Thermodynamic Properties of a single component fluid

Part 1

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Introduction

For a single-component, single-phase fluid at an arbitrary thermodynamic equation of state, we choose to define the state in terms of eight thermodynamic variables:

pressure	P	pascals
temperature	T	Kelvin
molar volume	V	meters^3/mole
internal energy	U	Joules/mole
enthalpy	H	Joules/mole
entropy	S	Joules/mole/K
Gibbs free energy	G	Joules/mole
Helmholtz free energy	A	Joules/mole

We have eight unknowns. We need to specify or define these with eight equations. From the phase rule, we know we can specify T and P independently. We use an equation of state to obtain the molar volume. We use a heat capacity, C_v or C_p, to define either H or U. This gives us four of the variables. We still need four more pieces of information. Three of these are thermodynamic relations:

$$H = U + PV \tag{1}$$

$$A = U - TS \tag{2}$$

$$G = H - TS \tag{3}$$

Now we are lacking only one piece of information, to completely define all variables. This last piece of information is the entropy of the fluid at some reference state.

We will now proceed to demonstrate how these eight pieces of information lead to a complete description of the material.

A. Equation of State

A fluid can be described by an equation of state. Take for example, the van der Waal's equation of state.

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

This is a cubic equation of state because we can rearrange the equation as a cubic polynomial in molar volume:

$$PV^3 + (-RT - bP)V^2 + aV - ba = 0 \tag{4.b}$$

Since this equation is a cubic polynomial, it has three roots for given values of P, T, R, a, and b. Each root has units of molar volume. Below the critical temperature, all three roots of the equation are real. Above the critical temperature, one of the roots is real and the other two roots are complex conjugates.

For a given V and T, the equation yields 1 pressure. For a given V and P, the equation yields 1 T, which we can explicitly see from

$$T = \frac{V-b}{R}\left(P + \frac{a}{V^2}\right) \tag{4.c}$$

There are two constants in the van der Waal's equation of state, a and b. b is the hard-sphere volume of a single molecule, multiplied by Avogadro's number. b has units of volume. a is an energetic attraction between molecules. It has units of energy-volume. For a van der Waal's gas a and b can be obtained from the critical properties.

$$a = \frac{27R^2 T_c^2}{64P_c} \tag{5}$$

and

$$b = \frac{RT_c}{8P_c} \tag{6}$$

For Argon ($T_c = 150.8\,\text{K}$, $P_c = 4.874 \cdot 10^6\,\text{Pa}$), we have values of a and b

$$a = 0.13606\,\text{J}\cdot\text{m}^3$$

$$b = 3.2154 \cdot 10^{-5}\,\frac{\text{m}^3}{\text{mole}}$$

B. Changes in Thermodynamic Properties

The properties U, H, S, G, and A should be considered as mathematical functions of T, P, and V. If we know two of the three variables in the set T, P, and V, then we can obtain all the other unknown properties, given that we know a reference value. If we don't know a reference value, then we can obtain changes in these properties.

As an example consider the arbitrary function, $f(T,P)$. We can express this function *exactly* as

$$f(T,P) = f(T_{ref},P_{ref}) + \int_{T_{ref}}^{T} \left(\frac{\partial f(T,P_{ref})}{\partial T}\right)_P dT + \int_{P_{ref}}^{P} \left(\frac{\partial f(T,P)}{\partial P}\right)_T dP \tag{7.a}$$

or

$$f(T,P) = f(T_{ref},P_{ref}) + \int_{T_{ref}}^{T} \left(\frac{\partial f(T,P)}{\partial T}\right)_P dT + \int_{P_{ref}}^{P} \left(\frac{\partial f(T_{ref},P)}{\partial P}\right)_T dP \tag{7.b}$$

These two statements differ only in the order in which we integrated the functions. Both are true and form the fundamental basis by which we calculate changes in thermodynamic properties. If we replace the function $f(T,P)$ with the enthalpy $H(T,P)$, then we can compute the enthalpy at any temperature and pressure assuming we know its value at some reference conditions.

$$H(T_1,P_1) = H(T_{ref},P_{ref}) + \int_{T_{ref}}^{T_1} \left(\frac{\partial H(T,P_{ref})}{\partial T}\right)_P dT + \int_{P_{ref}}^{P_1} \left(\frac{\partial H(T_1,P)}{\partial P}\right)_T dP \tag{8}$$

On the other hand, if we want to know the change in enthalpy in moving from (T_1,P_1) to (T_2,P_2) then we can consider (T_1,P_1) as our reference state, and evaluating equation (7.a) yields:

$$H(T_2,P_2) = H(T_1,P_1) + \int_{T_1}^{T_2} \left(\frac{\partial H(T,P_1)}{\partial T}\right)_P dT + \int_{P_1}^{P_2} \left(\frac{\partial H(T_2,P)}{\partial P}\right)_T dP$$

$$\Delta H = H(T_2,P_2) - H(T_1,P_1) = \int_{T_1}^{T_2} \left(\frac{\partial H(T,P_1)}{\partial T}\right)_P dT + \int_{P_1}^{P_2} \left(\frac{\partial H(T_2,P)}{\partial P}\right)_T dP \tag{9}$$

Now, all we are missing is the functional form of the partial derivatives. If we only had a table that would tell us what the partial derivatives, then all we would have to do is integrate the functions (either analytically or numerically) and we would be able to calculate the change in enthalpy from any one thermodynamic state to another.

