Prof. Dr. Deniz Uner
Chemical Engineering. Middle East Technical University, Ankara

THE THERMODYNAMICS OF THE REAL FLUIDS SELF STUDY MODULE

Objective

The objective of this module is to develop a basis for estimating properties of the real fluids, starting from our basis of the thermodynamics landscape. Upon successful completion of this module, the student should be able to estimate any thermodynamic state variable of any fluid, given basic information such as critical parameters.

Reading assignment

Read Chapter 6 Sandler’s Thermodynamics, 4th edition.

Remember

This section is borrowed from the self study module on the thermodynamic landscape, U, H, A, G. We will derive the energy introduced into a fluid confined in a piston and cylinder assembly by an impeller performing reversible shaft work, subject to different constraints. We will start from the most general form of the Energy balance and the entropy balance to find the answers under different constraints.

$$\frac{dU}{dt} = \sum_{all\ streams} \dot{m}_i \widehat{H}_i + \dot{Q} + \dot{W}_s - P\frac{dV}{dt}$$

$$\frac{dS}{dt} = \sum_{all\ streams} \dot{m}_i \hat{S}_i + \frac{\dot{Q}}{T} + \dot{S}_{generated}$$

Case 1: The system is closed, the process is adiabatic and the system is at constant volume

The energy balance simplifies to

$$\frac{dU}{dt} = \dot{W}_s$$

The entropy balance indicates that

$$\frac{dS}{dt} = 0$$

This result indicates that for a reversible and adiabatic process, entropy is constant.

Case 2: The system is closed, the process is adiabatic and the system is at constant pressure

The energy balance simplifies to

$$\frac{dU}{dt} = \dot{W}_s - P\frac{dV}{dt}$$

At constant pressure, it is possible to rearrange the expression as

$$\frac{dH}{dt} = \dot{W}_s$$

Similar to case 1,

$$\frac{dS}{dt} = 0$$

Case 3: The system is closed, the process is isothermal and the system is at constant volume

The energy balance simplifies to

$$\frac{dU}{dt} = \dot{Q} + \dot{W}_s$$

While the entropy balance yields

$\frac{dS}{dt} = \frac{\dot{Q}}{T}$ or $\dot{Q} = T\frac{dS}{dt}$ when this expression for $\dot{Q}$ is substituted in the energy balance, keeping in mind that the temperature is constant, the rearrangement gives

$$\frac{dA}{dt} = \dot{W}_s$$

Where A is the Helmholtz free energy defined by, A=U-TS

It is important to note here that we derive this expression for any fluid. The fact that at constant temperature U is also constant is valid only for the ideal gases, not for the real fluids. Therefore we keep U in our derivations.

Case 4: The system is closed, the process is isothermal and the system is at constant pressure

The energy balance simplifies to

$$\frac{dU}{dt} = \dot{Q} + \dot{W}_s - P\frac{dV}{dt}$$

While the entropy balance yields

$\frac{dS}{dt} = \frac{\dot{Q}}{T}$ or $\dot{Q} = T\frac{dS}{dt}$ when this expression for $\dot{Q}$ is substituted in the energy balance, keeping in mind that the temperature and pressure are constant, the rearrangement gives

$$\frac{dG}{dt} = \dot{W}_s$$

Where A is the Helmholtz free energy defined by, G=U+PV-TS

It is important to note here that we derive this expression for any fluid. The fact that at constant temperature U is also constant is valid only for the ideal gases, not for the real fluids. Therefore, we keep U in our expressions.

Now lets combine all of the cases along with their constraints in the table below. Realize that your independent variables are S, T, P and V and your dependent variables are U, H, A and G.

S and V constant $\frac{dU}{dt} = \dot{W}_s$	S and P constant $\frac{dH}{dt} = \dot{W}_s$ H=U+PV
T and V constant $\frac{dA}{dt} = \dot{W}_s$ A=U-TS	T and P constant $\frac{dG}{dt} = \dot{W}_s$ G=U+PV-TS

Derive

The analysis presented above gave us a perspective using Joule's experiment as a tool. Joules experiment was a classic revealing the relationship between work and total energy. We studied an ideal gas confined in a piston and cylinder assembly and realized that under different constraints, the amount of energy exchanged with the environment is different. The special constraint pairs gave rise to new forms of energy as defined above. We will use these energies and their relationships to generate a set of equations that will allow us to determine the real fluid properties.

