

process of reversible heating, whereby only infinitesimal temperature gradients existed at any time during the heating process. Thus,

$$\Delta S = \int_{T_1}^{T_2} \frac{d'q_{\text{rev}}}{T} = n \int_{T_1}^{T_2} \frac{c_p}{T} dT \quad (9)$$

**Entropy Changes in an Ideal Gas.** If one mole of an ideal gas is brought from  $p_1, v_1, T_1$  to  $p_2, v_2, T_2$ , the entropy change is determined by following an imaginary reversible path from state 1 to state 2, regardless of how the change may have actually taken place. While there is a wide choice of paths, it will be convenient first to change the temperature at constant pressure and then to change the pressure reversibly and isothermally.

For the first step,

$$\Delta S_1 = \int_{T_1}^{T_2} \frac{c_p}{T} dT \quad (10)$$

In the isothermal reversible change of pressure, the first law is applied:

$$d'q = dU + d'w_e \quad (11)$$

The reversible work of expansion,  $d'w_e$ , equals  $p dv$ . By definition, an ideal gas has the following characteristics: (1) It follows the simple gas law,  $pv = RT$ , and (2) its internal energy is a function of temperature alone, and is not affected by pressure. Accordingly,

$$dU = 0 \quad (12)$$

$$p dv + v dp = R dT = 0 \quad (13)$$

$$p dv = -v dp = -RT \frac{dp}{p} \quad (14)$$

Substituting in equation 11 yields

$$d'q = -RT \frac{dp}{p} \quad (15)$$

The entropy change for the second step is as follows:

$$\Delta S_2 = \int_{p_1}^{p_2} \frac{d'q}{T} = -R \int_{p_1}^{p_2} \frac{dp}{p} = -R \ln \frac{p_2}{p_1} \quad (16)$$

$$\Delta S_{\text{total}} = \Delta S_1 + \Delta S_2 = \int_{T_1}^{T_2} \frac{c_p}{T} dT - R \ln \frac{p_2}{p_1} \quad (17)$$

An alternative equation developed by first changing temperature at constant volume and then changing volume reversibly and isothermally is as follows:

$$\Delta S_{\text{total}} = \int_{T_1}^{T_2} \frac{c_v}{T} dT + R \ln \frac{v_2}{v_1} \quad (18)$$

conditions, it is important to derive specifications which must be fulfilled by any system at equilibrium. Such specifications, termed *criteria of equilibrium*, are the foundation for complete relationships among the various properties of a system at equilibrium.

From a thermodynamic standpoint, it is necessary that, in a system at equilibrium, every possible change that might take place to an infinitesimal extent shall be reversible, since any irreversible change would result in a displacement which would destroy the original equilibrium. As was previously pointed out, reversible processes are accompanied by no change in total entropy of the combined system and its surroundings, whereas every spontaneous process is accompanied by an increase in total entropy. Thus, a universal thermodynamic criterion of equilibrium is that, for any change that takes place, the total entropy of the system *and its surroundings* shall be constant. In a completely isolated system the entropy of the system itself is constant at equilibrium. From equation 1, defining entropy, it follows that, where heat is added to a system in which all changes of state are reversible,  $d'q = T dS$ , where  $S$  is the entropy of the system itself, not including its surroundings. This expression may also be taken as a criterion of reversibility and equilibrium. Since for all irreversible changes of state  $dS > d'q/T$ , if any incremental addition of heat to the system is accompanied by an entropy increase equal to and not greater than  $d'q/T$ , then all thermodynamic processes within the system must be reversible, and it follows that the system is in equilibrium.

**Stable and Unstable Equilibrium.** A system is in *stable* equilibrium if after a finite displacement it spontaneously returns to its original state when the displacing force is returned to its original value. A round pencil lying in the bottom of a cylindrical trough is a mechanical example of this type of equilibrium. If, however, this pencil is carefully balanced on its sharpened point, it will be in a state of *unstable* equilibrium such that finite displacement does not lead to a spontaneous return to its original conditions. Although, at equilibrium, any infinitesimal change is accompanied by no change in the total entropy of the system and its surroundings, thermodynamically a system is in unstable equilibrium if a finite displacement involves an increase in total entropy. For example, a finite displacement of the pencil balanced on its point results in an irreversible process whereby heat is developed and the entropy of the pencil and of its surroundings increases. In a system in stable equilibrium no finite change can be accompanied by an increase in total entropy. Thus, at stable equilibrium, for any change resulting from a temporarily applied extraneous force, not associated with the system or its normal surroundings,

$$dS_t = 0, \quad \Delta S_t \leq 0 \quad (47)$$

TABLE 40 (Continued)

