

Thermodynamic Properties of a single-component, single-phase fluid

Part 2

David Keffer
Department of Chemical Engineering
University of Tennessee, Knoxville
March, 2001
dkeffer@utk.edu

Table of Contents

E. State Variables	2
Example E.1. Ideal Gas	4
Example E.2. van der Waal's gas with vdW C_p	5
Example E.3. van der Waal's gas with cubic polynomial C_p	6
F.1. Isochoric Heating for Arbitrary Equation of State	8
F.2. Isochoric Heating for Ideal Gas	10
Example F.2. Numerical Example	13
F.3. Isochoric Heating for van der Waal's gas with vdW C_p	
Example F.3. Numerical Example	14
G.1. Isenthalpic Compression for Arbitrary Equation of State	15
G.2. Isenthalpic Compression for Ideal Gas	18
Example G.2. Numerical Example	20
G.3. Isenthalpic Compression for van der Waal's gas with vdW C_p	
Example G.3. Numerical Example	21
H.1. Isentropic Expansion for Arbitrary Equation of State	22
H.2. Isentropic Expansion for Ideal Gas	25
Example H.2. Numerical Example	28
H.3. Isentropic Expansion for van der Waal's gas with vdW C_p	
Example H.3. Numerical Example	29

E. State Variables

The two processes (an isothermal expansion/compression and an isobaric heating/cooling) that we have shown in parts C and D for are only two examples of processes which could take place. However, since a single-component, single-phase fluid is completely determined by its temperature and pressure, we can effect any change in thermodynamic state of a single component, single phase material by combining an isothermal expansion/compression step with an isobaric heating/cooling step. It doesn't matter if the real process used a different path to get from the initial to the final state, because U, H, S, G, and A are state variables. They are path independent. If we know the initial and final values of T and P, we can calculate any of these properties.

To Demonstrate that these variables are path independent, we can calculate the change in U, H, S, G, and A for (i) the case where we first undergo an isobaric heating from T_o to T_f followed by an isothermal expansion from P_o to P_f , and (ii) the case where we first undergo an isothermal expansion from P_o to P_f followed by an isobaric heating from T_o to T_f .

Let's take the enthalpy as an example. In case (i), we have first an isothermal change in pressure

$$\left(\frac{\partial H}{\partial P}\right)_T = T \frac{\left(\frac{\partial p}{\partial T}\right)_V}{\left(\frac{\partial p}{\partial V}\right)_T} + V$$

yielding an enthalpy change of

$$\Delta H_{\text{iso-T}} = H(T_1, P_2) - H(T_1, P_1) = \int_{P_1}^{P_2} \left[T_1 \frac{\left(\frac{\partial P}{\partial T}\right)_V}{\left(\frac{\partial V}{\partial T}\right)_T} + V \right] dP$$

We now have a gas at T_1 and P_2 . At a constant pressure of P_2 , we now isobarically heat the material.

$$\left(\frac{\partial H}{\partial T}\right)_P = C_p$$

$$\Delta H_{\text{iso-P}} = H(T_2, P_2) - H(T_1, P_2) = \int_{T_1}^{T_2} C_p(T, P_2) dT$$

The total change in enthalpy is

$$\Delta H = \Delta H_{\text{iso-T}} + \Delta H_{\text{iso-P}} = \int_{P_1}^{P_2} \left[T_1 \frac{\left(\frac{\partial P}{\partial T}\right)_V}{\left(\frac{\partial V}{\partial T}\right)_T} + V \right] dP + \int_{T_1}^{T_2} C_p(T, P_2) dT$$

In case (ii), we perform the steps in the opposite order. At a constant pressure of P_1 , we now isobarically heat the material. Then once the gas is at T_2 and P_1 , we isothermally change the temperature.

$$\Delta H = \Delta H_{\text{iso-P}} + \Delta H_{\text{iso-T}} = \int_{T_1}^{T_2} C_p(T, P_1) dT + \int_{P_1}^{P_2} \left[T_2 \left(\frac{\partial P}{\partial T} \right)_V + V \right] dP$$

We see that these two equations are not the same because the temperature integrals are evaluated at different pressures and the pressure-integrals are evaluated at different pressures. However, since H is a state function, the numerical result for ΔH must be the same.

We shall now demonstrate that U, H, S, G, and A are state functions, *given that you have chosen compatible equations of state and heat capacities.*

E.1. Numerical Example: Ideal Gas

Case (i): Let's first isothermally compress Argon from $(T_1, P_1) = (500 \text{ K}, 101325 \text{ Pa})$ to state $(T_1, P_2) = (500 \text{ K}, 202650 \text{ Pa})$. Second, we will isobarically heat the gas from $(T_1, P_2) = (500 \text{ K}, 202650 \text{ Pa})$ to $(T_2, P_2) = (600 \text{ K}, 202650 \text{ Pa})$. We will assume Argon is an Ideal Gas.

Single Component, single phase fluid: Ar
 Model: Ideal Gas
 Initial Condition: $T = 500.000000 \text{ (K)}$ and $P = 1.013250\text{e}+005 \text{ (Pa)}$ $V = 4.102640\text{e}-002 \text{ (m}^3\text{/mol)}$
 Final Condition: $T = 600.000000 \text{ (K)}$ and $P = 2.026500\text{e}+005 \text{ (Pa)}$ $V = 2.461584\text{e}-002 \text{ (m}^3\text{/mol)}$
 Heat Capacity: $C_p(T_o, P_o) = 2.078500\text{e}+001$ $C_p(T_f, P_f) = 2.078500\text{e}+001 \text{ (J/mol/K)}$
 Heat Capacity: $C_v(T_o, P_o) = 1.247100\text{e}+001$ $C_v(T_f, P_f) = 1.247100\text{e}+001 \text{ (J/mol/K)}$
 Changes due to Change in Temperature
 $\Delta U = 1.247100\text{e}+003 \text{ (J/mol)}$ $\Delta H = 2.078500\text{e}+003 \text{ (J/mol)}$ $\Delta S = 3.789554\text{e}+000 \text{ (J/mol/K)}$
 $\Delta G = -1.670550\text{e}+004 \text{ (J/mol)}$ $\Delta A = -1.753690\text{e}+004 \text{ (J/mol)}$
 Changes due to Change in Pressure
 $\Delta U = 0.000000\text{e}+000 \text{ (J/mol)}$ $\Delta H = 0.000000\text{e}+000 \text{ (J/mol)}$ $\Delta S = -5.762826\text{e}+000 \text{ (J/mol/K)}$
 $\Delta G = 3.457695\text{e}+003 \text{ (J/mol)}$ $\Delta A = 3.457695\text{e}+003 \text{ (J/mol)}$
 Total Changes
 $\Delta U = 1.247100\text{e}+003 \text{ (J/mol)}$ $\Delta H = 2.078500\text{e}+003 \text{ (J/mol)}$ $\Delta S = -1.973272\text{e}+000 \text{ (J/mol/K)}$
 $\Delta G = -1.324781\text{e}+004 \text{ (J/mol)}$ $\Delta A = -1.407921\text{e}+004 \text{ (J/mol)}$

Case (ii): Let's first isobarically heat the gas from $(T_1, P_1) = (500 \text{ K}, 101325 \text{ Pa})$ to $(T_2, P_1) = (600 \text{ K}, 101325 \text{ Pa})$. Second, we isothermally compress Argon from $(T_2, P_1) = (600 \text{ K}, 101325 \text{ Pa})$ to state $(T_2, P_2) = (600 \text{ K}, 202650 \text{ Pa})$.

