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Liquefied Natural Gas (LNG) - Thermodynamics and Liquefaction Systems Part 2

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Acknowledgments

Thanks is given to the National Institute of Science and Technology (NIST) for making a relatively inexpensive software available to aid in the understanding of thermodynamic processes. NIST has made the software very user-friendly. The identifying information on this software is shown in Figure 1.

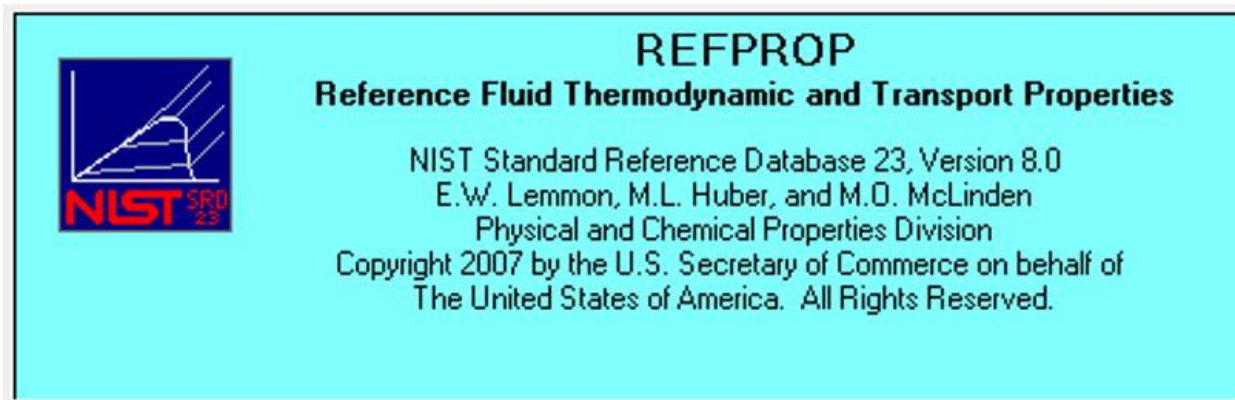


Figure 1: REFPROP information. Source REFPROP Software

A special thanks is given to Dr. Eric Lemmon of NIST. Over the past 15 years, he has continued to enhance this software and has always made himself available to explain its use. His contribution to making thermodynamic computation available to the masses has greatly benefited science and technology. His inspiring knowledge and willingness to help me to train others in the understanding of thermodynamics has been career changing and is much appreciated.

What Every Energy Engineer Needs to Know about Thermodynamics and Liquefaction Systems Part 2

What Every Energy Engineer Needs to Know about Thermodynamics and Liquefaction Systems Part 1, explained the basics of thermodynamics as applied to natural gas and LNG. It relied heavily on the use of pressure enthalpy charts for the pure substance methane. The use of these charts was good for building an understanding of the basics. However, the shortcomings of using these charts are the inaccuracy of reading the charts by eye and the inability to easily manage data for hydrocarbon mixtures. Also, it was tedious to scrutinize and interpolate the fine lines of various properties on the Ph diagrams, which sometimes resulted in learner frustration.

What Every Energy Engineer Needs to Know about Thermodynamics and Liquefaction Systems Part 2 builds on the information presented in Part 1, and introduces the use of software for understanding more complex concepts.

Although not essential, a companion list of conversions should be used with this book. The one used in this work is that published by the Sequoia Publishing Company in their pocket reference 4th edition. Further, although not essential, it is recommended that the Ph diagram used in the Part 1 learning (published in 1962 by Hydrocarbon Research) be used along with this work as there is some reference made to that diagram Ph diagram. The source information on the 1962 Ph diagram is as shown in Figure 2.

FROM: Canjar, Lawrence N.; Tejada, Victor M.; Manning, Francis S. "Thermo Properties of Methane". <u>Hydrocarbon Processing</u> , vol. 41, no. 9, Sep. 1962. pp

Figure 2: Source of Ph diagram used in Part 1 and Part 2 of this course

A copy of that Ph diagram accompanies this course.

Disclaimers

Although I believe this information to be correct no guarantee is given to its accuracy or completeness. It is the user's obligation to evaluate and use this information safely and to comply with all applicable laws and regulations. No statement made in this document shall be construed as a permission or recommendation for use of any product that might infringe existing patents or put persons or property at risk. No warranty is made, either express or implied.

The NIST software used in this book has its limitations. Cautions are given in the software and in the NIST documentation. The reader of this course is asked to read the NIST software documentation to better understand the limitations of the software. In particular, I show below, in Figure 3, the NIST caution that appears upon opening the software.

NIST uses its best efforts to deliver a high quality copy of the Database and to verify that the data contained therein have been selected on the basis of sound scientific judgement. However, NIST makes no warranties to that effect, and NIST shall not be liable for any damage that may result from errors or omissions in the Database.

Figure 3: NIST disclaimer (Source: REFPROP software)

Cautionary Notes

This document is intended to teach basic concepts. To accomplish this, a simplified approach is taken to explain thermodynamic processes.

Real plants have pressure drops associated with flows through piping, heat exchangers and other process equipment. Such pressure drops are not taken into account in the simplified examples given herein. Parts of the plant, such as the CO₂ and water removal systems were not included in the Part 2 analysis because their study is outside the scope of Part 2 but will be discussed in Part 3 of this course.

Rounded-off numbers are often used throughout to allow the reader to focus on concept and not get bogged down in numerical detail. Also, often pure methane is used as a study fluid when the real-world fluid would be natural gas as a mixture of many components.

It needs to be realized that different agencies use different values for Standard Temperature and Pressure or Normal Temperature and Pressure. Therefore, the reader needs to understand that before any analysis is attempted. The analyst needs to know the definition of Normal or Standard conditions for the calculation being made. Some of the various standard reference conditions are as shown below.

Table 1: Standard Reference Conditions. Source: Wikipedia

Standard reference conditions in current use			
Temperature	Absolute pressure	Relative humidity	Publishing or establishing entity
°C	kPa	% RH	
0	100.000		IUPAC (present definition) ^[1]
0	101.325		NIST, ^[7] ISO 10780, ^[8] formerly IUPAC ^[1]
15	101.325	0 ^{[9][10]}	ICAO's ISA, ^[9] ISO 13443, ^[10] EEA, ^[11] EGIA ^[12]
20	101.325		EPA, ^[13] NIST ^[14]
25	101.325		EPA ^[15]
25	100.000		SATP ^[16]
20	100.000	0	CAGI ^[17]
15	100.000		SPE ^[18]
20	101.3	50	ISO 5011 ^[19]
°F	psi	% RH	
60	14.696		SPE, ^[18] U.S. OSHA, ^[20] SCAQMD ^[21]
60	14.73		EGIA, ^[12] OPEC, ^[22] U.S. EIA ^[23]
59	14.503	78	U.S. Army Standard Metro ^{[24][25]}
59	14.696	60	ISO 2314, ISO 3977-2 ^[26]
°F	in Hg	% RH	
70	29.92	0	AMCA, ^{[27][28]} air density = 0.075 lbm/ft³. This AMCA standard applies only to air.
59 (15c)	29.92 (1013.25 hPa)		FAA, FAA's Pilot Handbook of Aeronautical Knowledge, Chapter 3 ^[29]

In this document the SI Normal Temperature and Pressure used are 1.01325 bar and 0 C unless otherwise stated. In this document the English Standard Temperature and Pressure used are 60 F and 14.696 unless otherwise stated.

1. A word about standard conditions

Take note that a scf is a mass measurement because it is a measure of a fixed number of molecules. That is because a scf is 1 cf at 60 F and 14.696 psia for the standard condition I chose to use. You need to determine which “Standard Conditions” you should use depending on what industry you are in and what your suppliers and customers are using.

For example, many in the Natural Gas Industry use 60 F and 14.73 psia as standard conditions. Although the difference in properties between 14.696 psia and 14.73 psia are small, when multiplied by billions of cubic feet, the mass delivered and associated dollar value can be large. For example, if an LNG ship is delivering \$30,000,000 worth of LNG, the difference between a standard pressure of 14.696 psia and 14.73 psia for contract calculations can equate to a

difference of approximately \$70,000 per shipload. If that error is made for 100 ships per year, the cumulative effect can be an error of \$7,000,000 per year.

UNLESS OTHERWISE STATED OR OBVIOUS BY THE NATURE OF THE PROBLEM, ALL PROCESS PROBLEMS PRESENTED IN THIS LEARNING ARE TO BE CONSIDERED AS STEADY STATE STEADY FLOW PROCESSES.

Prerequisites for Learning from this Book

The work herein presumes that the learner has completed and understands the concepts from *What Every Energy Engineer Needs to Know about Thermodynamics and Liquefaction Systems Part 1*.