**II. The Four Basic Equations and the Modified  $dU$  and  $dH$  Equations**

$$dU = T dS - p dV \quad (96)$$

$$= -T \left( \frac{\partial V}{\partial T} \right)_p dp - p dV + C_p dT \quad (97)$$

$$= - \left[ p + T \frac{(\partial V / \partial T)_p}{(\partial V / \partial p)_T} \right] dV + C_v dT \quad (98)$$

$$dH = T dS + V dp \quad (99)$$

$$= \left[ V - T \left( \frac{\partial V}{\partial T} \right)_p \right] dp + C_p dT \quad (100)$$

$$= V dp - T \left[ \frac{(\partial V / \partial T)_p}{(\partial V / \partial p)_T} \right] dV + C_v dT \quad (101)$$

$$dA = -S dT - p dV \quad (102)$$

$$dG = -S dT + V dp \quad (103)$$

**III. Two  $dS$  Equations**

$$dS = - \left( \frac{\partial V}{\partial T} \right)_p dp + \frac{C_p}{T} dT \quad (104)$$

$$dS = \left( \frac{\partial p}{\partial T} \right)_V dV + \frac{C_v}{T} dT \quad (105)$$

$$= - \left[ \frac{(\partial V / \partial T)_p}{(\partial V / \partial p)_T} \right] dV + \frac{C_v}{T} dT \quad (106)$$

**IV. Four Important Entropy Derivatives**

$$\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial p}{\partial T} \right)_V \quad (107)$$

$$\left( \frac{\partial S}{\partial p} \right)_T = - \left( \frac{\partial V}{\partial T} \right)_p \quad (108)$$

$$\left( \frac{\partial S}{\partial T} \right)_p = \frac{C_p}{T} \quad (109)$$

$$\left( \frac{\partial S}{\partial T} \right)_V = \frac{C_v}{T} \quad (110)$$

The 168 partial derivatives involving  $p$ ,  $V$ ,  $T$ ,  $S$ ,  $U$ ,  $H$ ,  $A$ , and  $G$  may be classified into six groups. A standard method of procedure for each of the six groups is outlined below. In the discussion that follows, the

through the use of the equations for  $dS$ ,  $dU$ ,  $dH$ ,  $dA$ , and  $dG$  as given in Table 40. They are then substituted in equation 95.

**Bridgman Table.** Table 41 developed by Bridgman<sup>3</sup> affords the quickest and simplest procedure for setting up the equation for any partial derivative involving  $p$ ,  $V$ ,  $T$ ,  $S$ ,  $U$ ,  $H$ ,  $A$ , and  $G$  in terms of  $C_p$ ,  $(\partial V/\partial T)_p$ , and  $(\partial V/\partial p)_T$ . The items entered in this table are based on equation 95 where the special symbol  $(\partial z)_y$  is used to designate the numerator, and the special symbol  $(\partial x)_y$  the denominator.

$$\left(\frac{\partial z}{\partial x}\right)_y = \frac{(\partial z/\partial T)_p(\partial y/\partial p)_T - (\partial z/\partial p)_T(\partial y/\partial T)_p}{(\partial x/\partial T)_p(\partial y/\partial p)_T - (\partial x/\partial p)_T(\partial y/\partial T)_p} = \frac{(\partial z)_y}{(\partial x)_y} \quad (138)$$

Bridgman worked out expressions for all the items of the type  $(\partial z)_y$  that involve the variables  $p$ ,  $V$ ,  $T$ ,  $S$ ,  $U$ ,  $H$ ,  $A$ , and  $G$ , and then assembled them in Table 41. The procedure followed is shown in Illustration 12.

**Illustration 12.** Verify the expression for  $(\partial S)_V$  given in the Bridgman table. According to the system of notation indicated by equation 138:

$$(\partial S)_V = \left[ \left( \frac{\partial S}{\partial T} \right)_p \left( \frac{\partial V}{\partial p} \right)_T - \left( \frac{\partial S}{\partial p} \right)_T \left( \frac{\partial V}{\partial T} \right)_p \right] \quad (a)$$

Substituting equations 109 and 108 in equation (a), gives

$$\begin{aligned} (\partial S)_V &= \frac{C_p}{T} \left( \frac{\partial V}{\partial p} \right)_T - \left( - \frac{\partial V}{\partial T} \right)_p \left( \frac{\partial V}{\partial T} \right)_p \\ &= \frac{1}{T} \left[ C_p \left( \frac{\partial V}{\partial p} \right)_T + T \left( \frac{\partial V}{\partial T} \right)_p^2 \right] \end{aligned} \quad (b)$$

The use of the Bridgman table follows from equation 138, which indicates the significance of the special notation adopted. Illustration 13 demonstrates the procedure employed.

**Illustration 13.** Using Table 41, develop an equation for  $(\partial A/\partial U)_p$ .

$$\left( \frac{\partial A}{\partial U} \right)_p = \frac{(\partial A)_p}{(\partial U)_p} \quad (a)$$

Expressions for  $(\partial A)_p$  and  $(\partial U)_p$  are selected from Table 41 and substituted in the foregoing equation to yield the following result:

$$\left( \frac{\partial A}{\partial U} \right)_p = \frac{-[S + p(\partial V/\partial T)_p]}{C_p - p(\partial V/\partial T)_p} \quad (b)$$

<sup>3</sup> P. W. Bridgman, *Condensed Collection of Thermodynamic Formulas*, Harvard University Press, Cambridge, Mass. (1926). This was first published in *Phys. Rev.* (2), **3**, 273 (1914). The original article contained two errors involving  $(\partial A)_U$  and  $(\partial A)_H$ . These errors were eliminated in the book published in 1926.