Oh, Lucky us! Such a table exists. Thermodynamics has been around a long time and a lot of good minds have scrutinized it. One such mind belonged to P.W. Bridgeman. He devised a table by which he could rapidly obtain any thermodynamic partial derivative for a pure component fluid of the form:

$$\left(\frac{\partial X}{\partial Y}\right)_Z$$

Since we have 8 different variables (T, P, V, U, H, S, G, & A) and three ways they can be entered into X, Y, and Z, we have a total of $8^3 = 512$ different partial derivatives. The Bridgeman Tables can give us any of these partials, although some are not as useful as others.

The Bridgeman Tables require (i) an equation of state, (ii) an expression for the heat capacity (either , C_v or C_p) and a single reference entropy at some (T_{ref}, P_{ref}). These three pieces of data are the absolute minimum necessary to determine these partial derivatives.

Let's say we are using a pressure explicit equation of state (e.g. van der Waal's EOS) and we have C_p. We select that table. If we want the enthalpy change with respect to temperature at constant pressure, we then proceed to the page marked pressure, because we are holding pressure constant. In the Bridgeman tables:

$$\left(\frac{\partial H}{\partial T}\right)_P = \frac{(\partial H)_P}{(\partial T)_P} = \frac{C_P\left(\frac{\partial p}{\partial V}\right)_T}{\left(\frac{\partial p}{\partial V}\right)_T} = C_P \tag{10}$$

If we want the enthalpy change with respect to pressure at constant temperature, we find:

$$\left(\frac{\partial H}{\partial P}\right)_T = \frac{(\partial H)_T}{(\partial P)_T} = \frac{-T\left(\frac{\partial p}{\partial T}\right)_V - V\left(\frac{\partial p}{\partial V}\right)_T}{-\left(\frac{\partial p}{\partial V}\right)_T} = \frac{T\left(\frac{\partial p}{\partial T}\right)_V}{\left(\frac{\partial p}{\partial V}\right)_T} + V \tag{11}$$

From the Bridgeman Tables, we can get the partial derivative of any variable in terms of any other variable, holding any variable constant.

The solutions are given in terms of only P, T, V, C_p, and derivatives which are easy to obtain from the equation of state, $\left(\frac{\partial p}{\partial T}\right)_V$ and $\left(\frac{\partial p}{\partial V}\right)_T$. For certain partial derivatives, we also need a reference entropy (as we will see later).

So, if we want the enthalpy for an arbitrary change in temperature and pressure, we substitute equations (10) and (11) into equation (9).

$$\Delta H = H(T_2, P_2) - H(T_1, P_1) = \int_{T_1}^{T_2} C_P(T, P_1)dT + \int_{P_1}^{P_2} \frac{T_2\left(\frac{\partial P}{\partial T}\right)_V}{\left(\frac{\partial P}{\partial V}\right)_T} + VdP \tag{12}$$

If we want to determine the change in temperature as we go from state (T_1, P_1) through an isentropic throttling valve to state $(T_2 = ?, P_2)$, then we have:

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{(\partial T)_S}{(\partial P)_S} = \frac{\left(\frac{\partial p}{\partial T}\right)_V}{-\frac{C_P}{T}\left(\frac{\partial p}{\partial V}\right)_T} = -\frac{T\left(\frac{\partial p}{\partial T}\right)_V}{C_P\left(\frac{\partial p}{\partial V}\right)_T} \tag{13}$$

$$\Delta T = T_2 - T_1 = \int_{P_1}^{P_2} \left(\frac{\partial T}{\partial P}\right)_S dP = \int_{P_1}^{P_2} -\frac{T_{iso-S}\left(\frac{\partial p}{\partial T}\right)_V}{C_P\left(\frac{\partial p}{\partial V}\right)_T} dP \qquad (14)$$

In equation (14), T_{iso-S} is a dummy variable that identifies the temperature that corresponds to the dummy variable of integration P, along an isentropic process.

If we want to determine the change in temperature as we go from state (T_1, P_1) through an isenthalpic turbine to state $(T_2 = ?, P_2)$, then we have:

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{(\partial T)_H}{(\partial P)_H} = \frac{T\left(\frac{\partial p}{\partial T}\right)_V + V\left(\frac{\partial p}{\partial V}\right)_T}{-C_P\left(\frac{\partial p}{\partial V}\right)_T} = -\frac{T\left(\frac{\partial p}{\partial T}\right)_V}{C_P\left(\frac{\partial p}{\partial V}\right)_T} - \frac{V}{C_P} \qquad (15)$$

$$\Delta T = T_2 - T_1 = \int_{P_1}^{P_2} \left(\frac{\partial T}{\partial P}\right)_H dP = \int_{P_1}^{P_2} \left[-\frac{T_{iso-H}\left(\frac{\partial p}{\partial T}\right)_V}{C_P\left(\frac{\partial p}{\partial V}\right)_T} - \frac{V}{C_P}\right] dP \qquad (16)$$

We will see that we have all the information we need from the equation of state and the heat capacity to determine the functional form of the integrand.

