

ENGRD 221: ENGINEERING THERMODYNAMICS

Lecture 18: October 25th, 2007

Topics covered:

- Review material from the last two lectures on thermodynamic relations.
- General relations for du , dh , df , ds and dg in terms of dT and dP .
- The general Jacobian approach in computing thermodynamic relations. For those who did not learn the Jacobian approach for solving a system of 2 equations with 2 unknowns, following the technique discussed in class will be just fine (i.e. equating the coefficients of the dT and dP terms on the left and right hand side of the equation leads to 2 equations with 2 unknowns that you can solve with your favorite method).
- General expression between c_p and c_v in terms of the volume expansivity (coefficient of volumetric expansion) β and isothermal compressibility α .

Chapter 5

General Procedure

In this chapter we will develop a general method for determining the relationship between thermodynamic variables. If your independent variables of choice happen to be T and P , then you can just look at the six expressions in the Summary of Thermodynamic functions for $dZ(P, T)$ and write down the various relationships that result by applying coefficient and Maxwell relations to the exact differentials. This is the trivial case. If on the other hand; however, you are interested in relationships that involve variables other than temperature and pressure then you need to do a bit more work. Let's proceed to develop a strategy for deriving these relationships.

Derivation of the General Procedure

1. The first step is to identify the variables of interest. If you have a system with only two degrees of freedom then you will have three variables, one dependent and two independent. Write down the dependent variable as a function of the two independent variables;

$$Z = Z(X, Y)$$

2. Write the total differential of Z :

$$dZ = MdX + NdY$$

where we know that the coefficients are just the partials

$$M = \left(\frac{\partial Z}{\partial X}\right)_Y$$

and

$$N = \left(\frac{\partial Z}{\partial Y}\right)_X$$

3. The third step is to convert the total differential from the independent variables of X and Y , to P and T . We do this by substituting in for dX and dY from the *Summary of Thermodynamic State Functions in terms of T and P* in the previous section. dX and dY are themselves exact differentials and so they are of the form

$$dX = \left(\frac{\partial X}{\partial P}\right)_T dP + \left(\frac{\partial X}{\partial T}\right)_P dT$$

and

$$dY = \left(\frac{\partial Y}{\partial P}\right)_T dP + \left(\frac{\partial Y}{\partial T}\right)_P dT$$

where we write $X_P = \left(\frac{\partial X}{\partial P}\right)_T$, $Y_P = \left(\frac{\partial Y}{\partial P}\right)_T$, etc. as shorthand for the partial derivatives. Notice that here that the subscripts in this notation refer to the independent variables that are *not* constant.

Then on substitution into dZ we obtain:

$$dZ = M(X_T dT + X_P dP) + N(Y_T dT + Y_P dP)$$

4. The fourth step is to collect like terms:

$$dZ = (MX_T + NY_T) dT + (MX_P + NY_P) dP$$

5. The fifth step involves writing

$$dZ = Z_T dT + Z_P dP$$

from the now obviously very useful *Summary of Thermodynamic State Functions in terms of T and P* . We now have two different expressions for $dZ(T, P)$. Since the variables T and P are both independent variables we can vary each one independent of the other and since the two expressions for dZ don't depend on the variation we know that the coefficients of dT and dP from the two expressions for dZ are equal to each other.

$$Z_T = MX_T + NY_T$$

and

$$Z_P = MX_P + NY_P$$

6. The Sixth step involves solving these two equations for M and N . Solving a system of two linear equations in two unknowns can be done by elimination of M or N and then solving for the other or by using the Jacobians of the system. For the two linear equations in the two unknowns M and N above the Jacobians are:

$$M = \frac{\begin{vmatrix} Z_T & Y_T \\ Z_P & Y_P \end{vmatrix}}{\begin{vmatrix} X_T & Y_T \\ X_P & Y_P \end{vmatrix}}$$

and

$$N = \frac{\begin{vmatrix} X_T & Z_T \\ X_P & Z_P \end{vmatrix}}{\begin{vmatrix} X_T & Y_T \\ X_P & Y_P \end{vmatrix}}$$

which of course gives you

$$M = \frac{Z_T Y_P - Z_P Y_T}{X_T Y_P - X_P Y_T}$$

and

$$N = \frac{Z_P X_T - Z_T X_P}{X_T Y_P - X_P Y_T}.$$

Now that we have outlined this procedure, let's apply it to several problems as examples (these examples are taken from DeHoff section 4.3.3).

General Procedure Examples

The following three examples involve using the General Procedure to find the thermodynamic relationship between three variables where one of the independent variables is either T or P . In the first example T is one of the independent variables.

T or P as an Independent Variable

Example 3 Write the entropy of a system as a function of its temperature and volume.