Units

In Part 1 of this course, English units were used. It is expected that the learner will need to easily be able to switch between English and SI units in the workplace. Thus, in order to maximize the learning experience and since our industry uses both English and SI units, both units are used in Part 2 of this course. See Figure 4.

In this work, unless otherwise stated, mixtures are molar mixtures and not mass mixtures. Thus, if a mixture is stated to be a 97/3 methane ethane mixture it is a molar mixture and not a mass mixture unless defined as a mass mixture in the text.

Figure 4: Statement on how to understand mixtures. Source: Self-made

Introduction

This course is intended to be an aid for Liquefied Natural Gas (LNG) engineers to help them better understand the basic thermodynamic principles they deal with daily. Although this learning specifically deals with LNG, methane gas and mixtures of natural gas, the principles certainly pertain to propane, refrigerants and other gases and that engineers manage.

LNG is an essential part of the gas industry supply portfolio. It is used during our most critical supply times, and it is available only because we have reliable equipment and a highly skilled staff of operators and engineers.

Currently, LNG accounts for only a few percent of the U.S. gas supply. However, during a peak day, LNG may account for 30% of a local distribution company's send out. LNG also allows local gas production and stored natural gas supplies to contribute to the global energy picture as this gas can be transported in liquid form around the world. LNG utilization has grown significantly over the next 10 years, and it is highly likely that LNG will play a very important role in the future U.S and global energy picture. Today there are numerous import and export terminals in operation and on the drawing boards, and the present fleet of worldwide LNG tankers is increasing at a rapid pace. This growth in the LNG industry will require a significant increase in the skilled workforce necessary to operate and maintain this production, processing, export, receiving, distributing, and vaporizing facilities.

To better respond to anomalies during plant operation, engineers need some understanding of thermodynamics. The thermodynamic principles presented in this Part 2 of the course are basic and based on application rather than theory. The cases studied are mostly steady-state (the properties of the fluid at any point do not change with time) and steady-flow (the flow rate does not change with time) type problems. All of the solutions are based on some simple calculations and or on the use of thermodynamic or software.

Software

In this learning, software developed by the National Institute of Standards and Technology (NIST) is used to determine the properties of fluids. The program name is:

NIST Standard Reference Database 23

NIST Reference Fluid Thermodynamic and Transport Properties – REFPROP

April 2007, Version 8.0

Later versions are available

It should be noted that, at the time of this writing, there is a Version 10 available. For this work, Version 8.0 is being used. For this work, the program will always be referred to as REFPROP.

1. Mechanics of using the Software

The first thing you will need to do is to obtain the software, read the related documentation and install the software on your computer. Once REFPROP is installed the icon, shown in Figure 5 should appear on your computer desktop. The file name should also appear in your list of programs.

Start the program by double clicking the REFPROP icon on your desktop or via your all programs list.



Figure 5: REFPROP shortcut icon found on your computer desktop. Source: Computer Desktop

Once the program opens the first screen will show the informational message shown in Figure 6. Take note, that this information screen does state that REFPROP is a “best efforts” program. To continue using the program you will need to click on the “continue” tab on the screen.

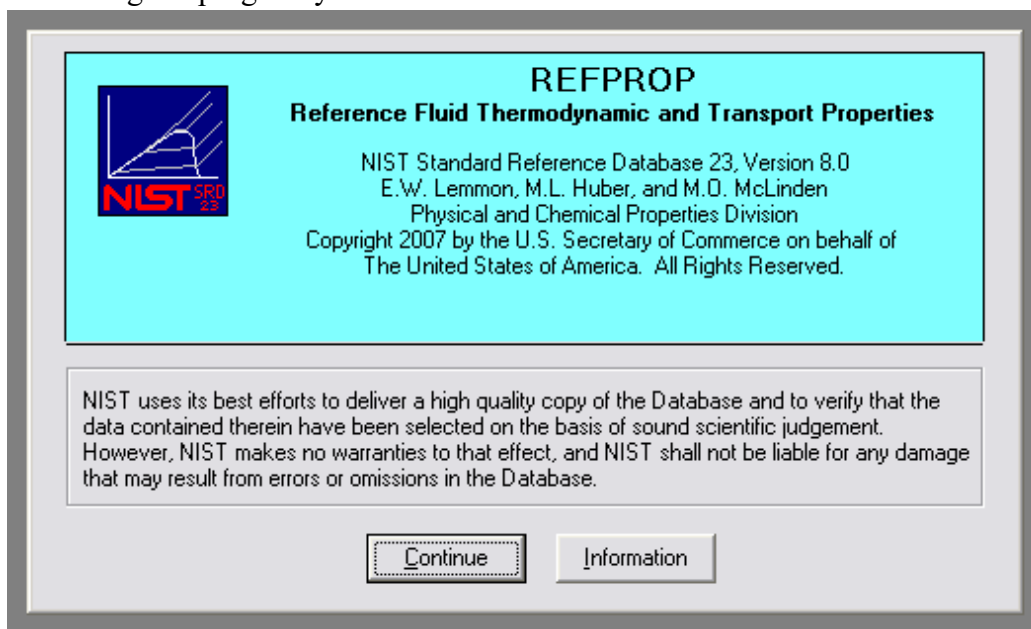


Figure 6: REFPROP opening statement – you must check on “continue” to use the program. Source: REFPROP

After you select “continue” and press enter, another information screen, as shown in Figure 7, will be displayed. This screen advises the user of the limitations of the REFPROP program.

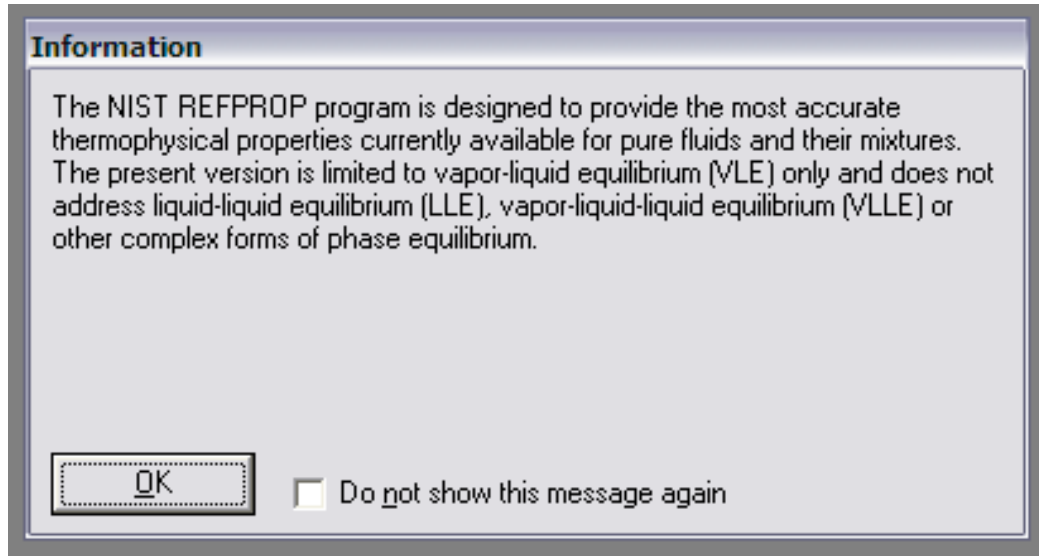


Figure 7: REFPROP opening statement – you must check on “OK” to use the program. Source: REFPROP

After you acknowledge the information shown in Figure 7, you will have displayed the screen shown in Figure 8. This screen has a blank display with a menu on the top of the screen. The menu is your interface to the REFPROP program. Take note, that at the very top of the screen it says “REFPROP (nitrogen)”. Every time you start the program the default fluid is nitrogen. One common mistake, learners make, is to open REFPROP, start using it and not realize that they need to change the fluid to the fluid they are studying. **Whenever you get strange data, check to assure that you have selected the correct fluid for your analysis.**