The internal energy

We have already learned that the internal energy carries information about vibrational, rotational, and translational degrees of freedom of a molecule. For the ideal gases, we also learned that the internal energy is only a function of temperature.

$$\frac{dU}{dT} = n\, C_v^*$$

In this module, we will ask the question of what happens if we do not have an ideal gas.

The assumptions of the ideal gas law

The ideal gas law has the following assumptions:

1. The volume occupied by the molecules, in comparison to the total volume, is negligible
2. The molecules do not interact.

Using this starting point, lord Kelvin discovered the absolute zero, by potting PV (a measure of energy) of a gas as a function of T. This plot had to features. The first feature of the plot, was that it was a straight line with a slope equal for all the gases investigated. The slope is what we call R, the universal gas constant. Universal indicate that the constant is valid for all of the gases under the conditions that they behave ideally. The second feature was the intercept of the Temperature axis. This temperature signified the condition where net energy is zero.

The van der Waals Equation of State

Let us now remove the assumptions of the ideal gas law one by one:

1. There is a finite volume that the molecules occupy. In fact, this is even more important when we move close to the liquid state. Lets call this volume b, such that the volume of voids that is calculated by the ideal gas law becomes $(\underline{V}-b)$ and the new equation of state is $P(\underline{V}-b)=RT$
2. We will also remove the second assumption by adding a term that represent the molecular interactions. For the discussion we will conduct here, the interaction parameter we chose will be $\frac{a}{\underline{V}^2}$, this parameter will correct the local pressures sensed by the molecules, for the attractive interactions.

   As a result, our new equation of state took the following form:

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

This is the van der Waals equation of state. It will be the basis of our discussions. The van der Waals (vDW) equation of state (EOS) is a cubic polynomial in terms of $\underline{V}$. There is a group of equations of state called cubic equations due to the fact that in all of these equations, the highest power of $\underline{V}$ is three, but the function does not have to be a polynomial. Now, in the Figure below, you see a plot of two isotherms emanating from VDW EOS. One of the isotherms (orange colored) is at the critical temperature, and the other one (blue) is at a temperature lower than the critical temperature, such that the vapor and liquid coexistence can be experienced.

The cubic equation of state exhibit three extrema: a maximum, a minimum, and a saddle point at which the concave curve and convex curve meet. These extrema are represented by the following mathematical equalities at the critical point.

$$\left(\frac{\partial P}{\partial \underline{V}}\right)_T = 0 = -\frac{RT}{\left(\underline{V} - b\right)^2} + 2\frac{a}{\underline{V}^3}$$

$$\left(\frac{\partial^2 P}{\partial \underline{V}^2}\right)_T = \frac{2RT}{\left(\underline{V} - b\right)^3} - 6\frac{a}{\underline{V}^4} = 0$$

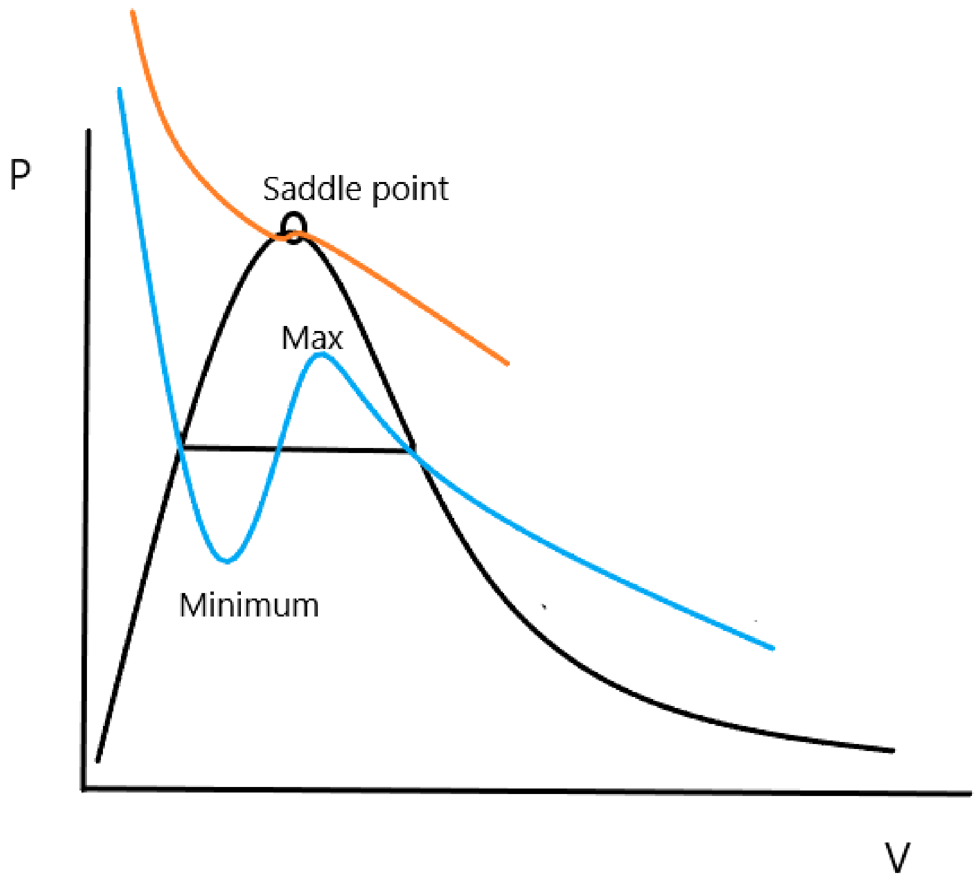
These two identities give us a set of equations that we can calculate and b

