THE MAXWELL RELATIONS

- The equations that relate the partial derivatives of properties *P, v, T,* and *s* of a simple compressible system to each other are called the *Maxwell relations.*

- They are obtained from the four Gibbs equations by exploiting the exactness of the differentials of thermodynamic properties

Two of the Gibbs relations were derived earlier in T-dS relations

$$du = T\,ds - P\,dv$$ -------- (Gibbs relation 1)

$$dh = T\,ds + v\,dP$$ -------- (Gibbs relation 2)

The other two Gibbs relations are based on two new combination properties— the **Helmholtz function** *a* and the **Gibbs function** *g,* defined as

$$a = u - Ts$$

$$g = h - Ts$$

Differentiating, we get

$$da = du - T\,ds - s\,dT$$
$$dg = dh - T\,ds - s\,dT$$

we obtain the other two Gibbs relations by simplifying the preceding relations

$$da = -s\,dT - P\,dv \quad \text{-------- (Gibbs relation 3)}$$

$$dg = -s\,dT + v\,dP \quad \text{-------- (Gibbs relation 4)}$$

A careful examination of the four Gibbs relations reveals that they are of the form

$$dz = M\,dx + N\,dy$$

with $$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

Applying the above differential relation to the Four Gibbs relations, we obtain

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

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

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

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

- These are called the **Maxwell relations**.

- They are extremely valuable in thermodynamics because they provide a means of determining the change in entropy, which cannot be measured directly, by simply measuring the changes in properties *P, v,* and *T*

CLAPEYRON–CLAUSIUS EQUATION

The Clapeyron equation enables us to determine the enthalpy change associated with a phase change (such as the enthalpy of vaporization h_{fg}) from a knowledge of P, v, and T data alone.

Consider the third Maxwell relation,

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

The partial derivative $(\partial P/\partial T)_v$ can be expressed as a total derivative $(dP/dT)_{sat}$, which is the slope of the saturation curve on a P-T diagram at a specified saturation state as it is independent of specific volume.
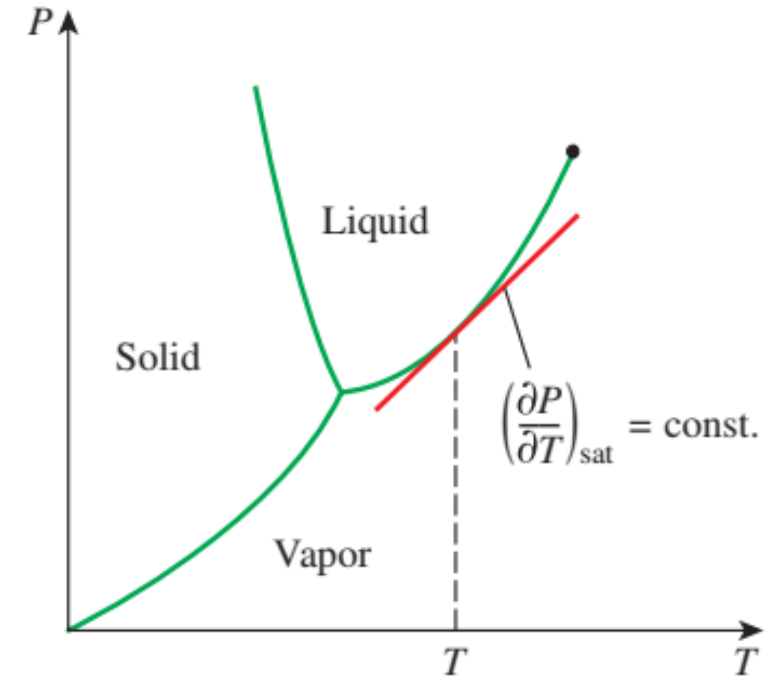

$$\left(\frac{\partial P}{\partial T}\right)_{sat} = \text{const.}$$

FIGURE 13–8

The slope of the saturation curve on a P-T diagram is constant at a constant T or P.

For an isothermal liquid–vapor phase-change process, for example, the integration yields

$$S_g - S_f = \left(\frac{dP}{dT}\right)_{sat} (\upsilon_g - \upsilon_f)$$

(or) $$\left(\frac{dP}{dT}\right)_{sat} = \frac{S_{fg}}{\upsilon_{fg}}$$

During this process the pressure also remains constant. Therefore,

$$dh = T\,ds + \upsilon\,dP\nearrow^{0}$$

$$\rightarrow \int_f^g dh = \int_f^g T\,ds$$

$$\rightarrow h_{fg} = Ts_{fg}$$

Substituting this result into above equation,

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

which is called the **Clapeyron equation**

This is an important thermodynamic relation since it enables us to determine the enthalpy of vaporization h_{fg} at a given temperature by simply measuring the slope of the saturation curve on a *P-T* diagram and the specific volume of saturated liquid and saturated vapor at the given temperature.

The Clapeyron equation can be simplified for liquid–vapor and solid–vapor phase changes by utilizing some approximations.

- At low pressures $v_g \gg v_f$, and thus $v_{fg} \cong v_g$.
- By treating the vapor as an ideal gas, we have $v_g = RT/P$.

$$\left(\frac{dP}{dT}\right)_{sat} = \frac{P h_{fg}}{RT^2}$$

$$\left(\frac{dP}{P}\right)_{sat} = \frac{h_{fg}}{R}\left(\frac{dT}{T^2}\right)_{sat}$$

Then integrating this equation between two saturation states yields

$$\ln\left(\frac{P_2}{P_1}\right)_{sat} \cong \frac{h_{fg}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)_{sat}$$

This equation is called the **Clapeyron–Clausius equation**

It can be used to determine the variation of saturation pressure with temperature.

THE JOULE-THOMSON COEFFICIENT

$T_1 = 20°C$

$P_1 = 800$ kPa

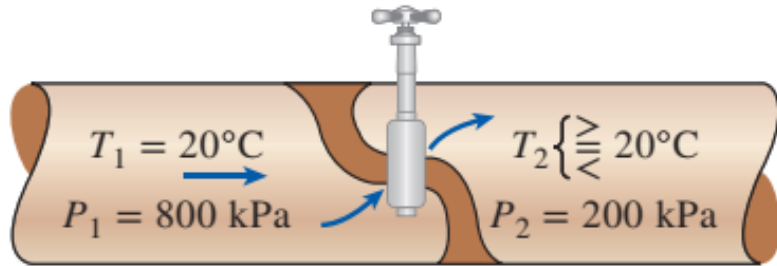$T_2 \begin{cases} \geq \\ = \\ < \end{cases} 20°C$

$P_2 = 200$ kPa

FIGURE 13–12

The temperature of a fluid may increase, decrease, or remain constant during a throttling process.

- When a fluid passes through a restriction such as a porous plug, a capillary tube, or an ordinary valve, its pressure decreases.

- the enthalpy of the fluid remains approximately constant during such a throttling process.

- A fluid may experience a large drop in its temperature as a result of throttling, which forms the basis of operation for refrigerators and air conditioners.

- This is not always the case, however. The temperature of the fluid may remain unchanged, or it may even increase during a throttling process

The temperature behavior of a fluid during a throttling ($h = $ constant) process is described by the **Joule-Thomson coefficient**, defined as

$$\mu = \left(\frac{\partial T}{\partial P}\right)_h \qquad\qquad \textbf{(13–51)}$$

Thus the Joule-Thomson coefficient is a measure of the change in temperature with pressure during a constant-enthalpy process. Notice that if

$$\mu_{JT} \begin{cases} < 0 & \text{temperature increases} \\ = 0 & \text{temperature remains constant} \\ > 0 & \text{temperature decreases} \end{cases}$$

during a throttling process.