Single Component, single phase fluid: Ar
 Model: Ideal Gas
 Initial Condition: $T = 500.000000 \text{ (K)}$ and $P = 1.013250\text{e}+005 \text{ (Pa)}$ $V = 4.102640\text{e}-002 \text{ (m}^3\text{/mol)}$
 Final Condition: $T = 600.000000 \text{ (K)}$ and $P = 2.026500\text{e}+005 \text{ (Pa)}$ $V = 2.461584\text{e}-002 \text{ (m}^3\text{/mol)}$
 Heat Capacity: $C_p(T_o, P_o) = 2.078500\text{e}+001$ $C_p(T_f, P_f) = 2.078500\text{e}+001 \text{ (J/mol/K)}$
 Heat Capacity: $C_v(T_o, P_o) = 1.247100\text{e}+001$ $C_v(T_f, P_f) = 1.247100\text{e}+001 \text{ (J/mol/K)}$
 Changes due to Change in Temperature
 $\Delta U = 1.247100\text{e}+003 \text{ (J/mol)}$ $\Delta H = 2.078500\text{e}+003 \text{ (J/mol)}$ $\Delta S = 3.789554\text{e}+000 \text{ (J/mol/K)}$
 $\Delta G = -1.612922\text{e}+004 \text{ (J/mol)}$ $\Delta A = -1.696062\text{e}+004 \text{ (J/mol)}$
 Changes due to Change in Pressure
 $\Delta U = 0.000000\text{e}+000 \text{ (J/mol)}$ $\Delta H = 0.000000\text{e}+000 \text{ (J/mol)}$ $\Delta S = -5.762826\text{e}+000 \text{ (J/mol/K)}$
 $\Delta G = 2.881413\text{e}+003 \text{ (J/mol)}$ $\Delta A = 2.881413\text{e}+003 \text{ (J/mol)}$
 Total Changes
 $\Delta U = 1.247100\text{e}+003 \text{ (J/mol)}$ $\Delta H = 2.078500\text{e}+003 \text{ (J/mol)}$ $\Delta S = -1.973272\text{e}+000 \text{ (J/mol/K)}$
 $\Delta G = -1.324781\text{e}+004 \text{ (J/mol)}$ $\Delta A = -1.407921\text{e}+004 \text{ (J/mol)}$

The relative errors for ΔU , ΔH , ΔS , ΔG , and ΔA between the two processes are respectively:

Error = $0.000000\text{e}+000$ $0.000000\text{e}+000$ $0.000000\text{e}+000$ $1.373049\text{e}-016$ $1.291968\text{e}-016$

The errors are zero to machine precision. Therefore, U, H, S, G, and A are state variables for an ideal gas.

E.2. Numerical Example: van der Waal's gas with rigorous C_p

Case (i): Let's first isothermally compress Argon from $(T_1, P_1) = (500 \text{ K}, 101325 \text{ Pa})$ to state $(T_1, P_2) = (500 \text{ K}, 202650 \text{ Pa})$. Second, we will isobarically heat the gas from $(T_1, P_2) = (500 \text{ K}, 202650 \text{ Pa})$ to $(T_2, P_2) = (600 \text{ K}, 202650 \text{ Pa})$. We will assume Argon is a van der Waal's gas with the rigorous heat capacity.

Single Component, single phase fluid: Ar
 Model: van der Waals Gas w/ vdW C_p
 Initial Condition: $T = 500.000000 \text{ (K)}$ and $P = 1.013250\text{e}+005 \text{ (Pa)}$ $V = 4.102585\text{e}-002 \text{ (m}^3\text{/mol)}$
 Final Condition: $T = 600.000000 \text{ (K)}$ and $P = 2.026500\text{e}+005 \text{ (Pa)}$ $V = 2.462076\text{e}-002 \text{ (m}^3\text{/mol)}$
 Heat Capacity: $C_p(T_o, P_o) = 2.079827\text{e}+001$ $C_p(T_f, P_f) = 2.080341\text{e}+001 \text{ (J/mol/K)}$
 Heat Capacity: $C_v(T_o, P_o) = 1.247764\text{e}+001$ $C_v(T_f, P_f) = 1.248022\text{e}+001 \text{ (J/mol/K)}$
 Changes due to Change in Temperature
 $\Delta U = 1.247653\text{e}+003 \text{ (J/mol)}$ $\Delta H = 2.079605\text{e}+003 \text{ (J/mol)}$ $\Delta S = 3.791580\text{e}+000 \text{ (J/mol/K)}$
 $\Delta G = -1.670495\text{e}+004 \text{ (J/mol)}$ $\Delta A = -1.753690\text{e}+004 \text{ (J/mol)}$
 Changes due to Change in Pressure
 $\Delta U = -2.762778\text{e}+000 \text{ (J/mol)}$ $\Delta H = -2.262133\text{e}+000 \text{ (J/mol)}$ $\Delta S = -5.767425\text{e}+000 \text{ (J/mol/K)}$
 $\Delta G = 3.458193\text{e}+003 \text{ (J/mol)}$ $\Delta A = 3.457692\text{e}+003 \text{ (J/mol)}$
 Total Changes
 $\Delta U = 1.244890\text{e}+003 \text{ (J/mol)}$ $\Delta H = 2.077343\text{e}+003 \text{ (J/mol)}$ $\Delta S = -1.975845\text{e}+000 \text{ (J/mol/K)}$
 $\Delta G = -1.324676\text{e}+004 \text{ (J/mol)}$ $\Delta A = -1.407921\text{e}+004 \text{ (J/mol)}$

Case (ii): Let's first isobarically heat the gas from $(T_1, P_1) = (500 \text{ K}, 101325 \text{ Pa})$ to $(T_2, P_1) = (600 \text{ K}, 101325 \text{ Pa})$. Second, we isothermally compress Argon from $(T_2, P_1) = (600 \text{ K}, 101325 \text{ Pa})$ to state $(T_2, P_2) = (600 \text{ K}, 202650 \text{ Pa})$.

Single Component, single phase fluid: Ar
 Model: van der Waals Gas w/ vdW C_p
 Initial Condition: $T = 500.000000 \text{ (K)}$ and $P = 1.013250\text{e}+005 \text{ (Pa)}$ $V = 4.102585\text{e}-002 \text{ (m}^3\text{/mol)}$
 Final Condition: $T = 600.000000 \text{ (K)}$ and $P = 2.026500\text{e}+005 \text{ (Pa)}$ $V = 2.462076\text{e}-002 \text{ (m}^3\text{/mol)}$
 Heat Capacity: $C_p(T_o, P_o) = 2.079827\text{e}+001$ $C_p(T_f, P_f) = 2.080341\text{e}+001 \text{ (J/mol/K)}$
 Heat Capacity: $C_v(T_o, P_o) = 1.247764\text{e}+001$ $C_v(T_f, P_f) = 1.248022\text{e}+001 \text{ (J/mol/K)}$
 Changes due to Change in Temperature
 $\Delta U = 1.248207\text{e}+003 \text{ (J/mol)}$ $\Delta H = 2.080710\text{e}+003 \text{ (J/mol)}$ $\Delta S = 3.793606\text{e}+000 \text{ (J/mol/K)}$
 $\Delta G = -1.612812\text{e}+004 \text{ (J/mol)}$ $\Delta A = -1.696062\text{e}+004 \text{ (J/mol)}$
 Changes due to Change in Pressure
 $\Delta U = -3.316454\text{e}+000 \text{ (J/mol)}$ $\Delta H = -3.367100\text{e}+000 \text{ (J/mol)}$ $\Delta S = -5.769451\text{e}+000 \text{ (J/mol/K)}$
 $\Delta G = 2.881358\text{e}+003 \text{ (J/mol)}$ $\Delta A = 2.881409\text{e}+003 \text{ (J/mol)}$
 Total Changes
 $\Delta U = 1.244890\text{e}+003 \text{ (J/mol)}$ $\Delta H = 2.077343\text{e}+003 \text{ (J/mol)}$ $\Delta S = -1.975845\text{e}+000 \text{ (J/mol/K)}$
 $\Delta G = -1.324676\text{e}+004 \text{ (J/mol)}$ $\Delta A = -1.407921\text{e}+004 \text{ (J/mol)}$

The relative errors for ΔU , ΔH , ΔS , ΔG , and ΔA between the two processes are respectively:

Error = $3.470266\text{e}-015$ $3.502530\text{e}-015$ $2.809489\text{e}-014$ $2.746316\text{e}-016$ $1.291968\text{e}-016$

The errors are zero to machine precision. Therefore, U, H, S, G, and A are state variables for this gas.

