

and eq.(5) becomes

$$V_l = \frac{(V_A^\circ)_l}{(V_A^\circ)_s} (V_A)_s - (\Delta V)_l x,$$

then being changed to the next form

$$\frac{V_l - V_s}{V_s^\circ} = \left\{ \Delta V_{s-l}^\circ \cdot \frac{V_s}{V_s^\circ} - (\Delta V)_l x \right\} / V_s^\circ, \quad (8)$$

where  $\Delta V_{s-l}$  denotes the volume change during melting at zero pressure. We use the notation *s* instead of *A* in eq.(8). In fact there is no difference between the notation *A* and *s*. This will be understood later, when the calculations will be performed. According to the Rapoport's assumption that  $(\Delta V)_l$  is roughly independent of pressure and temperature and using the observed values of  $(V_A)_s$  and  $(V_B)_s$  at room temperature<sup>9) 10)</sup>, we can calculate  $(\Delta V)_l$ . Since the thermal expansion of a solid is generally very small compared with the volume change during melting, we may use the values of  $(V_s^\circ)$  and  $V_s$  at room temperature instead of those at melting temperature in eq.(8). For cesium the values of  $\Delta V_{s-l}^\circ$  and  $(\Delta V)_l$  are 1.81 cm<sup>3</sup>/mole and 3.42 cm<sup>3</sup>/mole<sup>9) 11)</sup>. For tellurium they are 1.00 cm<sup>3</sup>/mole and 1.17 cm<sup>3</sup>/mole respectively<sup>10) 11)</sup>. Then we can perform the calculations of the right hand side of e.q.(8) along the melting curves for cesium and tellurium. We give the numerical results by the dashed curves in Fig. 1 and Fig. 2. From these results and the Clausius-Clapayron equation, we

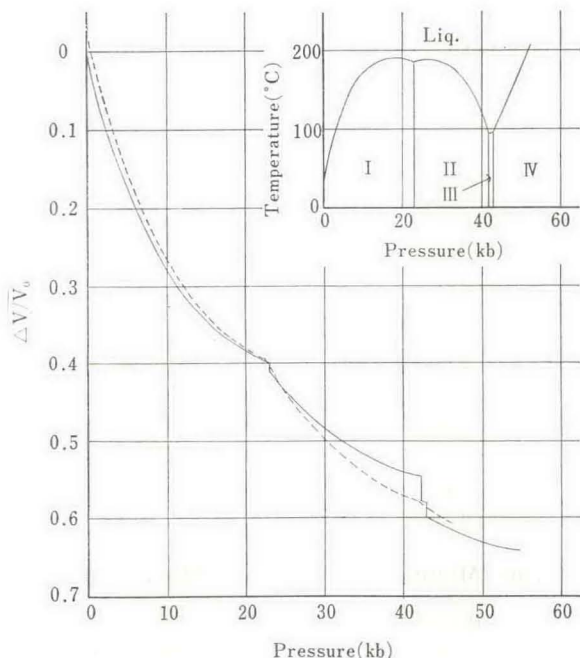


Fig. 1. The dashed curve shows the volume decrease of the liquid cesium at the melting temperature and the solid curve shows the volume decrease of the solid cesium at room temperature in terms of that at room temperature and pressure,  $V_0$  as unity.

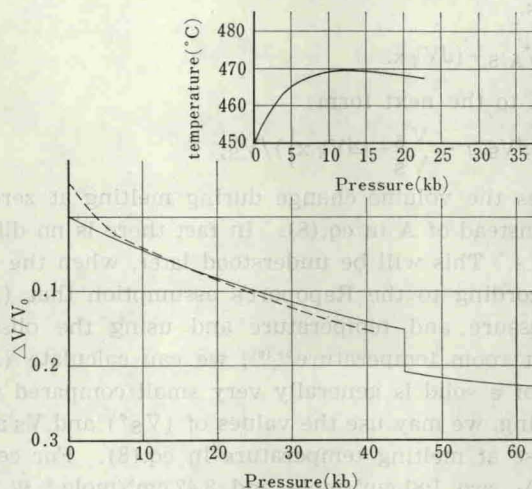


Fig. 2. The dashed curve shows the volume decrease of the liqued tellurium at the melting temperature and the solid curve shows the volume decrease of the solid tellurium at room temperature in terms of that at room temperature and pressure,  $V_0$  as unity.

find that the agreements with the observed phase diagrams<sup>12) 13)</sup> are quite good.

Now we shall derive the rough condition for a melting curve maximum from eq.(8). At this point the volume change during melting must be zero, hence, we have

$$x = \frac{\Delta V_{S-l}^{\circ}}{(\Delta V)_l} \cdot \frac{V_S^{\circ}}{V_S}$$

at this point.

If the melting curve maximum occurs below pressure  $P$ ,  $x$  must be smaller than unit, i. e.,

$$\frac{\Delta V_{S-l}^{\circ}}{(\Delta V)_l} \cdot \frac{V_S^{\circ}}{V_S} \leq 1. \quad (9)$$

The values of  $\Delta V_{S-l}$ 's have been obtained for most substances, hence, to calculate the left hand side we need only the value of  $V_S$ . Under the rough assumption, we may use a value of  $V_S$  at room temperature and the values of  $V_S$ 's have been obtained for many substances up to 80-100 kb. There are not many substances with the melting curves maxima in such pressure range, but the condition (9) is satisfied with those substances.

#### Entropy Changes during Melting on The Two Species Model

We shall derive the pressures at the entropy changes maxima along the melting curves for cesium and tellurium. We have the entropy of the liquid from eq.(4), i. e.,

$$S = - \left( \frac{\partial G}{\partial T} \right)_P = (S_A) - x_l (\Delta S)_l - R \{ (1-x) \ln (1-x) + x \ln x \},$$

where