eE_f} \int_{T_1}^{T_2} \left( \frac{E}{L_A} - \frac{E}{L_B} \right) dT \tag{34}
\]

The change in the absolute thermoelectric power becomes:

\[
\Delta s = \frac{d(\theta_A - \theta_B)}{dT} = \frac{\pi^2 k^2}{3eE_f} \left[ \frac{\partial \ln(L_A/L_B)}{\partial \ln E} \right]_{E_f} \tag{35}
\]

Writing \( L_A = L_B + \Delta L \), we see that:

\[
\frac{L_A}{L_B} = 1 + \frac{\Delta L}{L_B} \tag{36}
\]

where \( \Delta L \) is the change in the mean free path of the conduc-
tion electrons due to excess point defects. From the fact that \( \ln(1 + x) = x \) when \( 0 < x << 1 \) eqn. (35) can be written as:

\[
\Delta s = \frac{\pi^2 k^2 T}{3eE_f} \left[ \frac{\partial (\Delta L/L_B)}{\partial E} \right]_{E_f}
\]  

(37)

Gerstriken (18) used the thermoelectric power method to determine the energy of formation of vacancies in silver containing dissolved oxygen and the energy of migration of single and divacancies without realizing the fundamental principles. Their choice of this method was not based on the fact that the thermoelectric power is more sensitive to changes in the defect structure, than resistivity, but rather, it was based on the fact that electrical resistivity measurements did not provide any meaningful energies of motions for point defects.
ANALYSIS OF KINETIC DATA

Because the quenched specimens had the shape of a cylinder, it might be assumed that a solution of the radial diffusion equation would yield an expression for the diffusion coefficient, \( D \), of the form (28):

\[ (C_0 - C_t/C_0) = 4(Dt/r^2)^{1/2} \pi^{1/2} - (1/3)^{1/2}(Dt/r^2)^{3/2} + \ldots \]  \hspace{1cm} (38)

and for short times (10 minutes) eqn. (38) simplifies to:

\[ D = (C_0 - C_t/C_0)^2 \pi r^2/16t \]  \hspace{1cm} (39)

where \( r \) is the radius of the specimen and \( t \) is the annealing time at constant temperature. Since the thermoelectric force is proportional to the concentration of processes, eqn. (14) can be written in the form:

\[ D = (E_0 - E_t/E_0)^2 \pi r^2/16t \]  \hspace{1cm} (40)

where \( E \) is the thermoelectric force. Experiments on the diffusion of vacancies have shown that only an insignificant number are annihilated at the surface, so it is more appropriate to use an expression for the diffusion coefficient derived by Faingold, Gerstriken and Khaletskii (29) for annihilation at internal sinks. Their expression for \( D \) has the form:

\[ 2(Dt/r^2)^{3/2} - 3(Dt/r^2)^{1/2} + (C_0 - C_t/C_0)^{1/2} = 0 \]  \hspace{1cm} (41)
where \( r \) is the diffusion distance in this expression, and for short times eqn. (16) simplifies to:

\[
D = \left( E_0 - \frac{E_t}{E_0} \right)^2 \pi r^2 / 9t \tag{42}
\]

Although eqn. (42) is similar to eqn. (40) in form, eqn. (40) for the diffusion coefficient cannot be used because it is not independent of specimen shape, and in principle, it is not related to the physical process. It should be pointed out that \( D \) is an effective diffusivity, since there is usually more than one simultaneously diffusing species. \( D \) can be defined by the following relationship:

\[
D \frac{\partial Z}{\partial x} = \sum_{i=1}^{n} J_i \tag{43}
\]

where \( \frac{\partial Z}{\partial x} \) is the total void gradient in the \( x \) direction and \( J_i \) is the flux of voids of a particular with type defect.

The local void concentration \( Z \) is given by:

\[
Z = (C_1 + 2C_2 + 3C_3 + C_x + \ldots) \tag{44}
\]

By using the thermoelectric force method, one can determine \( D \) as a function of temperature from continuous curves of the change of thermoelectric force with annealing temperature for constant heating rate experiments, and from the temperature dependence of \( D \) the activation energy spectrum can be determined for the annealing process. Assuming that \( D \) does not change appreciably with concentration of point defects over a particular temperature range and writing the
temperature function as $T = \beta t$ where $\beta$ is the heating rate, one can write eqn. (17) as:

$$\left( E_0 - E_t/E_0 \right)^2 = \gamma t$$

or

$$\left( E_0 - E_t/E_0 \right)^2 = \gamma T/\beta$$

(45)

where $\gamma$ is a proportionality constant.

Differentiating eqn. (40) with respect to temperature yields:

$$\gamma = -2\left( E_0 - E_t \right)/E_0^2 \frac{dE_t}{dT}$$

(46)

The substitution of eqn. (46) into eqn. (45) yields:

$$t = -\frac{(E_0 - E_t)}{2E_0^2} \beta \frac{dE_t}{dT}$$

(47)

and the new expression for the diffusion coefficient becomes:

$$D = -\frac{2\pi r^2 \beta (E_0 - E_t)}{9E_0^2} \frac{dE_t}{dT}$$

(48)

This expression for $D$ now contains a term, $\frac{dE_t}{dT}$, which is the change in absolute thermoelectric power due to lattice defects.

In practice, a graph of thermoelectric force as a function of temperature can be determined for a constant rate of heating. This curve can then be graphically differentiated by means of a magnifying glass and a flat mirror. This technique gives the slope of the line perpendicular to the tangent of the curve, and $\frac{dE_t}{dT}$ is correspondingly the
negative of the reciprocal of this slope. The change in the absolute thermoelectric power can be obtained to an accuracy of about 0.1%. A schematic curve of thermoelectric force as a function of $T$ is given in Figure 13.

In general, the average diffusion distance $r$, appearing in eqn. (48) does not remain constant over the entire temperature range of the experiment. However, over the narrow temperature range where a constant activation energy is determined, $r$ can be assumed to remain constant.

The thermoelectric force as a function of temperature curves had a number of distinct recovery stages which are related to reactions between point defects and sinks that are energetically favorable. Each stage has its own effective activation energy, $E_m$, which is described by:

$$E_m = kT_1T_2/(T_2-T_1)/\ln \left[ \frac{\text{Rate}(T_2)}{\text{Rate}(T_1)} \right]$$

and the kinetics of the entire recovery process can be said to be distributed in activation energy. The kinetics of processes distributed in activation energy have been theoretically discussed by Primak (30-32) for cases involving radiation damage experiments. Processes distributed in activation energy occur because a number of different species are present which anneal independently of each other. Each defect can react with more than one sink having different chemical affinities for the defect. When the affinities for defect trapping are not widely separated there will only be a gradual change in the measured activation energy until a recovery
Slope At $(E_i T_i) = \frac{-1}{m}$

Temperature

Schematic of thermoelectric force as a function of temperature for an isochronal anneal.

$D = \frac{2\pi T^2 B}{9E_0^2} \left[ E_0 - E_i \right] \frac{dE_i}{dT} \text{cm}^2/\text{sec}$

Schematic illustrating the Arrhenius behavior of $\ln D$ for the different recovery stages of the isochronal anneal.

Figure 13
Schematic Curve Of Thermoelectric Force As A Function Of Temperature
Schematic illustrating an activation energy spectrum as a function of temperature for an isochronal anneal.

Figure 14
Schematic Behavior Of Activation Energy As A Function Of Temperature
Stage is reached which has a relatively high trapping energy. When the activation energy for a process which has a high trapping energy is observed to occur over a very narrow temperature range, then this energy is defined as a characteristic-activation energy provided it is followed by processes with decreasing activation energy. In order to determine the characteristic-activation energy, $E_m$ is measured as a function of time or temperature depending on whether or not the experiments are isothermal or constant heating rate experiments. The method for analyzing the experimental data is schematically illustrated in Figure 13 and Figure 14.