$$a = \frac{9\underline{V}_c R T_c}{8}$$

$$b = \frac{\underline{V}_c}{3}$$

Substitute these values to vdW to obtain the critical pressure.

$$P_c = \frac{a}{27b^2}$$



As seen, there is a horizontal line connecting the vapor equilibrium curve with that of the liquid equilibrium curve. The locus of this curve was decided such that the area remaining above the curve and below are equal.

We have removed the ideal gas assumptions from the equation of state. Now we will do the same for the internal energy.

Internal Energy of a Real Fluid

So far, we used The following identity to estimate the internal energy of the ideal gas

$\frac{dU}{dT} = n\,C_v^*$

For the real fluids, this expression will take the following form

$$\left(\frac{\partial U}{\partial T}\right)_V = n\,C_v$$

Notice the difference between these two expressions. The total derivative indicating U is only a function of temperature for an Ideal Gas is replaced with a particle derivative, indicating that U depends on more than one variable. In this section we will learn these parameters and their interrelationships.

In order to estimate the thermodynamic behavior of the real fluid, we need to start from the energy balance and the entropy balance. This time we will have a real fluid confined in a piston and cylinder assembly, under closed system configurations, and there is no shaft work. The energy balance reduces to

$\frac{dU}{dt} = \dot{Q} - P\frac{dV}{dt}$

Similarly, entropy balance reduces to (for situations that the entropy generation is not considered)

$$\frac{dS}{dt} = \frac{\dot{Q}}{T}$$

Hence, substitution yields,

$\frac{dU}{dt} = T\frac{dS}{dt} - P\frac{dV}{dt}$

We can eliminate the dt terms to have the most general expression of the internal energy:

dU=TdS-PdV

This expression tells us that U is a function of entropy and volume, U(S,V). This is the most fundamental level of defining the internal energy coordinate system. But similar to mathematics, where we change the variables in order to ease the calculations, we can do the same in thermodynamics. As we have seen so far, entropy is a difficult state variable to control or measure. Therefore, we will switch the coordinates to T, V instead (however, will always remember that internal energy is a function of entropy and volume, at the fundamental level) . The coordinate transformation will require defining entropy, S, as a function of T and V, S(T,V). Then we will substitute this function in the definition of internal energy equation.

If S (T,V) then, $\mathrm{dS} = \left(\frac{\partial \mathrm{S}}{\partial \mathrm{T}}\right)_{\mathrm{v}} \mathrm{dT} + \left(\frac{\partial \mathrm{S}}{\partial \mathrm{V}}\right)_{\mathrm{T}} \mathrm{dV}$

Now, we need to define $\left(\frac{\partial \mathrm{S}}{\partial \mathrm{T}}\right)_{\mathrm{v}}$ and $\left(\frac{\partial \mathrm{S}}{\partial \mathrm{V}}\right)_{\mathrm{T}}$.

