Callen

3.2-1 Find the relation among T, P, μ of

$$U = \left(\frac{v_0^2\theta}{R^3}\right)\frac{S^4}{NV^2}$$

$$T = \frac{dU}{dS} = \left(\frac{v_0^2\theta}{R^3}\right)\frac{4S^3}{NV^2},$$

$$P = -\frac{\partial U}{\partial V} = -\left(\frac{v_0^2\theta}{R^3}\right)\frac{S^4}{1}\frac{1}{N}(-2)\left(\frac{1}{V^3}\right)$$

$$= \left(\frac{v_0^2\theta}{R^3}\right)\frac{2S^4}{NV^3}.$$

$$\mu = \frac{dU}{dN} = -\left(\frac{v_0^2\theta}{R^3}\right)\frac{S^4}{N^2V^2}.$$

The Gibbs-Duhem relation gives

$$S\,dT - V\,dP + N\,d\mu = 0.$$

$$S\,d\left(\frac{4S^3}{NV^2}\right) - V\,d\left(\frac{2S^4}{NV^3}\right) - N\,d\left(\frac{S^4}{N^2V^2}\right) = 0.$$

$$d\left(\frac{4S^3}{NV^2}\right) = \frac{d(\cdots)}{dS}\Delta S + \frac{d(\cdots)}{dV}\Delta V + \frac{d(\cdots)}{dN}\Delta N$$

$$= \frac{12S^2}{NV^2}\,dS - \frac{8S^3}{NV^3}\,dV - \frac{4S^3}{N^2V^2}\,dN$$

$$d\left(\frac{2S^4}{NV^3}\right) = \frac{8S^3}{NV^3}dS - \frac{6S^4}{NV^4}dV - \frac{2S^4}{N^2V^3}dN$$

$\cancel{d(4S^3}$ $\cancel{d(S^4)}$

$$d\left(\frac{S^4}{N^2V^2}\right) = \frac{4S^3}{N^2V^2}dS - \frac{2S^4}{N^2V^3}dV - \frac{2S^4}{N^3V^2}dN.$$

$\Rightarrow$ The Gibbs-Duhem relation when expanded is.

$$\frac{12S^3}{NV^2}dS - \frac{8S^4}{NV^3}dV - \frac{4S^4}{N^2V^2}dN$$

$$-\frac{8S^3}{NV^2}dS + \frac{6S^4}{NV^3}dV + \frac{2S^4}{N^2V^2}dN$$

$$-\frac{4S^3}{NV^2}dS + \frac{2S^4}{NV^3}dV + \frac{2S^4}{N^2V^2}dN = 0.$$

$\bigstar$ which by inspection, is correct.