Processes distributed in activation energy are generally treated as chemical rate processes (21)(30). A list of chemical reactions and their rate constants is given in table 1 which are pertinent to quenched gold containing impurity atoms. These reactions will be used to interpret the experimental results.
EXPERIMENTAL APPARATUS AND PROCEDURE

Any experimental study of the kinetic processes involved in the decay of excess vacancies requires the determination of the effective rate constant, $K_e$, for each successive chemical reaction. The change of the absolute thermoelectric power of a metal has been determined to be more sensitive to the different point defects than electrical resistivity. Also, since $K_e$ determined by the isothermal annealing methods does not in general follow the Arrhenius equation, another technique must be used to develop the characteristic activation energies of the annealing process. The experimental studies of Blatt et al. (26) and Huebener (27) elucidate the fundamental principles underlying the use of the change of the absolute thermoelectric power for studying point defect reactions in quenched metals. Because of the sensitivity of the absolute thermoelectric power to lattice defects, this method was chosen to determine the tempering curves. The type of equipment and experimental procedures used are outlined in the paragraphs below.

The apparatus used in this work was patterned after a similar device first used by Huebener (27). The specimen assembly is shown schematically in Figure 15. The assembly consists of a cryostat and a specimen fixture. The cryostat
Figure 15
Schematic Of Specimen Assembly
contains a thin-walled stainless steel tube which was open at the top so that the specimen assembly can be inserted into the cryostat. The specimen fixture consists of a heat sink made of a copper plate approximately 4 mm thick which is brazed to an elbow attached to an open tube extending out of the cryostat. The open tube is brazed to a cap which makes a vacuum seal when the specimen fixture is inserted into the cryostat. Provisions are made in the cap to bring the electrical connections for the furnace and potential leads attached within the cryostat to the outside. The heat sink was painted with a thin coat of a General Electric R.T.V. No. 106 Silicone Rubber adhesive to provide electrical insulation from the heat sink. The specimen jig shown in Figure 16 is fixed to the sink by screws, and the specimen wires are held against the heat sink with a second copper plate. The heater consists of two hollowed out copper blocks which contains two heaters made of .25 mm nichrome wire of approximately 22 ohms total resistance. The copper blocks were clamped around the hot junction of the quenched and annealed gold wire. Thermocouples were attached to the copper block for temperature measurement and control, and another thermocouple (Iron-Constantan) was attached to the heat sink. The thermocouple wire had a diameter of 0.003 in. The thermocouple voltages were measured with a Honeywell Thermocouple Potentiometer Model 2713. The thermocouple wire was checked at the temperature of liquid nitrogen and ice water, and the
Figure 16
Scheme Of Specimen
voltage was found to deviate by less than 0.2% from the tables compiled by R. L. Powell (33).

Liquid nitrogen was used to cool the cryostat and the heat sink of the specimen assembly. Liquid nitrogen was pumped onto the heat sink at a rate of approximately one liter per minute, and as the temperature of the hot junction was raised the temperature shift of the heat sink was measured to be about 1°C over the temperature range of 77K to 500K. The annealed specimen wires were welded to extensions of 99.999% pure gold wire which lead out of the cryostat.

The specimen materials were 99.999% and 99.995% gold wire of 0.25 mm diameter which was obtained from Leytess, Inc., New York, N.Y. The specimen consisted of an annealed wire and a quenched wire attached backside to a stainless steel holder. Potential leads (0.05 mm diameter) were attached to short pieces of gold lead wire (0.375 mm diameter) which were attached to the holder. These potential leads were used to determine the specimen temperature. Each wire was bent as shown in Figure 16 to obtain a uniform temperature on heating and to assure good thermal contact with the heat sink.

After mounting, each of the specimen wires was annealed for 15 minutes at 900°C. Each specimen was cooled gradually by slowly reducing the heating current. The specimen that was to be quenched was heated again for two minutes prior to immersion into a water tank. The electrical circuit for the
for the quenching experiments is shown in Figure 17. The experiments were carried out for quench temperatures of 800°, 700°, and 600°C. A solid state switching device was used to switch the heating current off as soon as the wire touched the water, and the quenching rate for the wires was observed to be about $2 \times 10^7$°C/sec.

The specimen was rinsed with isopropyl alcohol after quenching and stored in liquid nitrogen. The specimens were subsequently spot welded while they were still cold, and they remained at room temperature less than three minutes after quenching. After sealing the stainless steel tube the cryostat was filled with dry helium gas and immersed into liquid nitrogen. As soon as the furnace surrounding the spot weld reached 77°K, the specimen was heated at a constant rate.

The measured resistivity of the 99.999% gold at room temperature ($\sim 25°C$) was $2.26 \times 10^{-6}$ ohm cm which is consistent with the lowest values reported for gold and the resistance ratio between room temperature and liquid helium temperature was between 1000 and 2000 for specimens annealed for 15 minutes at 900°C in air. The resistivity of the 99.995% gold at room temperature was $2.3 \times 10^{-6}$ ohm cm and the resistance ratio between room temperature and liquid helium temperature was 500-1000. A quantitative O.E. Spectrographic Analysis of the gold wires was made to estimate the ppm of impurity atoms present. The results showed that
Schematic of Heating Circuit

Figure 17
Schematic Of Heating And Quenching Circuit
the 99.999% gold had approximately 1.5 ppm copper and approximately .7 ppm silver present. The analysis of the 99.995% gold showed that approximately 4 ppm copper and 1 ppm silver to be present. The error in the values was estimated to be ± 3 ppm.

Two heating rates of 0.416°K/sec and 0.167°K/sec were used in these experiments. The temperature at any time t is given by the expression:

\[ T = t \beta + 77^\circ K \]  

(50)

where \( \beta \) is the heating rate.

The measurement of the thermoelectric force was made with a Keithley 148 nanovoltmeter. The Model 148 Nanovoltmeter measures very small dc potentials from low impedance sources. These are found in fundamental or applied research, laboratory standards work, cryogenic experiments and instrument development for space research. Typical uses include measuring small temperature differences and small temperature changes indicated by thermocouple outputs, small changes in conductance, super conductivity in the \( 10^{-6} \) ohm range, and thermopile outputs in narrow band spectrum analysis. Other uses are determining the thermoelectric power of metals, conducting Hall effect studies, and making Bolometer measurements. This instrument has an accuracy of 1% of full scale on all ranges. This accuracy includes noise levels. The stability of this instrument is 10 nanovolts per 24 hours,
and the long term drift is non-cumulative. The input noise is less than one \(1\) nanovolt peak-to-peak \(\left(10^{-9} \text{V}\right)\), and the resolution of the amplifier is greater than one \(1\) nanovolt. The resolution of the instrument is sufficiently good so that minute changes in the absolute thermoelectric power of the specimen can be detected. The output of the nanovoltmeter is one volt on all ranges, and this output was subsequently fed into a Honeywell Class 16 recorder which has an accuracy of \(0.25\%\) of full scale. A check on the system was made by measuring the thermoelectric force with a microvolt potentiometer capable of resolving \(0.01\) microvolt. The agreement between the two methods was good, but the higher sensitivity of the nanovoltmeter was advantageous to bringing out the details of the annealing curves. Several runs were made for each quench temperature, and the data was observed to be very reproducible. The leads to the nanovoltmeter and accessories were carefully screened from electric and magnetic fields by a special low-thermal input cable called Inter-8-Weave manufactured by the Perfection Mica Company. This cable reduces the signal noise ratio over the conventional twisted pair method by about 20 d.b. in the \(10^{-9}\) to \(10^{-8}\) V range. All measurements were made in a copper wire screened cage which was grounded to a copper bar driven into the ground.

