1. Hint to get started on probem 6 in the homework 1

To find the entropy we usually have to integrate unless we know one of thermodynamic potentials as a function of its natural variables. For example if we know $F(T, V, N)$ we can find the entropy as a partial derivative:

$$dF = -SdT - pdV + \mu dN$$

and

$$S = - \left(\frac{\partial F}{\partial T} \right)_{V,N}.$$

In the problem the internal energy U is given as a function of temperature $U = U(T)$ as is expected as for an equation of state derived from experiments. N is obviously constant and so is V but I now realize I should have stated that in the problem.

Recall the TD identity
$$dU =$$
and
$$dU =$$
U is given as $U(T)$ and you can calculate
$$dU =$$

.

You now have

Recall the TD identity

$$dU = TdS + \dots$$

and

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS = TdS$$

U is given as $U(T)$ and you can calculate

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT = CdT$$

.

You now have

$$dS = \frac{C}{T}dT$$

You now have

$$dS = \frac{C}{T} dT$$

which you can integrate on both sides with suitable initial conditions S_0 and T_0:

$$d\tilde{S} = \frac{C}{\tilde{T}} d\tilde{T}$$

You can also recognize the heat capacity at constant volume

$$C_V =$$

and in this problem

You now have

$$dS = \frac{C}{T}dT$$

which you can integrate on both sides with suitable initial conditions S_0 and T_0:

$$\int_{S_0}^{S} d\tilde{S} = \int_{T_0}^{T} \frac{C}{\tilde{T}}d\tilde{T}$$

You can also recognize the heat capacity at constant volume

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$$

and in this problem $C_V = C$ is constant.

2. Consequences of extensivity

Generalized forces are intensive, i.e. their value does not change if the size of the system is changed. Generalized displacements do change their value if the size of the system changes. Usually (but not in general) the change is proportional to the change in the size of the system, i.e. if I double U, V and N than S also doubles

$$S(2U, 2V, 2N) = 2S(U, V, N)$$

.

Systems with that property are called extensive and generalized displacements for such systems are extensive.

For what follow we assume an extensive system.

We can write more general

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

or

$$\lambda U(S, V, N) = U(\lambda S, \lambda V, \lambda N).$$

We differentiate on both sides with respect to λ:

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

and setting $\lambda = 1$ we get

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

We can write more general

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

or

$$\lambda U(S, V, N) = U(\lambda S, \lambda V, \lambda N).$$

We differentiate on both sides with respect to λ:

Euler equation

Identify the partial derivatives with T, p, μ using the TD identity, we arrive at

$$U = TS - pV + \mu N$$

This relation is known as Euler equation and is only true for extensive systems. It can also expressed in terms of the entropy S:

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

by either rewriting the first expression or deriving it directly from

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

Gibbs-Duhem relation

Calculate the total differential of the Euler relation $U = TS - pV + \mu N$:

Gibbs-Duhem relation

Calculate the total differential of the Euler relation $U = TS - pV + \mu N$:

$$dU = TdS + SdT - pdV - Vdp + \mu dN + Nd\mu$$

and inserting the thermodynamic identity

$$dU = TdS - pdV + \mu dN$$

we arrive at the Gibbs-Duhem relation

$$0 = SdT - Vdp + Nd\mu \,.$$

A direct consequence of the Gibbs-Duhem relation is that a extensive single component (only one particle species) system has only two thermodynamic degrees of freedom.

Generalized for r components (species) we have the TD indentity (= the differential form of the fundamental relation)

$$dU = TdS - pdV + \sum_{j=1}^{r} \mu_j dN_j$$

and the corresponding Gibbs-Duhem relation

$$0 = SdT - Vdp + \sum_{j=1}^{r} N_j d\mu_j \,.$$

A extensive system with r components has r+1 thermodynamic degrees of freedom.

We can solve for changes in chemical potential $d\mu$ in terms of dT and dP:

$$d\mu = -\left(\frac{S}{N}\right)dT + \left(\frac{V}{N}\right)dp$$

A frequently more convenient form (the entropy S is usually less readily avalable than the internal energy U) can be derived by starting from the entropy form of the Euler equation (today's exercise). We arrive at

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

We have previously dicussed that for a single component system we need three EOSs to reconstruct a fundamental relation. For example qe can find the internal energy $U(S,V,N)$ by integrating the three EOSs:

$$T(S,V,N), \qquad p(S,V,N), \qquad \mu(S,V,N).$$

For an extensive single component (only one particle species) system we can derive one EOS from the other two by integration.

Example: Ideal gas

$$pV = NkT$$

$$U = \frac{3}{2}NkT$$

To simplfy the calculation we introduce the internal enegy per particle $u = U/N$ and for the volume $v = V/N$:

Example: Ideal gas

$$pV = NkT$$

$$U = \frac{3}{2}NkT$$

To simplfy the calculation we introduce the internal enegy per particle $u = U/N$ and for the volume $v = V/N$:

$$\frac{p}{T} = k\frac{1}{v}$$

leads to

$$d\left(\frac{p}{T}\right) = -k\frac{1}{v^2}dv$$

and

$$\frac{1}{T} = \frac{3}{2}k\frac{1}{u}$$

leads to

$$d\left(\frac{1}{T}\right) = -\frac{3}{2}k\frac{1}{u^2}du \,.$$

Inserting into the Gibbs-Duhem relation

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

we find

$$d\left(\frac{\mu}{T}\right) =$$

Inserting into the Gibbs-Duhem relation

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

we find

$$d\left(\frac{\mu}{T}\right) = -u\frac{3}{2}k\frac{1}{u^2}du - vk\frac{1}{v^2}dv = -\frac{3}{2}k\frac{1}{u^1}du - k\frac{1}{v}dv \,.$$

Integrating

$$d\left(\frac{\mu}{T}\right) = -u\frac{3}{2}k\frac{1}{u^2}du - vk\frac{1}{v^2}dv = -\frac{3}{2}k\frac{1}{u^1}du - k\frac{1}{v}dv\,.$$

results in

Integrating

$$d\left(\frac{\mu}{T}\right) = -u\frac{3}{2}k\frac{1}{u^2}du - vk\frac{1}{v^2}dv = -\frac{3}{2}k\frac{1}{u^1}du - k\frac{1}{v}dv\,.$$

results in

$$\left(\frac{\mu}{T}\right) = -\frac{3}{2}k\ln(u) - k\ln(v) + X$$

and the chemical potential for a monoatomic ideal gas μ

$$\mu = -kT\left(\ln\left(\frac{V}{N}(kT)^{3/2}\right) + \tilde{X}\right)$$