

Hello,

On problem set #2, problem 2.4 we are asked to perform transformations of  $U(S,X)$ . These types of transformations were discussed in class, but I do not see the reasoning why sometimes you subtract terms and sometimes you add-- for example: We are given  $U(S,X)$  and want to know  $D(S,f)$ ,  $F(T,X)$  and  $K(T,f)$ . When we do this, we get  $D(S,f) = U - fX$ ,  $F(T,X) = U - TS$ ,  $K(T,f) = U - TS - fX$ .

I understand why we add the extra term of  $fX$  or  $TS$  (it depends on what is used in the  $U(S,X)$ ) but why are we subtracting these? How can I determine when to subtract and when to add them. It seems to me sometimes that for  $F$ ,  $G$  and  $H$  transformations of  $U$  when we add a  $u_{HM}$  (magnetic properties) sometimes we subtract the term and other times we add it.

Hi,

I am not sure I fully grasp your question, but let me try. In a Legendre transform you always subtract terms. However for work terms such as  $pdV$  the work term is actually  $p(-dV)$ , so subtracting that gives  $+PV$ . Is this what you meant?

Gerd Ceder

Hmm..

Not quite. Maybe I can reword my question. For the four basic functions,  $U$ ,  $G$ ,  $H$  and  $F$ , we have derived basic equations in class and recitation and in the Zemansky book. For some problems we are asked to look at things like, if  $U$  is now a function of  $S$  and  $X$  rather than  $P$  and  $V$ , such as pset 2, 2.4. We are given the letters  $D$ ,  $F$  and  $K$  instead of  $G$ ,  $H$  and  $F$ , and told they are functions of other values  $D(S,f)$ ,  $F(T,X)$  and  $K(T,f)$ . Then we need to write out all these transformations taking into account what they are now functions of.

For each of these, we end up basically having  $D$  or  $F$  or  $K$  equal to  $U$  minus some other thing(s). For instance,  $D = U - fX$ . I am wondering why I am subtracting the  $fX$  rather than adding it, which would seem more logical to me.

What I was trying to say was I thought that we'd seen similar relations when we were relating our  $U$  to  $H$ ,  $F$  and  $G$  and adding some magnetization value, but I recall us adding the values, not subtracting them. Am I incorrect in this? I don't quite understand why I would subtract in some cases/add in others.

An extra question-- What is the best way to think about the difference between an isolated system ( $dU=0$  and  $dV=0$ )? and an adiabatic system ( $dQ=0$ ). For instance, how are they described differently in a problem. Does isolated just tell me that  $W = Q$ , so  $pdV = TdS$ . There is still heat flow, right? It just is not affected by the environment?

Thanks again,

Dear X:

In general, whenever you want to make a Legendre Transform of the internal energy with respect to one or more intensive variables, you have to subtract the conjugate pair, except for the PV term, which is subtracted like this  $-(-PV)$ .

During the lectures, when we added some other conjugate pair, for example HM, or  $\mu N$ , it was because we had not done the Legendre Transforms in the intensive variables H or  $\mu$ . For example, consider that you have an HM term in the internal energy representation:

$$U=TS-PV+HM\dots$$

If you want to know the enthalpy of the system, you have to do the Legendre Transform"

$$H(P)=U+PV=TS-PV+HM+PV$$

See how we did not subtract HM from U, since we are not required to do the Legendre Transform for H.

I hope this helps, if not, I have office hours tomorrow, at 1:00 PM..

Good Luck!!

Sorry for not reading through the end of the e-mail...

With respect to the extra question, in an isolated system there is no energy exchange between the system and the environment. In this system  $dU=0$  and  $dV=0$  and  $dQ=0$  since there is no work that can be done on the system and the  $PdV$  should be cancelled.

In an isolated system there is no heat transfer between the environment and the system.  $dQ=0$  and  $PdV=0$ .

In an adiabatic system, while heat is not transferred between the environment and the system, work can still be exchanged, through flexible walls, for example.

An example of the ultimate isolated system: The Universe!! No heat transfer, no work done on it,  $dU=0$

I hope this works,