The main error in determining the activation energies for the different reactions arises from the error in the
measurement of the thermoelectric force, since the values of the thermoelectric force to be measured are small. The accuracy of the nanovoltmeter is 1% so the error involved in determining the activation energies should not exceed 3% of the calculated quantity.
EXPERIMENTAL RESULTS AND DISCUSSION

The complete annealing process was studied by means of constant heating rate experiments that allowed the complexity of the annealing process to be minimized by selecting a heating rate that was sufficiently fast to permit only the most mobile species to jump and to form only the simplest clusters. A heating rate of 0.416°K/sec was found to be fast enough to simplify the annealing process so that the differential equations adequately described the annealing process. The time spent by each defect in the neighborhood of a given temperature is approximately equal to the reciprocal of the linear heating rate. By controlling the time spent in the neighborhood of a given temperature the degree of defect clustering can be minimized. The $E_m$'s that were calculated from the data of the rapid heating experiments were interpreted with the aid of the solutions for the differential equations. When the heating rate was decreased to 0.167°K/sec the tempering curves became so complicated that the differential equations would no longer approximate the real situation. The differential equations broke down because of the problem of describing the rate of decomposition of impurity clusters which are distributed in both size and binding energy. The results of the experimental tempering curves are subsequently described.
Two compositions of gold were quenched from 800\(^\circ\)C, 700\(^\circ\)C, and 600\(^\circ\)C, and the effective energies of motion, \(E_m\), and the energies of decomposition of defect clusters, \(E_d\), were determined over a wide range of temperatures. Figures 18 - 23 show the results for the gold wires that were quenched from the above stated temperatures and continuously annealed from 77\(^\circ\)K to 375\(^\circ\)K. \(E_m\) at each temperature point was calculated according to eqn. (49). The rates of annealing were determined by a technique previously applied by Gerstriken et al. (18), namely, one in which all of the points were used to determine the effective rate at each point of temperature. Rate \((T_1)\) and Rate \((T_2)\) are given by \(\frac{2\pi\beta(E_0-E_t)(dE_t)}{9E_0^2} (\frac{dT}{dt})_1\) and \(\frac{2\pi\beta(E_0-E_t)(dE_t)}{9E_0^2} (\frac{dT}{dt})_2\) respectively. The activation energies generally increased from a very low value to a maximum value followed by a drop in activation energy. Whenever a maximum value was reached in the activation energy spectrum it was considered to be a characteristic activation energy that corresponded to a unique energy of migration or either and energy of decomposition.

In the annealing experiment single vacancies, divacancies, vacancy-impurity complexes, and higher order complexes will be present in the early stage of annealing. The higher order complexes will start to disappear when the ratio of \(T_3/T_2\) approaches unity where \(T_3\) is the average time required for a
Figure 18
Thermoelectric Force As A Function Of Temperature
For 99.999% Gold Quenched From 800°C
Figure 19
Thermoelectric Force As A Function Of Temperature
For 99.995% Gold Quenched From 800°C
Figure 20
Thermoelectric Force of 99.999% Gold as a Function of Temperature Quenched from 700°C

700°C Quench Temperature
99.999% Gold
Figure 21
Thermoelectric Force Of 99.995% Gold As A Function Of Temperature Quenched From 700°C
Figure 22
Thermoelectric Force of 99.999\% Gold As A Function Of Temperature Quenched From 600°C
Figure 23
Thermoelectric Force of 99.995% Gold As A Function Of Temperature Quenched from 600°C

600°C Quench Temperature
99.995% Gold

THERMOELECTRIC FORCE (MICROVOLTS)

TEMPERATURE (°K)

0
1.0
2.0

100 200 300 400
divacancy to encounter a single vacancy, $T_2$ is the time necessary to dissociate a divacancy. The ratio of $T_3/T_2$ is:

$$\frac{T_3}{T_2} = \frac{16V_2}{7V_1} C_1 \exp \left( \frac{E_m^1 + B_2 - E_m^2}{kT} \right)$$

(51)

As $C_1$ tends to 0 and as the temperature increases, the clusters begin to dissociate. Clustering can be eliminated by quenching from a temperature where $C_1$ is less than some critical concentration. 800°C has been determined to be a critical quenching temperature for 99.999% gold. The recovery of the quenched-in resistivity is supposed to be exponential for quenches below 800°C, but there has been considerable disagreement among the numerous investigators about this point. The time for the resistivity to decay to 50% of the initial value has varied considerably for gold specimens having the same nominal composition. The differing annealing kinetics after quenching seem to be due to impurity differences (34)(35). The 700°C quenches were probably low enough to prevent vacancy cluster formation, and at the same time, it should serve to enhance the impurity-vacancy interactions. The quenches from 600°C should definitely eliminate the possibility of vacancy clustering; however, Mori, Meshii and Kauffmann (16) solved the differential equations for isothermal recovery of vacancies and concluded that clustering was possible for quenches from below 500°C. Their conclusion depends on their choice of parameters ($E_m^1 = 0.80$ eV, $E_m^2 = 0.70$ eV and $B_2 = 0.3$ eV), since the condition for clustering depends on ($E_m^1 +$
B_2 - E_m^2) rather than simply B_2. The activation energy spectra for the three quenching temperatures for both compositions of the gold specimens will be discussed below.

**Activation energy spectra for gold tempered at a heating rate of 0.416°K/sec.**

The activation energy spectra for the three quenches are summarized graphically in Figures 24, 25, and 26, and the values are tabulated in tables 3 and 4. The graphical presentation illustrates the important fact that increasing the impurity content of gold shifts the activation energy spectra to higher temperatures. The quenches from 800°C had two characteristic peaks in the activation energy spectrum. The first peak had an E_m of .56 ± .02 eV for the low purity material which occurred between 217° and 244°K, and for the high purity material the peak occurred between 169° and 185°K. The next characteristic peak for the low purity material occurred between 316° and 357°K with an activation energy of 0.95 ± .03 eV. This peak was not observed for the high purity material for the same temperature range covered in the experiment. The high purity material had a characteristic activation energy of 0.89 ± .03 eV between 293° and 306°K. Other peaks occurred in the activation energy spectra for the 800°C quenches. These peaks are probably related to the mixed diffusion of defects. The impure specimen had a peak with an activation energy of 0.65 ± .02 eV. This had been
Figure 24
Activation Energy Spectra For Quenches From 800°C
Figure 25
Activation Energy Spectra For Quenches From 700°C
Figure 26
Activation Energy Spectra For Quenches From 600°C
### TABLE 3

**DISTRIBUTION OF ACTIVATION ENERGIES FOR THREE QUENCH TEMPERATURES**

**MINT GOLD (99.995%)**

**QUENCH TEMPERATURES**

<table>
<thead>
<tr>
<th>Temperature °K</th>
<th>Activation Energy electron volts/atom</th>
<th>Temperature °K</th>
<th>Activation Energy electron volts/atom</th>
<th>Temperature °K</th>
<th>Activation Energy electron volts/atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>1073°K 800°C</td>
<td></td>
<td>973°K 700°C</td>
<td></td>
<td>873°K 600°C</td>
<td></td>
</tr>
<tr>
<td>84-125</td>
<td>0.05</td>
<td>89-109</td>
<td>0.01</td>
<td>81-134</td>
<td>0.02</td>
</tr>
<tr>
<td>132-162</td>
<td>0.16</td>
<td>117-175</td>
<td>0.03</td>
<td>145-166</td>
<td>0.11</td>
</tr>
<tr>
<td>190-211</td>
<td>0.35+0.01</td>
<td>175-222</td>
<td>0.08</td>
<td>176-236</td>
<td>0.03</td>
</tr>
<tr>
<td>217-244</td>
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<td>0.56+0.02</td>
<td>246-264</td>
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<tr>
<td>252-277</td>
<td>0.25</td>
<td>278-302</td>
<td>0.06</td>
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<tr>
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<td>0.12</td>
<td>284-309</td>
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<tr>
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<td>0.33</td>
<td>318-325</td>
<td>0.26+0.02</td>
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TABLE 4
DISTRIBUTION OF ACTIVATION ENERGIES FOR THREE QUENCH TEMPERATURES
99.999% GOLD