Starting from dU=TdS-PdV , dividing both sides by dT and keeping volume constant, in other words, dV =0 gives us

$$\left(\frac{\partial \mathrm{U}}{\partial \mathrm{T}}\right)_{\mathrm{v}} = T\left(\frac{\partial \mathrm{S}}{\partial \mathrm{T}}\right)_{\mathrm{v}}$$

Remember

$$\left(\frac{\partial U}{\partial T}\right)_{V} = n\, C_v$$

Therefore

$$\left(\frac{\partial \mathrm{S}}{\partial \mathrm{T}}\right)_{\mathrm{v}} = n\,\frac{C_v}{T}$$

Being able to replace $\left(\frac{\partial \mathrm{S}}{\partial \mathrm{V}}\right)_{\mathrm{T}}$ will require a little bit more effort. We will bring the PVT equivalent of this term from the Helmholtz free energy based Maxwell relations.

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{V}}$$

With this substitution, we obtain an equation for the entropy:

$$\mathrm{dS} = n\frac{C_v}{T}\mathrm{dT} + \left(\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{V}}\mathrm{dV}$$

Substituting this will give us the relationship for the internal energy:

$$\mathrm{dU} = \mathrm{T}\left[n\frac{C_v}{T}\mathrm{dT} + \left(\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{V}}\mathrm{dV}\right] - PdV$$

rearranging gives:

$$\boxed{\mathrm{dU} = \mathrm{n}C_v\mathrm{dT} + \left[\left(\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{V}} - P\right]dV}$$

This is the equation we should use to determine the internal energy change.

Example

Determine the internal energy change for an ideal gas.

Solution

The equation of state for an ideal gas is given by $P = nRT/V$. We have to determine the function $\left(\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{V}} - P$ for the ideal gas.

$$\left(\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{V}} = nR/V$$

Upon substitution, we obtain

$$\left(\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{V}} - P = \frac{nRT}{V} - P = 0$$

Hence, for an ideal gas $\mathbf{dU} = \mathbf{n}\boldsymbol{C_v}\mathbf{dT}$

Example

Derive the function for internal energy change for a van der Waals equation of state.

Solution

Van Der Waals equation of state is given by $P = \frac{RT}{\underline{V}-b} - \frac{a}{\underline{V}^2}$. We have to determine the function $\left(\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{V}} - P$ for the ideal gas.

$$\left(\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{V}} = \frac{RT}{\underline{V} - b}$$

Upon substitution, we obtain

$$\left(\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{V}} - P = \frac{nRT}{V} - P = \frac{a}{\underline{V}^2}$$

Hence, for a van der Waals gas $\mathbf{dU} = \mathbf{n}\boldsymbol{C_v}\mathbf{dT} + \boldsymbol{\frac{a}{\underline{V}^2} dV}$

Maxwell relationships

First we have to derive Maxwell's relationships. Maxwell's relationships define how the thermodynamic independent parameters, T, S, P and V are related to each other. You may have already noticed from the example we used in the beginning of this document that we had four different forms of energy U, H, A and G. Each simplified a situation under a particular constraint so that we knew how much shaft work was done, through the changes in these energies. Now we will use these energies and their dependency on the variables T, S, P and V to establish relationships between the independent variables.

I will derive the relationship based on U function, and will leave the rest as an exercise for you (and if you attended the lecture, you know what to do). The internal energy at the fundamental level, (i.e. by the combination of the first and second laws) is a function of S and V.

U=U(S, V)

Therefore its derivative should look like

$$\mathrm{dU} = \left(\frac{\partial \mathrm{U}}{\partial \mathrm{S}}\right)_{\mathrm{v}} \mathrm{dS} + \left(\frac{\partial \mathrm{U}}{\partial \mathrm{V}}\right)_{\mathrm{S}} \mathrm{dV}$$

We started this course by taking energy as a conserved quantity. As such, the differential equation above is an exact differential, which allows the commutation of the differentiation operators. In other words,

$$\left(\frac{\partial}{\partial V}\left(\frac{\partial \mathrm{U}}{\partial \mathrm{S}}\right)_{\mathrm{v}}\right)_{S} = \left(\frac{\partial}{\partial S}\left(\frac{\partial \mathrm{U}}{\partial \mathrm{V}}\right)_{\mathrm{S}}\right)_{V}$$