In the sections that follow, we will derive the equations of change for four common processes for an arbitrary equation of state. After that, we will apply the results to three specific equations of state.

C.1. Isothermal Expansion/Compression for Arbitrary Equation of State

In this section we are going to provide formulae, obtained from the Bridgeman Tables, for the change in V, U, H, S, G, and A, due to an isothermal expansion/compression. In this problem, we move from state (T_1, P_1) to state (T_1, P_2). The relevant formulae in the Bridgeman Tables are of the form:

$$\left(\frac{\partial X}{\partial p}\right)_T$$

where X can be T, P, V, U, H, S, G, and A.

i. Temperature

Let's start with the simplest one, temperature. When we hold temperature constant, there is no change in pressure.

$$\left(\frac{\partial T}{\partial p}\right)_T = 0$$

ii. Pressure

When we vary pressure, the change in pressure is defined as $\Delta P = P_2 - P_1$

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

$$\Delta P \equiv P_2 - P_1 = \int_{P_1}^{P_2}\left(\frac{\partial p}{\partial p}\right)_T dP = \int_{P_1}^{P_2} dP = P_2 - P_1$$

iii. Volume

If we isothermally vary pressure, we have for the change in volume

$$\left(\frac{\partial V}{\partial p}\right)_T = \frac{(\partial V)_T}{(\partial p)_T} = \frac{-1}{-\left(\frac{\partial p}{\partial V}\right)_T} = \frac{1}{\left(\frac{\partial p}{\partial V}\right)_T}$$

This is an identity. We can obtain this derivative, $\left(\frac{\partial p}{\partial V}\right)_T$, from the equation of state.

$$\Delta V \equiv V_2 - V_1 = \int_{V_1}^{V_2}\frac{1}{\left(\frac{\partial p}{\partial V}\right)_T}dP = \int_{V_1}^{V_2}\left(\frac{\partial V}{\partial p}\right)_T dP = \int_{V_1}^{V_2} dV = V_2 - V_1$$

We then solve the equation of state for V_1 and V_2 because we know the initial and final temperature and pressure.

iv. Internal Energy

From the Bridgeman Tables we have:

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

yielding an internal energy change of

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

v. Enthalpy

From the Bridgeman Tables we have:

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

yielding an enthalpy change of

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

vi. Entropy

From the Bridgeman Tables we have:

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

yielding an entropy change of

$$\Delta S = S(T_1,P_2) - S(T_1,P_1) = \int_{P_1}^{P_2} \frac{\left(\frac{\partial p}{\partial T}\right)_V}{\left(\frac{\partial p}{\partial V}\right)_T} \, dP$$

vii. Gibbs Free Energy

From the Bridgeman Tables we have:

$$\left(\frac{\partial G}{\partial P}\right)_T = \frac{(\partial G)_T}{(\partial P)_T} = \frac{-V\left(\frac{\partial p}{\partial V}\right)_T}{-\left(\frac{\partial p}{\partial V}\right)_T} = V$$

yielding a Gibbs Free Energy change of

$$\Delta G = G(T_1,P_2) - G(T_1,P_1) = \int_{P_1}^{P_2} V \, dP$$

viii. Helmholtz Free Energy

From the Bridgeman Tables we have:

$$\left(\frac{\partial A}{\partial P}\right)_T = \frac{(\partial A)_T}{(\partial P)_T} = \frac{p}{-\left(\frac{\partial p}{\partial V}\right)_T}$$

yielding a Helmholtz Free Energy change of

$$\Delta A = A(T_1,P_2) - A(T_1,P_1) = \int_{P_1}^{P_2} \frac{p}{-\left(\frac{\partial p}{\partial V}\right)_T} \, dP$$

C.2. Isothermal Expansion/Compression for Ideal Gas

The Ideal Gas has an equation of state

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

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

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

The necessary derivatives are:

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{V^2}$$

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

i. Temperature

$$\Delta T = T_2 - T_1 = 0$$

ii. Pressure

$$\Delta P = P_2 - P_1$$

iii. Volume

$$\left(\frac{\partial V}{\partial p}\right)_T = \frac{1}{\left(\dfrac{\partial p}{\partial V}\right)_T} = \frac{1}{-\dfrac{RT}{V^2}} = -\frac{V^2}{RT} = -\frac{RT}{p^2}$$

$$\Delta V \equiv V_2 - V_1 = \int_{V_1}^{V_2} -\frac{RT}{p^2}dP = \frac{RT}{p_2} - \frac{RT}{p_1} = V_2 - V_1$$

iv. Internal Energy

$$\left(\frac{\partial U}{\partial P}\right)_T = \frac{p - T\dfrac{R}{V}}{\dfrac{RT}{V^2}} = \frac{p - p}{\dfrac{RT}{V^2}} = 0$$

