

## Chapter 6

### Thermodynamic Properties of Fluids

Initial purpose in this chapter is to develop from the first and second laws the fundamental property relations which underlie the mathematical structure of thermodynamics. From these, we derive equations which allow calculation of enthalpy and entropy values from PVT and heat-capacity data. We then discuss the diagrams and tables by which property values are presented for convenient use. Finally, we develop generalized correlations which provide estimates of property values in the absence of complete experimental information.

#### 6.1 PROPERTY RELATIONS FOR HOMOGENEOUS PHASES

The first law for a closed system of  $n$  moles is:

$$d(nU) = dQ + dW \quad (2.6)$$

For the special case of a reversible process,

$$d(nU) = dQ_{\text{rev}} + dW_{\text{rev}}$$

Equations (1.2) and (5.12) are here written:

$$dW_{\text{rev}} = -P d(nV) \quad dQ_{\text{rev}} = T d(nS)$$

Together these three equations give:

$$\boxed{d(nU) = T d(nS) - P d(nV)} \quad (6.1)$$

where  $U$ ,  $S$ , and  $V$  are molar values of the internal energy, entropy, and volume.

In Chap. 2 the enthalpy was defined as a matter of convenience by the equation:

$$\boxed{H \equiv U + PV} \quad (2.11)$$

Two additional properties, also defined for convenience, are the Helmholtz energy,

$$\boxed{A \equiv U - TS} \quad (6.2)$$

and the Gibbs energy,

$$\boxed{G \equiv H - TS} \quad (6.3)$$

Each of these defined properties leads directly to an equation like Eq. (6.1). Upon multiplication by  $n$ , Eq. (2.11) becomes:

$$nH = nU + P(nV)$$

Differentiation gives:

$$d(nH) = d(nU) + P d(nV) + (nV)dP$$

When  $d(nU)$  is replaced by Eq. (6.1), this reduces to:

$$\boxed{d(nH) = T d(nS) + (nV)dP} \quad (6.4)$$

Similarly, from Eq. (6.2),

$$d(nA) = d(nU) - T d(nS) - (nS)dT$$

Eliminating  $d(nU)$  by Eq. (6.1) gives:

$$\boxed{d(nA) = -P d(nV) - (nS)dT} \quad (6.5)$$

In analogous fashion, Eqs. (6.3) and (6.4) combine to yield:

$$\boxed{d(nG) = (nV)dP - (nS)dT} \quad (6.6)$$

Equations (6.4) through (6.6) are subject to the same restrictions as Eq. (6.1). All are written for the entire mass of any closed system.

Immediate application of these equations is to one mole (or to a unit mass) of a homogeneous fluid of constant composition. For this case, they simplify to:

$$\boxed{dU = T dS - P dV} \quad (6.7)$$

$$\boxed{dH = T dS + V dP} \quad (6.8)$$

$$\boxed{dA = -P dV - S dT} \quad (6.9)$$

$$\boxed{dG = V dP - S dT} \quad (6.10)$$

**These fundamental property relations are general equations for a homogeneous fluid of constant composition.**

The thermodynamic properties  $U$ ,  $H$ ,  $A$ , and  $G$  are known to be functions of the variables on the right sides of Eqs. (6.7) through (6.10); we may therefore write the relationship expressed for each of these equations:

$$\boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V} \quad (6.13)$$

$$\boxed{\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P} \quad (6.14)$$

$$\boxed{\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T} \quad (6.15)$$

$$\boxed{\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T} \quad (6.16)$$

*These are Maxwell's equations.*

**Enthalpy and Entropy as Functions of T and P:**

Consider first the temperature derivatives. Equation (2.20) defines the heat capacity at constant pressure:

$$\left(\frac{\partial H}{\partial T}\right)_P = C_P \quad (2.20)$$

Another expression for this quantity is obtained by division of Eq. (6.8) by dT and restriction of the result to constant P

$$\left(\frac{\partial H}{\partial T}\right)_P = T \left(\frac{\partial S}{\partial T}\right)_P$$

Combination of this equation with Eq. (2.20) gives:

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \quad (6.17)$$

The pressure derivative of the entropy results directly from Eq. (6.16):