E.3. Numerical Example: van der Waal's gas with approximate C_p

Case (i): Let's first isothermally compress Argon from $(T_1, P_1) = (500 \text{ K}, 101325 \text{ Pa})$ to state $(T_1, P_2) = (500 \text{ K}, 202650 \text{ Pa})$. Second, we will isobarically heat the gas from $(T_1, P_2) = (500 \text{ K}, 202650 \text{ Pa})$ to $(T_2, P_2) = (600 \text{ K}, 202650 \text{ Pa})$. We will assume Argon is a van der Waal's gas with the rigorous heat capacity.

Single Component, single phase fluid: Ar
 Model: van der Waals Gas w/ cubic polynomial C_p
 Initial Condition: $T = 500.000000 \text{ (K)}$ and $P = 1.013250\text{e}+005 \text{ (Pa)}$ $V = 4.102585\text{e}-002 \text{ (m}^3\text{/mol)}$
 Final Condition: $T = 600.000000 \text{ (K)}$ and $P = 2.026500\text{e}+005 \text{ (Pa)}$ $V = 2.462076\text{e}-002 \text{ (m}^3\text{/mol)}$
 Heat Capacity: $C_p(T_o, P_o) = 2.819216\text{e}+001$ $C_p(T_f, P_f) = 2.866217\text{e}+001 \text{ (J/mol/K)}$
 Heat Capacity: $C_v(T_o, P_o) = 1.986489\text{e}+001$ $C_v(T_f, P_f) = 2.032975\text{e}+001 \text{ (J/mol/K)}$
 Changes due to Change in Temperature
 $\Delta U = 2.009655\text{e}+003 \text{ (J/mol)}$ $\Delta H = 2.842160\text{e}+003 \text{ (J/mol)}$ $\Delta S = 5.180569\text{e}+000 \text{ (J/mol/K)}$
 $\Delta G = -1.713624\text{e}+004 \text{ (J/mol)}$ $\Delta A = -1.796820\text{e}+004 \text{ (J/mol)}$
 Changes due to Change in Pressure
 $\Delta U = -2.762778\text{e}+000 \text{ (J/mol)}$ $\Delta H = -2.262133\text{e}+000 \text{ (J/mol)}$ $\Delta S = -5.767425\text{e}+000 \text{ (J/mol/K)}$
 $\Delta G = 3.458193\text{e}+003 \text{ (J/mol)}$ $\Delta A = 3.457692\text{e}+003 \text{ (J/mol)}$
 Total Changes
 $\Delta U = 2.006892\text{e}+003 \text{ (J/mol)}$ $\Delta H = 2.839898\text{e}+003 \text{ (J/mol)}$ $\Delta S = -5.868560\text{e}-001 \text{ (J/mol/K)}$
 $\Delta G = -1.367805\text{e}+004 \text{ (J/mol)}$ $\Delta A = -1.451050\text{e}+004 \text{ (J/mol)}$

Case (ii): Let's first isobarically heat the gas from $(T_1, P_1) = (500 \text{ K}, 101325 \text{ Pa})$ to $(T_2, P_1) = (600 \text{ K}, 101325 \text{ Pa})$. Second, we isothermally compress Argon from $(T_2, P_1) = (600 \text{ K}, 101325 \text{ Pa})$ to state $(T_2, P_2) = (600 \text{ K}, 202650 \text{ Pa})$.

Single Component, single phase fluid: Ar
 Model: van der Waals Gas w/ cubic polynomial C_p
 Initial Condition: $T = 500.000000 \text{ (K)}$ and $P = 1.013250\text{e}+005 \text{ (Pa)}$ $V = 4.102585\text{e}-002 \text{ (m}^3\text{/mol)}$
 Final Condition: $T = 600.000000 \text{ (K)}$ and $P = 2.026500\text{e}+005 \text{ (Pa)}$ $V = 2.462076\text{e}-002 \text{ (m}^3\text{/mol)}$
 Heat Capacity: $C_p(T_o, P_o) = 2.819216\text{e}+001$ $C_p(T_f, P_f) = 2.866217\text{e}+001 \text{ (J/mol/K)}$
 Heat Capacity : $C_v(T_o, P_o) = 1.986489\text{e}+001$ $C_v(T_f, P_f) = 2.032975\text{e}+001 \text{ (J/mol/K)}$
 Changes due to Change in Temperature
 $\Delta U = 2.008550\text{e}+003 \text{ (J/mol)}$ $\Delta H = 2.842160\text{e}+003 \text{ (J/mol)}$ $\Delta S = 5.180569\text{e}+000 \text{ (J/mol/K)}$
 $\Delta G = -1.655941\text{e}+004 \text{ (J/mol)}$ $\Delta A = -1.739191\text{e}+004 \text{ (J/mol)}$
 Changes due to Change in Pressure
 $\Delta U = -3.316454\text{e}+000 \text{ (J/mol)}$ $\Delta H = -3.367100\text{e}+000 \text{ (J/mol)}$ $\Delta S = -5.769451\text{e}+000 \text{ (J/mol/K)}$
 $\Delta G = 2.881358\text{e}+003 \text{ (J/mol)}$ $\Delta A = 2.881409\text{e}+003 \text{ (J/mol)}$
 Total Changes
 $\Delta U = 2.005233\text{e}+003 \text{ (J/mol)}$ $\Delta H = 2.838793\text{e}+003 \text{ (J/mol)}$ $\Delta S = -5.888818\text{e}-001 \text{ (J/mol/K)}$
 $\Delta G = -1.367805\text{e}+004 \text{ (J/mol)}$ $\Delta A = -1.451050\text{e}+004 \text{ (J/mol)}$

The relative errors for ΔU , ΔH , ΔS , ΔG , and ΔA between the two processes are respectively:
 Error = $8.264738\text{e}-004$ $3.890870\text{e}-004$ $3.451961\text{e}-003$ $1.329860\text{e}-016$ $1.253567\text{e}-016$

The errors for ΔU , ΔH , and ΔS are **NOT** zero to machine precision. Therefore, U , H , and S are not state variables for a gas described by van der Waal's equation of state and an approximate heat capacity.

F.1. Isochoric Heating/Cooling for Arbitrary Equation of State

There are a variety of different ways for a gas to move from state (T_1, P_1) to state (T_2, P_2) and they don't necessarily involve an isothermal step and an isobaric step. Now, of course, if we know (T_1, P_1) and (T_2, P_2) , then the easiest way to calculate ΔU , ΔH , ΔS , ΔG , and ΔA is to use an isothermal step and an isobaric step, because we already have a code written that will do that. However, in engineering practice, we are faced with problems where we do not know both (T_2, P_2) .

Three common examples are isochoric (constant volume), isentropic, and isenthalpic processes. An isochoric problem occurs when you heat a fluid in a container of fixed volume. An isentropic process occurs when you release a gas from high pressure to low pressure through a throttling valve. An isenthalpic process occurs when you use an ideal turbine, which drops the pressure of a gas. In each of these cases, you don't know (T_2, P_2) . What you do know in an isochoric process is $(T_2, V_2 = V_1)$. In an isentropic throttling valve, generally you know $(T_2, S_2 = S_1)$. In an isenthalpic turbine, generally you know $(P_2, H_2 = H_1)$.

So we need to be able to deal with these other processes.

In this section we are going to provide formulae, obtained from the Bridgeman Tables, for the change in T , P , V , U , H , S , G , and A , due to an isochoric heating. In this problem, we move from state (T_1, P_1) to state $(T_2, V_2 = V_1)$.

We can do this one of two ways. The most fundamental way is to solve for P_2 given $(T_2, V_2 = V_1)$. If we know (T_2, P_2) , we can model the process as first an isobaric change in T from (T_1, P_1) to (T_2, P_1) , followed by an isothermal change in P from (T_2, P_1) to (T_2, P_2) . That would be the easiest thing to do, especially since we have a code to perform isothermal and isobaric steps.

A second way to solve this is to return to the Bridgeman Tables.

