

ChatGPT-4 & Questions from a Materials Thermodynamics Course

Question 2: Fundamental Equations & Equations of State

TLL Question 2:

A system obeys the equations:

$$U = a P(V/N)^2$$

$$P(V/N)^2 = b T$$

where a and b are constants. Find a fundamental equation, $S(U,V,N)$, for this system. Your answer should contain integration constants (e.g., S_0 , U_0 , V_0 , N_0).

ChatGPT4 answer:

We start with the two equations:

$$(1) U = a P(V/N)^2$$

$$(2) P(V/N)^2 = b T$$

We can substitute (2) into (1) to get $U = abT$.

But from ideal gas law, we have that $PV = NkT$, where k is the Boltzmann constant. So $P = NT/V$, therefore $U = ab(N^2T/V^2)$.

We can then substitute $T = PV/Nk$ from the ideal gas law into U to get:

$$U = ab(N^2(V/Nk)/V^2) = abkN/V.$$

For an ideal gas, we have the relation $S = Nk[\ln(V/N) + 5/2 + \ln(kT)]$, where S is the entropy, V is the volume, N is the number of particles, k is Boltzmann's constant, and T is the temperature.

From the equation for U we derived, we can write $T = UV/(abkN)$, and substitute this into the entropy equation to get:

$$S = Nk[\ln(V/N) + 5/2 + \ln(UV/(abkN^2))].$$

We can further simplify this equation and write it in terms of U , V , and N :

$$S = Nk \ln(V) - Nk \ln(N) + 5/2 Nk + Nk \ln(U) + Nk \ln(V) - Nk \ln(abk) - 2Nk \ln(N)$$

$$S = Nk \ln(UV^2/N^3) - Nk \ln(abk) + 5/2 Nk.$$

We would usually write the integration constants as additive terms, so finally, the fundamental equation for the system is:

$$S = Nk \ln(UV^2/N^3) + S_0 - Nk \ln(abk) + 5/2 Nk$$

where S_0 is an integration constant.

Please note that this derivation assumes that the given system behaves like an ideal gas and the equations of state given are applicable in all ranges which may not be the case in reality. Thus, this derivation may not hold in the general case and is based on the given equations.

TLL follow-up:

But from equation (2): $P(V/N)^2 = b T$ we know that the relationship between P , V & N is not given by the ideal gas law - so you cannot use $T = PV/Nk$ as you did above.

ChatGPT4 answer:

You're correct. My apologies for the oversight. We cannot use the ideal gas law as it won't be applicable given the provided equation $P(V/N)^2 = bT$. Let's approach it again:

Given the equations:

$$U = a P(V/N)^2$$

$$P(V/N)^2 = bT$$

Substituting (2) into (1) gives us:

$$U = abT.$$

We can write the differential of U , which gives us the number of ways we can distribute the system's energy, which is linked to the entropy S :

$$dU = ab dT.$$

Integrating, we find:

$$U = abT + U_0,$$

where U_0 is the integration constant.

Now, we know that in thermodynamics, temperature T is the derivative of the internal energy U with respect to the entropy S ($T = dU/dS$). So, we have:

$$T = dU/dS = ab.$$

Integrating this, we get:

$$abS = T + T_0,$$

where T_0 is another integration constant.

Substituting $T = abS - T_0$ into $U = abT + U_0$, we have:

$$U = ab^2S - abT_0 + U_0.$$

We can rewrite this as:

$$U - U_0 = ab^2S - abT_0.$$

Rearranging, we get the fundamental equation as:

$$S = (U - U_0) / (ab^2) + T_0/ab.$$

Remember, this solution assumes the equations provided in the question, and the actual behavior of a real system might deviate from these equations.

TLL follow-up:

If you take $T=dU/dS = ab$ and integrate, you get: $U - U_0 = ab(S - S_0) = T(S - S_0)$...I am not sure why should have a $T+T_0$ term. Can you explain?

ChatGPT4 answer:

I apologize for the confusion, you're right. My previous message contains a mistake.

If we take $T = dU/dS = ab$ and integrate, we indeed should get:

$$U - U_0 = ab (S - S_0)$$

not

$$abS = T + T_0.$$

That was an error on my part. The equation $T = dU/dS = ab$ signifies that the temperature T is a constant (ab) times the change in entropy, which gives:

$$U - U_0 = ab (S - S_0)$$

Or rearranged:

$$S = (U - U_0) / ab + S_0.$$

Here U_0 and S_0 are the integration constants. Thank you for pointing out the error.

TLL follow-up:

Your units don't work. Replacing $ab = UN/T$ in your equation above, we get $S - S_0 = U/(U/NT) - U_0/ab = NT - U_0/ab$, The dimensions of entropy are not (moles)(temperature) as your equation implies

ChatGPT4 answer:

You are correct and I apologize for the oversight. In thermodynamics, quantities need to be dimensionally consistent, and it's crucial that the units on both sides of the equations match. The dimension of entropy is typically energy/temperature, not moles x temperature.

Given the system of equations:

$$U = a P(V/N)^2$$

$$P(V/N)^2 = bT$$

We can substitute equation (2) into (1) to give:

$$U = abT.$$

The differential of U with respect to S while holding V and N constant is the definition of temperature (the first law of thermodynamics):

$$T = (dU/dS)_{(V,N)} = ab.$$

Then we can separate variables and integrate:

$$dU = ab dS \Rightarrow \int dU = \int ab dS \Rightarrow U - U_0 = ab (S - S_0)$$

where U_0 and S_0 are constants of integration.

Now we can substitute $ab = U_0/(S_0)$ to make the units consistent:

$$U - U_0 = (U_0/S_0) (S - S_0) \Rightarrow U/S_0 = U_0/S_0 + S - S_0 \Rightarrow S = (U/U_0)S_0 - S_0$$

Therefore, the entropy S as a function of U , V , and N can be expressed as:

$$S = (U/U_0)S_0 - S_0$$

Note that the constant terms (U_0 and S_0) should be chosen such that the units on both sides of the equation are consistent. In this case, U_0 has units of energy (same as U), and S_0 has units of entropy (energy/temperature).

Please note that the above derivation assumes that the temperature T can be written as a simple derivative of the internal energy U with respect to the entropy S . In more complex systems, there may be additional terms in the expression for T that reflect other kinds of interactions in the system.