Step 1. Identify variables:

$$S = S(T, V)$$

Step 2. Write the differential form:

$$dS = MdT + NdV$$

Step 3. Convert dV using $dV(P, T)$ from the summary:

$$dS = MdT + N(V\alpha dT - V\beta dP)$$

Step 4. Collect terms:

$$dS = (M + NV\alpha) dT - NV\beta dP$$

Step 5. Obtain $dS(P, T)$ from the summary and compare to dS we just derived:

$$dS = \left[\frac{C_p}{T} \right] dT - V\alpha dP$$

The coefficients are equal to each other so:

$$\frac{C_p}{T} = M + NV\alpha$$

and

$$V\alpha = NV\beta$$

Step 6. Since the algebra is simple we can just use elimination of N .

$$N = \frac{\alpha}{\beta} = \left(\frac{\partial S}{\partial V} \right)_T$$

and

$$M = \frac{C_p}{T} - \left(\frac{\alpha}{\beta}\right) V\alpha$$

$$M = \frac{C_p}{T} - \frac{\alpha^2}{\beta} V = \left(\frac{\partial S}{\partial T}\right)_V$$

and finally

$$dS = \left(\frac{C_p}{T} - \frac{\alpha^2}{\beta} V\right) dT + \frac{\alpha}{\beta} dV$$

This next example is very similar, however rather than T , P is one of the independent variables.

Example 4 Write the entropy of a system in terms of its pressure and volume

Step 1. Identify variables:

$$S = S(P, V)$$

Step 2. Write the differential form:

$$dS = MdP + NdV$$

Step 3. Convert dV using $dV(P, T)$ from the summary:

$$dS = MdP + N(V\alpha dT - V\beta dP)$$

Step 4. Collect terms:

$$dS = (M - NV\beta) dP + NV\alpha dT$$

Step 5. Obtain $dS(P, T)$ from the summary and compare to dS we just derived:

$$dS = \left[\frac{C_p}{T}\right] dT - V\alpha dP$$

The coefficients are equal to each other so:

$$\frac{C_p}{T} = NV\alpha$$

and

$$-V\alpha = M - NV\beta$$

Step 6. Since the algebra is simple again we can just use elimination of N .

$$N = \frac{C_p}{VT\alpha} = \left(\frac{\partial S}{\partial V}\right)_P$$

and

$$M = NV\beta - V\alpha$$

$$M = \frac{C_p\beta}{T\alpha} - V\alpha = \left(\frac{\partial S}{\partial P}\right)_V$$

and finally

$$dS = \left(\frac{C_p\beta}{T\alpha} - V\alpha\right) dP + \frac{C_p}{VT\alpha} dV$$

From the above two examples we can see that if either P or T is one of the independent variables then we do not have to substitute in for dP or dT in step 3. This results in simple algebra in step 5. Notice this again in the next example.

Example 5 Find the relationship needed to compute the change in Helmholtz free energy when the initial and final states are specified by their pressure and volume.

Step 1. Identify variables:

$$F = F(P, V)$$

Step 2. Write the differential form:

$$dF = MdP + NdV$$

Step 3. Convert dV using $dV(P, T)$ from the summary:

$$dF = MdP + N(V\alpha dT - V\beta dP)$$

Step 4. Collect terms:

$$dF = (M - NV\beta) dP + NV\alpha dT$$

Step 5. Obtain $dF(P, T)$ from the summary and compare to dF we just derived:

$$dF = -(S + PV\alpha)dT + PV\beta dP$$

The coefficients are equal to each other so:

$$-(S + PV\alpha) = NV\alpha$$

and

$$PV\beta = M - NV\beta$$

Step 6. Since the algebra is simple again we can just use elimination of N .

$$N = -\left(\frac{S}{V\alpha} + P\right) = \left(\frac{\partial F}{\partial V}\right)_P$$

and

$$M = (N + P)V\beta$$

$$M = \left(P - \frac{S}{V\alpha} - P\right)V\beta = -\frac{S\beta}{\alpha} = \left(\frac{\partial F}{\partial P}\right)_V$$

and finally

$$dF = -\frac{S\beta}{\alpha} dP - \left(\frac{S}{V\alpha} + P\right) dV$$

Independent Variables Not T or P

In the above three examples we solved for the thermodynamic relationship between three variables where one of the independent variables was either temperature or pressure. A slightly more complicated case involves solving for the relationship using the exact same steps of the General Procedure, but where neither of the independent variables are pressure nor temperature. The slight complication involves primarily the extra algebra of solving the two linear equations. Let's look at an example of this type.

Example 6 Write the enthalpy as a function of volume and entropy.