The relevant formulae in the Bridgeman Tables are of the form:

$$\left(\frac{\partial X}{\partial T}\right)_V$$

where X can be T , P , V , U , H , S , G , and A . In each case, it is understood that to obtain the macroscopic change, we must integrate the partial.

$$\Delta X \equiv X_2 - X_1 = \int_{T_1}^{T_2} \left(\frac{\partial X}{\partial T}\right)_V dT$$

Below, we simply present the partial derivatives.

i. Temperature

$$\left(\frac{\partial T}{\partial T}\right)_V = 1$$

ii. Pressure

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{(\partial p)_V}{(\partial T)_V} = \frac{\left(\frac{\partial p}{\partial T}\right)_V}{1} = \left(\frac{\partial p}{\partial T}\right)_V$$

iii. *Volume*

$$\left(\frac{\partial V}{\partial T}\right)_V = 0$$

iv. *Internal Energy*

$$\left(\frac{\partial U}{\partial T}\right)_V = \frac{(\partial U)_V}{(\partial T)_V} = C_P + \frac{T\left(\frac{\partial p}{\partial T}\right)_V^2}{\left(\frac{\partial p}{\partial V}\right)_T}$$

v. *Enthalpy*

$$\left(\frac{\partial H}{\partial T}\right)_V = \frac{(\partial H)_V}{(\partial T)_V} = C_P + \frac{T\left(\frac{\partial p}{\partial T}\right)_V^2}{\left(\frac{\partial p}{\partial V}\right)_T} + v\left(\frac{\partial p}{\partial T}\right)_V$$

vi. *Entropy*

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{(\partial S)_V}{(\partial T)_V} = \frac{C_P}{T} + \frac{\left(\frac{\partial p}{\partial T}\right)_V^2}{\left(\frac{\partial p}{\partial V}\right)_T}$$

vii. *Gibbs Free Energy*

$$\left(\frac{\partial G}{\partial T}\right)_V = \frac{(\partial G)_V}{(\partial T)_V} = -S + v\left(\frac{\partial p}{\partial T}\right)_V$$

viii. *Helmholtz Free Energy*

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

F.2. Isochoric Heating/Cooling for Ideal Gas

The Ideal Gas has an equation of state

$$PV = RT \quad \text{or} \quad P = \frac{RT}{V}$$

and, for a monatomic ideal gas, it has a heat capacity

$$C_p = \frac{5}{2}R$$

The necessary derivatives are:

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{V^2} \quad \text{and} \quad \left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V}$$

i. Temperature

$$\Delta T = T_2 - T_1$$

ii. Pressure

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V}$$

$$\Delta P = \int_{T_1}^{T_2} \frac{R}{V} dT = \frac{R}{V}(T_2 - T_1)$$

iii. Volume

$$\Delta V = V_2 - V_1 = 0$$

iv. Internal Energy

$$\left(\frac{\partial U}{\partial T}\right)_V = C_p + \frac{T\left(\frac{\partial p}{\partial T}\right)_V^2}{\left(\frac{\partial p}{\partial V}\right)_T} = \frac{5}{2}R + \frac{T\frac{R^2}{V^2}}{-\frac{RT}{V^2}} = \frac{3}{2}R$$

$$\Delta U = \int_{T_1}^{T_2} \frac{3}{2}R dT = \frac{3}{2}R(T_2 - T_1)$$

v. *Enthalpy*

$$\left(\frac{\partial H}{\partial T}\right)_V = C_P + \frac{T\left(\frac{\partial p}{\partial T}\right)_V^2}{\left(\frac{\partial p}{\partial V}\right)_T} + V\left(\frac{\partial p}{\partial T}\right)_V = \frac{5}{2}R$$

$$\Delta H = \int_{T_1}^{T_2} \frac{5}{2}R dT = \frac{5}{2}R(T_2 - T_1)$$

 vi. *Entropy*

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_P}{T} + \frac{\left(\frac{\partial p}{\partial T}\right)_V^2}{\left(\frac{\partial p}{\partial V}\right)_T} = \frac{3R}{2T}$$

$$\Delta S = \int_{T_1}^{T_2} \frac{3R}{2T} dT = \frac{3}{2}R \ln\left(\frac{T_2}{T_1}\right)$$

 vii. *Gibbs Free Energy*

$$\left(\frac{\partial G}{\partial T}\right)_V = -S + V\left(\frac{\partial p}{\partial T}\right)_V = -S + R$$

$$\Delta G = \int_{T_1}^{T_2} -S + R dT = \int_{T_1}^{T_2} -S dT + R(T_2 - T_1)$$

where the entropy is given as

$$S(T,P) = S(T_{\text{ref}},P_{\text{ref}}) + \int_{T_{\text{ref}}}^T \frac{C_P(T,P_{\text{ref}})}{T} dT + \int_{P_{\text{ref}}}^P \frac{\left(\frac{\partial p}{\partial T}\right)_V}{\left(\frac{\partial p}{\partial V}\right)_T} dP$$

$$\int_{T_1}^{T_2} -S dT = \left[-S_{\text{ref}} + \frac{5}{2}R \ln(T_{\text{ref}}) + R \ln\left(\frac{P}{P_{\text{ref}}}\right) \right] (T_2 - T_1) - \frac{5}{2}R[(T_2 \ln(T_2) - T_2) - (T_1 \ln(T_1) - T_1)]$$

 viii. *Helmholtz Free Energy*

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

$$\Delta A = \int_{T_1}^{T_2} -S \, dT = \Delta G - R(T_2 - T_1)$$

Example F.2. Numerical Example: Isochoric Heating/Cooling for Ideal Gas

Let's isothermally compress Argon from $(T_1, P_1) = (500 \text{ K}, 101325 \text{ Pa})$ where $V_1 = 0.0410264 \frac{\text{m}^3}{\text{mol}}$ to state $(T_2, V_2 = V_1) = (600 \text{ K}, V_1)$. We will assume Argon is an Ideal Gas.

We can write a simple code in MATLAB, which implements the equations in Section F.2. This has been done. The output of the code is as follows:

```

Single Component, single phase fluid: Ar
Model: Ideal Gas
Initial Condition: T = 500.000000 (K) and P = 1.013250e+005 (Pa) V = 4.102640e-002 (m^3/mol)
Final Condition: T = 600.000000 (K) and P = 1.215900e+005 (Pa) V = 4.102640e-002 (m^3/mol)
Heat Capacity: Cp(To,Po) = 2.078500e+001 Cp(Tf,Pf) = 2.078500e+001 (J/mol/K)
Heat Capacity: Cv(To,Po) = 1.247100e+001 Cv(Tf,Pf) = 1.247100e+001 (J/mol/K)
Changes due to Change in Temperature
Delta U = 1.247100e+003 (J/mol) Delta H = 2.078500e+003 (J/mol) Delta S = 3.789554e+000 (J/mol/K)
Delta G = -1.670550e+004 (J/mol) Delta A = -1.753690e+004 (J/mol)
Changes due to Change in Pressure
Delta U = 0.000000e+000 (J/mol) Delta H = 0.000000e+000 (J/mol) Delta S = -1.515821e+000 (J/mol/K)
Delta G = 9.094929e+002 (J/mol) Delta A = 9.094929e+002 (J/mol)
Total Changes
Delta U = 1.247100e+003 (J/mol) Delta H = 2.078500e+003 (J/mol) Delta S = 2.273732e+000 (J/mol/K)
Delta G = -1.579601e+004 (J/mol) Delta A = -1.662741e+004 (J/mol)
    
```

We can see that the molar volume was constant. We can also see that the pressure increased with increasing temperature. The increase in temperature caused an increase in U, H, and S, which dominated the net effect of the isochoric heating.

Example F.2. Numerical Example: Isochoric Heating/Cooling for van der Waal's Gas

We can evaluate the partial derivatives given in section F.1 for the van der Waal's gas with equation of state

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \quad (4.a)$$

and, for a monatomic vdW gas, a heat capacity

$$C_p = \frac{R}{2} \left(\frac{5PV^3 - Va + 6ab}{PV^3 - Va + 2ab} \right)$$

The particular forms of the partial derivatives are not given here.

Let's isothermally compress Argon from $(T_1, P_1) = (500 \text{ K}, 101325 \text{ Pa})$ where

$V_1 = 0.0410259 \frac{\text{m}^3}{\text{mol}}$ to state $(T_1, V_2 = V_1) = (600 \text{ K}, V_1)$. We will assume Argon is a van der Waal's

Gas with critical properties $T_c = 150.8 \text{ K}$ and $P_c = 4.874 \cdot 10^6 \text{ Pa}$.