$$\Delta U = U(T_1,P_2) - U(T_1,P_1) = 0$$

v. Enthalpy

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

$$\Delta H = H(T_1, P_2) - H(T_1, P_1) = 0$$

vi. Entropy

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

$$\Delta S = S(T_1, P_2) - S(T_1, P_1) = \int_{P_1}^{P_2} -\frac{R}{P}\, dP = -R\ln\left(\frac{P_2}{P_1}\right) = R\ln\left(\frac{P_1}{P_2}\right)$$

vii. Gibbs Free Energy

$$\left(\frac{\partial G}{\partial P}\right)_T = \frac{-V\left(\frac{\partial p}{\partial V}\right)_T}{-\left(\frac{\partial p}{\partial V}\right)_T} = V = \frac{RT}{P}$$

$$\Delta G = G(T_1, P_2) - G(T_1, P_1) = \int_{P_1}^{P_2} \frac{RT}{P}\, dP = RT\ln\left(\frac{P_2}{P_1}\right)$$

viii. Helmholtz Free Energy

$$\left(\frac{\partial A}{\partial P}\right)_T = \frac{p}{-\left(\frac{\partial p}{\partial V}\right)_T} = \frac{p}{\frac{RT}{V^2}} = \frac{RT}{P}$$

$$\Delta A = A(T_1, P_2) - A(T_1, P_1) = \int_{P_1}^{P_2} \frac{RT}{P}\, dP = RT\ln\left(\frac{P_2}{P_1}\right)$$

Example C.2. Numerical Example: Isothermal Expansion/Compression for Ideal Gas

Let's isothermally compress Argon from $(T_1, P_1) = (500\,\text{K}, 101325\,\text{Pa})$ to state
$(T_1, P_2) = (500\,\text{K}, 202650\,\text{Pa})$. We will assume Argon is an Ideal Gas.

We can write a simple code in MATLAB, which implements the equations in Section C.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 = 2.026500e+005 (Pa) V = 2.051320e-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 = 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 = -5.762826e+000 (J/mol/K)
Delta G = 2.881413e+003 (J/mol) Delta A = 2.881413e+003 (J/mol)
Total Changes
Delta U = 0.000000e+000 (J/mol) Delta H = 0.000000e+000 (J/mol) Delta S = -5.762826e+000 (J/mol/K)
Delta G = 2.881413e+003 (J/mol) Delta A = 2.881413e+003 (J/mol)

An ideal gas does not have a change in U or H when undergoing an isothermal compression. The Change in entropy is negative, because the gas is more dense at the final state. The values of ΔG and ΔA are the same. This is just a chance occurrence. For other gases undergoing this process and for an ideal gas undergoing a different process, this would not be the case.

C.3. Isothermal Expansion/Compression for van der Waal's Gas

The van der Waal's Gas has an equation of state

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

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

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

This functional form of the heat capacity was derived using statistical mechanics. It cannot be derived using classical thermodynamics. If you are interested in the derivation, you might just have an inclination to be a statistical thermodynamicist/molecular modeler and you ought to take a course in statistical mechanics.

The only necessary derivatives of the equation of state are:

$$\left(\frac{\partial p}{\partial V} \right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3}$$

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

i. Temperature

$$\Delta T = T_2 - T_1 = 0$$

ii. Pressure

$$\Delta P = P_2 - P_1$$

iii. Volume

$$\left(\frac{\partial V}{\partial p} \right)_T = \frac{1}{\left(\frac{\partial p}{\partial V} \right)_T} = \frac{1}{-\frac{RT}{(V-b)^2} + \frac{2a}{V^3}}$$

$$\Delta V \equiv V_2 - V_1 = \int_{P_1}^{P_2} \frac{1}{-\frac{RT}{(V-b)^2} + \frac{2a}{V^3}} dP$$

This integral is not easily evaluated analytically. Instead, we evaluate the integral numerically. When we discretize the range of integration, we evaluate the integrand at each point. We've discretized along the pressure, so we know the values of P. Our system is isothermal so we know the value of T. The value of V at each point,

must be obtained by solving the vdW EOS, and selecting the root that corresponds to the phase which we are in. These comments apply to the integrals involved in obtaining the changes in U, H, S, G, and A as well.

iv. Internal Energy

$$\left(\frac{\partial U}{\partial P}\right)_T = \frac{p - T\left(\frac{\partial p}{\partial T}\right)_V}{-\left(\frac{\partial p}{\partial V}\right)_T} = \frac{p - T\dfrac{R}{V - b}}{\dfrac{RT}{(V - b)^2} - \dfrac{2a}{V^3}}$$

$$\Delta U = U(T_1, P_2) - U(T_1, P_1) = \int_{P_1}^{P_2}\left[\frac{p - T\dfrac{R}{V - b}}{\dfrac{RT}{(V - b)^2} - \dfrac{2a}{V^3}}\right]dP$$

