

CHEM 3410: Physical Chemistry I — Fall 2009

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Lecture 10: Combined first and second law

References

1. Levine, *Physical Chemistry*, Sections 4.1–4.3

Key Concepts

- We can combine the First and Second laws into a fundamental relationship. We wrote the first law as:

$$dU = \partial q + \partial w$$

For systems where pressure-volume work is the only contribution to work, $\partial w = -PdV$. Using the definition of entropy, we write $\partial q_{rev} = TdS$. Since U is a state function, as long as some reversible path exists, we can combine these two relations to yield:

$$\boxed{dU = TdS - PdV}$$

- This relationship shows us that the “natural variables” of U are S and T , or that $U = U(S, V)$. In general, U is a function of all the extensive variables. Thus if we had additional work terms, such as surface work, we would add a term in the form of γdA , and $U = U(S, V, A)$.
- Because U is a state function, or an exact differential, we can write dU in another way, much like we did on the first day of class for dV :

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

Compared to the relation above we see that:

$$\left(\frac{\partial U}{\partial S}\right)_V = T \text{ and } \left(\frac{\partial U}{\partial V}\right)_S = -P$$

- Since the order of partial derivatives doesn't matter for an exact differential (state function), we derived the first of several Maxwell Relations:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

- Having a thermodynamic potential that is a function of S and V is not very handy when looking at real systems, since we can't really control S and V in the lab. We already saw one step towards a more useful function, namely, enthalpy which we defined as:

$$H = U + PV$$

- Written in differential form:

$$dH = dU + d(PV) = dU + PdV + VdP = TdS - PdV + PdV + VdP$$

$$dH = TdS + VdP$$

Enthalpy is therefore a function of S and P , $H(S, P)$. This is a more useful thermodynamic potential since we usually work at constant pressure, and can therefore fix pressure. We saw this is helpful because enthalpy is the heat transferred at constant pressure.

- This type of variable transformation is very handy in thermodynamics. It allows us to transform from internal energy, which is a function of the extensive variables (like S and V), to other more convenient variables that fit the system we are actually looking at.
- For example, we will shortly look at systems at constant T and P , which are the typical conditions which we work. Therefore, a thermodynamic potential which is a function of T and P would be really helpful. So we define G , using a similar approach as with H :

$$G = U - TS + PV$$

This will switch us to T and P :

$$dG = dU - d(TS) + d(PV) = dU - TdS - SdT + PdV + VdP = TdS - PdV - TdS - SdT + PdV + VdP$$

$$dG = -SdT + VdP$$

So, the trick is to always start with U as a function of all the extensive variables and then go to your other functions. To go from $S \rightarrow T$ we switch the variables and change the sign: $TdS \rightarrow -SdT$.