

$$\kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T, \quad (2.53)$$

and gives the fractional change of volume under pressure at constant temperature. Since volume decreases with increasing pressure, the negative sign is used to ensure that  $\kappa$  is a positive number. Using these definitions, the equation of state can be expressed in an alternative form. First, we write the differential of  $V$  in terms of  $P$  and  $T$ :

$$dV = \left( \frac{\partial V}{\partial T} \right)_P dT + \left( \frac{\partial V}{\partial P} \right)_T dP. \quad (2.54)$$

Using eqs. (2.52) and (2.53) to eliminate the partial derivatives that appear in eq. (2.54), this equation becomes

$$\frac{dV}{V} = \beta dT - \kappa dP. \quad (2.55)$$

If the coefficients  $\beta$  and  $\kappa$  are known, this equation can be integrated to calculate changes in  $V$ .

These coefficients are themselves functions of pressure and temperature, but for liquids, the effect of pressure is quite weak; we may take them to depend on temperature only. The coefficient of isothermal compressibility expresses the degree to which the volume of a liquid responds to pressure. Since liquids at temperatures well below the critical are nearly incompressible, the coefficient of isothermal compressibility is approximately zero. The coefficient of thermal expansion is usually small, as liquids expand much less than gases, but it is not zero. *Perry's Chemical Engineers' Handbook* provides data on the thermal expansion of selected liquids.

## 2.11 Empirical Equations for Density

**Rackett Equation** A useful and accurate method for the calculation of liquid molar volumes at saturation is the Rackett equation. In its modified form, it gives the molar volume of saturated liquid as

$$V_L = \frac{RT_c}{P_c} Z_R^{1+(1-T_r)^{2/7}} \quad (2.56)$$

where  $V_L$  is the molar volume at saturation,  $T_c$  is the critical temperature,  $P_c$  is the critical pressure,  $T_r = T/T_c$  is the reduced temperature and  $Z_R$  is a parameter specific to the fluid. *Perry's Chemical Engineers' Handbook* [2] lists the values for