

## Chapter 11 SUMMARY

- Some thermodynamic properties can be measured directly, but many others cannot. Therefore, it is necessary to develop some relations between these two groups so that the properties that cannot be measured directly can be evaluated. The derivations are based on the fact that properties are point functions, and the state of a simple, compressible system is completely specified by any two independent, intensive properties.
- The equations that relate the partial derivatives of properties  $P$ ,  $v$ ,  $T$ , and  $s$  of a simple compressible substance to each other are called the *Maxwell relations*. They are obtained from *the four Gibbs equations*, expressed as

$$du = Tds - Pdv$$

$$dh = Tds + vdP$$

$$da = -sdT - Pdv$$

$$dg = -sdT + vdP$$

- The *Maxwell relations* are

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v$$

$$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P$$

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$$

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

- The *Clapeyron equation* enables us to determine the enthalpy change associated with a phase change from knowledge of  $P$ ,  $v$ , and  $T$  data alone. It is expressed as

$$\left(\frac{dP}{dT}\right)_{\text{sat}} = \frac{h_{fg}}{Tv_{fg}}$$

- For liquid-vapor and solid-vapor phase-change processes at low pressures, the Clapeyron equation can be approximated as

$$\ln \left( \frac{P_2}{P_1} \right)_{\text{sat}} \cong \frac{h_{fg}}{R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)_{\text{sat}}$$

- The changes in internal energy, enthalpy, and entropy of a simple, compressible substance can be expressed in terms of pressure, specific volume, temperature, and specific heats alone as

$$du = C_v dT + \left[ T \left( \frac{\partial P}{\partial T} \right)_v - P \right] dv$$

$$dh = C_p dT + \left[ v - T \left( \frac{\partial v}{\partial T} \right)_P \right] dP$$

$$ds = \frac{C_v}{T} dT + \left( \frac{\partial P}{\partial T} \right)_v dv$$

$$ds = \frac{C_p}{T} dT - \left( \frac{\partial v}{\partial T} \right)_P dP$$

- For specific heats, we have the following general relations:

$$\left( \frac{\partial C_v}{\partial v} \right)_T = T \left( \frac{\partial^2 P}{\partial T^2} \right)_v$$

$$\left( \frac{\partial C_p}{\partial P} \right)_T = -T \left( \frac{\partial^2 v}{\partial T^2} \right)_P$$

$$C_{p,T} - C_{p0,T} = -T \int_0^P \left( \frac{\partial^2 v}{\partial T^2} \right)_P dP$$

$$C_p - C_v = -T \left( \frac{\partial v}{\partial T} \right)_P^2 \left( \frac{\partial P}{\partial v} \right)_T$$

$$C_p - C_v = \frac{vT\beta^2}{\alpha}$$

where  $\beta$  is the *volume expansivity* and  $\alpha$  is the *isothermal compressibility*, defined as

$$\beta = \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_P \quad \text{and} \quad \alpha = -\frac{1}{v} \left( \frac{\partial v}{\partial P} \right)_T$$

- The difference  $C_p - C_v$  is equal to  $R$  for ideal gases and to zero for incompressible substances.
- The temperature behavior of a fluid during a throttling ( $h = \text{constant}$ ) process is described by the *Joule-Thomson coefficient*, defined as

$$\mu_{JT} = \left( \frac{\partial T}{\partial P} \right)_h$$

The Joule-Thomson coefficient is a measure of the change in temperature of a substance with pressure during a constant-enthalpy process, and it can also be expressed as

$$\mu_{JT} = -\frac{1}{C_p} \left[ v - T \left( \frac{\partial v}{\partial T} \right)_P \right]$$

- The enthalpy, internal energy, and entropy changes of real gases can be determined accurately by utilizing *generalized enthalpy* or *entropy departure charts* to account for the deviation from the ideal-gas behavior by using the following relations:

$$\bar{h}_2 - \bar{h}_1 = (\bar{h}_2 - \bar{h}_1)_{\text{ideal}} - R_u T_{\text{cr}} (Z_{h_2} - Z_{h_1})$$

$$\bar{u}_2 - \bar{u}_1 = (\bar{h}_2 - \bar{h}_1) - R_u (Z_2 T_2 - Z_1 T_1)$$

$$\bar{s}_2 - \bar{s}_1 = (\bar{s}_2 - \bar{s}_1)_{\text{ideal}} - R_u (Z_{s_2} - Z_{s_1})$$

where the values of  $Z_h$  and  $Z_s$  are determined from the generalized charts.