

Quiz problem 1: The entropy is an extensive state function for weakly interacting large systems and both the internal energy and the entropy are homogeneous functions of order 1

$$U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N) \quad (1)$$

$$S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N) \quad (2)$$

From the entropy equation directly derive the Euler relation (a)

$$S = \frac{1}{T}U + \frac{p}{T}V - \frac{\mu}{T}N \quad (3)$$

and the corresponding form of the Gibbs-Duhem relation (b):

$$d\left(\frac{\mu}{T}\right) = \left(\frac{U}{N}\right)d\left(\frac{1}{T}\right) + \left(\frac{V}{N}\right)d\left(\frac{p}{T}\right) \quad (4)$$

(a) **Solution:**

First we can start by differentiating equation 2 with respect to λ

$$S(U, V, N) = \frac{\partial S(\lambda U, \lambda V, \lambda N)}{\partial \lambda U} \frac{\partial \lambda U}{\partial \lambda} + \frac{\partial S(\lambda U, \lambda V, \lambda N)}{\partial \lambda V} \frac{\partial \lambda V}{\partial \lambda} + \frac{\partial S(\lambda U, \lambda V, \lambda N)}{\partial \lambda N} \frac{\partial \lambda N}{\partial \lambda} \quad (5)$$

Now, assume λ has a constant value of 1.

$$S(U, V, N) = \frac{\partial S(U, V, N)}{\partial U} U + \frac{\partial S(U, V, N)}{\partial V} V + \frac{\partial S(U, V, N)}{\partial N} N \quad (6)$$

Recall TD equation,

$$dU = Tds - pdV + \mu dN \quad (7)$$

Solving for dS we get

$$dS = \frac{dU}{T} + \frac{pdV}{T} - \frac{\mu dN}{T} \quad (8)$$

From this we know that

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T}; \quad \left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{p}{T}; \quad \left(\frac{\partial S}{\partial N}\right)_{U,V} = \frac{\mu}{T} \quad (9)$$

Combining equation 9 with equation 6, we get

$$S = \frac{1}{T}U + \frac{p}{T}V - \frac{\mu}{T}N \quad (10)$$

(b) **Solution:**

Now to get the Gibbs-Duhem relation, first we take the total differential of the Euler Relation: $U = TS - pV + \mu N$ and solve for dS .

$$dU = TdS + SdT - pdV - Vdp + \mu dN + Nd\mu \quad (11)$$

$$dS = \frac{dU}{T} - \frac{SdT}{T} + \frac{pdV}{T} + \frac{Vdp}{T} - \frac{\mu dN}{T} - \frac{Nd\mu}{T} \quad (12)$$

We can also take the total derivative of equation 10 and get

$$dS = \frac{1}{T}dU + U d\frac{1}{T} + \frac{p}{T}dV + V d\frac{p}{T} - \frac{\mu}{T}dN - Nd\frac{\mu}{T} \quad (13)$$

Now combining our two expressions for dS we get,

$$-\frac{SdT}{T} + \frac{Vdp}{T} - \frac{Nd\mu}{T} = U d\frac{1}{T} + V d\frac{p}{T} - Nd\frac{\mu}{T} \quad (14)$$

AAANNNNDDDDDD... for some reason I have extra terms in this expression and I am unsure about how to remove them.