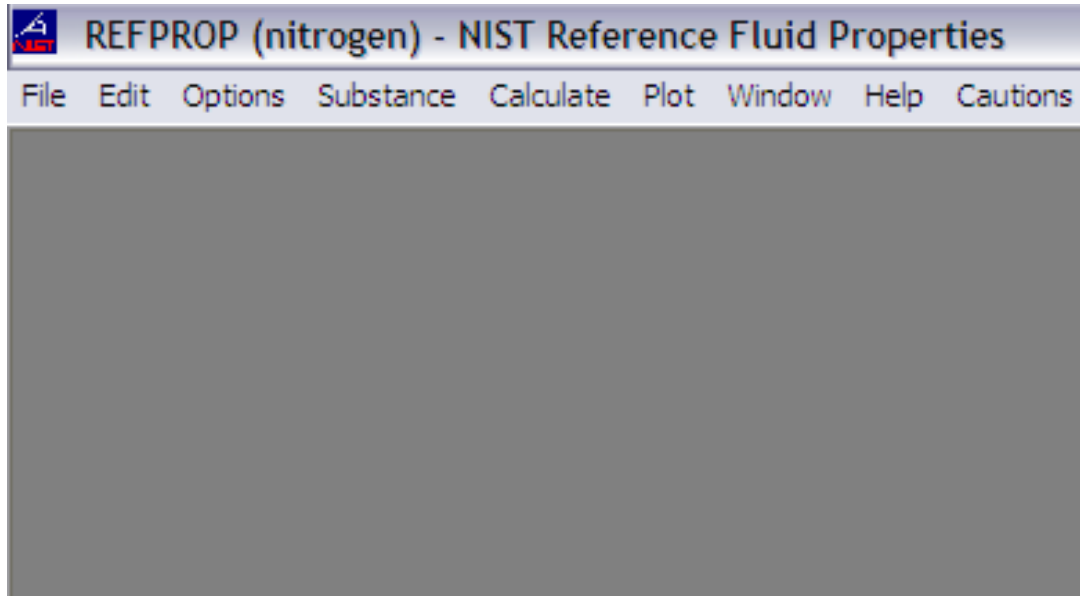


Figure 8: Menu screen shown when you open REFPROP (note, the default substance is nitrogen). Source: REFPROP

The menu line shows multiple selections for interfacing with the program. Rather than review each of these, at this point, we will jump right into showing the sub-options and using the program. Then the use of the menu will become self-evident. Figures 9 through 18 show various menu sub-options.

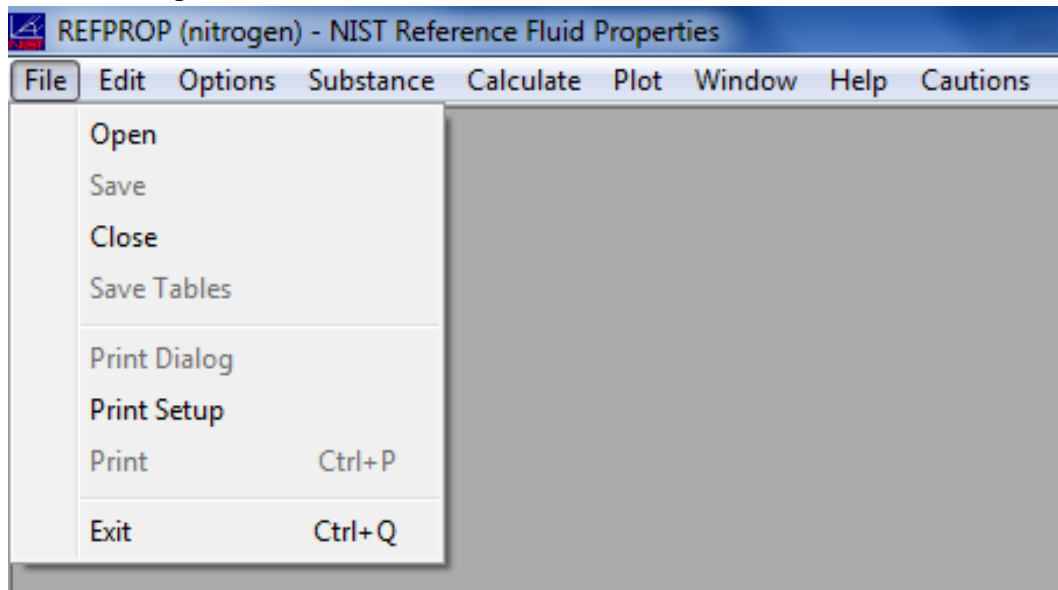


Figure 9: Menu screen shown with sub-options of file. Source: REFPROP

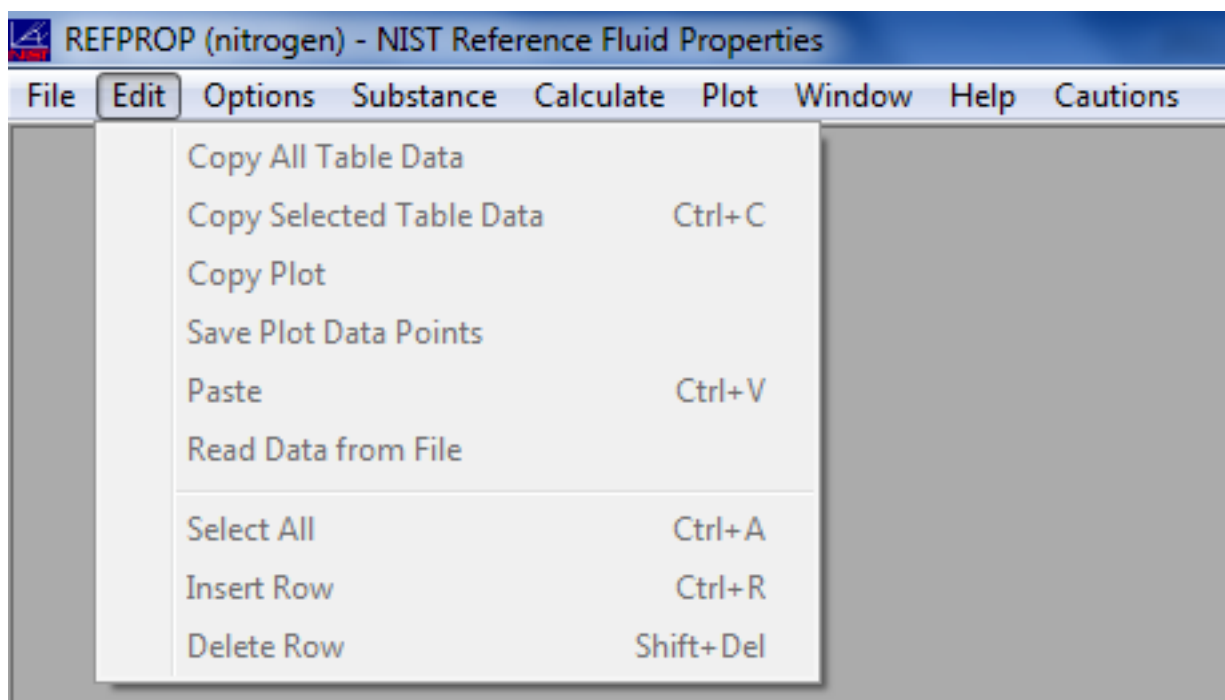


Figure 10: Menu screen shown with sub-options of edit. Source: REFPROP

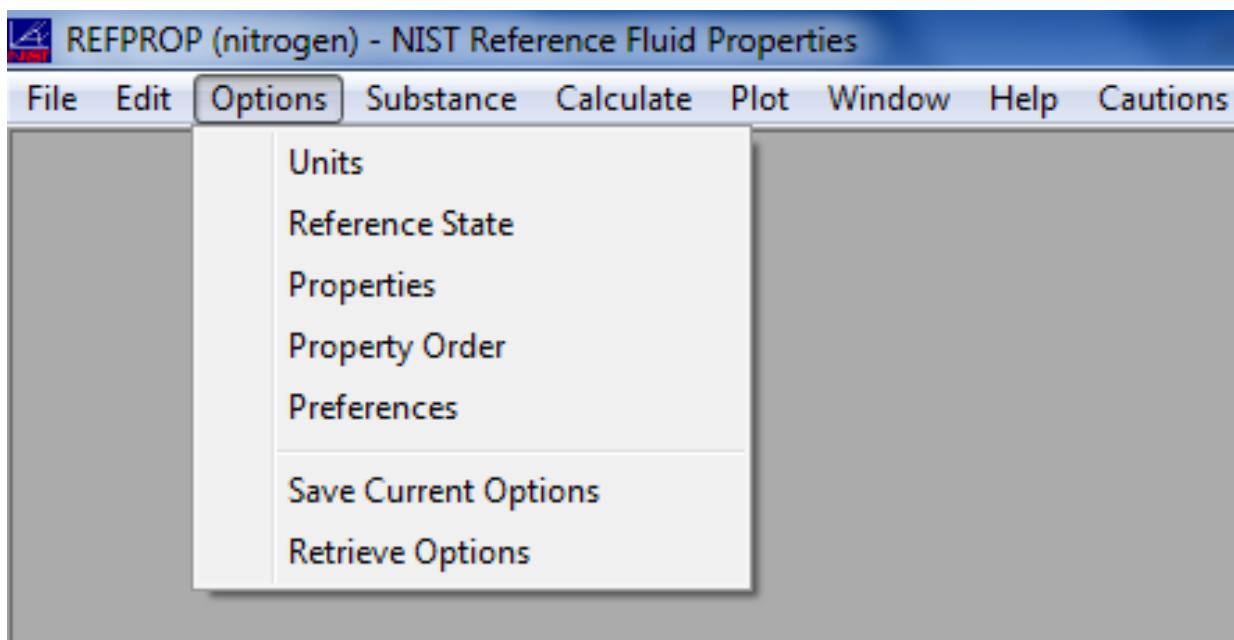


Figure 11: Menu screen shown with sub-options of options.

