

tion about a vacancy, and it must be included before the theoretical calculation of the relaxation about a vacant site in an infinite lattice may be directly compared with experimental results.

It is also possible to compare the result of the present experiment with expressions relating the activation volume to other known quantities. Nachtrieb, Resing, and Rice<sup>8</sup> and Rice and Nachtrieb<sup>36</sup> showed that

$$\Delta V = (\Delta H / \Delta H_m) \Delta V_m,$$

where  $\Delta H_m$  and  $\Delta V_m$  are the enthalpy and volume change upon melting. Using 42 kcal/mole<sup>23</sup> for  $\Delta H$ , 3.0 kcal/mole<sup>37</sup> for  $\Delta H_m$ , and 0.51 cm<sup>3</sup>/mole<sup>37</sup> for  $\Delta V_m$ , one finds that  $\Delta V$  is equal to 7.1 cm<sup>3</sup>/mole, in startling agreement with the present results.

Keyes<sup>38</sup> noted that many materials follow the semi-empirical relationship

$$\Delta V = 4K_T \Delta H.$$

Using  $6.0 \times 10^{-7}$  bar<sup>-1</sup> for  $K_T$ , and 42 kcal/mole for  $\Delta H$ , one obtains the value 4.2 cm<sup>3</sup>/mole for  $\Delta V$ . In a later paper<sup>39</sup> Keyes derived the expression

$$\Delta V = 2(\gamma_G - \frac{2}{3})K_T \Delta G.$$

There is some doubt about the correct value of  $\gamma_G$  for gold.<sup>40</sup> A compromise between the value of  $\gamma_G$  derived from compressibility data and from shock-wave experiments suggests the value 2.0. With this value, and with  $\Delta G \approx \Delta H = 42$  kcal/mole,  $\Delta V$  is equal to only 2.8 cm<sup>3</sup>/mole. However, a derivation of  $\gamma_G$  from the heat capacity at constant volume gives a value of 3.0. If this is used in the above equation, then  $\Delta V$  is equal to 4.9 cm<sup>3</sup>/mole.

Lawson *et al.*<sup>29</sup> also derived an approximate relation between the activation volume of formation  $\Delta V_f$  and the molar volume

$$\Delta V_f / V_M = 1 / (\gamma_G - \frac{1}{3}).$$

With  $\gamma_G = 3.0$ ,  $\Delta V_f$  is 3.8 cm<sup>3</sup>/mole, but with  $\gamma_G = 2.0$ ,  $\Delta V_f$  is 6.1 cm<sup>3</sup>/mole.

Many of the calculations cited are but rough approximations. However, many of the experimental results cited also are quite limited in their certainty by large experimental errors. In the present investigation,

<sup>36</sup> S. A. Rice and N. H. Nachtrieb, *J. Chem. Phys.* **31**, 139 (1959).

<sup>37</sup> C. J. Smithells, *Metals Reference Book* (Butterworths Scientific Publications Ltd., London, 1962), 3rd ed., Vol. 2, p. 618.

<sup>38</sup> R. W. Keyes, *J. Chem. Phys.* **29**, 467 (1958).

<sup>39</sup> R. W. Keyes, in *Solids Under Pressure*, edited by W. Paul and D. M. Warschauer (McGraw-Hill Book Company, Inc., New York, 1963), p. 71.

<sup>40</sup> K. A. Gschneidner, Jr., *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York), Vol. 16 (to be published).

TABLE IV. Theoretical values for volume relaxation about vacancies in copper. Potentials  $a$ ,  $b$ ,  $V_1$ , and  $V_2$  are Born-Mayer repulsive potentials. The explicit form of  $V_1$  is due to Huntington,<sup>a</sup> and that of  $V_2$  is due to Huntington and Seitz.<sup>b</sup>  $V_3$  is a Morse repulsive potential whose explicit form is due to Girifalco and Weizer.<sup>c</sup> The constant  $\delta$  is the Eshelby factor (Ref. 35), which is equal to  $3(1-\sigma)/(1+\sigma)$ , where  $\sigma$  is Poisson's ratio.

Source	Nearest-neighbor potential	Fractional volume relaxation	$\Delta V_f / V_M$
Tewordt <sup>d</sup> ( $\delta = 1.5$ )	$V_1$	-0.53	0.47
	$V_2$	-0.45	0.55
Seeger and Mann <sup>e</sup> ( $\delta = 1.5$ )	$a$	-0.09	0.91
	$b$	-0.19	0.81
Bennemann and Tewordt <sup>f</sup> ( $\delta = 1.2$ )	$V_1$	-0.29	0.71
	$V_2$	-0.38	0.62
	$V_3$	-0.32	0.68
	$V_3$	-0.44	0.56
	$V_1$	-0.46	0.54
	$V_2$	-0.39	0.61
Bennemann <sup>g</sup> ( $\delta = 1.2$ )	$V_3$	-0.53	0.47
	$V_1$	-0.40	0.60
Johnson and Brown <sup>h</sup> ( $\delta = 1.5$ )	$V_1$	-0.48	0.52

<sup>a</sup> H. B. Huntington, *Phys. Rev.* **91**, 1092 (1953).

<sup>b</sup> H. B. Huntington and F. Seitz, *Phys. Rev.* **61**, 315 (1942).

<sup>c</sup> L. A. Girifalco and V. G. Weizer, *Phys. Rev.* **114**, 687 (1959).

<sup>d</sup> See Ref. 31.

<sup>e</sup> See Ref. 33.

<sup>f</sup> See Ref. 32.

<sup>g</sup> See Ref. 31.

<sup>h</sup> See Ref. 13.

limitations in accuracy of the experimental data made it impossible to draw any conclusions with respect to the temperature dependence of the activation volume or the pressure dependence of the activation energy. These limitations are due to the difficulties involved in the measurement, reproducibility, and control of the temperature. A reasonable value for the error in the temperature measurement was estimated to be  $\pm 5^\circ\text{C}$ , and the error limits in Fig. 6 are based upon this estimate. It is probable that the cause of the irregular thermocouple deteriorations which were observed was due to contamination of the thermocouple wires by uncontrollable impurities in the gas, furnace parts, or vessel parts, although precautions were taken to minimize this possibility. Measurement of an accurate temperature in a small furnace of the type used in this experiment also is limited by the presence of temperature gradients. Once these difficulties are overcome, more reliable data can be obtained from measurements of the type made in this investigation.

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