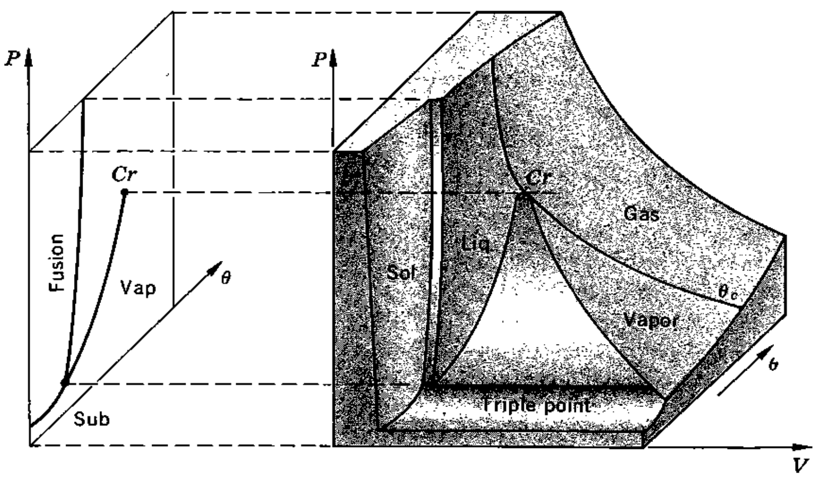

Fig. 2-4 *Surface for a substance that expands on melting.*

All the triple points of water are shown on the *PVt* surface shown in Fig. 2-5, which was constructed by Verwiebe on the basis of measurements by Bridgman.

2-5 Equations of State

It is impossible to express the complete behavior of a substance over the whole range of measured values of P, V, and θ by means of one simple equation. There have been over sixty equations of state suggested to represent only the liquid, vapor, and liquid-vapor regions, ranging from the ideal gas equation

$$Pv = R\theta, \tag{2-1}$$

which holds only at low pressures in the vapor and gas regions, to the Beattie-Bridgman equation:

$$P = \frac{R\theta(1-\epsilon)}{v^2}(v+B) - \frac{A}{v^2}, \tag{2-2}$$

where $A = A_0\left(1 - \frac{a}{v}\right)$, $B = B_0\left(1 - \frac{b}{v}\right)$, $\epsilon = \frac{c}{v\theta^3}$,

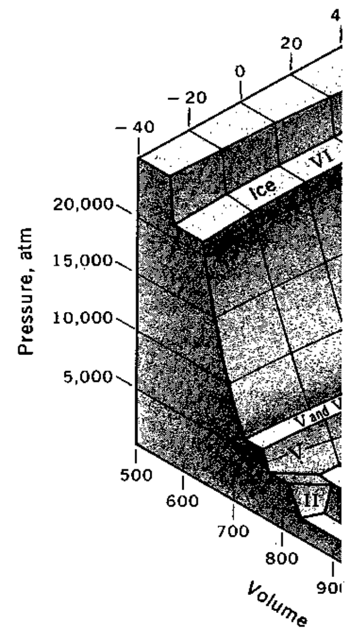

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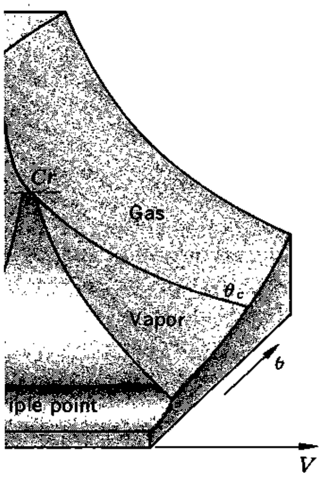
Fig. 2-5 *Surface for water, showi basis of measurements by Bridgman.)*

which, because of its five adjust the whole range above the tri

Some of these equations are closely as possible the measure retical, having been calculate One of the most famous of the t tions concerning molecular beh Waals equation of state:

$$\left(P + \right.$$

This equation holds fairly wel near and above the critical po



nelting.

he PVt surface shown in Fig. 2-5,
the basis of measurements by

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θ by means of one simple equa-
of state suggested to represent
ions, ranging from the ideal gas

(2-1)

vapor and gas regions, to the

$$B) - \frac{A}{v^2}, \qquad (2\text{-}2)$$

$$- \frac{b}{v}\Big), \qquad \epsilon = \frac{c}{v\theta^3},$$

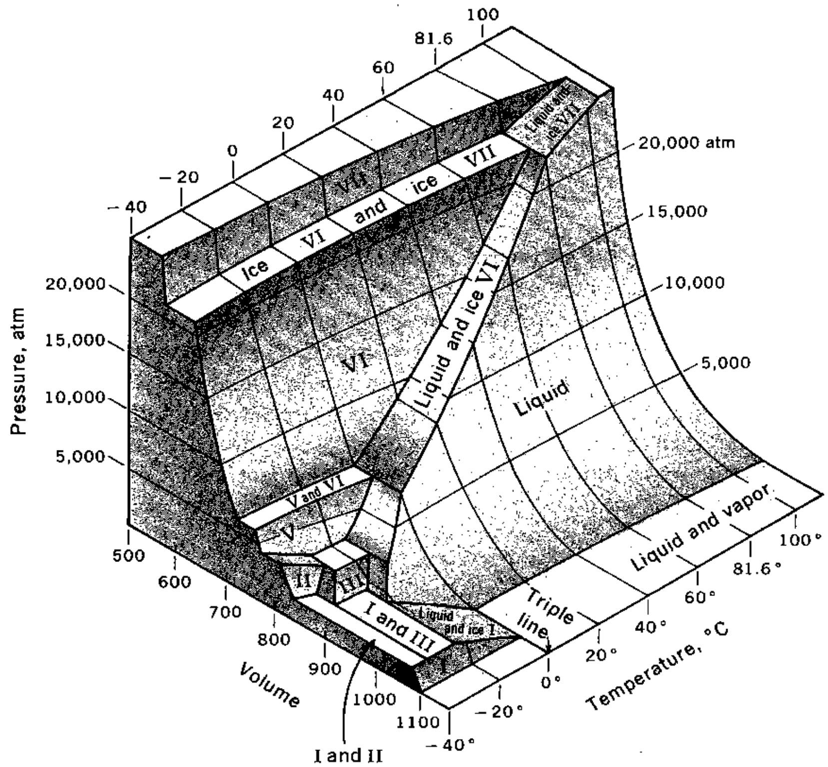

Fig. 2-5 *Surface for water, showing all the triple points. (Constructed by Verwiebe on the basis of measurements by Bridgman.)*

which, because of its five adjustable constants, represents with some accuracy the whole range above the triple point.

Some of these equations are frankly empirical, designed to represent as closely as possible the measured values of P, V, and θ, while others are theoretical, having been calculated on the basis of the kinetic theory of gases. One of the most famous of the theoretical equations of state, based on assumptions concerning molecular behavior that are still of use today, is the van der Waals equation of state:

$$\left(P + \frac{a}{v^2}\right)(v - b) = R\theta. \qquad (2\text{-}3)$$

This equation holds fairly well in the liquid region, the vapor region, and near and above the critical point.