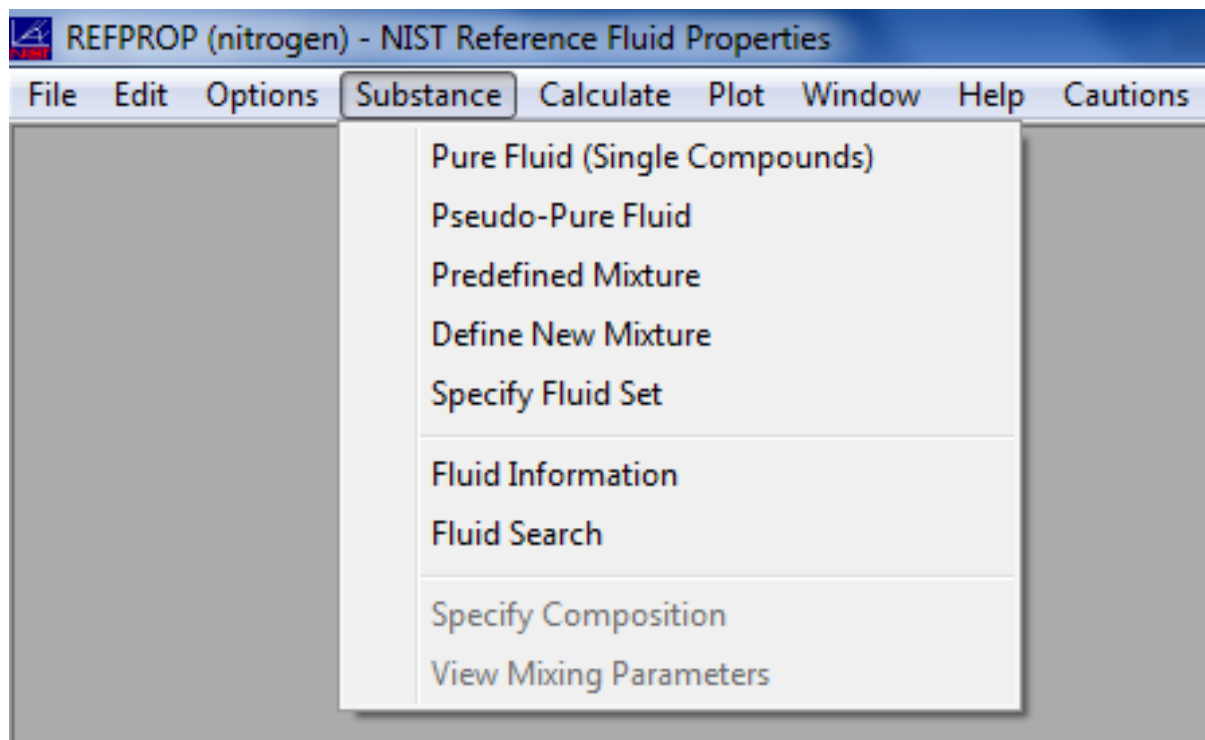


Figure 12: Menu screen shown with sub-options of substance. Source: REFPROP

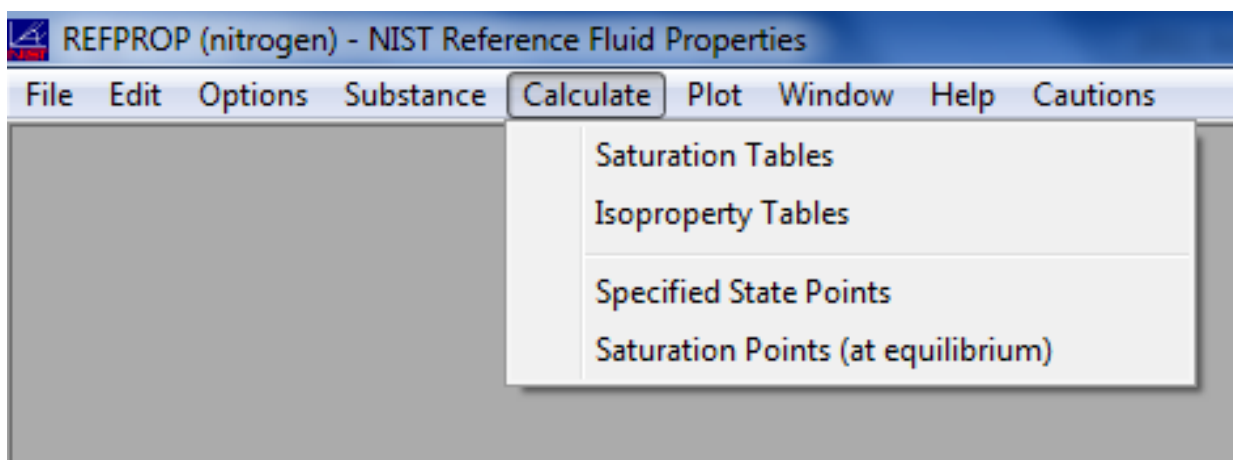


Figure 13: Menu screen shown with sub-options of calculate. Source: REFPROP

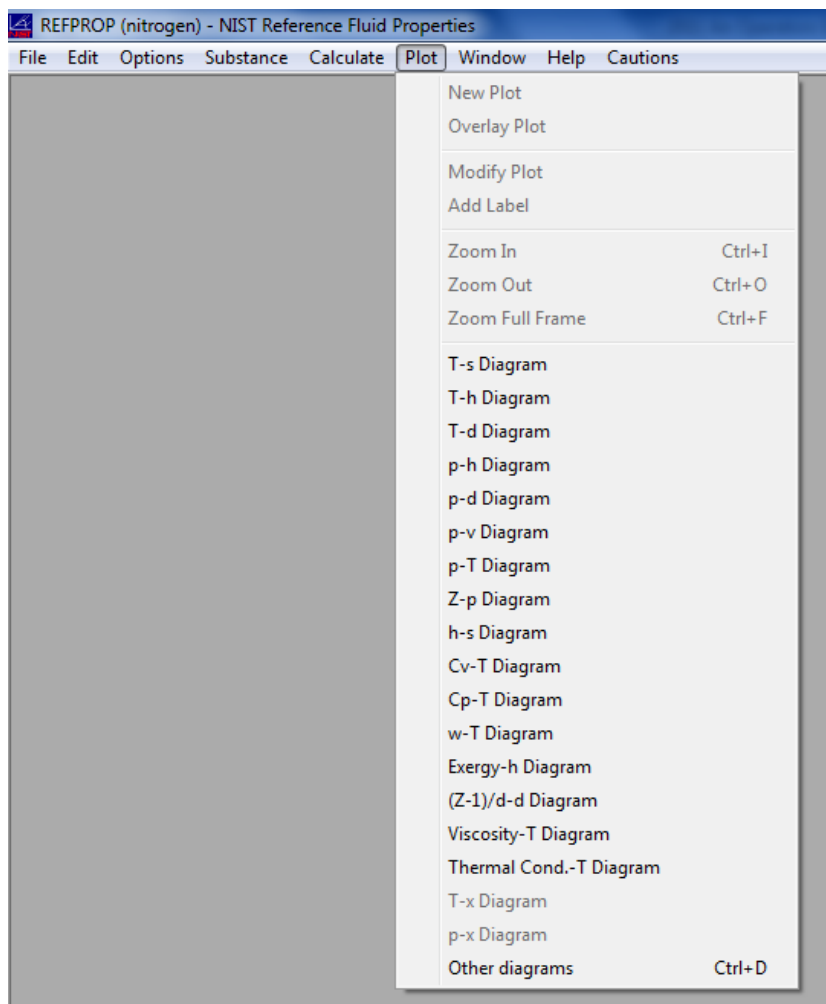


Figure 14: Menu screen shown with sub-options of plot. Source: REFPROP

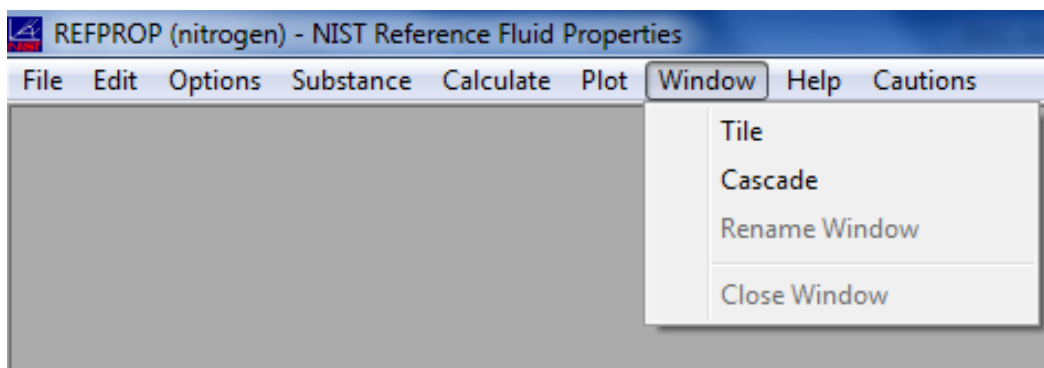


Figure 15: Menu screen shown with sub-options of windows. Source: REFPROP

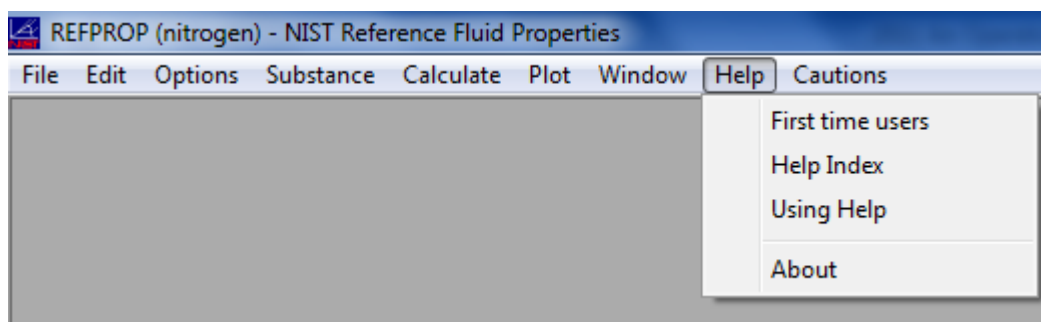


Figure 16: Menu screen shown with sub-options of help. Source: REFPROP

Cautions

Users of the REFPROP program should be aware of several potential pitfalls:

If you experience large differences in your expected values of enthalpy or entropy as compared to those calculated by the program, see information on [reference states](#).

Changing the units in the Options/Units menu does not change the units on the tables already created, but only for new tables and plots.

The equation parameters for mixtures composed of natural gas fluids come from the 2008 GERG model (see [references](#) for the reference). The default pure fluid equations of state in REFPROP are not the same as those used in the GERG model, rather they are more complex with lower uncertainties. The GERG equations for the pure fluids are shorter, less complex, and faster, but slightly less accurate. To use the GERG model, as published, choose the corresponding option under Options/Preferences. The preference screen also has an option to use the AGA8 model for natural gas calculations.

The NIST REFPROP program is designed to provide the most accurate thermophysical properties currently available for pure fluids and their mixtures. The present version is limited to vapor-liquid equilibrium (VLE) only and does not address liquid-liquid equilibrium (LLE), vapor-liquid-liquid equilibrium (VLLE) or other complex forms of phase equilibrium. The program does not know the location of the freezing line for mixtures. Certain mixtures can potentially enter into these areas without giving warnings to the user.

Some mixtures have components with a wide range of volatilities (i.e., large differences in boiling points), as indicated by a critical temperature ratio greater than 2. Certain calculations, especially saturation calculations, may fail without generating warnings. Plotting the calculation results may reveal such cases—looking for discontinuities in density is a good check. Such mixtures, including many with hydrogen, helium, or water, may not have Type I critical behavior, that is they do not have a continuous critical line from one pure component to the other. The estimated critical parameters specified in the Substance/Fluid Information screen for these types of mixtures will not be displayed.