We can write a simple code in MATLAB, which implements the equations in Section F.1. where we put in the form of the van der Waal's equation of state and heat capacity. This has been done. We use a Fourth-Order Simpson's Method with 20 intervals to numerically integrate all the functions. The output of the code is as follows:

```

Single Component, single phase fluid: Ar
Model: van der Waals Gas w/ vdW Cp
Initial Condition: T = 500.000000 (K) and P = 1.013250e+005 (Pa) V = 4.102585e-002 (m^3/mol)
Final Condition: T = 600.000000 (K) and P = 1.216062e+005 (Pa) V = 4.102585e-002 (m^3/mol)
Heat Capacity: Cp(To,Po) = 2.079827e+001 Cp(Tf,Pf) = 2.079605e+001 (J/mol/K)
Heat Capacity: Cv(To,Po) = 1.247764e+001 Cv(Tf,Pf) = 1.247653e+001 (J/mol/K)
Changes due to Change in Temperature
Delta U = 1.247653e+003 (J/mol) Delta H = 2.079605e+003 (J/mol) Delta S = 3.791580e+000 (J/mol/K)
Delta G = -1.670495e+004 (J/mol) Delta A = -1.753690e+004 (J/mol)
Changes due to Change in Pressure
Delta U = -5.530410e-001 (J/mol) Delta H = -4.531654e-001 (J/mol) Delta S = -1.517848e+000 (J/mol/K)
Delta G = 9.102555e+002 (J/mol) Delta A = 9.101556e+002 (J/mol)
Total Changes
Delta U = 1.247100e+003 (J/mol) Delta H = 2.079152e+003 (J/mol) Delta S = 2.273732e+000 (J/mol/K)
Delta G = -1.579470e+004 (J/mol) Delta A = -1.662675e+004 (J/mol)

```

We see that there are slight differences between the van der Waal's gas and the ideal gas. First, the molar volume which we maintain as constant is different than that used for the ideal gas, because what we specified was (T_1, P_1) .

G.1. Isenthalpic Compression for Arbitrary Equation of State

Turbines are often approximated as an isenthalpic process. In this case, the gas moves from state (T_1, P_1) to state (T_2, P_2) . However, what we generally know about the outlet state is the pressure and the fact that the enthalpy of the second state is the same as the enthalpy of the initial state, $(P_2, H_2 = H_1)$.

In this section we are going to provide formulae, obtained from the Bridgeman Tables, for the change in $T, P, V, U, H, S, G,$ and $A,$ due to an isenthalpic compression. In this problem, we move from state (T_1, P_1) to state $(P_2, H_2 = H_1)$.

We can do this one of two ways. The most fundamental way is to solve for T_2 given $(P_2, H_2 = H_1)$. If we know (T_2, P_2) , we can model the process as first an isobaric change in T from (T_1, P_1) to (T_2, P_1) , followed by an isothermal change in P from (T_2, P_1) to (T_2, P_2) . That would be the easiest thing to do, especially since we have a code to perform isothermal and isobaric steps.

A second way to solve this is to return to the Bridgeman Tables. The relevant formulae in the Bridgeman Tables are of the form:

$$\left(\frac{\partial X}{\partial P} \right)_H$$

where X can be $T, P, V, U, H, S, G,$ and $A.$ In each case, it is understood that to obtain the macroscopic change, we must integrate the partial.

$$\Delta X \equiv X_2 - X_1 = \int_{P_1}^{P_2} \left(\frac{\partial X}{\partial P} \right)_H dP$$

The advantage of the first method is that we already have a code to calculate changes in properties from (T_2, P_1) to (T_2, P_2) . The disadvantage of the first method is that we must first find, T_2 given $(P_2, H_2 = H_1)$. This is an iterative process and requires the solution of

$$\Delta H = \Delta H_{\text{iso-T}} + \Delta H_{\text{iso-P}} = \int_{P_1}^{P_2} \left[T_1 \frac{\left(\frac{\partial P}{\partial T} \right)_V}{\left(\frac{\partial P}{\partial V} \right)_T} + V \right] dP + \int_{T_1}^{T_2} C_p(T, P_2) dT = 0$$

or

$$-\Delta H_{\text{iso-P}} = \Delta H_{\text{iso-T}}$$

$$-\int_{P_1}^{P_2} \left[T_1 \frac{\left(\frac{\partial P}{\partial T} \right)_V}{\left(\frac{\partial P}{\partial V} \right)_T} + V \right] dP = \int_{T_1}^{T_2} C_p(T, P_2) dT$$

In this process, we evaluate the right-hand side once and iteratively guess T_2 until the system converges. In terms of the computational effort involved, this method is less efficient because we have to evaluate the integrals for each guess of T_2 .

If we used the Bridgeman Tables, we would only have to evaluate the integrals once. Therefore, this is the preferred method. Admittedly, this is not the method I used in the examples in the following sections because I already had a code to solve the equations by iterative solution of T_2 .

Below, we simply present the partial derivatives from the Bridgeman Tables

i. Temperature

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{(\partial T)_H}{(\partial p)_H} = \frac{T\left(\frac{\partial p}{\partial T}\right)_V + V\left(\frac{\partial p}{\partial V}\right)_T}{-C_P\left(\frac{\partial p}{\partial V}\right)_T} = -\frac{T\left(\frac{\partial p}{\partial T}\right)_V}{C_P\left(\frac{\partial p}{\partial V}\right)_T} - \frac{V}{C_P}$$

ii. Pressure

$$\left(\frac{\partial p}{\partial p}\right)_H = 1$$

iii. Volume

$$\left(\frac{\partial V}{\partial P}\right)_H = \frac{(\partial V)_H}{(\partial p)_H} = \frac{-C_P - \frac{T\left(\frac{\partial p}{\partial T}\right)_V^2}{\left(\frac{\partial p}{\partial V}\right)_T} - V\left(\frac{\partial p}{\partial T}\right)_V}{-C_P\left(\frac{\partial p}{\partial V}\right)_T}$$

iv. Internal Energy

$$\left(\frac{\partial U}{\partial P}\right)_H = \frac{(\partial U)_H}{(\partial p)_H} = \frac{p\left[C_P + \frac{T\left(\frac{\partial p}{\partial T}\right)_V^2}{\left(\frac{\partial p}{\partial V}\right)_T} + V\left(\frac{\partial p}{\partial T}\right)_V\right] + V\left[C_P\left(\frac{\partial p}{\partial V}\right)_T\right]}{-C_P\left(\frac{\partial p}{\partial V}\right)_T}$$

v. Enthalpy

$$\left(\frac{\partial H}{\partial P}\right)_H = 0$$

vi. *Entropy*

$$\left(\frac{\partial S}{\partial P}\right)_H = \frac{(\partial S)_H}{(\partial p)_H} = \frac{\frac{V}{T} \left[C_P \left(\frac{\partial p}{\partial V}\right)_T \right]}{-C_P \left(\frac{\partial p}{\partial V}\right)_T} = -\frac{V}{T}$$

vii. *Gibbs Free Energy*

$$\left(\frac{\partial G}{\partial P}\right)_H = \frac{(\partial G)_H}{(\partial p)_H} = \frac{-V \left[C_P + S \left(\frac{\partial p}{\partial V}\right)_T \right] - ST \left(\frac{\partial p}{\partial T}\right)_V}{-C_P \left(\frac{\partial p}{\partial V}\right)_T}$$

viii. *Helmholtz Free Energy*

$$\left(\frac{\partial A}{\partial P}\right)_H = \frac{(\partial A)_H}{(\partial p)_H} = \frac{\rho \left[C_P + \frac{T \left(\frac{\partial p}{\partial T}\right)_V^2}{\left(\frac{\partial p}{\partial V}\right)_T} \right] + [\rho V - ST] \left(\frac{\partial p}{\partial T}\right)_V - SV \left(\frac{\partial p}{\partial V}\right)_T}{-C_P \left(\frac{\partial p}{\partial V}\right)_T}$$

Many of the function forms of the partials are quite ugly, but it doesn't matter since we are going to numerically integrate them anyway.