QUENCH TEMPERATURES

<table>
<thead>
<tr>
<th>Temperature (^\circ\text{K})</th>
<th>Activation Energy (\text{volts/atom})</th>
<th>Temperature (^\circ\text{K})</th>
<th>Activation Energy (\text{volts/atom})</th>
<th>Temperature (^\circ\text{K})</th>
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<td>.03</td>
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<td>.03</td>
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<td>.03</td>
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<tr>
<td>236-254</td>
<td>.27</td>
<td>263-299</td>
<td>.10</td>
<td>256-265</td>
<td>0.64±.03</td>
</tr>
<tr>
<td>265-293</td>
<td>.13</td>
<td>299-337</td>
<td>.31</td>
<td>273-311</td>
<td>0.11</td>
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<tr>
<td>293-306</td>
<td>.89±.03</td>
<td>337-365</td>
<td>.64</td>
<td>311-340</td>
<td>0.55±.03</td>
</tr>
<tr>
<td>312-321</td>
<td>.80±.03</td>
<td>372-391</td>
<td>.97±.03</td>
<td>343-374</td>
<td>0.41±.03</td>
</tr>
<tr>
<td>328-346</td>
<td>.06</td>
<td>382-426</td>
<td>0.67±.03</td>
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<tr>
<td>337-373</td>
<td>.66±.03</td>
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</table>
reported to be equal to the migration energy of a divacancy. $E_m^2$ occurred between $279^\circ - 304^\circ K$. The concentration of divacancies reaches its maximum value around $300^\circ K$ for this experiment, and because the jump frequency of a divacancy is about 300 times that of a single vacancy, this activation energy can be attributed to the migration energy of a divacancy. de Jong and Koehler (3) report a value for $E_m^2$ of $0.66 \pm 0.06$ eV, so our value is within the uncertainty of their results. A value for $E_m^2$ was not observed for the high purity material, because within the same temperature range divacancy decomposition should occur for the high purity material. Values of $E_m$ less than that of $E_m^2$ and less than that of the characteristic activation energies are related to mixed diffusion of point defects. The mobile species in this experiment are reasoned to be monovacancies, divacancies and vacancy-impurity complexes.

The quenches from $700^\circ C$ had several characteristic activation energies. The maximum characteristic activation energy occurred between $348^\circ$ and $366^\circ K$ with an activation energy of $0.93 \pm 0.03$ eV for the low purity material. A value of $0.97 \pm 0.03$ eV was observed for the high purity material to occur between $372^\circ$ and $391^\circ K$. These two values are related to the same process, namely, the decomposition of the vacancy-impurity complex, and the values are within the uncertainty of the experiment. The high purity material had an activation energy of $0.64 \pm 0.03$ eV between $337^\circ - 365^\circ K$. It is
not likely that this energy of migration is equal to $E_m^2$, since $\tau_s/\tau_2$ is greater than unity in this temperature range. $E_m = 0.64$ eV is probably an effective diffusivity due to mixed diffusion of $C_x$, $C_1$, and possibly $C_2$. An activation energy of $0.56 \pm 0.02$ eV was observed in the temperature range of $232^\circ - 245^\circ K$. The same activation energy occurred for the $800^\circ C$ quench over the same temperature range for the low purity material. This value is probably the energy of migration of the vacancy-impurity complex $E_m^C$. An identical value was observed for the high purity material between $169^\circ$ and $185^\circ K$.

The activation energy spectrum for the $600^\circ C$ quenches was distributed in activation energy up to a maximum $0.83 \pm 0.03$ eV for the low purity material, this corresponds to the activation energy of motion for a monovacancy, and it is within the uncertainty of the value of $E_m^1 = 0.82 \pm 0.03$ eV reported by de Jong and Koehler (3). $E_m^1$ occurred between $344^\circ$ and $349^\circ K$ and it is in the temperature range where one expects monovacancy diffusion. The high purity material did not produce an activation energy for $E_m^1$, but it produced a characteristic activation energy of $0.67 \pm 0.02$ eV which is well within the uncertainty of the values reported in the literature for $E_m^2$. The value for $E_m^2$ occurred between $256^\circ$ and $265^\circ K$ and this is close to the temperature range for the $800^\circ C$ quench of the impure material ($279^\circ - 304^\circ K$) which had a value of $0.65 \pm 0.02$ eV for $E_m^2$. Impurity effects shift the
$E_m$'s to higher temperatures, so that this particular value can be taken to be that for $E_m^2$. The formation of clusters predicted by Mori, Meshii and Kauffman for quenches as low as 500°C supports this conclusion.

Annealing involving the slow heating rate

The quenching experiments were repeated using a slow heating rate of 0.167°K/sec, and the effective activation energy, $E_m$, was determined for each recovery stage. The effective activation energies that were calculated were unexpectedly high, and they could not be interpreted with the aid of calculated tempering curves. The calculated values were:

0.41, 0.57, 0.64, 0.65, 0.66, 0.71, 0.72, 0.77, 0.83, 0.89, 0.95, 1.04, 1.27, 1.30 and 1.98 eV.

The activation energies were measured over a range of initial vacancy concentrations, and there did not appear to be any systematic temperature dependence for the appearance of a particular recovery stage as was found for the activation energies calculated for the fast heating rate studies. The only new values for $E_m$ that appeared were $0.71 \pm 0.03$ eV + $0.77 \pm 0.03$ eV and the $E_m$'s that were greater than 1 eV. The high values were not anticipated, and their significance can only be speculated. One thing is for certain; their appearance perturbs the recovery process. The high $E_m$'s occurred intermittently over the entire temperature range. Cattaneo
and Germagnoli (10) also observed an $E_m$ greater than 1 eV for the high temperature annealing of quenched gold doped with silver which they could not explain. An interesting feature of the recovery stage was that every time an $E_m$ greater than 1 eV was calculated an activation energy that ranged between 0.71 eV and 0.77 eV was observed. Moreover, a value of 0.71 eV was not calculated from the data that evolved from the rapid heating experiments. Ytterhius and Balluffi (35) have recently measured an $E_m$ of 0.71 ± 0.03 eV in 99.999% gold over a wide range of defect concentration and annealing temperature. They concluded that it must correspond to some type of relatively tightly bound cluster. Their candidate for this cluster was a divacancy. The results from the fast heating rate experiments do not agree with this conclusion nor do the results from the slow heating experiments owing to the fact that it only occurs after an $E_m$ greater than 1 eV.

The results of this work suggest that the $E_m$'s greater than 1 eV correspond to the decomposition of solute clusters, and that the 0.71 ± 0.03 eV activation energy corresponds to the migration energy of some impurity-vacancy complex that forms as a result of the decomposition of an impurity atom cluster.

The effects of impurity atoms on the recovery behavior of quenched gold is illustrated by the complexity of the tempering curve developed by slowly heating the specimens.
It is evident that dilute concentrations of solute atoms with a low binding energy to vacancies can act as nuclei for the formation of impurity clusters. These conclusions appear to be consistent with the electron transmission microscopy work of Cotterill (6) and Cotterill and Segall (36). They found that increased impurities tended to promote the heterogeneous nucleation of black spot precipitates in specimens quenched from both high and low temperatures.

The results of the two heating rate experiments describe the annealing behavior of vacancies in gold containing small amounts of impurity atoms more conclusively than the well established resistivity methods. The effect of impurity atoms on vacancy annealing was nicely illustrated by the rapid heating experiments owing to the fact that the activation energy spectra were shifted to higher temperatures with increasing copper and silver content. It is also apparent from this study that the exponential decay of residual resistivity does not necessarily describe first order kinetics, and this point was thoroughly discussed by Damask and Dienes (8). The effective rate constant, $K_e$, determined from the exponential decay curves of residual resistivity will generally yield values for $E_m$ that will range from $E_m^1$ to $(E_m^1 + B_x)$ when $I_0$ is greater than $C_x$. Thus, in order to determine $E_m$ accurately from measurements of $K_e$, $I_0$ must be less than $10^{-6}$ when the impurity atom is bound to a vacancy by a binding energy of 0.15 eV, if the impurity concentration is to be neg-
lected in the calculation of $E_m^1$. $E_m^1$ calculated from this study was found to be $0.83 \pm .03$ eV.

The slow heating rate experiments showed the effects of impurity atom segregation on the annealing kinetics of quenched gold. Impurity clustering that apparently occurred during the tempering perturbed all stages of recovery and introduced activation energies that were apparently related to the decomposition of impurity clusters.