There are cases where an input state point can result in two separate valid states. The most common is temperature-enthalpy inputs. Viewing a T-H diagram will help show how there can be two valid states points for a given input. For example, nitrogen at 140 K and 1000 J/mol can exist at 6.85 MPa and at 60.87 MPa. When this situation occurs, REFPROP returns the state with the higher density. See the [Specified State Points](#) section for information on calculating the upper and lower roots.

There are certain properties pertaining only to the saturation line, such as dp/dT . For most cases, displayed properties at saturation states are those for the single phase on the saturation boundary. Thus, derivative properties at saturation as well as saturation properties that are given along constant property paths, such as C_v , C_p , or C_{sat} , pertain to their state in the single phase. Those properties label with a [sat] indicate a path along the saturation line.

For pure fluids, when the 'Show 2-phase' option in the plot menu is selected, the generated lines for pressure and temperature represent metastable fluid states and the calculated lines between them. These are calculations from the equation of state disregarding any saturation states and generally have no physical significance.

Two equations of state are available for hydrogen to account for the different quantum spin states of the molecule. Normal hydrogen should be used in applications where it was created and stored at 250 K or above, or when it was cooled to below 250 K and stored without a catalyst for less than a day. The parahydrogen equation should be used where hydrogen was catalyzed or stored for several days at the normal boiling point (NBP) and used at any temperature within 1 day of storage at the NBP. Since the rate of conversion between quantum states is dependent on temperature, pressure, and the storage container, these values are only estimates. For more information, see the Leachman et al. literature reference in the Fluid Information window for hydrogen.

Figure 17: Menu screen shown after selecting “cautions”. Source: REFPROP

Let's get right into using REFPROP. Toggle on the menu “Options” and select “Units” as shown in Figure 18 Then click on “Units”. You will get the screen shown in Figure 19. Take note, on this screen, temperature has been highlighted by the user.

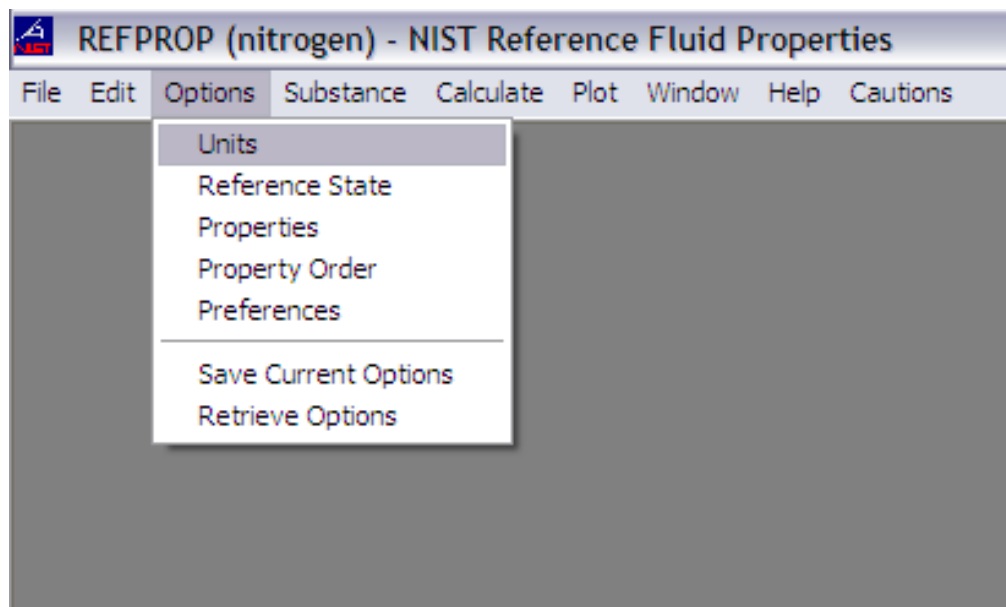


Figure 18: Menu screen shown with sub-options of options with units selected. Source: REFPROP

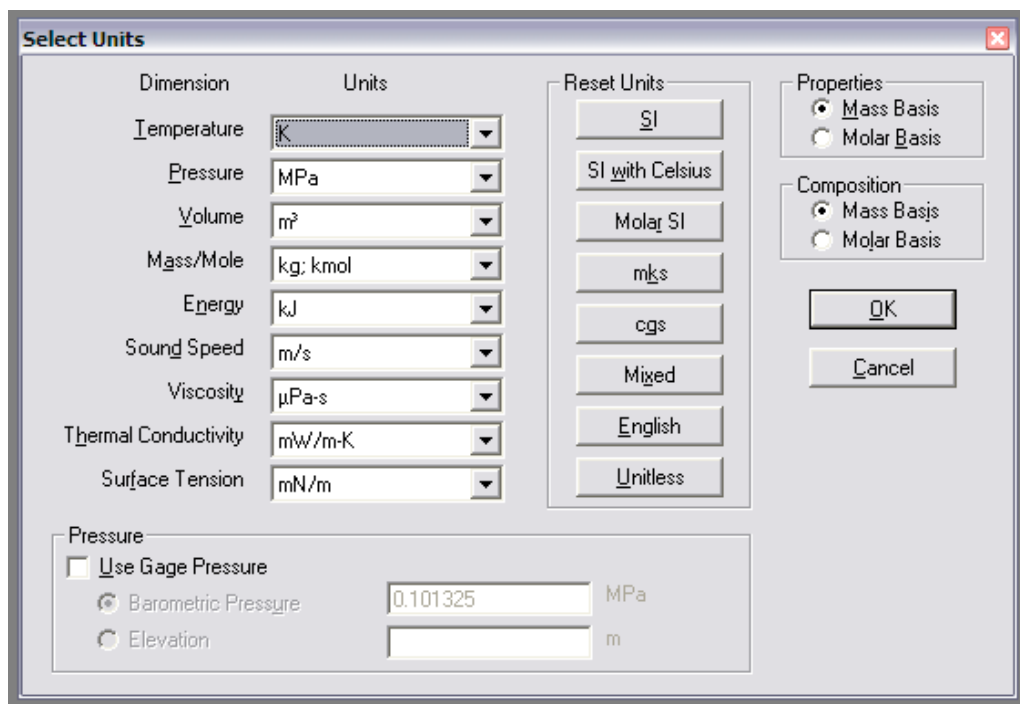


Figure 19: Screen showing units for analysis work (temperature is highlighted). Source: REFPROP

On the unit's screen to the right of temperature select the pull-down menu arrow. Select temperature to be measured in degree "C". Take note, you could have also selected "SI Units with Celsius" to achieve the same results. See Figures 20 and 21.