G.2. Isenthalpic Compression for Ideal Gas

The Ideal Gas has an equation of state

$$PV = RT \quad \text{or} \quad P = \frac{RT}{V}$$

and, for a monatomic ideal gas, it has a heat capacity and pressure derivatives given by

$$C_p = \frac{5}{2}R, \quad \left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{V^2} \quad \text{and} \quad \left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V}$$

i. Temperature

$$\left(\frac{\partial T}{\partial P}\right)_H = -\frac{T\left(\frac{\partial p}{\partial T}\right)_V}{C_p\left(\frac{\partial p}{\partial V}\right)_T} - \frac{V}{C_p} = \frac{T\frac{R}{V}}{\frac{5}{2}R\frac{RT}{V^2}} - \frac{V}{\frac{5}{2}R} = 0$$

ii. Pressure

$$\left(\frac{\partial p}{\partial p}\right)_H = 1$$

iii. Volume

$$\left(\frac{\partial V}{\partial P}\right)_H = \frac{-C_p - \frac{T\left(\frac{\partial p}{\partial T}\right)_V^2}{\left(\frac{\partial p}{\partial V}\right)_T} - V\left(\frac{\partial p}{\partial T}\right)_V}{-C_p\left(\frac{\partial p}{\partial V}\right)_T} = \frac{-\frac{5}{2}R - \frac{T\frac{R^2}{V^2}}{-\frac{RT}{V^2}} - V\frac{R}{V}}{\frac{5}{2}R\frac{RT}{V^2}} = \frac{-V^2}{RT}$$

iv. Internal Energy

$$\left(\frac{\partial U}{\partial P}\right)_H = \frac{p\left[C_p + \frac{T\left(\frac{\partial p}{\partial T}\right)_V^2}{\left(\frac{\partial p}{\partial V}\right)_T} + V\left(\frac{\partial p}{\partial T}\right)_V\right] + V\left[C_p\left(\frac{\partial p}{\partial V}\right)_T\right]}{-C_p\left(\frac{\partial p}{\partial V}\right)_T} = \frac{p + V\left[\left(\frac{\partial p}{\partial V}\right)_T\right]}{-\left(\frac{\partial p}{\partial V}\right)_T} = 0$$

v. *Enthalpy*

$$\left(\frac{\partial H}{\partial P}\right)_H = 0$$

 vi. *Entropy*

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

$$\Delta S = -R \ln\left(\frac{P_2}{P_1}\right)$$

 vii. *Gibbs Free Energy*

$$\left(\frac{\partial G}{\partial P}\right)_H = \frac{-V\left[C_P + S\left(\frac{\partial p}{\partial V}\right)_T - ST\left(\frac{\partial p}{\partial T}\right)_V\right]}{-C_P\left(\frac{\partial p}{\partial V}\right)_T} = V$$

$$\Delta G = RT \ln\left(\frac{P_2}{P_1}\right)$$

 viii. *Helmholtz Free Energy*

$$\left(\frac{\partial A}{\partial P}\right)_H = \frac{p\left[C_P + \frac{T\left(\frac{\partial p}{\partial T}\right)_V^2}{\left(\frac{\partial p}{\partial V}\right)_T}\right] + [pV - ST\left(\frac{\partial p}{\partial T}\right)_V - SV\left(\frac{\partial p}{\partial V}\right)_T]}{-C_P\left(\frac{\partial p}{\partial V}\right)_T} = V$$

$$\Delta A = \Delta G = RT \ln\left(\frac{P_2}{P_1}\right)$$

Example G.2. Numerical Example: Isenthalpic Compression of an Ideal Gas

Let's isenthalpically compress Argon from $(T_1, P_1) = (500 \text{ K}, 101325 \text{ Pa})$ to state $(P_2 = 10P_1, H_2 = H_1)$. We will assume Argon is an Ideal Gas.

We can write a simple code in MATLAB, which implements the equations in Section G.2. This has been done. The output of the code is as follows:

```

Single Component, single phase fluid: Ar
Model: Ideal Gas
Initial Condition: T = 500.000000 (K) and P = 1.013250e+005 (Pa) V = 4.102640e-002 (m^3/mol)
Final Condition: T = 500.000000 (K) and P = 1.013250e+006 (Pa) V = 4.102640e-003 (m^3/mol)
Heat Capacity: Cp(To, Po) = 2.078500e+001 Cp(Tf, Pf) = 2.078500e+001 (J/mol/K)
Heat Capacity: Cv(To, Po) = 1.247100e+001 Cv(Tf, Pf) = 1.247100e+001 (J/mol/K)
Changes due to Change in Temperature
Delta U = 0.000000e+000 (J/mol) Delta H = 0.000000e+000 (J/mol) Delta S = 0.000000e+000 (J/mol/K)
Delta G = 0.000000e+000 (J/mol) Delta A = 0.000000e+000 (J/mol)
Changes due to Change in Pressure
Delta U = 0.000000e+000 (J/mol) Delta H = 0.000000e+000 (J/mol) Delta S = -1.914369e+001 (J/mol/K)
Delta G = 9.571846e+003 (J/mol) Delta A = 9.571846e+003 (J/mol)
Total Changes
Delta U = 0.000000e+000 (J/mol) Delta H = 0.000000e+000 (J/mol) Delta S = -1.914369e+001 (J/mol/K)
Delta G = 9.571846e+003 (J/mol) Delta A = 9.571846e+003 (J/mol)

```

We see that there is no temperature change associated with an isenthalpic compression of an ideal gas.

$T_2 = T_1 = 500 \text{ K}$. We see that the entropy is given by $\Delta S = -R \ln\left(\frac{P_2}{P_1}\right)$ and $\Delta A = \Delta G = RT \ln\left(\frac{P_2}{P_1}\right)$.

The entropy change is negative because we are reducing the molar volume of the gas by compressing it. The free energy changes are positive since only the entropic effect is present and it is multiplied by $-T$ in the definition of the free energy.

Example G.3. Numerical Example: Isenthalpic Compression of a van der Waal's Gas

We can evaluate the partial derivatives given in section G.1 for the van der Waal's gas with equation of state

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \quad (4.a)$$

and, for a monatomic vdW gas, a heat capacity

$$C_p = \frac{R}{2} \left(\frac{5PV^3 - Va + 6ab}{PV^3 - Va + 2ab} \right)$$

The particular forms of the partial derivatives are not given here.

Let's isenthalpically compress Argon from $(T_1, P_1) = (500 \text{ K}, 101325 \text{ Pa})$ to state $(P_2 = 10P_1, H_2 = H_1)$.

We can write a simple code in MATLAB, which implements the equations in Section G.1. where we put in the form of the van der Waal's equation of state and heat capacity. This has been done. We use a Fourth-Order Simpson's Method with 20 intervals to numerically integrate all the functions. The output of the code is as follows:

```

Single Component, single phase fluid: Ar
Model: van der Waals Gas w/ vdW Cp
Initial Condition: T = 500.000000 (K) and P = 1.013250e+005 (Pa) V = 4.102585e-002 (m^3/mol)
Final Condition: T = 501.439937 (K) and P = 1.013250e+006 (Pa) V = 4.114227e-003 (m^3/mol)
Heat Capacity: Cp(T0,P0) = 2.079827e+001 Cp(Tf,Pf) = 2.091691e+001 (J/mol/K)
Heat Capacity: Cv(T0,P0) = 1.247764e+001 Cv(Tf,Pf) = 1.253747e+001 (J/mol/K)
Changes due to Change in Temperature
Delta U = 1.796698e+001 (J/mol) Delta H = 2.994814e+001 (J/mol) Delta S = 5.981019e-002 (J/mol/K)
Delta G = -2.377710e+002 (J/mol) Delta A = -2.497522e+002 (J/mol)
Changes due to Change in Pressure
Delta U = -2.976305e+001 (J/mol) Delta H = -2.994814e+001 (J/mol) Delta S = -1.920628e+001 (J/mol/K)
Delta G = 9.600846e+003 (J/mol) Delta A = 9.601031e+003 (J/mol)
Total Changes
Delta U = -1.179606e+001 (J/mol) Delta H = 7.354117e-013 (J/mol) Delta S = -1.914647e+001 (J/mol/K)
Delta G = 9.363075e+003 (J/mol) Delta A = 9.351279e+003 (J/mol)

```

We see that there are slight change in temperature for the isenthalpic compression of a van der Waal's gas. This results in small changes in U. However, see that the total change in the enthalpy is still zero (within machine precision) because the process is isenthalpic.