**Binding energy of a divacancy**

The theoretical annealing curve for gold quenched from $-800^\circ$C calculated by inserting numerical values for $E_m^1$, $E_m^2$, $E_m^C$, $B_2$, $B_3$ and $B_x$ presented in Figure 5 gives the temperature at which divacancies decompose into single vacancies. The maximum concentration of divacancies occurs at $310^\circ$K. The temperature range where the decomposition occurs is estimated to be from approximately $290^\circ$K to approximately $325^\circ$K. This is in excellent agreement with the experimental results where the temperature range was observed to be from $293^\circ$K to $306^\circ$K. The experimentally determined activation energy was found to be equal to $0.89 \pm .03$ eV. The chemical reaction for the decomposition of a divacancy is $C_2 \xrightarrow{K_{10}} 2C_1$ where the rate constant $K_{10}$ is equal to $14V_1 \exp\left(-\frac{(E_m^1 + B_2)}{kT}\right)$. The energy term $(E_m^1 + B_2)$ is therefore equal to $0.89 \pm .03$ eV. If one takes $E_m^1$ to be equal to $0.82 \pm .03$ eV, then $B_2$ is equal to $0.07 \pm .03$ eV. de Jong and Koehler (3) were not able to
measure \((E_{m}^{1} + B_{2} - E_{m}^{2}) = .26 \pm .03\) eV based on the analysis of \(E_{m}\) for mixed diffusion of vacancies and divacancies. If \(E_{m}^{2}\) is taken equal to \(0.66 \pm .06\) eV, then \((E_{m}^{1} + B_{2} - E_{m}^{2}) = (0.89 - .66) = 0.23 \pm .06\) eV which is within the uncertainty of the value for \(E_{m}^{2}\), and it falls within the uncertainty range determined by de Jong and Koehler. An analysis including trivacancies by de Jong and Koehler as a mobile defect lead to \(B_{2} = 0.07 \pm .03\) eV which is the exact value calculated by the thermoelectric force method. Assuming that our value is correct, one can conclude that trivacancies must also be considered a mobile defect.

Binding energy of a trivacancy

Trivacancies have not been studied in detail with the exception of some theoretical considerations to determine their stable configuration (37) (38). Many different configurations were found to have energies that were so close to each other that the stable form could not be accurately selected. Vineyard's calculations suggested that the tetrahedral configuration of the trivacancy having a relaxed atom in the center was the most stable configuration for the copper trivacancy. Intuition says that the planar configuration of 3-vacancies would be the most stable because it has shorter bond distances between them. Since there are three divacancy type bonds in the planar configuration, \(B_{3}\) might be expected to be about \(0.21\) eV.
The theoretical isochronal annealing curve computed for these experiments had a maximum occurring for the trivacancy concentration at 312°K for an 800°C quench. $B_3$ was assumed to be 0.21 eV for this calculation. The temperature range associated with the dissociation of the trivacancy is contained in the temperature range for the dissociation of a divacancy. Assuming that the chemical reaction describing the dissociation is $C_3 \rightarrow C_2 + C_1$ where $K_{11} = \frac{N^2}{2} \exp\left(-\frac{(E_m^2 + B_3)}{kT}\right)$, then the energy term associated with the dissociation reaction is $(E_m^2 + B_3)$. Taking $E_m^2$ to equal 0.66 eV the energy term could be approximately equal to 0.87 eV. If another possibility for the dissociation reaction is considered such that:

$$K_{12}$$

where $K_{12} = 15 \nu_1 \exp\left(-\frac{(E_m^1 + B_3)}{kT}\right)$ then $(E_m^1 + B_3)$ equals approximately 1.03 eV when $E_m^1$ is taken equal to 0.82 eV. Thus, the measured energy of dissociation in the neighborhood of 310°K is expected to have the range $0.87 \leq E_d \leq 1.03$ eV. A value of $0.89 \pm 0.03$ eV was measured in this range. If $E_d$ for divacancies and trivacancies were equal, then:

$$E_d = E_d^2 = E_d^3 = 0.89 \text{ eV}$$

Assuming $E_d^3$ is equal to $0.89 \pm 0.03$ eV then $B_3$ is equal to $0.23 \pm 0.06$ eV. The uncertainty of $\pm 0.06$ eV is assigned because of the uncertainty of $E_m^2$. 

Schottky in discussing the entropy of formation of divacancies and higher clusters pointed out that the tightly bound planar trivacancy must decompose to a more loosely bound trivacancy called a dogleg if it is to be considered to be mobile. When the trivacancy is allowed to be mobile the effective migration energy $E_m$ will be influenced. This effect was discussed by de Jong and Koehler. When it is included in the analysis of the effective activation energy $B_2$ is equal to $0.07 \pm 0.03$ eV which is the precise value calculated from the thermoelectric force measurements. $B_3$ is $\leq 0.3$ eV when $B_2$ is equal to 0.07 eV. The value estimated from our data was $B_3 = 0.23 \pm 0.06$ eV and is in excellent agreement with the proposed limits of $B_3$.

**Binding energy of the copper-vacancy complex**

Vacancy-impurity complexes have been neglected, and information about $B_x$ is lacking. As long as $B_x$ is greater than 0, some impurities will be associated with vacancies; these interactions constitute an important vacancy trapping mechanism. There are two parts (21)(39) to the binding energy of a complex: (1) The change in strain energy and (2) electrostatic interaction between the impurity and the defect. The change in strain energy around the impurity contributes an important term to the binding energy of the vacancy-impurity complex. When a vacancy is placed near an oversized atom the strain interaction term is very important. Copper is an
undersized atom in gold, so the strain interaction term may not be as great. No specific calculations have been made for the binding energy of a vacancy to an impurity atom by strain. A value of \( B_x = 0.15 \text{ eV} \) was assumed and the isochronal annealing curve calculated. The maximum in \( C_x \) occurred at \( 328^\circ\text{K} \). The temperature range where the recovery is expected to be observed is from approximately \( 310^\circ\text{K} \) to approximately \( 340^\circ\text{K} \). A characteristic activation energy was experimentally found to exist over the temperature range of \( 316^\circ\text{K} \) to \( 357^\circ\text{K} \). This is shown in Figure 5 for the impure metal. The activation energy measured was \( 0.95 \pm 0.03 \text{ eV} \). Similar activation energies were observed for different quenches and also for the high purity material. The average value for \( E_d \) was \( 0.95 \pm 0.03 \text{ eV} \). The chemical reaction describing the dissociation of the vacancy-impurity complex is

\[
\begin{align*}
K_{13} & \quad C_x \longrightarrow C_1 + I \\
& \quad \text{where } K_{13} \text{ is equal to } 7 \nu_1 \exp\left(-\left(E_m^1 + B_x\right)/kT\right).
\end{align*}
\]

On the basis of the calculated annealing curve \( (E_m^1 + B_x) = 0.95 \pm 0.03 \text{ eV} \). Taking \( E_m^1 \) to equal \( 0.82 \pm 0.03 \text{ eV} \), \( B_x \) is then to \( 0.13 \pm 0.03 \text{ eV} \). This is a very low value for the binding energy of the copper vacancy complex. Since no theoretical calculations have been made to estimate \( B_x \), this value cannot be compared to any calculated numbers. It stands to reason that since copper is an undersized atom, the strain energy part of \( B_x \) should be less than if it were an oversized atom. The binding energy of the undersized atom may arise from the fact that there may be a configurational effect on \( B_x \) in an
analogue fashion as was pointed out by Hasiguti (39) for the case of an oversized atom being bound to an interstitial if the two are arranged in a suitable crystallographic orientation.