v. Enthalpy

$$\left(\frac{\partial H}{\partial P}\right)_T = \frac{T\left(\frac{\partial p}{\partial T}\right)_V}{\left(\frac{\partial p}{\partial V}\right)_T} + V = \frac{T\dfrac{R}{V - b}}{-\dfrac{RT}{(V - b)^2} + \dfrac{2a}{V^3}} + V$$

$$\Delta H = H(T_1, P_2) - H(T_1, P_1) = \int_{P_1}^{P_2}\left[\frac{T\dfrac{R}{V - b}}{-\dfrac{RT}{(V - b)^2} + \dfrac{2a}{V^3}} + V\right]dP$$

vi. Entropy

$$\left(\frac{\partial S}{\partial P}\right)_T = \frac{-\left(\frac{\partial p}{\partial T}\right)_V}{-\left(\frac{\partial p}{\partial V}\right)_T} = -\frac{\dfrac{R}{V - b}}{\dfrac{RT}{(V - b)^2} - \dfrac{2a}{V^3}}$$

$$\Delta S = S(T_1, P_2) - S(T_1, P_1) = \int_{P_1}^{P_2}\left[-\frac{\dfrac{R}{V - b}}{\dfrac{RT}{(V - b)^2} - \dfrac{2a}{V^3}}\right]dP$$

vii. Gibbs Free Energy

$$\left(\frac{\partial G}{\partial P}\right)_T = \frac{-V\left(\frac{\partial p}{\partial V}\right)_T}{-\left(\frac{\partial p}{\partial V}\right)_T} = -\frac{(V-b)V}{R}\left[\frac{RT}{(V-b)^2} - \frac{2a}{V^3}\right]$$

$$\Delta G = G(T_1,P_2) - G(T_1,P_1) = \int_{P_1}^{P_2} -\frac{(V-b)V}{R}\left[\frac{RT}{(V-b)^2} - \frac{2a}{V^3}\right] dP$$

viii. *Helmholtz Free Energy*

$$\left(\frac{\partial A}{\partial P}\right)_T = \frac{p}{-\left(\frac{\partial p}{\partial V}\right)_T} = \frac{p}{\dfrac{RT}{(V-b)^2} - \dfrac{2a}{V^3}}$$

$$\Delta A = A(T_1,P_2) - A(T_1,P_1) = \int_{P_1}^{P_2} \frac{p}{\dfrac{RT}{(V-b)^2} - \dfrac{2a}{V^3}} dP$$

Example C.3. Numerical Example: Isothermal Expansion/Compression for van der Waal's Gas

Let's isothermally compress Argon from $(T_1, P_1) = (500\,K, 101325\,Pa)$ to state $(T_1, P_2) = (500\,K, 202650\,Pa)$. We will assume Argon is a van der Waal's Gas with critical properties $T_c = 150.8\,K$ and $P_c = 4.874 \cdot 10^6\,Pa$.

We can write a simple code in MATLAB, which implements the equations in Section C.3. 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 = 500.000000 (K) and P = 2.026500e+005 (Pa) V = 2.051268e-002 (m^3/mol)
Heat Capacity   : Cp(To,Po) = 2.079827e+001 Cp(Tf,Pf) = 2.081153e+001 (J/mol/K)
Heat Capacity   : Cv(To,Po) = 1.247764e+001 Cv(Tf,Pf) = 1.248429e+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 = -3.316454e+000 (J/mol) Delta H = -3.367100e+000 (J/mol) Delta S = -5.769451e+000 (J/mol/K)
Delta G = 2.881358e+003 (J/mol) Delta A = 2.881409e+003 (J/mol)
Total Changes
Delta U = -3.316454e+000 (J/mol) Delta H = -3.367100e+000 (J/mol) Delta S = -5.769451e+000 (J/mol/K)
Delta G = 2.881358e+003 (J/mol) Delta A = 2.881409e+003 (J/mol)

Unlike an ideal gas, a vdW gas does have a change in U or H when undergoing an isothermal compression. The change in U and H are negative. The change in entropy is negative, because the gas is more dense at the final state. The values of ΔG and ΔA are not the same, as they were for the ideal gas.

D.1. Isobaric Heating/Cooling for Arbitrary Equation of State

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 isobaric heating/cooling. In this problem, we move from state (T_1, P_1) to state (T_2, P_1). In each case, the relevant formulae in the Bridgeman Tables are of the form:

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

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.