Also take note that we have selected to show properties on a mass basis and on the bottom, we have chosen to use absolute pressure by not checking the box "Use Gauge Pressure".

Figure 20: Screen showing units with degree C selected for units via using drop down menu. Source: REFPROP

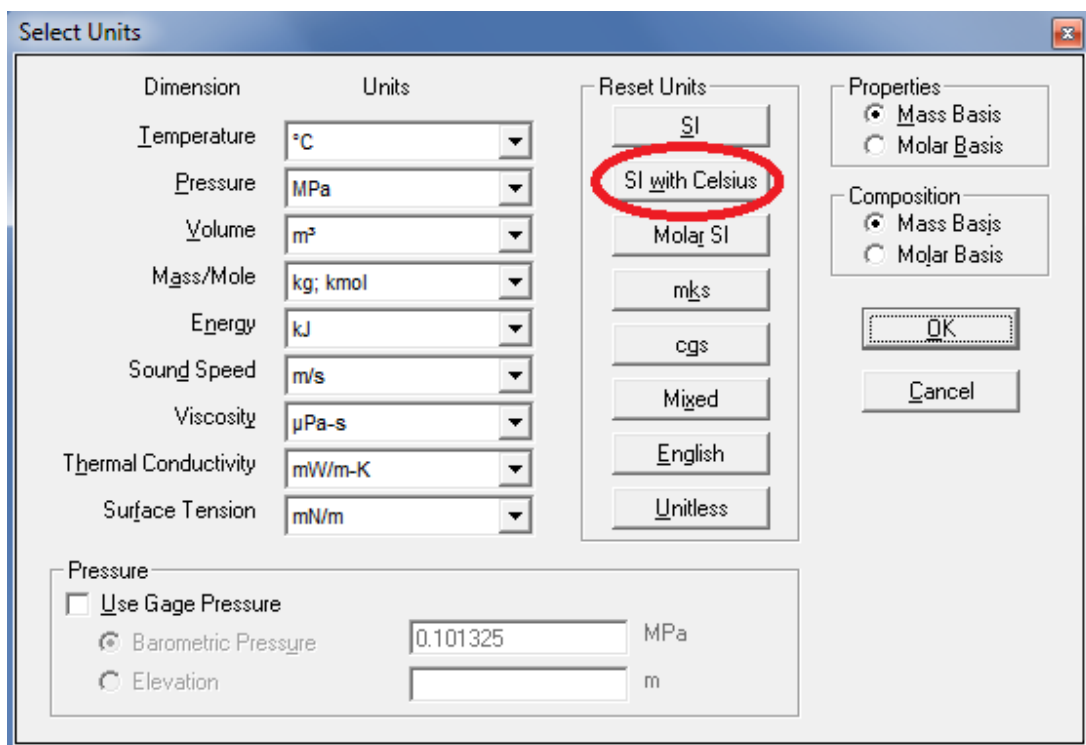


Figure 21: Screen showing units with degree C selected for units via using reset units. Source: REFPROP

Let's solve problems using REFPROP.

2. Applying the Software to Sample Problems, Analysis and Graphing

2.1 Problem #1.1 – Mass and Weight of Nitrogen in a Room

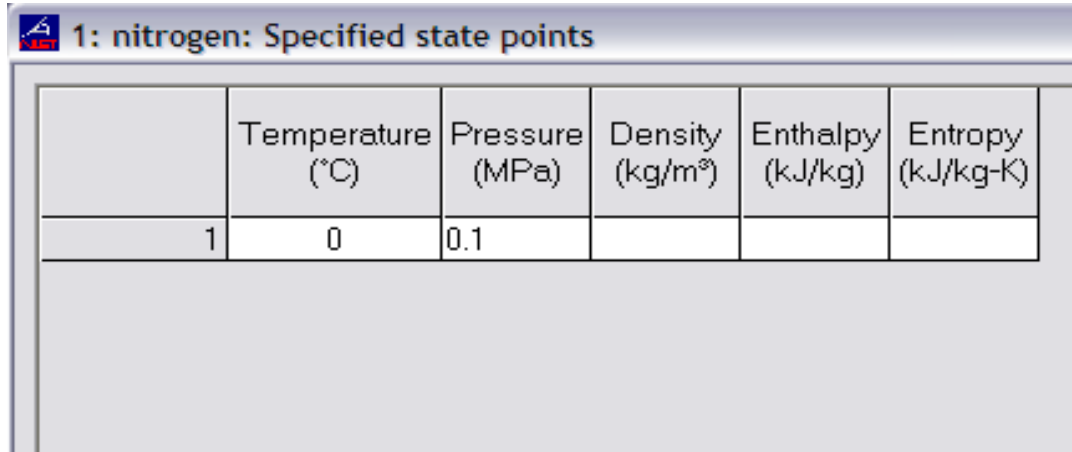
What is the mass of Nitrogen in a 10 m x 10 m x 10 m room? What is the weight of the nitrogen. Note, the room is filled with nitrogen, not air.

2.2 Solution #1.1

Answer – It depends!!!

The mass amount depends on the nitrogen's state! Define any two “intensive properties” and you have defined the state. Assume 1 bara and 0 degree C as two intensive properties. The weight of the nitrogen depends on the mass and the gravitational field strength. Assume 9.8 m/sec^2 as the gravitational acceleration.

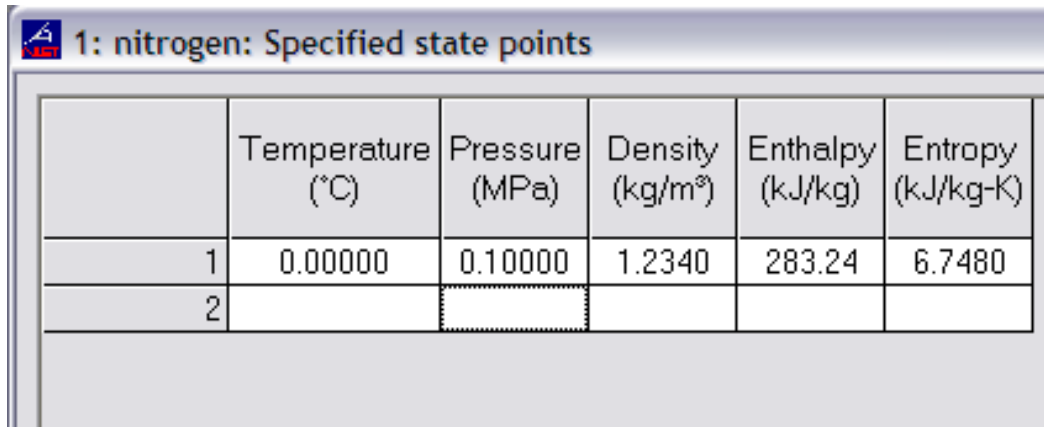
Now use REFPROP to find the density in order to find out the mass of nitrogen in the room. The REFPROP default substance is nitrogen, so we do not need to change the substance. We have already selected temperature units in degree C and we are already in SI units. Now go to the menu and select “Calculate” and select “Specific State Points”. The screen shown in Figure 22 will be displayed. Input the values of 0 for degree C and 0.1 MPa for pressure. Note, 1 bar = 100 kPa which is equal to 0.1 MPa. Remember, REFPROP is presently set up to have the pressure input in “absolute” pressure values (See Figure 21).



	Temperature (°C)	Pressure (MPa)	Density (kg/m³)	Enthalpy (kJ/kg)	Entropy (kJ/kg-K)
1	0	0.1			

Figure 22: Screen showing specified state points under the calculate menu (take note that the 2 intensive properties of pressure and temperature have been input).

When you press enter you get a new screen showing the data you need to solve the problem. This is shown in Figure 23, where you see density, enthalpy and entropy displayed.



