3/24/20

thermodynamics

ch 5 entropy and the second and third laws of thermodynamics

5.12 using the fact that S is a state function to determine the dependence of S on V and T

- dS is an exact differential
- dS w/ respect to V and T

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \quad (1)$$

$$dS = \frac{1}{T} dU + \frac{P}{T} dV \quad (2)$$

→ evaluating $(\partial S/\partial T)_V$ and $(\partial S/\partial V)_T$

$$(3)\ dS = \frac{1}{T}\left[C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV\right] + \frac{P}{T} dV = \frac{C_V}{T} dT + \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV$$

→ equating the co. of dT and dV

$$(4)\ \left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \text{ and } \left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]$$

→ the temperature dependence of entropy at constant volume can be calculated straight-forwardly using the first equality

$$dS = \frac{C_V}{T} dT, \text{ constant } V \quad (5)$$

→ to show dS is a differential

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right)_T\right)_V = \left(\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial T}\right)_V\right)_T \quad (6)$$

$$\left(\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial V}\right)_V\right)_T = \frac{1}{T}\left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_V\right)_T$$

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right)_T\right)_V = \frac{1}{T}\left[\left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T\right)_V\right] - \frac{1}{T^2}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] \quad (7)$$

→ substituting 6 for second derivatives canceling the double mixed derivative of U that appears on both sides of the equation and simplifying

$$P + \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V \quad (8)$$

→ comparing equation (8) with the second equality in (4) and a practical equation is obtained for the dependence of entropy on volume under constant temp. conditions

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = -\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T} = \frac{\beta}{\kappa} \quad (9)$$

* β = coefficient for thermal expansion at constant pressure and κ is the isothermal compressibility