A careful look at its defining equation reveals that the Joule-Thomson coefficient represents the slope of $h = $ constant lines on a *T-P* diagram.
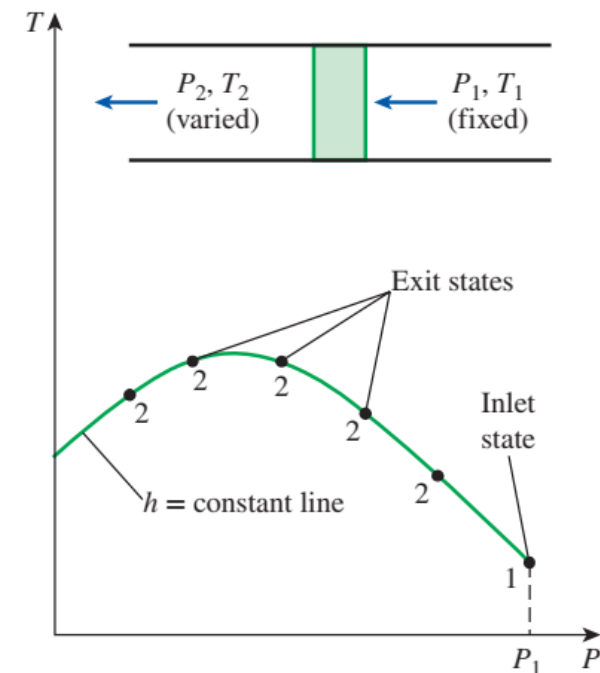

FIGURE 13–13

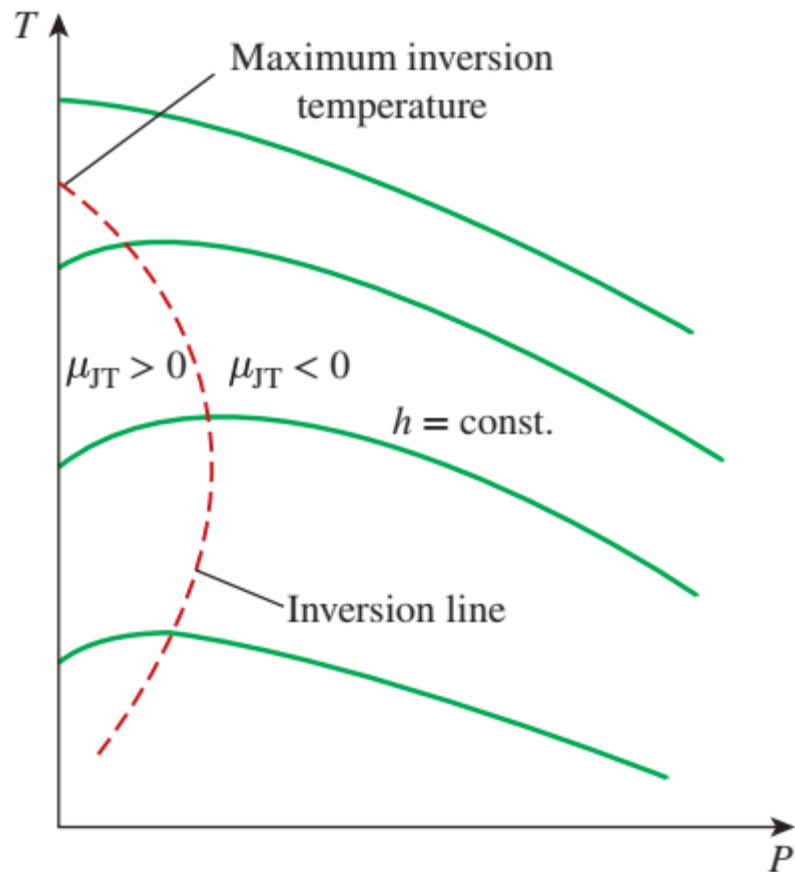The development of an $h = $ constant line on a *T-P* diagram.

FIGURE 13–14

Constant-enthalpy lines of a substance on a T-P diagram.

- Some constant-enthalpy lines on the *T-P* diagram pass through a point of zero slope or zero Joule-Thomson coefficient.

- The line that passes through these points is called the **inversion line**, and the temperature at a point where a constant enthalpy line intersects the inversion line is called the **inversion temperature**.

- The temperature at the intersection of the $P = 0$ line (ordinate) and the upper part of the inversion line is called the **maximum inversion temperature**.

- Notice that the slopes of the $h =$ constant lines are negative ($\mu_{JT} < 0$) at states to the right of the inversion line and positive ($\mu_{JT} > 0$) to the left of the inversion line.

➢ the temperature of a fluid increases during a throttling process that takes place on the right-hand side of the inversion line.

➢ However, the fluid temperature decreases during a throttling process that takes place on the left-hand side of the inversion line.