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad (6.18)$$

The corresponding derivative for the enthalpy is found by division of Eq. (6.8) by dP and restriction to constant T:

$$\left(\frac{\partial H}{\partial P}\right)_T = T \left(\frac{\partial S}{\partial P}\right)_T + V$$

As a result of Eq. (6.18) this becomes:

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T \left(\frac{\partial V}{\partial T}\right)_P \quad (6.19)$$

The functional relations chosen here for H and S are:

$$H = H(T, P) \quad \text{and} \quad S = S(T, P)$$

whence

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \quad \text{and} \quad dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

The partial derivatives in these two equations are given by Eqs. (2.20) and (6.17) through (6.19):

$$\boxed{dH = C_P dT + \left[ V - T \left( \frac{\partial V}{\partial T} \right)_P \right] dP} \quad (6.20)$$

$$\boxed{dS = C_P \frac{dT}{T} - \left( \frac{\partial V}{\partial T} \right)_P dP} \quad (6.21)$$

These are general equations relating the properties of homogeneous fluids of constant composition to temperature and pressure.

### Internal Energy as a Function of P

The pressure dependence of the internal energy is obtained by differentiation of the equation,  $U=H-PV$ :

$$\left( \frac{\partial U}{\partial P} \right)_T = \left( \frac{\partial H}{\partial P} \right)_T - P \left( \frac{\partial V}{\partial P} \right)_T - V$$

Then by Eq. (6.19),

$$\left( \frac{\partial U}{\partial P} \right)_T = -T \left( \frac{\partial V}{\partial T} \right)_P - P \left( \frac{\partial V}{\partial P} \right)_T - V \quad (6.22)$$

### The Ideal-Gas State:

The coefficients of  $dT$  and  $dP$  in Eqs. (6.20) and (6.21) are evaluated from heat-capacity and PVT data. The ideal-gas state provides an example of PVT behavior:

$$PV^{ig} = RT \quad \left( \frac{\partial V^{ig}}{\partial T} \right)_P = \frac{R}{P}$$

Substituting these equations into Eqs. (6.20) and (6.21) reduces them to:

$$dH^{ig} = C_P^{ig} dT \quad (6.23)$$

$$dS^{ig} = C_P^{ig} \frac{dT}{T} - R \frac{dP}{P} \quad (6.24)$$

where superscript "ig" denotes an ideal-gas value. These are merely restatements of equations for ideal gases presented in Secs. 3.3 and 5.5.

### Alternative Forms for Liquids

Alternative form Equations (6.18) and (6.19) result when  $(\partial V/\partial T)_P$  replaced by  $\beta V$  Eq. (3.2)

$$\left(\frac{\partial S}{\partial P}\right)_T = -\beta V \quad (6.25)$$

$$\left(\frac{\partial H}{\partial P}\right)_T = (1 - \beta T)V \quad (6.26)$$

An alternative form Equations (6.22) results if, in addition  $(\partial V/\partial P)_T$  is replaced by  $-kV$  Eq. (3.3)

$$\left(\frac{\partial U}{\partial P}\right)_T = (\kappa P - \beta T)V \quad (6.27)$$

These equations, incorporating  $\beta$  and  $k$ , although general, are usually applied only to liquids. However, for liquids not near the critical point, the volume itself is small, as are  $\beta$  and  $K$ . Thus at most conditions pressure has little effect on the properties of liquids.

When  $(\partial V/\partial T)_P$  is replaced in Eqs. (6.20) and (6.21) in favor of the volume expansivity, they become:

$$dH = C_P dT + (1 - \beta T)V dP \quad (6.28)$$

$$dS = C_P \frac{dT}{T} - \beta V dP \quad (6.29)$$

Since  $\beta$  and  $k$  are weak functions of pressure for liquids, they are usually assumed constant at appropriate average values for integration of the final terms of Eqs. (6.28) and (6.29).

### Example 6.1

Determine the enthalpy and entropy changes of liquid water for a change of state from 1 bar and 25°C to 1,000 bar and 50°C. Data for water are given in the following table.