H.1. Isentropic Expansion for Arbitrary Equation of State

Expansion valves are often approximated as an isentropic process. In this case, the gas moves from state (T_1, P_1) to state (T_2, P_2) . However, what we generally know about the outlet state is the pressure and the fact that the entropy of the second state is the same as the enthalpy of the initial state, $(P_2, S_2 = S_1)$.

In this section we are going to provide formulae, obtained from the Bridgeman Tables, for the change in T, P, V, U, H, S, G, and A, due to an isentropic expansion. In this problem, we move from state (T_1, P_1) to state $(P_2, S_2 = S_1)$.

We can do this one of two ways. The most fundamental way is to solve for T_2 given $(P_2, S_2 = S_1)$. If we know (T_2, P_2) , we can model the process as first an isobaric change in T from (T_1, P_1) to (T_2, P_1) , followed by an isothermal change in P from (T_2, P_1) to (T_2, P_2) . That would be the easiest thing to do, especially since we have a code to perform isothermal and isobaric steps.

A second way to solve this is to return to the Bridgeman Tables. The relevant formulae in the Bridgeman Tables are of the form:

$$\left(\frac{\partial X}{\partial P}\right)_S$$

where X can be T, P, V, U, H, S, G, and A. In each case, it is understood that to obtain the macroscopic change, we must integrate the partial.

$$\Delta X \equiv X_2 - X_1 = \int_{P_1}^{P_2} \left(\frac{\partial X}{\partial P}\right)_S dP$$

The advantage of the first method is that we already have a code to calculate changes in properties from (T_2, P_1) to (T_2, P_2) . The disadvantage of the first method is that we must first find, T_2 given $(P_2, S_2 = S_1)$. This is an iterative process and requires the solution of

$$\Delta S = \Delta S_{\text{iso-T}} + \Delta S_{\text{iso-P}} = \int_{P_1}^{P_2} \left[\frac{\left(\frac{\partial p}{\partial T}\right)_V}{\left(\frac{\partial p}{\partial V}\right)_T} \right]_{T=T_1} dP + \int_{T_1}^{T_2} \frac{C_P(T, P_2)}{T} dT = 0$$

or

$$-\Delta S_{\text{iso-P}} = \Delta S_{\text{iso-T}}$$

$$-\int_{P_1}^{P_2} \left[\frac{\left(\frac{\partial p}{\partial T}\right)_V}{\left(\frac{\partial p}{\partial V}\right)_T} \right]_{T=T_1} dP = \int_{T_1}^{T_2} \frac{C_P(T, P_2)}{T} dT$$

In this process, we evaluate the right-hand side once and iteratively guess T_2 until the system converges. In terms of the computational effort involved, this method is less efficient because we have to evaluate the integrals for each guess of T_2 .

If we used the Bridgeman Tables, we would only have to evaluate the integrals once. Therefore, this is the preferred method. Admittedly, this is not the method I used in the examples in the following sections because I already had a code to solve the equations by iterative solution of T_2 .

Below, we simply present the partial derivatives from the Bridgeman Tables

i. Temperature

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

ii. Pressure

$$\left(\frac{\partial p}{\partial p}\right)_S = 1$$

iii. Volume

$$\left(\frac{\partial V}{\partial P}\right)_S = \frac{(\partial V)_S}{(\partial p)_S} = \frac{-\frac{C_P}{T}\left(\frac{\partial p}{\partial T}\right)_V}{-\frac{C_P}{T}\left(\frac{\partial p}{\partial V}\right)_T} = \frac{1}{\left(\frac{\partial p}{\partial V}\right)_T} + \frac{T}{C_P} \frac{\left(\frac{\partial p}{\partial T}\right)_V^2}{\left(\frac{\partial p}{\partial V}\right)_T^2}$$

iv. Internal Energy

$$\left(\frac{\partial U}{\partial P}\right)_S = \frac{(\partial U)_S}{(\partial p)_S} = \frac{p \left[\frac{C_P}{T} + \frac{\left(\frac{\partial p}{\partial T}\right)_V^2}{\left(\frac{\partial p}{\partial V}\right)_T} \right]}{-\frac{C_P}{T}\left(\frac{\partial p}{\partial V}\right)_T} = -p \left(\frac{\partial V}{\partial P}\right)_S$$

v. Enthalpy

$$\left(\frac{\partial H}{\partial P}\right)_S = \frac{(\partial H)_S}{(\partial p)_S} = \frac{-\frac{V}{T} \left[C_P \left(\frac{\partial p}{\partial V}\right)_T \right]}{-\frac{C_P}{T} \left(\frac{\partial p}{\partial V}\right)_T} = V$$

vi. Entropy

$$\left(\frac{\partial S}{\partial P}\right)_S = 0$$

vii. Gibbs Free Energy

$$\left(\frac{\partial G}{\partial P}\right)_S = \frac{(\partial G)_S}{(\partial p)_S} = \frac{-\frac{V}{T} \left[C_P \left(\frac{\partial p}{\partial V}\right)_T \right] - S \left(\frac{\partial p}{\partial T}\right)_V}{-\frac{C_P}{T} \left(\frac{\partial p}{\partial V}\right)_T} = V + \frac{TS}{C_P} \left(\frac{\partial p}{\partial V}\right)_T$$

viii. Helmholtz Free Energy

$$\left(\frac{\partial A}{\partial P}\right)_S = \frac{(\partial A)_S}{(\partial p)_S} = \frac{p \left[\frac{C_P}{T} + \frac{\left(\frac{\partial p}{\partial T}\right)_V^2}{\left(\frac{\partial p}{\partial V}\right)_T} \right] - S \left(\frac{\partial p}{\partial T}\right)_V}{-\frac{C_P}{T} \left(\frac{\partial p}{\partial V}\right)_T} = -p \left(\frac{\partial V}{\partial P}\right)_S + \frac{TS}{C_P} \left(\frac{\partial p}{\partial V}\right)_T$$

Many of the function forms of the partials are quite ugly, but it doesn't matter since we are going to numerically integrate them anyway.

H.2. Isentropic Expansion for Ideal Gas

The Ideal Gas has an equation of state

$$PV = RT \quad \text{or} \quad P = \frac{RT}{V}$$

and, for a monatomic ideal gas, it has a heat capacity and pressure derivatives given by

$$C_p = \frac{5}{2}R, \quad \left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{V^2} \quad \text{and} \quad \left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V}$$

i. Temperature

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{\left(\frac{\partial p}{\partial T}\right)_V}{-C_p \left(\frac{\partial p}{\partial V}\right)_T} = \frac{2V}{5R} = \frac{2T}{5P}$$

$$\int_{T_1}^{T_2} \frac{1}{T} dT = \frac{2}{5} \int_{P_1}^{P_2} \frac{1}{P} dP$$

$$\ln\left(\frac{T_2}{T_1}\right) = \frac{2}{5} \ln\left(\frac{P_2}{P_1}\right)$$