Step 1. Identify variables:

$$H = H(S, V)$$

Step 2. Write the differential form:

$$dH = MdS + NdV$$

Step 3. Convert dS and dV using $dS(P, T)$ and $dV(P, T)$ from the summary:

$$dH = M \left(\frac{C_P}{T} dT - V\alpha dP \right) + N (V\alpha dT - V\beta dP)$$

Step 4. Collect terms:

$$dH = - (MV\alpha + NV\beta) dP + \left(M\frac{C_P}{T} + NV\alpha \right) dT$$

Step 5. Obtain $dH(P, T)$ from the summary and compare to dH we just derived:

$$dH = C_P dT + V (1 - T\alpha) dP$$

The coefficients are equal to each other so:

$$V (1 - T\alpha) = - (MV\alpha + NV\beta)$$

and

$$C_P = \left(M\frac{C_P}{T} + NV\alpha \right)$$

Step 6. Here we can multiply the top equation by α and the bottom equation by β and add the two equations or use the Jacobians. We'll use the Jacobians in this case just to illustrate their use.

$$\begin{aligned}
M &= \frac{\begin{vmatrix} H_T & V_T \\ H_P & V_P \end{vmatrix}}{\begin{vmatrix} S_T & V_T \\ S_P & V_P \end{vmatrix}} = \frac{H_T V_P - H_P V_T}{S_T V_P - S_P V_T} \\
&= \frac{-C_P V \beta - V(1-T\alpha)V\alpha}{-\frac{C_P}{T}V\beta + V\alpha V\alpha} \\
&= \frac{-C_P \beta - (V\alpha - TV\alpha^2)}{-\frac{C_P}{T}\beta + V\alpha^2} \\
&= \frac{\beta\left(C_P + \frac{V\alpha}{\beta} - \frac{TV\alpha^2}{\beta}\right)}{\frac{\beta}{T}\left(C_P - \frac{TV\alpha^2}{\beta}\right)} \\
M &= \frac{T\left(C_P + \frac{V\alpha}{\beta} - \frac{TV\alpha^2}{\beta}\right)}{\left(C_P - \frac{TV\alpha^2}{\beta}\right)}
\end{aligned}$$

Now although this is a perfectly valid equation, it is not in its simplest form. If one of the independent variables is volume it is usually the case that a simpler form results if we express the coefficients in terms of C_V rather than C_P . To do this we note that from the first example of using the General Procedure we found that

$$dS = \left(\frac{C_P}{T} - \frac{\alpha^2}{\beta}V\right) dT + \frac{\alpha}{\beta}dV$$

which has a coefficient relation of dT which states that

$$\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{C_P}{T} - \frac{\alpha^2}{\beta}V\right)$$

We also know from the section in this chapter on definitions that

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$$

So we find that

$$C_V = C_P - \frac{TV\alpha^2}{\beta}.$$

Substituting this into our expression for M gives us a simpler looking form:

$$M = \frac{T}{C_V} \left(C_V + \frac{V\alpha}{\beta}\right) = \left(\frac{\partial H}{\partial S}\right)_V$$

and

$$N = \frac{\begin{vmatrix} S_T & H_T \\ S_P & H_P \end{vmatrix}}{\begin{vmatrix} S_T & V_T \\ S_P & V_P \end{vmatrix}} = \frac{S_T H_P - S_P H_T}{S_T V_P - S_P V_T}$$

which can be expanded as M was to obtain

$$N = \frac{-C_P}{\beta C_V}.$$

T or P as the Dependent Variable

The next example of using the General Procedure involves cases where the dependent variable is either temperature T or pressure P . For example, how would one go about solving for the relationship $P(S, F)$? In this case we would just rewrite the equation $P = P(S, F)$ as either $F = F(P, S)$ or $S = S(P, F)$ and then use the General Procedure to determine this relationship. The final step would then be to rearrange the total differentials of either S or F to the total differential dP .

Example 7 Write an expression that shows the dependence of pressure on entropy and Helmholtz free energy.

First we identify variables: $P = P(S, F)$

Next we rewrite our master equation since in this case the dependent variable is pressure P .

$$S = S(P, F)$$

We can then write the Jacobians for the partials directly:

$$\left(\frac{\partial S}{\partial P}\right)_F = \frac{\left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial F}{\partial P}\right)_T - \left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial F}{\partial T}\right)_P}{\left(\frac{\partial P}{\partial T}\right)_P \left(\frac{\partial F}{\partial P}\right)_T - \left(\frac{\partial P}{\partial F}\right)_T \left(\frac{\partial F}{\partial T}\right)_P}$$

and

$$\left(\frac{\partial S}{\partial F}\right)_P = \frac{\left(\frac{\partial P}{\partial T}\right)_P \left(\frac{\partial S}{\partial P}\right)_T - \left(\frac{\partial P}{\partial F}\right)_T \left(\frac{\partial S}{\partial T}\right)_P}{\left(\frac{\partial P}{\partial T}\right)_P \left(\frac{\partial F}{\partial P}\right)_T - \left(\frac{\partial P}{\partial F}\right)_T \left(\frac{\partial F}{\partial T}\right)_P}$$

Which are just M and N , respectively. We'll start with simplifying the first expression. Notice that the partial derivatives of the pressure with respect to the temperature and pressure are zero and one, respectively:

$$\begin{aligned} \left(\frac{\partial S}{\partial P}\right)_F &= \frac{\left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial F}{\partial P}\right)_T - \left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial F}{\partial T}\right)_P}{0 \left(\frac{\partial F}{\partial P}\right)_T - 1 \left(\frac{\partial F}{\partial T}\right)_P} \\ &= \frac{-\left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial F}{\partial P}\right)_T}{\left(\frac{\partial F}{\partial T}\right)_P} + \left(\frac{\partial S}{\partial P}\right)_T \end{aligned}$$

The second partial simplifies even further:

$$\left(\frac{\partial S}{\partial F}\right)_P = \frac{0 \left(\frac{\partial S}{\partial P}\right)_T - 1 \left(\frac{\partial S}{\partial T}\right)_P}{0 \left(\frac{\partial F}{\partial P}\right)_T - 1 \left(\frac{\partial F}{\partial T}\right)_P} = \frac{\left(\frac{\partial S}{\partial T}\right)_P}{\left(\frac{\partial F}{\partial T}\right)_P}$$

Now that we have general expressions for the partials (we could substitute in for the various partials from the summary of thermodynamic relations, but we'll refrain from that here) we can write our total differential:

$$dS = MdP + NdF$$

and rearranging gives

$$dP = \frac{dS}{M} - \frac{NdF}{M}$$

$$dP = \left[\left(\frac{\partial S}{\partial P} \right)_F \right]^{-1} dS - \left[\left(\frac{\partial S}{\partial P} \right)_F \right]^{-1} \left[\frac{\left(\frac{\partial S}{\partial T} \right)_P}{\left(\frac{\partial F}{\partial T} \right)_P} \right] dF$$

Notice that when I have the partials of one state function with respect to another at either a constant temperature or constant pressure that this partial becomes just the ratio of the two partials with respect to T or P (which ever is not held constant). That is

$$\left(\frac{\partial X}{\partial Y} \right)_P = \frac{\left(\frac{\partial P}{\partial T} \right)_P \left(\frac{\partial X}{\partial P} \right)_T - \left(\frac{\partial P}{\partial T} \right)_T \left(\frac{\partial X}{\partial T} \right)_P}{\left(\frac{\partial P}{\partial T} \right)_P \left(\frac{\partial Y}{\partial P} \right)_T - \left(\frac{\partial P}{\partial T} \right)_T \left(\frac{\partial Y}{\partial T} \right)_P}$$

which simplifies by

$$\left(\frac{\partial X}{\partial Y} \right)_P = \frac{0 \left(\frac{\partial X}{\partial P} \right)_T - 1 \left(\frac{\partial X}{\partial T} \right)_P}{0 \left(\frac{\partial Y}{\partial P} \right)_T - 1 \left(\frac{\partial Y}{\partial T} \right)_P}$$

so that

$$\left(\frac{\partial X}{\partial Y} \right)_P = \frac{\left(\frac{\partial X}{\partial T} \right)_P}{\left(\frac{\partial Y}{\partial T} \right)_P}$$

Applications to Ideal Gases

The above General Procedure is useful and as the name implies General. That is, we don't have to specify any materials properties in order to apply the General Procedure to derive thermodynamic relationships. On the other hand, the general relationships we derive can be applied to specific cases when we have some measured property for the specific case. The ideal gas is the most trivial case. Remember that for one mole of an ideal gas

$$PV = RT$$

The thermal expansion coefficient then becomes

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{1}{V} \left(\frac{\partial(RT/P)}{\partial T} \right)_P = \frac{R}{PV}$$

$$\alpha = \frac{1}{T}$$

and the compressibility for an ideal gas becomes

$$\beta = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = -\frac{P}{RT} \left(\frac{\partial(RT/P)}{\partial P} \right)_T = -\frac{P}{RT} \left(\frac{-RT}{P^2} \right)$$

$$\beta = \frac{1}{P}$$

Applying these results to the general relationship between C_V and C_P we get

$$\begin{aligned} C_V &= C_P - \frac{TV\alpha^2}{\beta} = C_P - \frac{TV\beta}{T^2} \\ C_V &= C_P - \frac{PV}{T} \\ C_V &= C_P - R \end{aligned}$$

which is the same relationship we had derived earlier while discussing ideal gases. Also note that we can apply the ideal gas equation of state to any of the six state functions written as functions of temperature and pressure. The following summarizes the results of substituting in the explicit forms of α and β into our six state functions:

$$\begin{aligned} dS &= \left(\frac{C_P}{T} dT - \frac{V}{T} dP\right) \\ dV &= \frac{V}{T} dT - \frac{V}{P} dP \\ dU &= C_V dT \\ dH &= C_P dT \\ dF &= -\left(S + \frac{PV}{T}\right) dT + V dP \\ dG &= -S dT + V dP \end{aligned}$$

Using these expressions we can then find the changes in the various thermodynamic quantities for a particular change of state. Let's look at an example that does just this.

Example 8 *What is the heat absorbed by one mole of an ideal gas for a reversible isothermal change in pressure? The relationship that describes this process is $S = S(T, P)$ and from the above we write*

$$dS = \left(\frac{C_P}{T} dT - \frac{V}{T} dP\right)$$

and since the process is isothermal this becomes

$$dS_T = -\frac{V}{T} dP_T = -\frac{RT}{P} \frac{1}{T} dP_T = -\frac{R}{P} dP_T$$

Using the relationship between the heat flow in a reversible process and the change in entropy we can write

$$\begin{aligned} \delta q_{T,rev} &= T dS_T = -\frac{RT}{P} dP_T \\ \text{which on integration becomes} \\ q_{T,rev} &= -\int_{P_1}^{P_2} \frac{RT}{P} dP_T = -RT \ln\left(\frac{P_2}{P_1}\right) \end{aligned}$$

If instead we were interested in the heat absorbed by an ideal gas during an isobaric expansion we would need to find a different thermodynamic relationship to describe the process. Let's look at this case as another example.

Example 9 *What is the heat adsorbed by an ideal gas during an expansion at constant pressure?*

The variables for this case are entropy (because we are interested in heat), volume (because the gas expands) and pressure (because the process is done with $dP = 0$). So

$$S = S(P, V)$$

*We found this expression previously in **Example 15** using the General Procedure:*

$$dS = \left(\frac{C_P \beta}{T \alpha} - V \alpha \right) dP + \frac{C_P}{V T \alpha} dV$$

and for an isobaric expansion this becomes

$$dS_P = \frac{C_P}{V T \alpha} dV_P$$

Since we have $T \alpha = 1$ for an ideal gas we obtain

$$dS_P = \frac{C_P}{V} dV_P$$

To calculate the heat absorbed we multiply by temperature

$$\delta q_{P,rev} = T dS_P = \frac{T C_P}{V} dV_P = \frac{P C_P}{R} dV_P$$

which we integrate to get

$$q_{P,rev} = \int_{V_1}^{V_2} \frac{P C_P}{R} dV_P = \frac{P C_P}{R} (V_2 - V_1)$$

and

$$q_{P,rev} = C_P (T_2 - T_1)$$

Note that we implicitly assumed that C_P is independent of T . This is not necessarily the case. In cases where there is a significant change in T this assumption might not hold and an explicit description of $C_P(T)$ should be included in the more complicated integral.

Applications to Solids

Although ideal gases make for simple examples to demonstrate the use of the various strategies we have been developing, and although we can often times approximate the thermodynamic behavior of real gases by assuming that a gas behaves like an ideal gas, we are most interested in the thermodynamics of solids. In fact this course is titled *Solid State Thermodynamics* and the thermodynamics of materials is what we ultimately hope to learn in this course. So let's take a look at the application of our newly developed thermodynamic tools to the analysis of solid state thermodynamics.

We know from experience that in contrast to gases, solids and liquids are not very compressible, nor do they expand a great deal on heating. We also know from experiment that also unlike gases, the heat capacity of condensed phases is not a strong function of temperature. However, in many cases materials processing involves heating a material over a large temperature range. So while it is still true that the compressibility β , thermal expansion coefficient α , and heat capacity C_P are not strong functions of temperature, the temperature changes enough so that we cannot assume these properties to be constant without having a significant error.

Example 10 *In the processing of a mole of nickel at 100,000 atm of pressure you suddenly reduce the pressure down to 1atm. You realize that similar to the expansion of an ideal gas you are going to create entropy during this irreversible process of expanding your ingot. Although the change in pressure is significant, we showed previously that the work done by expanding condensed phases is very small (the change in enthalpy and internal energies are almost identical). If you allow this expansion to take place in a thermally insulating vessel we know that there is no entropy associated with heat transfer with the surroundings. Since the ingot does negligible work and absorbs no heat from the surroundings this is approximately a constant internal energy process:*

$$dU = 0$$

Since we are interested in the entropy change during a pressure change with $dU = 0$ we can write our master equation as

$$S = S(P, U)$$

and

$$dS = \left(\frac{\partial S}{\partial P}\right)_U dP + \left(\frac{\partial S}{\partial U}\right)_P dU$$

Now since $dU = 0$ we know that

$$dS_U = \left(\frac{\partial S}{\partial P}\right)_U dP_U$$

The Jacobian for the partial derivative coefficient is just

$$\begin{aligned} \left(\frac{\partial S}{\partial P}\right)_U &= \frac{\left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial U}{\partial P}\right)_T - \left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial U}{\partial T}\right)_P}{\left(\frac{\partial P}{\partial T}\right)_P \left(\frac{\partial U}{\partial P}\right)_T - \left(\frac{\partial P}{\partial T}\right)_T \left(\frac{\partial U}{\partial T}\right)_P} \\ \left(\frac{\partial S}{\partial P}\right)_U &= \frac{\left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial U}{\partial P}\right)_T - \left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial U}{\partial T}\right)_P}{-\left(\frac{\partial U}{\partial T}\right)_P} \\ \left(\frac{\partial S}{\partial P}\right)_U &= \frac{\left(\frac{C_P}{T}\right) V(P\beta - T\alpha) + V\alpha(C_P - PV\alpha)}{-(C_P - PV\alpha)} \\ \left(\frac{\partial S}{\partial P}\right)_U &= -\frac{PV(C_P\beta - VT\alpha^2)}{T(C_P - PV\alpha)} \end{aligned}$$

and so

$$dS_U = -\frac{PV(C_P\beta - VT\alpha^2)}{T(C_P - PV\alpha)} dP$$

Now to find the change in entropy of this process we just need to integrate dS over the changes in pressure and temperature etc. The typical strategy one uses in solving for the change in a state function for some irreversible process is to find a simpler reversible process which connects the same two end points. In this case the simplest process (which we have already implicitly chosen since we derived dS for constant internal energy U) is an expansion of our solid at constant internal energy.

In addition to determining the best specific process to use for the integration, we also need to know the dependence of the various materials properties over the range of pressures in the integration. Unfortunately we don't have this information. What we do know is that

$$\begin{aligned} \alpha &= 4 \times 10^{-5} (K^{-1}), \\ \beta &= 1.5 \times 10^{-6} (atm^{-1}) \\ C_P &= 16.99 + 2.95 \times 10^{-2} T (J/mol \cdot K) \\ V &= 6.6 (cc/mol), T = 300 (K) \end{aligned}$$

A good approach here is to look at the integrand and see if some terms are negligible:

$$\begin{aligned} VT\alpha^2 &= \left[6.6 \left(\frac{cc}{mol}\right)\right] \cdot 300 (K) \cdot [4 \times 10^{-5} (K^{-1})]^2 \\ VT\alpha^2 &= 3.2 \times 10^{-6} \left(\frac{cc}{mol \cdot K}\right) \end{aligned}$$

and

$$\begin{aligned} C_P\beta &= \left[16.99 \left(\frac{J}{mol \cdot K}\right) + 2.95 \times 10^{-2} \left(\frac{J}{mol \cdot K^2}\right) (300K)\right] 1.5 \times 10^{-6} \left(\frac{1}{atm}\right) \\ C_P\beta &= 3.876 \times 10^{-5} \frac{J}{mol \cdot atm \cdot K} \end{aligned}$$

Converting units gives

$$C_P\beta = 3.876 \times 10^{-5} \frac{J}{\text{mol}\cdot\text{atm}\cdot K} \left(9.869 \frac{\text{cc}\cdot\text{atm}}{J}\right)$$

$$C_P\beta = 3.8 \times 10^{-4} \frac{\text{cc}}{\text{mol}\cdot K}$$

So

$$C_P\beta - VT\alpha^2 \cong C_P\beta$$

since $C_P\beta$ is more than a hundred times larger than $VT\alpha^2$. Comparing terms in the denominator of

$$dS_U = -\frac{PV(C_P\beta - VT\alpha^2)}{T(C_P - PV\alpha)} dP$$

shows that even at the maximum pressure of 100,000 atmospheres

$$PV\alpha = 26.4 \left(\frac{\text{atm}\cdot\text{CC}}{K}\right)$$

is still 10 times smaller than

$$C_P(@300K) = 255 \left(\frac{\text{atm}\cdot\text{CC}}{K}\right)$$

With these comparisons we then make the approximation that

$$\begin{aligned} \Delta S_U &= -\int_{P_1}^{P_2} \frac{PV\beta}{T} dP = \frac{V\beta}{2T} (P_1^2 - P_2^2) \\ &= \frac{(6.6\text{cc})[1.5 \times 10^{-6}(\text{atm}^{-1})]}{2(300K)} (100,000\text{atm})^2 \\ \Delta S_U &= 170 \frac{\text{cc}\cdot\text{atm}}{K} \text{ or } 17\text{J}/K \end{aligned}$$

where we have assumed that the temperature is nearly constant.

