two-phase region, whether of compositional (1st order) or order-disorder (1st or 2nd order) type, is not known because of the sluggish nature of the system and contamination problems with the furnace cell and thermocouple for long-term experiments in this high-temperature range. Particularly on the basis of the volume measurements and, in addition, on the basis of the observance of the (220) split it seems that the temperature maximum will occur near to 1:1 molar composition. The splitting occurs at 1400°C but not at 1450°C when the pressure is 30 kb. Taking the critical temperature as approximately 1435°C and using the equations for critical unmixing (Guggenheim, 1949, p. 210 and following), one can calculate the pressure effect on the critical temperature. Assuming the entropy term ($\overline{S}m$) to be of the form

$$-R[(x_1 \ln x_1 + (1 - x_1) \ln (1 - x_1)],$$

the excess free energy of mixing ($\overline{G}m^e$) is of the form

$$(x_1)(1 - x_1)\, w$$

The w used here is sometimes called "Guggenheim's w" or the mismatch free energy. The quantity w has the dimensions of molar energy and is identical to Hildebrand's (1964) "interchange energy," which is the work done on the system by mixing. Guggenheim has shown that

$$w = 2RT$$

when T is critical. For 30 kb, 1708°K we have

$$w = 6.79 \text{ kcal/mole}$$
$$\text{and } x_{1(Tc)} = 0.5$$

Because the data do not violate Guggenheim's simple-mixture approximation, dw/dp can be calculated as a further consequence.

$$V^e = (x_1)(1 - x_1)(dw/dp) = (x_1)(1 - x_1)\, 2.56$$

Accordingly,

$$\Delta w_{(30K)} = \frac{2.56}{41.83} \int_{30 \times 10^3}^{P} dp$$

Here the excess molar volume of mixing function has been written as an approximation to the measured data (table 2) and is compared in figure 5. Working back from this function it is possible to evaluate w at 50 kb in order to average the pressure effect:

$$w_{(50 \text{ kb})} = 6790 + \frac{(2.56)(20 \times 10^3)}{41.83}$$
$$= 8.015 \text{ kal/mole}$$

The Tc (50 kb) = w/2R = 2015°K = 1742°C. This can be written dw/dp = 15°/kb (for w independent of T). While there is no particular reason for the slope to be constant there is nonetheless a strong pressure

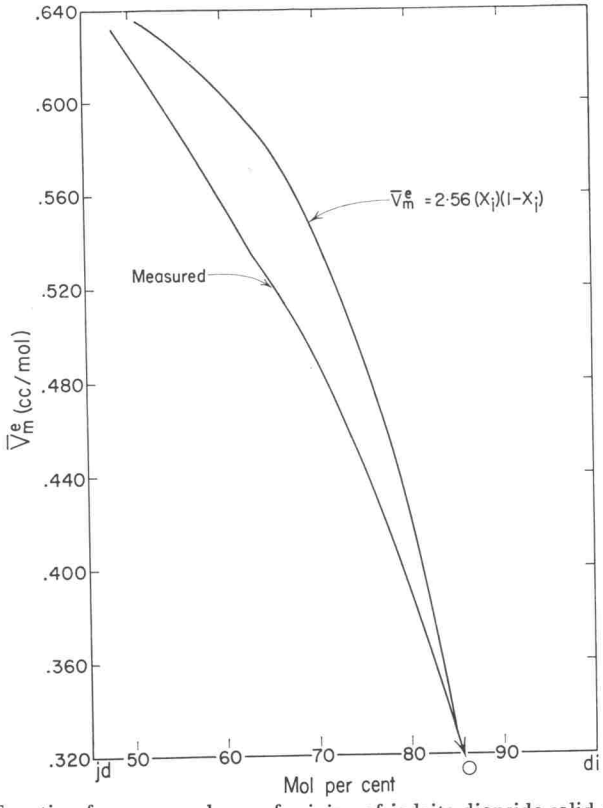

Fig. 5. Function for excess volume of mixing of jadeite-diopside solid solutions.

effect on the critical temperature so the two-phase region will occur at much lower temperatures at low pressures.

An attempt was made to unmix or disorder a natural omphacite for comparison with results in the synthetic system. The natural omphacite is an ordered, approximately 1/1 molar, jadeite-diopside from Kaminaljuj, Guatemala. This very pure omphacite was kindly supplied by Dr. J. Papike, who analyzed the experimental results by X-ray. The material was treated at 1350°C, 30 kb, for 6 hours. This was not enough time for complete equilibration, but it is significant that a very minor peak in addition to the (220) was observed. The pyroxene was determined to be completely ordered before the experiment (that is, $V^e = O$) on the basis of single crystal measurements. A positive value of excess volume was recorded after the experiment, however, only about one-half that reported for the synthetic product. This observation does tend to support the synthetic results.

Continuing with Guggenheim's simple-mixture approximation it is advantageous in lieu of experimental data to predict relations in the subsolidus. In particular, the reaction