5.13 The dependence of S on T and P

- substituting expression (4) for ∂H

$$\partial S = \frac{C_P}{T}\,\partial T + \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]\partial P = \left(\frac{\partial S}{\partial T}\right)_P \partial T + \left(\frac{\partial S}{\partial P}\right)_T \partial P \quad (5)$$

- $\partial T = \partial P$

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \text{ and } \left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right] \quad (6)$$

→ C_P/T = positive → S is monotically increasing function of temperature

- just as in our evaluation $(\partial S/\partial V)_T$ we equate the mixed second partial derivatives of $(\partial S/\partial T)_P$ and $(\partial S/\partial P)_T$:

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial P}\right)_T\right)_P = \left(\frac{\partial}{\partial P}\left(\frac{\partial S}{\partial T}\right)_P\right)_T \quad (7)$$

→ the mixed partial derivatives can be evaluated using (6)

$$\left(\frac{\partial}{\partial P}\left(\frac{\partial S}{\partial T}\right)_P\right)_T = \frac{1}{T}\left(\frac{\partial C_P}{\partial P}\right)_T = \frac{1}{T}\left(\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial T}\right)_P\right)_T \quad (8)$$

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial P}\right)_T\right)_P = \frac{1}{T}\left[\left(\frac{\partial}{\partial T}\left(\frac{\partial H}{\partial P}\right)_T\right)_P - \left(\frac{\partial V}{\partial T}\right)_P\right] - \frac{1}{T^2}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right] \quad (9)$$

→ equating (8) + (9)

$$\frac{1}{T}\left(\frac{\partial}{\partial T}\left(\frac{\partial H}{\partial P}\right)_T\right)_P = \frac{1}{T}\left[\left(\frac{\partial}{\partial T}\left(\frac{\partial H}{\partial P}\right)_T\right)_P - \left(\frac{\partial V}{\partial T}\right)_P\right] - \frac{1}{T^2}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right] \quad (10)$$

→ simplifying this equation

$$\left(\frac{\partial H}{\partial P}\right)_T - V = -T\left(\frac{\partial V}{\partial T}\right)_P \quad (11)$$

→ using (6) the pressure dependence of the entropy at constant temperature

$$\boxed{\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -V\beta} \quad (12)$$

→ using this result the total differential dS

$$\partial S = \frac{C_P}{T}\,\partial T - V\beta\,\partial P \quad (13)$$

→ integration of both sides

$$\boxed{\Delta S = \int_{T_i}^{T_f} \frac{C_P}{T}\,\partial T - \int_{P_i}^{P_f} V\beta\,\partial P} \quad (14)$$

idea diagram: