

to eq. (5.17), which gives the differential of the Gibbs free energy. We write this equation for the saturated vapor and liquid:

$$\begin{aligned}dG_V &= -S_V dT + V_V dP^{\text{sat}}, \\dG_L &= -S_L dT + V_L dP^{\text{sat}}.\end{aligned}$$

Because the difference between  $G_V$  and  $G_L$  is zero, we must have  $dG_V - dG_L = 0$ . Taking the difference between the two equations we have

$$0 = \Delta S_{\text{vap}} dT + (V_V - V_L) dP^{\text{sat}}$$

and using  $\Delta S_{\text{vap}} = \Delta H_{\text{vap}}/T$  the result becomes

$$\frac{dP^{\text{sat}}}{dT} = \frac{\Delta H_{\text{vap}}}{T(V_V - V_L)}.$$

This is an exact relationship between temperature and pressure at saturation. A practical result is obtained if we make the approximation that the liquid molar volume is negligible compared to the vapor volume (i.e.,  $V_V - V_L \approx V_V$ ), and that the vapor volume can be calculated by the ideal-gas law (i.e.,  $V_V \approx RT/P^{\text{sat}}$ ). Both approximations are acceptable at pressure well below the critical, and both become poor close to the critical point. Using these approximations, the relationship between temperature and saturation pressure becomes

$$\frac{dP^{\text{sat}}}{P^{\text{sat}}} \approx \frac{\Delta H_{\text{vap}}}{RT^2} dT$$

dT is missing from the right-hand side

The final approximation is to treat the enthalpy of vaporization as constant. Integrating from  $(T', P^{\text{sat}'})$  to  $(T, P^{\text{sat}})$ , we obtain the Clausius-Clapeyron equation:

important result  
place in box

$$\ln \frac{P^{\text{sat}}}{P^{\text{sat}'}} \approx -\frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T} - \frac{1}{T'} \right). \quad (7.5)$$

The enthalpy of vaporization is not constant, of course, it decreases with temperature and vanishes at the critical point. Therefore, the above result should be treated as an approximation over short temperature intervals. Despite its approximate nature, the Clausius-Clapeyron equation is useful in that it allows us to calculate the saturation pressure at a temperature, if its value is known at another. According to this equation, the logarithm of the saturation pressure is a linear function of inverse temperature with slope  $-\Delta H_{\text{vap}}/R$ . Saturation pressure is often plotted in semi-log axes against  $1/T$ . In this form the resulting graph is approximately linear.