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

Below, we simply present the partial derivatives.

i. Temperature

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

ii. Pressure

$$\left(\frac{\partial p}{\partial T}\right)_P = 0$$

iii. Volume

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

iv. Internal Energy

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

v. Enthalpy

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$$\left(\frac{\partial H}{\partial T}\right)_P = \frac{(\partial H)_P}{(\partial T)_P} = \frac{C_P\left(\frac{\partial p}{\partial V}\right)_T}{\left(\frac{\partial p}{\partial V}\right)_T} = C_p$$

vi. Entropy

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{(\partial S)_P}{(\partial T)_P} = \frac{\frac{C_P}{T}\left(\frac{\partial p}{\partial V}\right)_T}{\left(\frac{\partial p}{\partial V}\right)_T} = \frac{C_P}{T}$$

vii. Gibbs Free Energy

$$\left(\frac{\partial G}{\partial T}\right)_P = \frac{(\partial G)_P}{(\partial T)_P} = \frac{-S\left(\frac{\partial p}{\partial V}\right)_T}{\left(\frac{\partial p}{\partial V}\right)_T} = -S$$

viii. Helmholtz Free Energy

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

We see that in order to obtain the changes in G and A, we need the entropy at an arbitrary temperature and pressure. It's worthwhile to see how we get this. We know that we can express the entropy at any arbitrary T and P as

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

Using the Bridgeman Tables to get the partial derivatives, we have:

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

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So if we know the reference entropy at one point, we can calculate the entropy at any other (T,P) state. However, notice that once we have S, that only gives us the partial derivative required to obtain G or A. So, we will have to integrate again, to obtain ΔG and ΔA. Furthermore, if the first integral (over T) in the definition of S is evaluated at Pref (the lower limit of the P-integration), then the second integral (over P) must be evaluated at T (the upper limit of the T-integration). This is because we first isobarically heat the fluid at the reference pressure. Then we isothermally compress the fluid at the arbitrary T.

Where can we get the reference entropy from? Well, we can't get it from classical thermodynamics. However, we can get it from statistical thermodynamics. The entropy of an ideal *monatomic* gas is:

$$S_{ref} = S(T_{ref}, P_{ref}) = R \ln\left[\frac{1}{N_{av}} \frac{V}{\Lambda^3} e^{\frac{5}{2}}\right] = R \ln\left[\frac{1}{N_{av}} \frac{RT_{ref}}{P_{ref}\Lambda^3} e^{\frac{5}{2}}\right]$$

This equation is called the Sackur-Tetrode Equation. V is the molar volume. N_{av} is Avogadro's number. The thermal de Broglie wavelength has units of length and is defined as

$$\Lambda = \sqrt{\frac{h^2}{2\pi mkT_{ref}}}$$

where h is Planck's constant, k is Boltzmann's constant, and m is the mass of the atom. The ideal gas must have a reference temperature which is large enough that the ideal gas assumption is valid.

The Sackur-Tetrode equation applies to monatomic gases only. If we have a more complicated atom, then we need to either derive the entropy from statistical mechanics, or we need to find a table of reference entropies. Either way, once we have the reference entropy, we can proceed to calculate the change in the Gibbs free energy.

D.2. Isobaric Heating/Cooling for an Ideal Gas

The Ideal Gas has an equation of state

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

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

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

The necessary derivatives are:

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{V^2}$$

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

i. Temperature

$$\Delta T \equiv T_2 - T_1$$

ii. Pressure

$$\Delta P \equiv P_2 - P_1 = 0$$

iii. Volume

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

$$\Delta V = V_2 - V_1 = \int_{T_1}^{T_2}\left(\frac{\partial V}{\partial T}\right)_P dT = \int_{T_1}^{T_2}\frac{R}{P}dT = \frac{RT_2}{P} - \frac{RT_1}{P}$$

iv. Internal Energy

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

$$\Delta U = U_2 - U_1 = \int_{T_1}^{T_2}\left(\frac{\partial U}{\partial T}\right)_P dT = \int_{T_1}^{T_2}\frac{3}{2}RdT = \frac{3}{2}R(T_2 - T_1)$$

v. Enthalpy

$$\left(\frac{\partial H}{\partial T}\right)_P = C_p = \frac{5}{2}R$$

$$\Delta H = H_2 - H_1 = \int_{T_1}^{T_2}\left(\frac{\partial H}{\partial T}\right)_P dT = \int_{T_1}^{T_2}\frac{5}{2}RdT = \frac{5}{2}R(T_2 - T_1)$$

vi. Entropy

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} = \frac{5}{2}\frac{R}{T}$$

$$\Delta S = S_2 - S_1 = \int_{T_1}^{T_2}\left(\frac{\partial S}{\partial T}\right)_P dT = \int_{T_1}^{T_2}\frac{5}{2}\frac{R}{T}dT = \frac{5}{2}R\ln\left(\frac{T_2}{T_1}\right)$$

vii. Gibbs Free Energy

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

At this point, we need the entropy of an ideal gas.

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

$$S(T,P) = R\ln\left[\frac{1}{N_{av}}\frac{RT_{ref}}{P_{ref}\Lambda^3}e^{\frac{5}{2}}\right] + \frac{5}{2}R\ln\left(\frac{T}{T_{ref}}\right) - R\ln\left(\frac{P}{P_{ref}}\right)$$

This is the entropy that gives the partial derivative for G. It is a function of T and P.

$$\Delta G = G_2 - G_1 = \int_{T_1}^{T_2} \left(\frac{\partial G}{\partial T}\right)_P dT = \int_{T_1}^{T_2} -\left\{ R\ln\left[\frac{1}{N_{av}}\frac{RT_{ref}}{P_{ref}\Lambda^3}e^{\frac{5}{2}}\right] + \frac{5}{2}R\ln\left(\frac{T}{T_{ref}}\right) - R\ln\left(\frac{P}{P_{ref}}\right)\right\}dT$$

