

ENGRD 221: ENGINEERING THERMODYNAMICS

Lecture 16: October 18, 2007

Reading Assignments (from Moran & Shapiro, Sixth Edition): Sections 9.1, 9.2 and 9.3. Please read the remaining of chapter 9 as it provides many examples that re-enforce property and process calculations that have been discussed in class. The 2nd part of the lecture requires class attendance!

Particular topics reviewed:

- The spark ignition (SI) engine, the air-standard compression ignition engine, the Diesel cycle
- Key parameters: The compression, expansion and cutoff ratios
- Thermal efficiency of the standard Diesel cycle as a function of compression and cutoff ratios
- Efficiency comparisons between the Otto and Diesel cycles (basic ideas)
- Example problems
- Introduction to Legendre transformations of U
- Introducing enthalpy, Helmholtz free energy and Gibbs free energy
- Combined first and second laws in terms of U, H, F and G.

THERMODYNAMIC VARIABLES AND RELATIONS

Thermodynamic property relations

- How do the property tables are prepared?
- How some unknown properties can be obtained from limited available data?
- T,P,V can be measured directly. How about U,H,S,...?

**WE NEED RELATIONS BETWEEN
THERMODYNAMIC PROPERTIES**

Legendre transformations

- Let $Y(X_1, X_2, \dots, X_n)$ where X_1, X_2, \dots, X_n are n-independent natural variables. Then

$$\begin{aligned} dY &= \frac{\partial Y}{\partial X_1} dX_1 + \frac{\partial Y}{\partial X_2} dX_2 + \dots + \frac{\partial Y}{\partial X_n} dX_n = \\ &= C_1 dX_1 + C_2 dX_2 + \dots + C_n dX_n \end{aligned}$$

where $C_i = \frac{\partial Y}{\partial X_i} \Big|_{X_1, X_2, \dots, X_{i-1}, X_{i+1}, \dots, X_n}$

Legendre transformations

$$dY = C_1 dX_1 + C_2 dX_2 + \dots + C_n dX_n$$

- Note that 'in some sense' C_1 is conjugate to X_1 ,
 C_2 to X_2 , etc. Conjugate means that they come in pair in the expression for dY .
- We can define new functions replacing one or more of the X_i 's with their conjugate variables C_i 's.
- You can do that using Legendre transformations.

Legendre transformations

$$dY = C_1 dX_1 + C_2 dX_2 + \dots + C_n dX_n$$

- We want to replace X_1 with C_1 . To do so, we define:

$$\Omega_1(C_1, X_2, \dots, X_n) = Y(X_1, X_2, \dots, X_n) - C_1 X_1$$

- Then note that:

$$d\Omega_1 = C_1 dX_1 + C_2 dX_2 + \dots + C_n dX_n - C_1 dX_1 - X_1 dC_1$$

or
$$d\Omega_1 = -X_1 dC_1 + C_2 dX_2 + \dots + C_n dX_n$$

Note that the independent variables in Ω_1 are now: C_1, X_2, \dots, X_n .

Legendre transformations

$$dY = C_1 dX_1 + C_2 dX_2 + \dots + C_n dX_n$$

- Similarly you can define

$$\Omega_2(X_1, C_2, \dots, X_n) = Y(X_1, X_2, \dots, X_n) - C_2 X_2$$

(replaces X_2 with C_2)

$$\Omega_{1,2}(C_1, C_2, X_3, \dots, X_n) = Y(X_1, X_2, \dots, X_n) - C_1 X_1 - C_2 X_2$$

(replaces X_1 and X_2 with C_1, C_2)

Legendre transformations of U

- In order to simplify our derivations of thermodynamic variable relationships we will apply Legendre transformations to U using our combined statement of the 1st and 2nd laws:

$$dU = TdS - PdV$$

S and V are the natural variables of U

Enthalpy: $H = U + PV$

$$dU = TdS - PdV$$

- First, let's decide to make a new function out of U which replaces one of its natural variables, volume V with pressure P .
- Using the Legendre transformation, we can define a new function H which subtracts off from U the conjugate pair $(-PV)$ from the original function.

$$H = U - (-PV) = U + PV$$

Enthalpy: $H = U + PV$

$$H = U - (-PV) = U + PV$$

Compression work



- The above transformation replaces V with P as a natural variable.

Enthalpy

$$H = U + PV$$

- The differential of this new function is just

$$dH = dU + PdV + VdP$$

- If we substitute in our combined statement of the 1st and 2nd laws:

$$dU = TdS - PdV$$

- We obtain:

$$dH = TdS - PdV + PdV + VdP = TdS + VdP$$

Enthalpy

$$dH = TdS + VdP$$

- As we planned this has replaced V with its conjugate pair P .
- That is, this new function H has natural variables of entropy S and pressure P , $H=H(S,P)$. This energy function is just the enthalpy H that we defined weeks earlier.