The above example is representative of the way the General Procedure can be used to determine the thermodynamics of a system. Although we made some assumptions because we didn't know the details of how the materials properties depended on temperature, this strategy lead to an explicit answer in a straightforward way. Let's look at one more example which is even more straightforward than the last.

Example 11 A student studying electromigration problems in aluminum (Al) interconnects processes a mole of Al by increasing the temperature and pressure from $T = 300K$ and $P = 1\text{atm}$ to $T = 350K$ and $P = 1000\text{atm}$ in a pressurized furnace.

a) Estimate the change in internal energy per mole of Al for this process?

The independent variable is U and the dependent variables are P , and T . Since the independent variables are P and T we can just use the table of the summary of thermodynamic functions in the course notes:

$$dU = (C_P - PV\alpha) dT + V(P\beta - T\alpha) dP$$

Since U is a **state function** I can break the process of getting the temperature and pressure changes into **two** steps; a) one isothermal, and b) the other isobaric and get the same change in internal energy.

$$\begin{aligned} dU_{dT=0} &= V(P\beta - T\alpha) dP \\ dU_{dP=0} &= (C_P - PV\alpha) dT \end{aligned}$$

For the isothermal step

$$\Delta U_{dT=0} = \int_{1atm}^{1000atm} V(P\beta - T\alpha) dP$$

Here I assume that the compressibility is **not** pressure dependent, and that the volume change on pressurization is also negligible. I then get:

$$\begin{aligned} \Delta U_{dT=0} &= V\beta \int_{1atm}^{1000atm} PdP - VT\alpha \int_{1atm}^{1000atm} dP \\ \Delta U_{dT=0} &= V\beta \frac{P^2}{2} \Big|_{1atm}^{1000atm} - VT\alpha P \Big|_{1atm}^{1000atm} \end{aligned}$$

To integrate $dU_{dP=0}$ I'll assume volume and the thermal expansion coefficient are approximately temperature independent.

$$\begin{aligned} \Delta U_{dP=0} &= \int_{300K}^{350K} (C_P - PV\alpha) dT \\ \Delta U_{dP=0} &= \int_{300K}^{350K} (a + bT) dT - PV\alpha \int_{300K}^{350K} dT \\ \Delta U_{dP=0} &= \left(aT + \frac{bT^2}{2} \right) \Big|_{300K}^{350K} - PV\alpha T \Big|_{300K}^{350K} \end{aligned}$$

If the isothermal step is first:

$$\begin{aligned} \Delta U_{dT=0} &= \left(10 \frac{cc}{mole} \right) (1.2 \times 10^{-6} atm^{-1}) \frac{[(1000)^2 - 1^2] atm^2}{2} \\ &\quad - \left(10 \frac{cc}{mole} \right) (300K) (7 \times 10^{-5} K^{-1}) (1000 - 1) atm \\ \Delta U_{dT=0} &= -203.79 \frac{atm \cdot cc}{mole} \end{aligned}$$

If the isobaric step is carried out second ($T = 300K$, $P = 1000atm$)

$$\begin{aligned} \Delta U_{dP=0} &= 206 \frac{cc \cdot atm}{mole \cdot K} (350K - 300K) + 0.12 \left(\frac{cc \cdot atm}{mole \cdot K^2} \right) \frac{[(350K)^2 - (300K)^2]}{2} \\ &\quad - (1000atm) \left(10 \frac{cc}{mole} \right) (7 \times 10^{-5} K^{-1}) (350K - 300K) \\ \Delta U_{dP=0} &= 12215 \frac{atm \cdot cc}{mole} \\ \Delta U &= \Delta U_{dP=0} + \Delta U_{dT=0} \\ \Delta U &= 12215 \frac{atm \cdot cm^3}{mole} - 203.79 \frac{atm \cdot cm^3}{mole} = 12011 \frac{atm \cdot cm^3}{mole} \end{aligned}$$