	Temperature (°C)	Pressure (MPa)	Density (kg/m³)	Enthalpy (kJ/kg)	Entropy (kJ/kg-K)
1	0.00000	0.10000	1.2340	283.24	6.7480
2					

Figure 23: Screen showing specified state points, under the calculate menu, showing density, enthalpy, and entropy.

You do need density to solve this problem but you do not need enthalpy or entropy. Why did enthalpy and entropy show on the screen? It showed because it had been selected on the “Properties” sub menu under “Options”. This is shown in Figure 24.

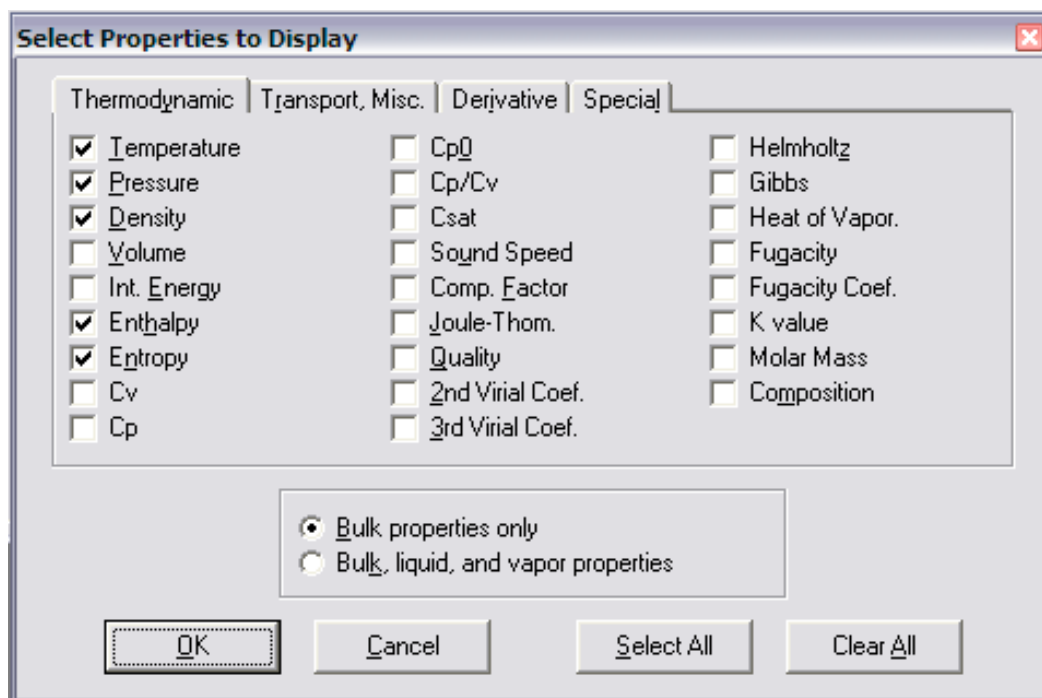
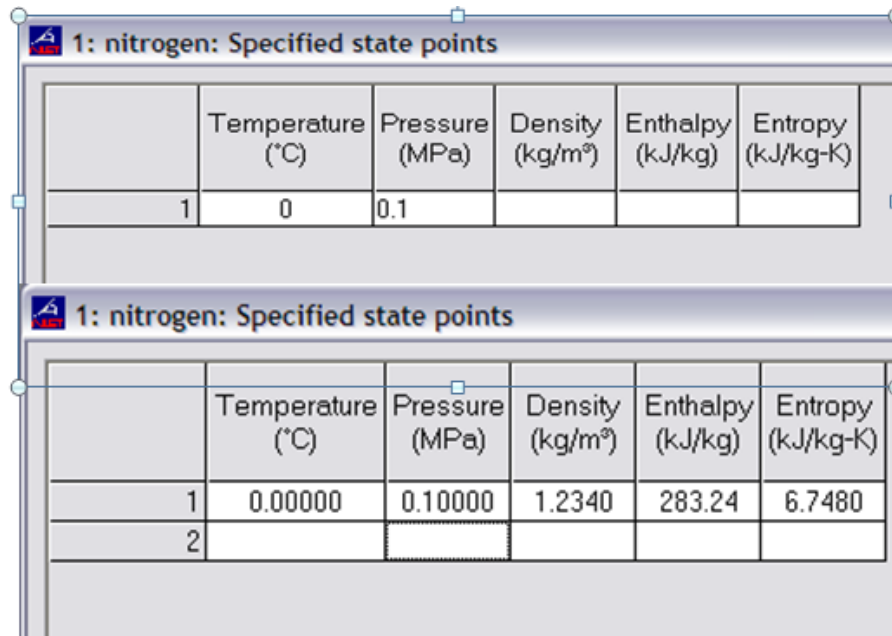


Figure 24: Properties screen showing pressure, temperature, density, enthalpy, and entropy selected.

Let's now again use REFPROP to determine the density at 0 C and 0.1 MPa. As shown in Figure 25, the density is 1.234 kg/m³ (Figures 22 and 23 combined).



	Temperature (°C)	Pressure (MPa)	Density (kg/m³)	Enthalpy (kJ/kg)	Entropy (kJ/kg-K)
1	0	0.1			

	Temperature (°C)	Pressure (MPa)	Density (kg/m³)	Enthalpy (kJ/kg)	Entropy (kJ/kg-K)
1	0.00000	0.10000	1.2340	283.24	6.7480
2					

Figure 25: Properties screen showing density as 1.234 kg/m³.

The mass in the room is equal to the volume of the room multiplied by the density of the fluid in the room. The volume of the room is 1,000 m³ and the density of the nitrogen is 1.234 kg/m³. Thus, the mass of nitrogen in the room is 1,000 m³ x 1.234 kg/m³. Doing this multiplication gives us a mass of nitrogen of 1,234 kg. (Answer).


The weight of a substance is a function of the mass of the substance and the gravitational field the substance is experiencing. We have assumed the gravitational acceleration is 9.8 m/sec². This means that 1 kg results in a weight of 9.8 Newtons. Thus, 1,234 kg x 9.8 m/sec² x (sec² x Newton) / (kg x m) = 12,093.2 Newtons. (Answer).

2.2 Problem # 1.2 – Nitrogen in a Vessel - 1 to 10 Bara

A 100m³ vessel is maintained at 0 C. On day 1 it is at a pressure of 1 bara. Two days later it is at 10 bara. How much nitrogen was added? How much “more” does the vessel weigh?

2.3 Solution # 1.2

The initial mass of the nitrogen was 123.4 kg (1.234 kg/m³ x 100 m³). The final mass of the nitrogen is it’s density x 100 m³. Use REFPROP to find the final density. On the same REFPROP screen you have already opened, look at the density of nitrogen at 1 bar (0.1 MPa) and 10 bar (1 MPa). This is shown in Figure 26.

 1: nitrogen: Specified state points

	Temperature (°C)	Pressure (MPa)	Density (kg/m³)	Enthalpy (kJ/kg)	Entropy (kJ/kg-K)
1	0.00000	0.10000	1.2340	283.24	6.7480
2	0.00000	1.0000	12.388	280.83	6.0570
3					
4					

Figure 26: Properties screen showing density as 12.388 kg/m³ at 10 bara (1 MPa).

In the earlier problem the volume was given as 1,000 m³, but in this problem the volume of the vessel is 100 m³. The mass of nitrogen initially in the vessel is 100 m³ x 1.234 kg/m³. Thus, the initial mass in the vessel is 123.4 kg.

The final mass in the vessel is the volume of the vessel times the density at 10 bara. The final mass of nitrogen in the vessel is calculated as 100 m³ x 12.388 kg/m³ which is equal to 1238.8 kg.

The difference in the vessel's mass between 1 bara and 10 bara is 1,238.8 kg – 123.4 kg = 1,115 kg.

(Answer).

The change in weight is the change in mass x gravitational acceleration. That is 1,115 kg x 9.8 m/sec² x (sec² x Newton) / (kg x m) = 10,930.92 Newtons.

(Answer).

2.5 Problem # 1.3 – Nitrogen in a Vessel - 1 to 10 Barg

A 100 m³ vessel is maintained at 0 C. On day 1 it is at a pressure of 1 barg. Two days later, it is at 10 barg. How much nitrogen was added? How much “more” does the vessel weigh?

2.6 Solution # 1.3

This problem is slightly different than problem # 1.2 in that in problem # 1.2 absolute pressure was used and in problem # 1.3, gauge pressure is used. Use REFPROP to solve problem # 1.3.