Recall or look in a Table of Integrals for:

$$\int \ln(x) = x\ln(x) - x$$

$$\Delta G = \left[-S_{ref} + \frac{5}{2}R\ln(T_{ref}) + R\ln\left(\frac{P}{P_{ref}}\right)\right](T_f - T_o) - \frac{5}{2}R[(T_f\ln(T_f) - T_f) - (T_o\ln(T_o) - T_o)]$$

viii. Helmholtz Free Energy

$$\left(\frac{\partial A}{\partial T}\right)_P = \frac{p\left(\frac{\partial p}{\partial T}\right)_V}{\left(\frac{\partial p}{\partial V}\right)_T} - S = \frac{p\frac{R}{V}}{-\frac{RT}{V^2}} - S = -R - S$$

$$\Delta A = A_2 - A_1 = \int_{T_1}^{T_2}\left(\frac{\partial A}{\partial T}\right)_P dT = \int_{T_1}^{T_2} -RdT + \Delta G = R(T_f - T_o) + \Delta G$$

Example D.2. Numerical Example: Isobaric Heating/Cooling for Ideal Gas

Let's isobarically heat Argon from $(T_1, P_1) = (500\,K, 101325\,Pa)$ to state
$(T_2, P_1) = (600\,K, 101325\,Pa)$.   We will assume Argon is an Ideal Gas.

We can write a simple code in MATLAB, which implements the equations in Section D.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 = 1.013250e+005 (Pa) V = 4.923168e-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 = 0.000000e+000 (J/mol/K)
Delta G = 0.000000e+000 (J/mol) Delta A = 0.000000e+000 (J/mol)
Total Changes
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)

The change in U and H for an ideal gas undergoing an isobaric heating is positive. The entropy also increases
because the gas is now less dense, so the molar volume has increased. Finally G and A decrease because the
entropic term (-TS) is larger than the energetic term (U or H).

D.3. Isobaric Heating/Cooling for a van der Waal's gas

The van der Waal's Gas has an equation of state

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

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

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

We will also need the reference entropy of a monatomic van der Waal's gas

$$S_{ref} = S(T_{ref}, P_{ref}) = R\ln\left[\frac{1}{N_{av}}\frac{V_{ref}-b}{\Lambda^3}e^{\frac{5}{2}}\right]$$

The only necessary derivatives of the equation of state are:

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3}$$

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

i. Temperature

$$\Delta T \equiv T_2 - T_1$$

ii. Pressure

$$\Delta P \equiv P_2 - P_1 = 0$$

iii. Volume
.

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{-\left(\frac{\partial p}{\partial T}\right)_V}{\left(\frac{\partial p}{\partial V}\right)_T} = \frac{-\frac{R}{V-b}}{\frac{RT}{(V-b)^2} - \frac{2a}{V^3}}$$

$$\Delta V = V_2 - V_1 = \int_{T_1}^{T_2} \left(\frac{\partial V}{\partial T}\right)_P dT = \int_{T_1}^{T_2} \frac{-\dfrac{R}{V-b}}{\dfrac{RT}{(V-b)^2} - \dfrac{2a}{V^3}} dT$$

iv. Internal Energy

$$\left(\frac{\partial U}{\partial T}\right)_P = C_p + \frac{p\left(\dfrac{\partial p}{\partial T}\right)_V}{\left(\dfrac{\partial p}{\partial V}\right)_T} = \frac{R}{2}\left(\frac{5PV^3 - Va + 6ab}{PV^3 - Va + 2ab}\right) + \frac{p\dfrac{R}{V-b}}{-\dfrac{RT}{(V-b)^2} + \dfrac{2a}{V^3}}$$

$$\Delta U = U_2 - U_1 = \int_{T_1}^{T_2} \left(\frac{\partial U}{\partial T}\right)_P dT = \int_{T_1}^{T_2} \frac{R}{2}\left(\frac{5PV^3 - Va + 6ab}{PV^3 - Va + 2ab}\right) + \frac{p\dfrac{R}{V-b}}{-\dfrac{RT}{(V-b)^2} + \dfrac{2a}{V^3}} dT$$

v. Enthalpy

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

$$\Delta H = H_2 - H_1 = \int_{T_1}^{T_2} \left(\frac{\partial H}{\partial T}\right)_P dT = \int_{T_1}^{T_2} \frac{R}{2}\left(\frac{5PV^3 - Va + 6ab}{PV^3 - Va + 2ab}\right) dT$$

vi. Entropy

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} = \frac{R}{2T}\left(\frac{5PV^3 - Va + 6ab}{PV^3 - Va + 2ab}\right)$$

$$\Delta S = S_2 - S_1 = \int_{T_1}^{T_2} \left(\frac{\partial S}{\partial T}\right)_P dT = \int_{T_1}^{T_2} \frac{R}{2T}\left(\frac{5PV^3 - Va + 6ab}{PV^3 - Va + 2ab}\right) dT$$

vii. Gibbs Free Energy

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

At this point, we need the entropy of a monatomic vdW gas.

