

Taking the differential, we obtain

$$dP = \left(\frac{\partial P}{\partial v}\right)_T dv + \left(\frac{\partial P}{\partial T}\right)_v dT. \quad (2.21)$$

Since we are assuming that the cooling takes place at constant volume, the first term on the right-hand side is zero. Thus

$$P_2 - P_1 = \int_{T_1}^{T_2} \left(\frac{\partial P}{\partial T}\right)_v dT. \quad (2.22)$$

Unfortunately, the integrand is unknown. However, using the cyclical relation given in Appendix A, we have

$$\left(\frac{\partial P}{\partial T}\right)_v \left(\frac{\partial T}{\partial v}\right)_P \left(\frac{\partial v}{\partial P}\right)_T = -1.$$

Thus

$$\left(\frac{\partial P}{\partial T}\right)_v = -\frac{1}{\left(\frac{\partial T}{\partial v}\right)_P \left(\frac{\partial v}{\partial P}\right)_T} = -\frac{\left(\frac{\partial v}{\partial T}\right)_P}{\left(\frac{\partial v}{\partial P}\right)_T} \beta. \quad \kappa.$$

Substituting this result in Equation (2.22), we obtain

$$P_2 - P_1 = \frac{\beta}{\kappa} (T_2 - T_1), \quad (2.23)$$

if  $\beta$  and  $\kappa$  are independent of  $T$ . This is negative if  $T_2 < T_1$ , indicating that the pressure is reduced on cooling. Note that this result could have been obtained immediately from Equation (2.18).

In practice, the cooling would not be reversible because one simply heats the fluid and lets it cool. The result would be large temperature gradients within the fluid itself and between the fluid and its surroundings. Thus the intermediate states are not equilibrium states and the equation of state cannot be applied.

However, the initial and final states are equilibrium states, and it doesn't matter how we go from state 1 to state 2 to determine the change in the state variable  $P$ . This is because  $\Delta P = P_2 - P_1$  is independent of the path, being determined only by the end points. We can choose any convenient path to calculate changes in state functions for processes between a pair of equilibrium states. The most convenient path is a reversible path.

Our fundamental state variables  $P$ ,  $v$ , and  $T$  are all exact differentials whose integrals are independent of the path. Formulating all thermodynamic relations in terms of state variables will be a goal of the theoretical development; this is called the *condition of integrability*. When we encounter a thermodynamic quantity whose differential is imperfect, we will seek an integrating factor to give us a quantity that we prefer to work with. Appendix A includes a comprehensive discussion of exact and inexact differentials.

## PROBLEMS

**2-1** How many kilograms of helium gas are contained in a vessel of 1 liter volume at 50°C if the pressure is one atmosphere? (The atomic weight of helium is 4.)

**2-2** A tank of volume 0.5 m<sup>3</sup> contains oxygen at a pressure of  $1.5 \times 10^6$  Pa and a temperature of 20°C. Assume that oxygen behaves like an ideal gas.

- How many kilomoles of oxygen are in the tank?
- How many kilograms?
- Find the pressure if the temperature is increased to 500°C.
- At a temperature of 20°C, how many kilomoles can be withdrawn from the tank before the pressure falls to 10 percent of the original pressure?

**2-3** A cylinder provided with a movable piston contains an ideal gas at a pressure  $P_1$ , specific volume  $v_1$ , and temperature  $T_1$ . The pressure and volume are simultaneously increased so that at every instant  $P$  and  $v$  are related by the equation

$$P = Av, \quad A = \text{constant}$$

- Express  $A$  in terms of the pressure  $P_1$ , the temperature  $T_1$ , and the gas constant  $R$ .
- Make a sketch representing the process in the  $P$ - $v$  plane.
- Find the temperature when the specific volume has doubled, if  $T_1 = 200$  K.

**2-4** For an ideal gas the slope of an isotherm is given by

$$\left(\frac{\partial P}{\partial v}\right)_T = -\frac{P}{v},$$

and that of an isochore is

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{P}{T}.$$

Show that these relations give  $Pv = RT$ , the equation of state.

**2-5** Noting that at the critical point, the three roots of the van der Waals equation are equal (i.e.,  $(v - v_c)^3 = 0$ ), show that the critical values of the specific volume, temperature, and pressure are given by Equation (2.10). Show that, in