NOTE: If I would have reversed the order of the steps I'd get (hold your breath!):

$$\Delta U_{dP=0} = 206 \frac{CC \cdot atm}{mole \cdot K} (350K - 300K) + 0.12 \left(\frac{CC \cdot atm}{mole \cdot K^2} \right) \frac{[(350K)^2 - (300K)^2]}{2} \\ - (1atm) \left(10 \frac{cc}{mole} \right) (7 \times 10^{-5} K^{-1}) (350K - 300K) \\ \Delta U_{dP=0} = 12250.0 \frac{atm \cdot cm^3}{mole}$$

and

$$\Delta U_{dT=0} = \left(10 \frac{cc}{mole} \right) (1.2 \times 10^{-6} atm^{-1}) \frac{[(1000)^2 - 1^2] atm^2}{2} \\ - \left(10 \frac{cc}{mole} \right) (350K) (7 \times 10^{-5} K^{-1}) (1000 - 1) atm \\ \Delta U_{dT=0} = -238.76 \frac{atm \cdot cm^3}{mole} \\ \Delta U = \Delta U_{dP=0} + \Delta U_{dT=0} \\ \Delta U = 12250 \frac{atm \cdot cm^3}{mole} - 238.76 \frac{atm \cdot cm^3}{mole} = 12011 \frac{atm \cdot cm^3}{mole}$$

Excellent! This is the same result as we obtained when we had the isothermal step followed by the isobaric step so we can continue to believe in the power of state functions.

b) Estimate the percentage change in volume of the Al?

$$V = V_0 (1 + \alpha \Delta T)$$

$$V = V_0 (1 - \beta \Delta P)$$

Now if the process occurs by two steps the V_0 for the second step is the V at the end of the first step. So we find that:

$$V = V_0 (1 - \beta \Delta P) (1 + \alpha \Delta T) \\ \frac{V}{V_0} = [1 - (1.2 \times 10^{-6} atm^{-1}) (999atm)] [1 + (7 \times 10^{-5} K^{-1}) (50K)] \\ \frac{V}{V_0} = 1.0023$$

The volume change is approximately 0.23%

NOTE: We could have also used

$$dV = V \alpha dT - V \beta dP$$

and broken the process up into two steps to get the equation

$$V = V_0 (1 - \beta \Delta P) (1 + \alpha \Delta T).$$

Check the constant volume approximation: If I would not have assumed the volume was pressure independent then

$$\Delta U_{dT=0} = \beta \int_{1atm}^{1000atm} V P dP - T \alpha \int_{1atm}^{1000atm} V dP \\ \Delta U_{dT=0} = \beta \int_{1atm}^{1000atm} V_0 (1 - \beta \Delta P) P dP - T \alpha \int_{1atm}^{1000atm} V_0 (1 - \beta \Delta P) dP$$

The ΔU is different from the constant volume assumption by the integral

$$\begin{aligned}\Delta U'_{dT=0} &= \beta \int_{1atm}^{1000atm} V_0 P \beta (P - P_0) dP - T\alpha \int_{1atm}^{1000atm} V_0 \beta (P - P_0) dP \\ \Delta U'_{dT=0} &= \left[V_0 \beta^2 \left(\frac{P^3}{3} - P_0 \frac{P^2}{2} \right) - T\alpha V_0 \beta \left(\frac{P^2}{2} - P_0 P \right) \right] \Big|_{1atm}^{1000atm} \\ \Delta U'_{dT=0} &= 10 (1.2 \times 10^{-6})^2 \left(\frac{(1000)^3}{3} - \frac{(999)^2}{2} \right) - \\ &300 (7 \times 10^{-5}) 10 (1.2 \times 10^{-6}) \left(\frac{1000^2}{2} - 999 \right) \Delta U' = -1.2095 \times 10^{-1} \\ &\quad \frac{atm \cdot cm^3}{mole}\end{aligned}$$

which is much smaller than

$$\Delta U_{dT=0} = -203.79 \frac{atm \cdot cm^3}{mole}$$

so the constant volume approximation works well in this case. A similar treatment can show that the approximation is also good for the isobaric step. In either case, the result of part (b) that the volume change is only $0.023V_0$ justifies our approximation.

Now although the General Procedure proves very useful and simple to use, it does not by itself allow us to determine the special state variable relationships that occur when a material is in equilibrium. Those relationships are derived in the next section.

Chapter 5 Main Points

- The General Procedure can be used to derive the thermodynamic relationship between any three thermodynamic variables. The process can be followed step by step, or by using the Jacobian expressions for the necessary partial derivatives.
- Often times the partial derivatives that can be derived using the General Procedure are more easily obtained by using the Coefficient Relations or Maxwell Relations.
- In cases where the dependent variable is either T or P , rewrite the function so that neither T or P are the independent variable, then use the General Procedure and finally rearrange the resulting expression for dT or dP , whichever is the dependent variable.