The binding energy $B_X$ of a vacancy-silver complex in gold was estimated to be about 0.3 eV by Cattaneo et al. (10). Their work on nickel and antimony in gold suggests that $B_X$ for nickel is low and that $B_X$ for antimony is at least as large as that for silver. The distance of closest approach for Au, Sb, Cu, Ni and Ag is 2.884, 2.903, 2.556, 2.491 and 2.888 angstroms respectively. Nickel and copper are undersized in gold while silver and antimony are oversized atoms in gold. The strain interaction effect on the binding energy may be an important term. The undersized atoms appear to have a low binding energy while the oversized atoms tend to have a higher binding energy.
Migration energies for point defect configurations

The migration energies determined from the fast heating rate experiments were used in fitting the calculated tempering curves to the experimental activation energy spectra determined from specimens quenched from 800°C, 700°C, and 600°C. The best results obtained for the migration energy of a monovacancy, a divacancy and a vacancy-impurity configuration are:

- Monovacancy: \( E_m^1 = 0.83 \pm 0.03 \text{ eV} \)
- Divacancy: \( E_m^1 = 0.65 \pm 0.03 \text{ eV} \)
- Vacancy-Copper Complex: \( E_m^c = 0.56 \pm 0.02 \text{ eV} \)

A comparison between other activation energies as measured by other investigators is made in table 5. The comparison of activation energies shows that the \( E_m \) values measured by the thermoelectric force method agrees well with those determined by electrical resistivity methods. In fact, every value of \( E_m \) reported in table 5 was obtained in this study. It is believed that the computer solutions of the simultaneous nonlinear differential equations provided a means for interpreting the measured activation energies.
<table>
<thead>
<tr>
<th>Investigators</th>
<th>Quenching Temperature (°C)</th>
<th>$E_m$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>De Sorbo (40)</td>
<td>820</td>
<td>0.73</td>
</tr>
<tr>
<td></td>
<td>890</td>
<td>0.64</td>
</tr>
<tr>
<td></td>
<td>920</td>
<td>0.62</td>
</tr>
<tr>
<td>Schule et al. (41)</td>
<td>700</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>0.60</td>
</tr>
<tr>
<td>Emrick (42)</td>
<td>708</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>723</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>718</td>
<td>0.82</td>
</tr>
<tr>
<td>Bradshaw et al. (43)</td>
<td>960</td>
<td>0.68</td>
</tr>
<tr>
<td>Bauerle et al. (44)</td>
<td>700</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>0.65-0.67</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>0.55-0.61</td>
</tr>
<tr>
<td>Cattaneo et al. (10)</td>
<td>700</td>
<td>0.84</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.04</td>
</tr>
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</table>
ATHERMAL CLUSTERING OF POINT DEFECT CONFIGURATIONS

In an earlier chapter it was shown that impurity atoms trap vacancies to form associated complexes. These complexes may be nuclei for the formation of larger defect clusters. The quenching rate is an important variable in the nucleation of clusters (45)(46).

In the case of precipitation hardening alloys (46), slow quenching rates tend to produce a coarse precipitate and coarse dispersion even though no precipitation is observed during the quench. Slow quenching generally allows the nucleation of clusters at higher temperatures where more diffusion can occur. The result of slow quenching is a coarse distribution of nuclei. The distribution of nuclei will be different for different quenching rates. Fast quenching rates produce finer particle sizes. The distribution of vacancy configurations should also be sensitive to quenching procedure.

The effect of quenching rate on the distribution of point defect structures can qualitatively be shown by comparing microhardness numbers determined as a function of quenching temperature and quenching rate. Figure 27 and Figure 28 presents a comparison for both the 99.999% gold and 99.995% gold quenched in water and mineral oil for different quenching temperatures.
Figure 27
As Quenched Microhardness of 99.999% Gold as a Function of Quenching Temperature After Quenching Into Water and Mineral Oil
Figure 28
As Quenched Microhardness of 99.995% Gold As A Function Of Quenching Temperature After Quenching Into Water And Mineral Oil
There is a remarkable difference between the microhardness numbers of the water quenched specimens and the microhardness numbers of the mineral oil quenched specimens. The water quenched specimens had two distinct peaks centered around quenching temperatures of 600°C and 850°C respectively. The exact cause of the two peaks is not known, but they are probably related to the interactions of the strain fields associated with the different point defect configurations. An effect due to impurity atom concentration can possibly be inferred from the relative peak heights of the specimens. The gold specimens that were of higher purity had as-quenched microhardness values that were higher than those for the 99.995% gold specimens. This effect can probably be attributed to the decrease in strain energy that results when an impurity atom associates with a vacancy type point defect configuration. The specimens having a higher concentration of impurity atoms show a larger amount of strain relaxation as reflected by the microhardness measurements.

The difference in appearance of the microhardness data of the mineral oil quenched specimens can in part be explained by the quenching rate effect. At the end of the cooling period both gold specimens have approximately the same supersaturation of vacancies, but they differ in solute concentration. This suggests that the distribution and size of nuclei must be different. It is probable that a fine dispersion of nuclei (Vacancy-Impurity Configurations) form during the slow cool-
ing period. The fact that the impurity content of one gold specimen is larger, accounts for the fact that this material is harder than the high purity gold specimens. The smooth increase in the hardness curve with increasing quenching temperature suggests that the number of nuclei that forms is increasing in the same fashion as the vacancy concentration increases with temperature and the hardness increases with increasing volume fraction of nuclei.

The isochronal annealing experiments verified the fact that the condition for impurity segregation exists in this system being studied, since $E_C < E_m$ was found to be less than $E_m$. The probable sequence for the formation of a spherical cluster in this system is Vacancy-Impurity Combination $\rightarrow$ Spherical Cluster. This particular sequence is logical, since Cotterill (6)(36) showed that gold specimens quenched from $800^\circ C$ and subsequently aged at $100^\circ C$ did not produce tetrahedra, but black spots were produced in their place. The average diameter of the spots that were observed was approximately 25 angstroms. The stages which are assumed to be responsible for the formation of the spherical clusters are described by the chemical reactions:

$$C_I + I \xrightarrow{K_5} \frac{K_5}{K_6} C_X$$

$$C_X \rightarrow \text{Spherical Clusters} + C_I$$

The above reactions are identical to those described in table 1, but the shape of the cluster has been specified as being spherical. The second reaction was written because the ex-
perimental results implied that there was a production of vacancies simultaneous to the formation of the clusters. The implication came from the fact that the effective diffusivity that was calculated corresponded to one that would occur if a high concentration of free vacancies were present in the crystal. The second reaction then provides for a continuous supply of vacancies that can be used to deplete the matrix material of free impurity atoms which subsequently diffuse to the interface of the growing nuclei. The stages of cluster formation that are being discussed here may be considered to be pre-precipitation stages that occur in classical precipitation hardening systems. The rate of depletion of solute atoms from the matrix, the rate of change in monovacancies and solute-vacancy pairs are

\[
\frac{\partial I}{\partial t} = -C_1 I \ K_5
\]

\[
\frac{\partial C_1}{\partial t} = -C_1 I \ K_5 + D_1 \ \frac{\partial^2 C_1}{\partial x^2}
\]

\[
\frac{\partial C_x}{\partial t} = C_1 I \ K_5 - C_x K_6 + D_x \ \frac{\partial^2 C_x}{\partial x^2}
\]

where \(D_1\) and \(D_x\) are the diffusivities for monovacancies and vacancy-solute complexes respectively. The law of mass action for the steady state on \(C_x\) yields:

\[
\frac{C_1 I \ K_5}{K_6} = C_x
\]
The substitution of eqn. (55) into the above expressions uncouples the above set of nonlinear simultaneous differential equations and the result is

\[
\frac{\partial r}{\partial t} = -C_X \frac{V_1}{x} e^{-\frac{(E_m^1 + B_{x})}{kT}} \tag{56}
\]

\[
\frac{\partial c_1}{\partial t} = -C_X \frac{V_1}{x} e^{-\frac{(E_m^1 + B_{x})}{kT}} + D \frac{\partial^2 c_1}{\partial r^2} \tag{57}
\]

\[
\frac{\partial c_X}{\partial t} = +D \frac{\partial^2 c_X}{\partial r^2} \tag{58}
\]

