

Oct. 02 2002: Lecture 12:

Thermodynamic Functions for General Systems

Last Time

Internal Energy of an Ideal Gas is a Function only of T

Physical Interpretation of $U(N, T)$

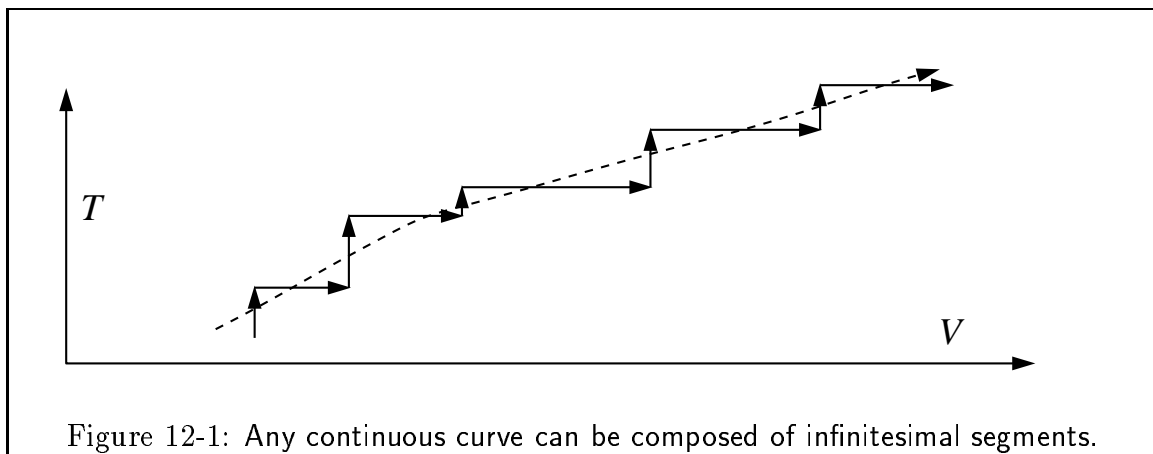
The Unexpected State Function: Entropy

We determined that for an ideal gas:

$$\frac{dq_{rev}}{T} = \frac{C_V}{T} dT + \frac{nR}{V} dV \quad (12-1)$$

Notice that we have separated the equation into something that is integrable over segments of dT (holding V constant) and dV (holding T constant).

Therefore, over any curve that we can divide up into small orthogonal segments:



Therefore, for an ideal gas, $\frac{dq_{rev}}{T}$ is a “perfect differential.”

The integral of $\frac{dq_{rev}}{T}$ depends only on its endpoints; therefore it has the properties of a state function.

Let's call the perfect differential in Equation 13-21 dS and S is defined as the new state function *entropy*.

$$\int_{\text{state}_0}^{\text{arbitrary state}} \frac{dq_{rev}}{T} = \int_{\text{state}_0}^{\text{arbitrary state}} dS = S(\text{arbitrary state}) - S_0 \quad (12-2)$$

The numerical value of entropy depends only on the state itself relative to some reference state.

Question: According to the definition in Equation 13-22, is entropy an intensive or extensive quantity?

Therefore, for an ideal gas at least,

$$dU = TdS - PdV \quad (12-3)$$

Notice that:

T is conjugate to S in the same way as $-P$ is conjugate to V

This gives a new interpretation of T :

Another Thermodynamic Function

The interpretation of S suggests that we can construct a new thermodynamic function in the same manner that we considered the physical interpretation enthalpy, H , in Eq. 13-12.

This new thermodynamic is formed by subtracting off the “thermal energy” part from U :

$$F \equiv U - TS \quad (12-4)$$

This should be a function expressing how much compression work can be done by any body at constant T . This function is called the Helmholtz free energy.

(But this is getting ahead of ourselves since we have only been discussing ideal gases.)

We have found the entropy is a state function for an ideal gas, a generalization of this entropy for any system makes up the first part of the second law.

The new functions that we have developed must also be state functions—we will find that their interpretation makes them very useful indeed.

Yet Another (and Very Important) Thermodynamic Function

There is one more thermodynamic function that we can define by the same means that we found both the enthalpy and the Helmholtz free energy.

This new thermodynamic is formed by subtracting off the “thermal energy” and the “compressive energy” from U :

$$G = U + PV - TS = H - TS = F + PV \quad (12-5)$$

This should be a function expressing how much work could be extracted from a fluid at constant pressure and temperature. This function is called the Gibbs free energy—and it is a pleasure to introduce you to one of my dear friends—I am sure that you will find many topics of common interest.

So, if we have subtracted off the “stored compressive energy” and the “stored thermal energy” from the potential energy, then what is left? Suppose that the system that we are considering has some other “internal degrees of freedom” that can be changed at constant pressure and temperature, then this is the energy associated with those internal degrees of freedom.

Question: Can you identify some variables that describe how a system can change at constant pressure and temperature?