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

$$\Delta G = G_2 - G_1 = \int_{T_1}^{T_2} \left(\frac{\partial S}{\partial T}\right)_P dT = \int_{T_1}^{T_2} -S \, dT$$

viii. Helmholtz Free Energy

$$\left(\frac{\partial A}{\partial T}\right)_P = \frac{p\left(\frac{\partial p}{\partial T}\right)_V}{\left(\frac{\partial p}{\partial V}\right)_T} - S = \frac{p\frac{R}{V-b}}{-\frac{RT}{(V-b)^2} + \frac{2a}{V^3}} - S$$

$$\Delta A = A_2 - A_1 = \int_{T_1}^{T_2} \left(\frac{\partial A}{\partial T}\right)_P dT = \int_{T_1}^{T_2} \frac{p\frac{R}{V-b}}{-\frac{RT}{(V-b)^2} + \frac{2a}{V^3}} dT + \Delta G$$

Example D.3. Numerical Example: Isobaric Heating/Cooling for van der Waal's Gas

Let's isobarically heat Argon from $(T_1, P_1) = (500\,K, 101325\,Pa)$ to state
$(T_2, P_1) = (600\,K, 101325\,Pa)$. We will assume Argon is a vdW Gas.

We can write a simple code in MATLAB, which implements the equations in Section D.3. This has been done.
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 = 1.013250e+005 (Pa) V = 4.923658e-002 (m^3/mol)
Heat Capacity   : Cp(To,Po) = 2.079827e+001 Cp(Tf,Pf) = 2.079421e+001 (J/mol/K)
Heat Capacity   : Cv(To,Po) = 1.247764e+001 Cv(Tf,Pf) = 1.247561e+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 = 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)
Total Changes
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)

You can compare these results to those obtained for an ideal gas, to see how the van der Waal's gas behaved
differently.

Ideal Gas:
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)

D.4. Isobaric Heating/Cooling for a van der Waal's gas with Cubic Polynomial C_p

Frequently engineers do not use the rigorous van der Waal's heat capacity

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

Instead they use a heat capacity fitted from data to a cubic polynomial in temperature. Generally we can find fitted models for C_P for common materials. In Sandler, we find the model

$$C_p = a + bT + cT^2 + dT^3$$

with tables of the coefficients for a variety of fluids. These heat capacities are only approximations. Notably, there is no pressure dependence in the approximate heat capacity. We will see that using them violates (to a small extent) a fundamental precept of thermodynamics, namely that U, H, S, G, and A are state (path-independent) variables.

If we choose to use such an approximation, as we often do, we can still use the equations derived above for the heat capacity. However, we must substitute our approximation in for C_p rather than the rigorous definition.

Example D.4. Numerical Example: Isobaric Heating/Cooling for van der Waal's Gas w/ approximate C_p

Let's isobarically heat Argon from $(T_1,P_1) = (500\,K,101325\,Pa)$ to state $(T_2,P_1) = (600\,K,101325\,Pa)$. We will assume Argon is a vdW Gas with a heat capacity approximated by a cubic polynomial. We will use the following values for the constants in the polynomial.

      Cpcon = [6.529; -0.03753; 0.1930; -0.6861];
      a = 4.184*Cpcon(1)
      b = 4.184*Cpcon(2)*1.0e-2
      c = 4.184*Cpcon(3)*1.0e-5
      d = 4.184*Cpcon(4)*1.0e-9

This will give us a heat capacity in J/mole for a temperature given in K. These values are taken from Sandler.

We can write a simple code in MATLAB, which implements the equations in Section D.4. This has been done. The output of the code is as follows:

Single Component, single phase fluid: Ar
Model: van der Waals Gas w/ cubic polynomial 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 = 1.013250e+005 (Pa) V = 4.923658e-002 (m^3/mol)
Heat Capacity   : Cp(To,Po) = 2.819216e+001 Cp(Tf,Pf) = 2.866217e+001 (J/mol/K)
Heat Capacity   : Cv(To,Po) = 1.986489e+001 Cv(Tf,Pf) = 2.033896e+001 (J/mol/K)
Changes due to Change in Temperature
Delta U = 2.009655e+003 (J/mol) Delta H = 2.842160e+003 (J/mol) Delta S = 5.180569e+000 (J/mol/K)
Delta G = -1.713624e+004 (J/mol) Delta A = -1.796820e+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 = 0.000000e+000 (J/mol/K)
Delta G = 0.000000e+000 (J/mol) Delta A = 0.000000e+000 (J/mol)
Total Changes
Delta U = 2.009655e+003 (J/mol) Delta H = 2.842160e+003 (J/mol) Delta S = 5.180569e+000 (J/mol/K)
Delta G = -1.713624e+004 (J/mol) Delta A = -1.796820e+004 (J/mol)

You can compare these results to those obtained for a van der Waal's gas with a rigorous C_p, to see how the approximate heat capacity changed the results..

Total Changes from van der Waal's gas with rigorous heat capacity.
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)