CONTINUATION OF ΔS CALCULATIONS FROM LECTURE #10 – cases 4), 4’), 5), 5’) and 6) – AND SOME NEW DERVIATIONS – case 7)

7) To calculate entropy changes for non-ideal gases, and for liquids and solids, we need to use the general relation (derived just below)

\[ dS = \frac{C_v}{T} dT + \frac{\beta}{\kappa} dV, \]

implying

\[ \Delta S \approx C_v \ln \frac{T_f}{T_i} + \frac{\beta}{\kappa} (V_f - V_i) \]

for \( T_i, V_i \to T_f, V_f \) changes of state.

Similarly, we can use \( dS = \frac{C_p}{T} dT - V \beta \ dP \) (which you’ll derive in the next problem set) to obtain

\[ \Delta S \approx C_p \ln \frac{T_f}{T_i} - V \beta (P_f - P_i) \]

for \( T_i, P_i \to T_f, P_f \) changes of state.

**Derivation of** \( dS = \frac{C_v}{T} dT + \frac{\beta}{\kappa} dV \)

Start with the following statement of the 1st law: \( dU = \ddot{q}_{rev} - PdV = TdS - PdV \), which implies

\[ dS = \frac{1}{T} \frac{dU}{dV}. \quad (1) \]

But we also have

\[ dS = \left( \frac{\partial S}{\partial V} \right)_T dT + \left( \frac{\partial S}{\partial T} \right)_V dV. \quad (2) \]

Now use \( dU = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV \) and \( \left( \frac{\partial U}{\partial T} \right)_V = C_v \) to write (1) as

\[ dS = \frac{1}{T} \left[ C_v dT + \left( \frac{\partial U}{\partial V} \right)_T dV \right] + \frac{P}{T} dV, \quad \text{or} \]

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

Comparing (3) with (2), we have

\[ \frac{\partial S}{\partial T} = \frac{C_v}{T}, \quad \text{and} \quad \left( \frac{\partial S}{\partial V} \right)_T = \frac{1}{T} [P + \left( \frac{\partial U}{\partial V} \right)_T]. \quad (4a) \]

“Apply” \( \frac{\partial}{\partial V} \left( \frac{\partial S}{\partial T} \right)_T \) to equation (4a):

\[ \left( \frac{\partial}{\partial V} \left( \frac{\partial S}{\partial T} \right)_T \right)_V = \frac{1}{T} \left( \frac{\partial C_v}{\partial V} \right)_T = \frac{1}{T} \left( \frac{\partial}{\partial V} \left( \frac{\partial U}{\partial T} \right)_V \right)_T. \quad (5a) \]

Similarly, “Apply” \( \frac{\partial}{\partial T} \left( \frac{\partial S}{\partial V} \right)_T \) to equation (4b):

\[ \left( \frac{\partial}{\partial T} \left( \frac{\partial S}{\partial V} \right)_T \right)_V = \frac{1}{T} \left[ \left( \frac{\partial P}{\partial V} \right)_T + \left( \frac{\partial}{\partial T} \left( \frac{\partial U}{\partial V} \right)_T \right)_V \right] - \frac{1}{T^2} [P + \left( \frac{\partial U}{\partial V} \right)_T]. \quad (5b) \]

NOTE that the left-hand sides of (5a) and (5b) are equal, because of the equality of mixed 2nd derivatives. We can then equate the right-hand sides, and use \( \left( \frac{\partial}{\partial T} \left( \frac{\partial U}{\partial V} \right)_T \right)_V = \left( \frac{\partial}{\partial T} \left( \frac{\partial U}{\partial V} \right)_T \right)_V \) to obtain

\[ 0 = \frac{1}{T} \left( \frac{\partial P}{\partial T} \right)_V - \frac{P}{T^2} - \frac{1}{T^2} \left( \frac{\partial U}{\partial V} \right)_T, \quad (6) \]

or

\[ \left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P, \quad (7) \]

which we have used (and promised ourselves to derive!) many times in earlier lectures....
Finally, using (7) in (4b) implies $(\frac{\partial S}{\partial V})_T = (\frac{\partial p}{\partial T})_V = -\frac{\partial V}{\partial p} = +\frac{\beta}{\kappa}$, where we have used the “reciprocal” and “cyclic” rules in the next-to-last step. It then follows that

$$dS = \frac{c_v}{T} dT + \frac{\beta}{\kappa} dV,$$

as we set out to prove.

Similarly, in the next problem set, you will show that

$$(\frac{\partial H}{\partial P})_T = V - T(\frac{\partial V}{\partial T})_P,$$

and that

$$dS = \frac{c_p}{T} dT - V\beta \ dP.$$