Solving partial differential eqn. (58) with the appropriate boundary conditions will yield the solution for \(C_X(r,t)\), and thus the equation for the rate of growth of spherical clusters can be derived. However, if the above reactions are assumed to be similar to the classical non-steady state diffusion in a semi-infinite medium discussed by Darken (47), then the equation giving the vacancy-solute concentration at a distance \(r\) from the boundary of the nucleus at any time \(t\) is

\[
C_X(r,t) = \frac{C_{x}^Q}{\sqrt{\frac{D_X t}{\pi}}} \left\{ \text{erf} \left[ \frac{r}{2 \sqrt{D_X t}} \right] \right\} \tag{59}
\]

where \(C_{x}^Q\) is the initial concentration in the matrix. The rate of growth of the spherical cluster is

\[
\frac{dv}{dt} = -J_{X}Ag \tag{60}
\]
where $J_x$ is the flux of solute-vacancy complexes at the interface, $A$ is the surface area, and $g$ is the volume/atom.

$$\frac{dR}{dt} = -gJ_x$$  \hspace{1cm} (61)

where $R$ is the radius of the spherical cluster. The gradient, $(\frac{\partial C_x}{\partial r})_{R=r}$, is given by the expression:

$$\left[ \frac{\partial C_x(r,t)}{\partial r} \right]_{R=r} = \frac{C^0_x}{\sqrt{D_x t \pi}} e^{-\left(\frac{R^2}{D_x t}\right)}$$ \hspace{1cm} (62)

Thus the rate of growth of a spherical cluster is:

$$\frac{dR}{dt} = \frac{Ng D_x C^0_x}{\sqrt{D_x t \pi}} e^{-\frac{R^2}{D_x t}}$$ \hspace{1cm} (63)

If it is assumed that $\sqrt{D_x t}$ is approximately equal to $R$, then the rate equation becomes:

$$\frac{dR}{dt} = \frac{Ng D_x C^0_x}{R \sqrt{\pi}} e^{-\frac{R^2}{D_x t}}$$ \hspace{1cm} (64)

According to De Sorbo et al. (13) an approximate expression for $D_x$ is:

$$D_x \approx 10^{-2} \pm 1 \ e^{-0.56/kT} \text{ cm}^2/\text{sec.}$$ \hspace{1cm} (65)

where .56 ev is the migration energy of the solute-vacancy pair determined in this study. Eqn. (65) then gives $D_x \approx 10^{-10} \pm 1 \text{ cm}^2/\text{sec.}$ For a radius of 25 angstroms, and taking $10^{-6}$ as an upper limit for $C_x^0$, we have for $dR/dt$ according to eqn. (64):

$$\frac{dR}{dt} \approx 0.12 \text{ Angstroms/sec.}$$
This value for the rate of growth of a spherical cluster is a reasonable estimate, since it is in good agreement with the experimental observations of Cotterill (6). Cotterill took special precautions to minimize the hold time at room temperature prior to observations in the electron microscope. In spite of the precautions, the total time to direct observation by electron transmission can be expected to be approximately 3-5 minutes. The approximate growth rate for the clusters is \((25 \text{ angstroms/200 sec.}) = 0.125 \text{ angstroms/sec.}\). The rate equation that was derived shows a decreasing rate of growth of the spherical cluster with time. In fact, it implies that the growth of the cluster occurs predominantly during the latter stages of the cooling period, and the subsequent growth of the cluster is stopped after a critical size is reached. Table 6 presents the rate of growth of spherical clusters for different \(D_x t\) values.

**TABLE 6**

RATE OF GROWTH OF SPHERICAL CLUSTERS FOR DIFFERENT \(D_x t\) VALUES

<table>
<thead>
<tr>
<th>(D_x t)</th>
<th>(R = \sqrt[3]{D_x t})</th>
<th>(\text{d}R/\text{d}t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10^{-14})</td>
<td>10</td>
<td>0.386</td>
</tr>
<tr>
<td>(10^{-12})</td>
<td>100</td>
<td>0.0386</td>
</tr>
<tr>
<td>(10^{-10})</td>
<td>1000</td>
<td>0.00386</td>
</tr>
</tbody>
</table>

\(D\) was taken to equal \(10^{-10} \text{ cm/sec.}\), and \(g\) was taken to be \(\frac{4}{3}\pi r^3\) where \(r^3\) is the cube of the radius of an impurity
atom taken to equal $2.76 \times 10^{-24}$ cm$^3$. Ytterhuis and Balluffi (35) reported $R$ values of approximately 44 Å after 4.7 hours of annealing indicating that the size of the cluster was not much larger than it was shortly after quenching. The size of the cluster observed by transmission electron microscopy is also a function of the initial impurity content of the system, and this hypothesis is supported by the behavior of the mineral oil quenched specimens. The specimens having a higher impurity content had a higher hardness. The size of the spherical cluster is a function of both the initial vacancy content and initial impurity content, and this is in agreement with the law of mass action.

It is not possible to directly observe the nucleation process by electron transmission microscopy, because it is impossible to image point defect configurations in the lattice. The role of vacancies in solute cluster nucleation must subsequently be inferred. The experimental results suggested that gold containing copper solute atoms has the necessary requisites for solute segregation.

The characteristics of the gold specimens are:

1. The binding energy between a copper atom and a vacancy is $0.13 \pm 0.03$ eV so that when $I_0 \gg C_x$ most of the vacancies will exist as solute-vacancy complexes.

2. The migration energy of the solute-vacancy complex is less than that for the motion of a single vacancy or a solute atom. The diffusivity, $D_x$, of the solute-vacancy
pair is approximately $10^{-2} \pm 1 \exp(-.56/kT)$ cm$^2$/sec which corresponds to a diffusivity of about $10^{-10}$ cm$^2$/sec at 373°K.

The tempering curves for the slow heating rate of 0.167°K/sec were too complex to interpret in terms of the energies of motion of the mobile defects or the decomposition of the single clusters. Many of the activation energies were greater than 1 eV. It is believed that these high activation energies are related to the thermal decomposition of solute clusters. The activation energy for decomposition of solute clusters would increase with increasing number of solute bonds, i.e., the binding energy of the cluster increases with an increase in the size of the cluster (48). If vacancy-solute complexes are responsible for the growth of the clusters, then a scheme must exist for the dissociation of the complex at the interface between the nucleus and the matrix. One possibility would be the relaxation of misfit strain energy between the nucleus and the matrix if the solute would dissociate from its vacancy and become attached to the cluster owing to the binding energy of the solute to the cluster being greater than the binding energy of the vacancy-solute cluster. Once the impurity atom becomes bound to the cluster the vacancy is free to diffuse to the matrix and recombine with another solute atom and to repeat the process (49). Another possibility for the dissociation of the cluster which does not involve emitting all of the vacancies from the cluster during growth exists.
When a cluster forms that consists primarily of impurity atoms that are smaller than the solvent atoms and vacancies, it is possible to develop a strain pattern that has regions of compression and regions of tension in an analogous fashion to the displacement of atoms around a vacancy. Figure 29 illustrates the behavior of atoms around a vacancy.

![Figure 29 Schematic Behavior Of Atoms When A Vacancy Is Inserted Into A Lattice (After J. R. Beeler, Jr.)](image)

Vacancies will not be emitted from those regions of the cluster configuration that are in compression, but they can be emitted from the tension regions. This appears to be a more realistic model for the structure of the impurity-vacancy cluster configurations. The impurity configuration will thus be surrounded by an atmosphere of vacancies which might serve as a barrier to the rapid growth of these clusters. A possible model for the dissociation of the cluster configuration is:

1. Assume that the cluster is in an initially tightly bound configuration (T.B.C.). In order to dissociate it, it is necessary to convert the T.B.C. to a loosely bound cluster (L.B.C.).

2. Assume that the L.B.C. is dissociated by the forma-
tion of impurity-vacancy pairs which subsequently must migrate away from the cluster configuration to complete the dissociation process.