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{2}{5}}$$

$$T_2 = T_1 \left(\frac{P_2}{P_1}\right)^{\frac{2}{5}}$$

$$\Delta T = T_2 - T_1 = T_1 \left(\frac{P_2}{P_1}\right)^{\frac{2}{5}} - T_1 = T_1 \left[\left(\frac{P_2}{P_1}\right)^{\frac{2}{5}} - 1 \right]$$

ii. Pressure

$$\left(\frac{\partial p}{\partial p}\right)_S = 1$$

iii. Volume

$$\left(\frac{\partial V}{\partial P}\right)_S = \frac{1}{\left(\frac{\partial p}{\partial V}\right)_T} + \frac{T}{C_p} \frac{\left(\frac{\partial p}{\partial T}\right)_V^2}{\left(\frac{\partial p}{\partial V}\right)_T} = \frac{1}{\left(\frac{\partial p}{\partial V}\right)_T} + \frac{T}{C_p} \frac{\left(\frac{\partial p}{\partial T}\right)_V^2}{\left(\frac{\partial p}{\partial V}\right)_T} = -\frac{3V^2}{5RT} = -\frac{3V}{5p}$$

$$\int_{V_1}^{V_2} \frac{1}{V} dV = -\frac{3}{5} \int_{P_1}^{P_2} \frac{1}{P} dP$$

$$V_2 = V_1 \left(\frac{P_2}{P_1}\right)^{-\frac{3}{5}}$$

$$\Delta V = V_2 - V_1 = V_1 \left(\frac{P_2}{P_1}\right)^{-\frac{3}{5}} - V_1 = V_1 \left[\left(\frac{P_2}{P_1}\right)^{-\frac{3}{5}} - 1 \right]$$

iv. Internal Energy

$$\left(\frac{\partial U}{\partial P}\right)_S = -p \left(\frac{\partial V}{\partial P}\right)_S = \frac{3RT}{5p}$$

We have already solved T as a function of p above. Substitute the result in.

$$\left(\frac{\partial U}{\partial P}\right)_S = \frac{3R}{5P} T_1 \left(\frac{P}{P_1}\right)^{\frac{2}{5}}$$

$$\Delta U = \frac{3RT_1}{5} \left(\frac{1}{P_1}\right)^{\frac{2}{5}} \int_{P_1}^{P_2} \frac{1}{P} (P)^{\frac{2}{5}} dP = \frac{3RT_1}{5} \left(\frac{1}{P_1}\right)^{\frac{2}{5}} \int_{P_1}^{P_2} P^{-\frac{3}{5}} dP$$

$$\Delta U = \frac{3RT_1}{2} \left[\left(\frac{P_2}{P_1}\right)^{\frac{2}{5}} - 1 \right]$$

v. Enthalpy

$$\left(\frac{\partial H}{\partial P}\right)_S = V = \frac{RT}{P}$$

$$\Delta H = \frac{5}{3}\Delta U = \frac{5RT_1}{2} \left[\left(\frac{P_2}{P_1}\right)^{\frac{2}{5}} - 1 \right]$$

vi. *Entropy*

$$\left(\frac{\partial S}{\partial P}\right)_S = 0$$

$$\Delta S = 0$$

vii. *Gibbs Free Energy*

$$\left(\frac{\partial G}{\partial P}\right)_S = V + \frac{TS}{C_P} \frac{\left(\frac{\partial p}{\partial T}\right)_V}{\left(\frac{\partial p}{\partial V}\right)_T} = V \left[1 - \frac{2S}{5R} \right] = \frac{T}{p} \left[R - \frac{2S}{5} \right]$$

viii. *Helmholtz Free Energy*

$$\left(\frac{\partial A}{\partial P}\right)_S = -p \left(\frac{\partial V}{\partial P}\right)_S + \frac{TS}{C_P} \frac{\left(\frac{\partial p}{\partial T}\right)_V}{\left(\frac{\partial p}{\partial V}\right)_T} = \frac{3RT}{5p} - \frac{2ST}{5p} = \frac{T}{5p} [3R - 2S]$$

We leave the functional evaluation of ΔG and ΔA to the reader. This will get a little ugly since the entropy has its own temperature and pressure dependence.

Example H.2. Numerical Example: Isentropic Expansion of an Ideal Gas

Let's isentropically expand Argon from $(T_1, P_1) = (500 \text{ K}, 101325 \text{ Pa})$ to state $(P_2 = \frac{P_1}{2}, S_2 = S_1)$.

We will assume Argon is an Ideal Gas.

We can write a simple code in MATLAB, which implements the equations in Section H.2. This has been done. The output of the code is as follows:

```

Single Component, single phase fluid: Ar
Model: Ideal Gas
Initial Condition: T = 500.000000 (K) and P = 1.013250e+005 (Pa) V = 4.102640e-002 (m^3/mol)
Final Condition: T = 378.929142 (K) and P = 5.066250e+004 (Pa) V = 6.218439e-002 (m^3/mol)
Heat Capacity: Cp(To, Po) = 2.078500e+001 Cp(Tf, Pf) = 2.078500e+001 (J/mol/K)
Heat Capacity: Cv(To, Po) = 1.247100e+001 Cv(Tf, Pf) = 1.247100e+001 (J/mol/K)
Changes due to Change in Temperature
Delta U = -1.509875e+003 (J/mol) Delta H = -2.516458e+003 (J/mol) Delta S = -5.762826e+000 (J/mol/K)
Delta G = 1.965637e+004 (J/mol) Delta A = 2.066296e+004 (J/mol)
Changes due to Change in Pressure
Delta U = 0.000000e+000 (J/mol) Delta H = 0.000000e+000 (J/mol) Delta S = 5.762826e+000 (J/mol/K)
Delta G = -2.183703e+003 (J/mol) Delta A = -2.183703e+003 (J/mol)
Total Changes
Delta U = -1.509875e+003 (J/mol) Delta H = -2.516458e+003 (J/mol) Delta S = 8.881784e-016 (J/mol/K)
Delta G = 1.747267e+004 (J/mol) Delta A = 1.847925e+004 (J/mol)
    
```

We see that there is no temperature change associated with an isentropic expansion of an ideal gas. We see also that the change in temperature is negative, i.e. the gas cools. This is the principle behind a flash tank. We see that the change in entropy is zero (to machine precision), since the process is isentropic.

Example H.3. Numerical Example: Isentropic Expansion of a van der Waal's Gas

We can evaluate the partial derivatives given in section H.1 for the van der Waal's gas with equation of state

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \quad (4.a)$$

and, for a monatomic vdW gas, a heat capacity

$$C_p = \frac{R}{2} \left(\frac{5PV^3 - Va + 6ab}{PV^3 - Va + 2ab} \right)$$

The particular forms of the partial derivatives are not given here.

Let's isentropically expand Argon from $(T_1, P_1) = (500 \text{ K}, 101325 \text{ Pa})$ to state

$$(P_2 = \frac{P_1}{2}, S_2 = S_1).$$

We can write a simple code in MATLAB, which implements the equations in Section H.1. where we put in the form of the van der Waal's equation of state and heat capacity. This has been done. We use a Fourth-Order Simpson's Method with 20 intervals to numerically integrate all the functions. The output of the code is as follows:

```

Single Component, single phase fluid: Ar
Model: van der Waals Gas w/ vdW Cp
Initial Condition: T = 500.000000 (K) and P = 1.013250e+005 (Pa) V = 4.102585e-002 (m^3/mol)
Final Condition: T = 378.913543 (K) and P = 5.066250e+004 (Pa) V = 6.217081e-002 (m^3/mol)
Heat Capacity: Cp(To,Po) = 2.079827e+001 Cp(Tf,Pf) = 2.079656e+001 (J/mol/K)
Heat Capacity: Cv(To,Po) = 1.247764e+001 Cv(Tf,Pf) = 1.247678e+001 (J/mol/K)
Changes due to Change in Temperature
Delta U = -1.511130e+003 (J/mol) Delta H = -2.518903e+003 (J/mol) Delta S = -5.768600e+000 (J/mol/K)
Delta G = 1.965780e+004 (J/mol) Delta A = 2.066557e+004 (J/mol)
Changes due to Change in Pressure
Delta U = 2.189213e+000 (J/mol) Delta H = 2.746023e+000 (J/mol) Delta S = 5.768600e+000 (J/mol/K)
Delta G = -2.183055e+003 (J/mol) Delta A = -2.183612e+003 (J/mol)
Total Changes
Delta U = -1.508941e+003 (J/mol) Delta H = -2.516157e+003 (J/mol) Delta S = 8.881784e-016 (J/mol/K)
Delta G = 1.747474e+004 (J/mol) Delta A = 1.848196e+004 (J/mol)

```

We can compare these results to those for the ideal gas to determine the effects of the van der Waal's equation of state.