$t/^\circ\text{C}$	$P/\text{bar}$	$C_P/\text{J mol}^{-1} \text{K}^{-1}$	$V/\text{cm}^3 \text{mol}^{-1}$	$\beta/\text{K}^{-1}$
25	1	75.305	18.071	$256 \times 10^{-6}$
25	1,000	.....	18.012	$366 \times 10^{-6}$
50	1	75.314	18.234	$458 \times 10^{-6}$
50	1,000	.....	18.174	$568 \times 10^{-6}$

### Solution 6.1

For application to the change of state described, Eqs. (6.28) and (6.29) require integration. Enthalpy and entropy are state functions, and the path of integration is arbitrary; the path most suited to the given data is shown in Fig. 6.1. Because the data indicate that  $C_P$  is a weak function of  $T$  and that both  $V$  and  $\beta$  are weak functions of  $P$ , integration with arithmetic means is satisfactory. The integrated forms of Eqs. (6.28) and (6.29) that result are:

$$\Delta H = \langle C_P \rangle (T_2 - T_1) + (1 - \langle \beta \rangle T_2) \langle V \rangle (P_2 - P_1)$$

$$\Delta S = \langle C_P \rangle \ln \frac{T_2}{T_1} - \langle \beta \rangle \langle V \rangle (P_2 - P_1)$$

For  $P = 1$  bar,

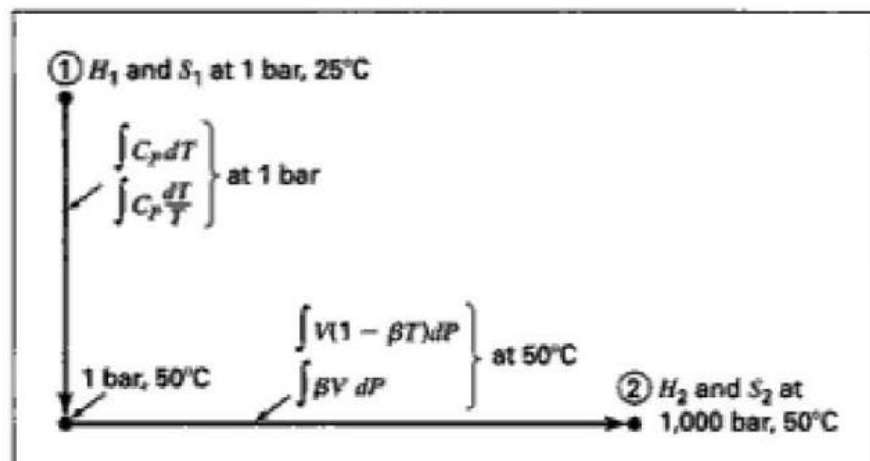
$$\langle C_P \rangle = \frac{75.305 + 75.314}{2} = 75.310 \text{ J mol}^{-1} \text{ K}^{-1}$$

and for  $t = 50^\circ\text{C}$ ,

$$\langle V \rangle = \frac{18.234 + 18.174}{2} = 18.204 \text{ cm}^3 \text{ mol}^{-1}$$

$$\langle \beta \rangle = \frac{458 + 568}{2} \times 10^{-6} = 513 \times 10^{-6} \text{ K}^{-1}$$

Figure 6.1:  
Calculational path for  
Ex. 6.1.



Substitution of these numerical values into the equation for  $\Delta H$  gives:

$$\begin{aligned}\Delta H &= 75.310(323.15 - 298.15) \\ &\quad + \frac{[1 - (513 \times 10^{-6})(323.15)](18.204)(1,000 - 1)}{10 \text{ cm}^3 \text{ bar J}^{-1}} \\ &= 1,883 + 1,517 = 3,400 \text{ J mol}^{-1}\end{aligned}$$

Similarly for  $\Delta S$ ,

$$\begin{aligned}\Delta S &= 75.310 \ln \frac{323.15}{298.15} - \frac{(513 \times 10^{-6})(18.204)(1,000 - 1)}{10 \text{ cm}^3 \text{ bar J}^{-1}} \\ &= 6.06 - 0.93 = 5.13 \text{ J mol}^{-1} \text{ K}^{-1}\end{aligned}$$

Note that the effect of a pressure change of almost 1,000 bar on the enthalpy and entropy of liquid water is less than that of a temperature change of only 25°C.