There is a second step: We also know that dU=TdS-PdV if we compare

dU=TdS-PdV and $\mathrm{dU} = \left(\frac{\partial \mathrm{U}}{\partial \mathrm{S}}\right)_{\mathrm{v}} \mathrm{dS} + \left(\frac{\partial \mathrm{U}}{\partial \mathrm{V}}\right)_{\mathrm{S}} \mathrm{dV}$, we notice that

$\left(\frac{\partial \mathrm{U}}{\partial \mathrm{S}}\right)_{\mathrm{v}} = T$ and $\left(\frac{\partial \mathrm{U}}{\partial \mathrm{V}}\right)_{\mathrm{S}} = -P$

So let us substitute these equalities in $\left(\frac{\partial}{\partial V}\left(\frac{\partial \mathrm{U}}{\partial \mathrm{S}}\right)_{\mathrm{v}}\right)_{S} = \left(\frac{\partial}{\partial S}\left(\frac{\partial \mathrm{U}}{\partial \mathrm{V}}\right)_{\mathrm{S}}\right)_{V}$ to obtain,

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

This last equality is the Maxwell relationship. It relates T, V,P and S to each other.

enthalpy

We will relate T,V, P and S to each other starting from the equation for H.

H=U+PV

dH= dU + d(PV) = TdS-PdV+ PdV + VdP

dH= TdS+VdP

Exercise: Using the tools of mathematics, derive the following relationships

$\left(\frac{\partial \mathrm{H}}{\partial \mathrm{S}}\right)_{\mathrm{P}} = T$ and $\left(\frac{\partial \mathrm{H}}{\partial \mathrm{P}}\right)_{\mathrm{S}} = V$

$$\left(\frac{\partial T}{\partial P}\right)_{S} = \left(\frac{\partial \mathrm{V}}{\partial \mathrm{S}}\right)_{\mathrm{P}}$$

Helmholtz Free Energy

We will relate T, V, P and S to each other starting from the equation for A.

A=U-TS

dA= dU - d(TS) = TdS-PdV-TdS-SdT

dA= -SdT-PdV

Exercise: Using the same tools of mathematics we used above for internal energy based derivations, derive the following relationships

$\left(\frac{\partial \mathrm{A}}{\partial \mathrm{T}}\right)_{\mathrm{V}} = -S$ and $\left(\frac{\partial \mathrm{A}}{\partial \mathrm{V}}\right)_{\mathrm{T}} = -P$

The corresponding Maxwell relationship is

$$\left(\frac{\partial S}{\partial V}\right)_{T} = \left(\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{V}}$$

Gibbs Free Energy

We will relate T, V, P and S to each other starting from the equation for G.

G=H-TS

dG= dH - d(TS) = TdS+VdP-TdS-SdT

dG= -SdT+VdP

Exercise: Using the same tools of mathematics we used above for internal energy based derivations, derive the following relationships

$\left(\frac{\partial \mathrm{G}}{\partial \mathrm{T}}\right)_{\mathrm{P}} = -S$ and $\left(\frac{\partial \mathrm{G}}{\partial \mathrm{P}}\right)_{\mathrm{T}} = V$

The corresponding Maxwell relationship is

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

Let us solve for dS from dU=TdS-PdV,

$$dS = \frac{1}{T}dU + \frac{P}{T}dV$$

. *Calculate*

1. Determine the reversible shaft work needed to increase the temperature of a monoatomic ideal gas from 300 K to 500 K.
    a. If the process is conducted under constant volume and adiabatic conditions. What is the final pressure?
    b. If the process is conducted under constant pressure and adiabatic conditions. What is the final volume?
2. A monoatomic ideal gas, initially at 1 atm and 300 K is kept in a 1 L container. Determine the reversible shaft work needed to increase the pressure to 2 atm while keeping the temperature and volume constant.
3. A monoatomic ideal gas, initially at 1 atm and 300 K is kept in a 1 L container. Determine the reversible shaft work needed to increase the volume to 2 liters, while keeping the temperature and pressure constant.

Evaluate yourself

Check if you have answers to the following questions:

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Chemical Engineering. Middle East Technical University, Ankara

1. Why do we need these four different forms of energy, i.e., U, H, G and A?
2. What is the difference between internal energy and enthalpy?
3. What is the difference between Helmholtz free energy and Gibbs Free Energy?
4. Why Helmholtz Free Energy and Gibbs Free Energy are called free energies? What makes them free? Is there a bound energy?
5. Why is entropy an independent variable in the thermodynamic landscape?