The scheme for the dissociation process is

$$\text{T.B.C.} \xrightarrow{H_b} \text{L.B.C.} \xrightarrow{K_b} \text{C}_x$$

where $H_b$ is the energy required to convert the T.B.C. to a L.B.C. and $K_b$ is the rate constant for final breakup of the L.B.C. The form of $K_b$ is:

$$K_b = f V_x e^{-\left(\frac{E_m^C + B_x^1}{kT}\right)}$$

where $f$ is a geometric factor and $B_x^1$ is the binding energy of the L.B.C. Since it was noted that the activation energies that ranged between 0.71 eV and 0.77 eV always followed an $E_m$ greater than 1 eV, it is hypothesized that $0.71 \text{ eV} \leq \left(\frac{E_m^C + B_x^1}{kT}\right) \leq 0.77 \text{ eV}$. The variation of the activation energy is assumed to be due to the difference in the binding energy of the different possible point defect configurations. Thus possible values of $B_x^1$ for the L.B.C. will range from 0.15 eV to 0.21 eV when $E_m^C$ is taken to be 0.56 eV.

It can be concluded from the microhardness data that quenching procedure affects the distribution of cluster nuclei, and that solute content of the specimens can alter the size and distribution of the cluster nuclei. The equation that was derived for the rate of growth of a spherical cluster predicts that the cluster will achieve a size that is very nearly equal to its maximum size early in the annealing process,
and, in fact, it will probably accomplish this during the cooling period of a very slow quench. The maximum size of the cluster will be a function of $I_0$, since the maximum concentration of vacancy-solute pairs, $C_{x}^0$, is given by $C_{x}^0 = \kappa C_1$. This hypothesis is supported in part by the fact that the microhardness values of the 99.995% gold were greater than those for the 99.999% gold specimens that were quenched in mineral oil. From the slow heating rate experiments it can be inferred that cluster configurations consisting of solute atoms and vacancies form during tempering, and that the activation energies whose values ranged from 0.71 eV to 0.77 eV are associated with the dissociation of a loosely bound vacancy-solute configuration. It can also be concluded that high solute supersaturations are not necessary for the formation of clusters containing solute atoms.
INTERNAL OXIDATION OF GOLD

Differing annealing kinetics after quenching in different atmospheres was observed by Jeanotte and Machlin (34). They postulated that their results were due to a high solubility of oxygen in gold. Toole and Johnson (50) and Eichenauer and Liebschen (51) determined the solubility of oxygen in gold and found it to be so low that Jeanotte and Machlin's argument does not appear to be valid. In order to determine the possibility of internal oxidation in gold, alloys of 0.005, 0.014, 0.064, 0.070 and 0.074 mole fraction of indium were exposed to air for different times up to 25 hours in the temperature range of 850°-950°C. No internal oxidation bands were observed. The 99.999% gold and 99.995% gold wires were also heated in air for times up to 25 hours in the temperature range of 800°-1000°C, and no internal oxidation bands were observed by microscopic examination at 1200X. However, a difference in color was observed on the surface of the two wires. The high purity gold wire had a yellow color initially and remained yellow after annealing, but the 99.995% gold wire acquired a bronze color after annealing. This color change is an indication that oxidation occurred only at the surface and that internal oxidation does not occur in gold.

Weight gain measurements on the gold-indium alloys in-
dicated that two different processes successively controlled the rate of oxidation (52). The initial oxidation rate was found to be controlled by the diffusion of indium through indium oxide and the second oxidation rate was found to be controlled by the diffusion of indium in the alloy. Subsequent optical microscopy revealed that the formation of a stable layer was controlled by the diffusion of indium in indium oxide and the unstable oxide was controlled by the diffusion of indium in the alloy. The transition from a stable oxide to an unstable oxide was found to occur at a critical concentration. These observations support the hypothesis that impurity atoms in gold tend to diffuse towards the surface of the specimen (6)(35). Further work is required to determine the behavior of impurities in gold during prequenching treatments.
SUMMARY AND CONCLUSIONS

The thermoelectric power of a metal is its most sensitive electronic transport property, since it governs all the various thermoelectric phenomena. The thermoelectric power of a specimen was measured as a function of temperature while the specimen temperature was raised at a constant rate (0.416°K/sec and 0.167°K/sec) from 77° to 375°K. Following the ideas of Damask and Dienes, it was assumed that the effective rate constant $K_e$ is proportional to the effective defect diffusion coefficient in a very dilute alloy, and the activation energies of the various chemical processes were subsequently determined from the temperature dependence of the effective diffusivity. The interpretation of the data for the experiments involving the heating rate of 0.416°K/sec was based on the numerical solution of simultaneous, nonlinear coupled differential equations for the concentrations of mono, di, tri, and tetravacancies, and a vacancy-impurity complex. Activation energies of 0.65 eV, 0.56 eV, and 0.83 eV were determined for the migration of a divacancy, vacancy-impurity complex, and a monovacancy, respectively. These values are consistent with the results of de Jong and Koehler for 99.999% gold. In all cases studied an increase in the solute content shifted the activation energy spectrum.
towards higher temperatures. Binding energies of 0.07 eV, 0.13 eV, and 0.23 eV were determined for a divacancy, vacancy-impurity complex and trivacancy, respectively.

The 0.167°C/sec tempering experiments were too complex to be interpreted with the aid of computer solutions for the differential equations. Impurity clusters simultaneously form and dissociate during the tempering process to perturb the activation energy spectrum. Activation energies having values greater than 1 eV appeared intermittently in the activation energy spectrum. These values were always followed by activation energies that had values ranging between 0.71 eV and 0.77 eV. This behavior of the determined activation energies is believed to be associated with the dissociation of small impurity type clusters. Assuming that the migration energy of the vacancy-impurity complex is 0.56 eV, the binding energy for a loosely bound cluster was found to range between 0.15 eV and 0.21 eV. The activation energies that are greater than 1 eV are believed to be related to the primary dissociation of a tightly bound impurity configuration into a loosely bound cluster. The binding energy of the loosely bound cluster may be a function of the crystallographic orientation of the defect.

An attempt was made to determine the effect of quenching rate on defect clustering. As-quenched microhardness values determined for specimens quenched from temperatures ranging between approximately 900°C and 500°C into water and mineral
oil showed a quenching procedure effect for both the 99.999% gold and the 99.995% gold specimens. Water quenching produced two peaks centered around 600°C and 850°C, respectively. The height of the peak centered around 850°C for the 99.999% gold was higher than that for the 99.995%. The difference in the height of this peak may be due to point defect hardening associated with divacancies, since the strain field associated with divacancies is non-cubic. The microhardness values of the mineral oil quenched specimens exhibited a smooth increase in hardness with increasing quenching temperature. The 99.995% gold specimens had higher hardness values than the 99.999% gold. This behavior can possibly be attributed to the size and number of the impurity clusters which formed during the quenching period. A rate equation that predicts the rate of growth of a spherical cluster was derived. Calculated growth rates showed rapid initial rates which subsequently decreases to small values after times not longer than the cooling period of the mineral oil quench.

Internal oxidation studies using dilute gold-indium alloys (.005 mole fraction) and gold specimens (4 ppm Cu and 1.5 ppm Cu) were made, and no evidence of internal oxidation was found. The gold-indium alloys exhibited classical noble metal oxidation predicted by Wagner, and the high purity gold specimens showed a difference in the color of their surface after oxidation. The 99.995% gold specimen developed a bronze color on its surface whereas the 99.999% gold did
not appear to change color. It thus appears that impurity atoms in gold tend to diffuse towards the surface during prequenching heat treatments.
RECOMMENDATIONS

A systematic investigation should be made to determine how solute atoms having different diffusivities and atomic diameters influence the activation energy spectrum of quenched gold. The solute contents should converge on extremely high purity gold so that values for the migration energy of the simple defect configurations can be accurately ascertained. Theory shows that slowly diffusing solute atoms do not influence single vacancy diffusion whereas fast diffusing species can easily yield incorrect activation energies. An error in the activation energy will be observed because recovery occurs at relatively low temperatures, so appreciable differences in jump frequencies will produce differences in the activation energy of defect motion.
REFERENCES


52. Gegel, H., Kosak, R. and Saxer, R., to be submitted for publication.