Enthalpy

$$dH = TdS + VdP$$

- Notice that if during a process we hold pressure constant that

$$dH_P = TdS$$

and that if the process is carried out quasi-statically, or reversibly in other words, that we can equate TdS to the heat flow so that

$$dH_P = \delta q_{rev}$$

- This is consistent with what we discussed earlier in the course.

Helmholtz free energy: $F=U-TS$

$$dU = TdS - PdV$$

- Another transformation we could have made is defining a new function to replace S with T as the natural variable.
- To do this we subtract from U the conjugate pair TS which defines a new function F

$$F = U - TS$$

with the natural variables of V and T .

Helmholtz free energy: $F=U-TS$

$$F = U - TS$$

- TS is the `thermal work'. So we subtract from U the `thermal work'

Helmholtz free energy $F=U-TS$

$$F = U - TS$$

- Taking the total derivative of this we find that

$$dF = dU - TdS - SdT$$

- and if we substitute in the combined statements of the 1st and 2nd laws as we results in

$$dF = TdS - PdV - TdS - SdT = -PdV - SdT$$

Helmholtz free energy $F=U-TS$

$$dF = -PdV - SdT$$

- The newly defined function F has natural variables T and V . We call this new function the Helmholtz free energy.
- Notice that if we have a process which is carried out reversibly (why?) at constant T then

$$dF_T = -PdV = \delta w_{rev}$$

- This says that the Helmholtz free energy is then just equal to the work done on the system during an isothermal process.

Gibbs free energy $G=U-TS+PV$

$$dU = TdS - PdV$$

- The last possible Legendre transformation we can perform on a system with only two independent variables is to replace both independent natural variables simultaneously. Starting from $U(S,V)$, we'll create a new function with **T and P as the new natural variables**.
- To do this let's define the new function $G=G(T,P)$ with $G = U - TS + PV$

Gibbs free energy $G=U-TS+PV$

$$G = U - TS - (-PV)$$

Thermal energy

Compression energy

- What is left after you subtract from U the thermal and mechanical (compression) energy?

Chemical energy

- G is the most important state function in thermodynamics

Gibbs free energy $G=U-TS+PV$

$$G = U - TS + PV$$

- Taking the total derivative of this we find that

$$dG = dU - TdS - SdT + PdV + VdP$$

- Substituting in the expression for the combined 1st and 2nd laws results in:

$$dG = -PdV - SdT + PdV + VdP = -SdT + VdP$$

Gibbs free energy

$$dG = -SdT + VdP$$

- $G=G(T,P)$ would be the most practical energy function in many cases since it has the most convenient pair of natural variables, P and T which are both easy to control in the laboratory.
- U on the other hand, although it is theoretically convenient (because we can connect changes in to heat flow and work done) has the inconvenient variables of S and V .

$$dU = TdS - PdV$$

- Performing experiments in a constant V chamber is more cumbersome than using a constant P condition, and because creating a constant S condition is not well understood or practical to achieve in the laboratory.

Energy functions: Enthalpy

- Above we defined three new functions using a Legendre transformation on U .
- Note that the Legendre Transformation doesn't change the units. That is the units of the new function are the same as the units of the original function since they are both made up of conjugate pairs whose products have the same units.
- In this particular case, the three new functions have the units of energy, as does U . We called the first new function the enthalpy H .

$$H = U + PV$$

Energy functions: Helmholtz and Gibbs free energies

- The two new functions we hadn't seen before in this course, although you are probably familiar from your chemistry classes, are G and F . The function

$$F = U - TS$$

which we called the Helmholtz free energy function and the function

$$G = U - TS + PV$$

which we called the Gibbs Free Energy.

Helmholtz and Gibbs free energies

- F and G are two of the most commonly used functions because both remove S as a natural variable and replace it with T, which is much easier to control using constant T baths, etc.
- All together then we have four energy functions:

Summary

$$U(S, V)$$

$$H(S, P) = U + PV$$

$$F(T, V) = U - TS$$

$$G(T, P) = U + PV - TS$$

Notice that we can also write that:

$$G(T, P) = H - TS$$

$$G(T, P) = F + PV$$

Differential forms (1st and 2nd laws)

- We will commonly use the differential forms of these energy functions which we summarize here:

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

$$dF = -PdV - SdT$$

$$dG = -SdT + VdP$$