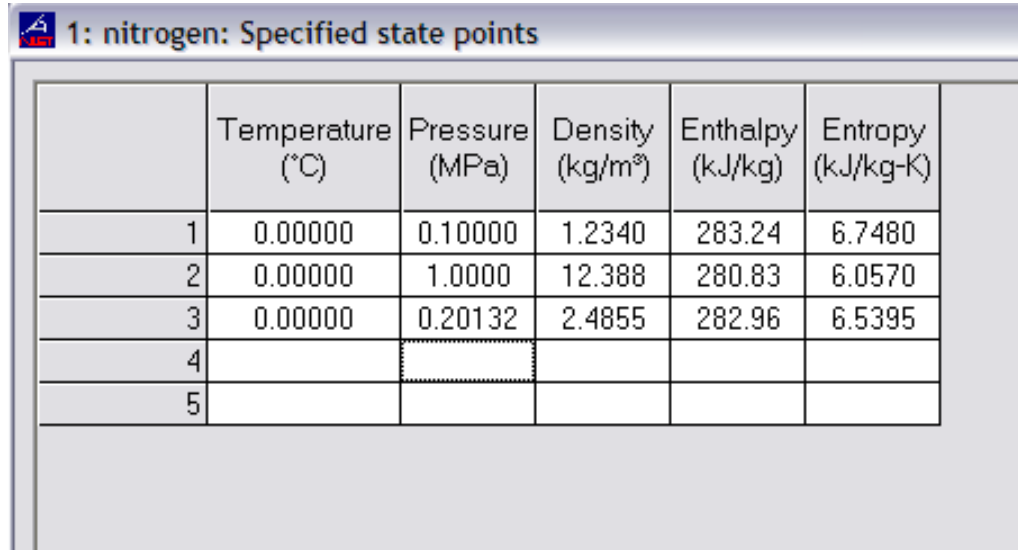
If we are going to use REFPROP with absolute pressure, we must convert gauge pressure to absolute pressure. See Figure 27.

$$1 \text{ bar} = 100 \text{ kPa} = 0.1 \text{ MPa} = 100 \text{ kN/m}^2$$

$$1 \text{ atm} = 1.01325 \text{ bar} = 101.325 \text{ kPa etc.}$$

$$1 \text{ barg} = 2.01325 \text{ bara} (1 \text{ bar} + 1.01325 \text{ bar})$$

Use REFPROP with the pressure at 2.01325 bara (0.201325 MPa).




	Temperature (°C)	Pressure (MPa)	Density (kg/m³)	Enthalpy (kJ/kg)	Entropy (kJ/kg-K)
1	0.00000	0.10000	1.2340	283.24	6.7480
2	0.00000	1.0000	12.388	280.83	6.0570
3	0.00000	0.20132	2.4855	282.96	6.5395
4					
5					

Figure 27: Properties screen showing density as 2.4855 kg/m³ at 1 barg (note, “g” means gauge). Note, 1 barg = 2.01325 bara = 0.201325 MPa.

Take note the density at 1 barg is close to twice that of the density at 1 bara. The density at 1 barg is 2.4855 kg/m³ and the density at 1 bara is 1.234 kg/m³.

Next compute the density of the nitrogen at 10 barg. Keep in mind that 10 barg = 11.01325 bara. Also note, 11.01325 bara = 1.101325 MPa. See Figure 28

 2: nitrogen: Specified state points

	Temperature (°C)	Pressure (MPa)	Density (kg/m³)	Enthalpy (kJ/kg)	Entropy (kJ/kg-K)
1	0.00000	0.10000	1.2340	283.24	6.7480
2	0.00000	1.0000	12.388	280.83	6.0570
3	0.00000	0.20132	2.4855	282.96	6.5395
4	0.00000	1.1013	13.648	280.56	6.0274
5					

Figure 28: Properties screen showing density as 13.672 kg/m³ at 10 barg (1 MPa gauge = 1.101325 MPa absolute).

The mass of nitrogen in the vessel initially was $2.4855 \text{ kg/m}^3 \times 100 \text{ m}^3 = 248.55 \text{ kg}$. The mass of nitrogen in the vessel @ 10 barg is $13.648 \text{ kg/m}^3 \times 100 \text{ m}^3 = 1,364.8 \text{ kg}$.

The difference in mass is 1,364.8 kg – 248.55 kg = 1,116.25 kg. (Answer)

The weight of the nitrogen added is 1,116.25 kg x 9.8 m/sec² x (sec² x Newton) / (kg x m) = 10,939.25 N. (Answer)

2.7 Switch to Using Methane and Bar Absolute Pressure

On the main menu select substance and then “Pure Fluid (Single Compounds)”. This is shown in Figure 29. Then select “methane” (See Figure 30) and enter “OK”.

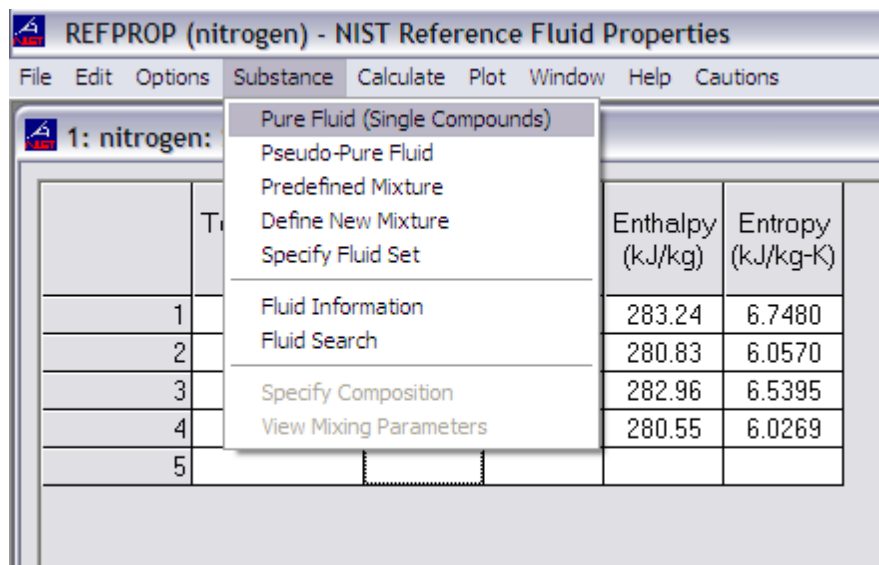


Figure 29: Switching fluid by selecting “Pure Fluid (Single Compounds)”.

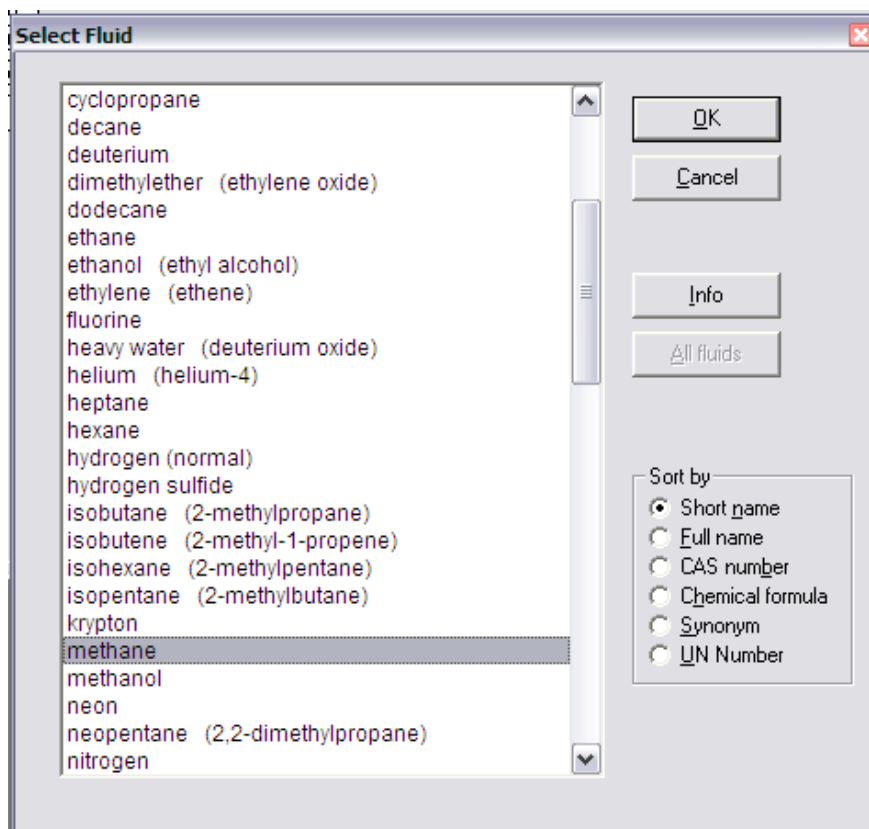


Figure 30: Switching fluid by selecting “methane”.

IT IS CRITICALLY IMPORTANT TO CLOSE ANY CALCULATION WINDOWS AFTER YOU CHANGE THE FLUID. IF YOU FAIL TO CLOSE THE CALCULATION WINDOWS YOU WILL BE STILL CALCULATING ON THE OLD FLUID.

Now select “Options” and then “Units” and then use the pressure drop down menu to select “bar” and click “ok”. This is shown in Figure 31.

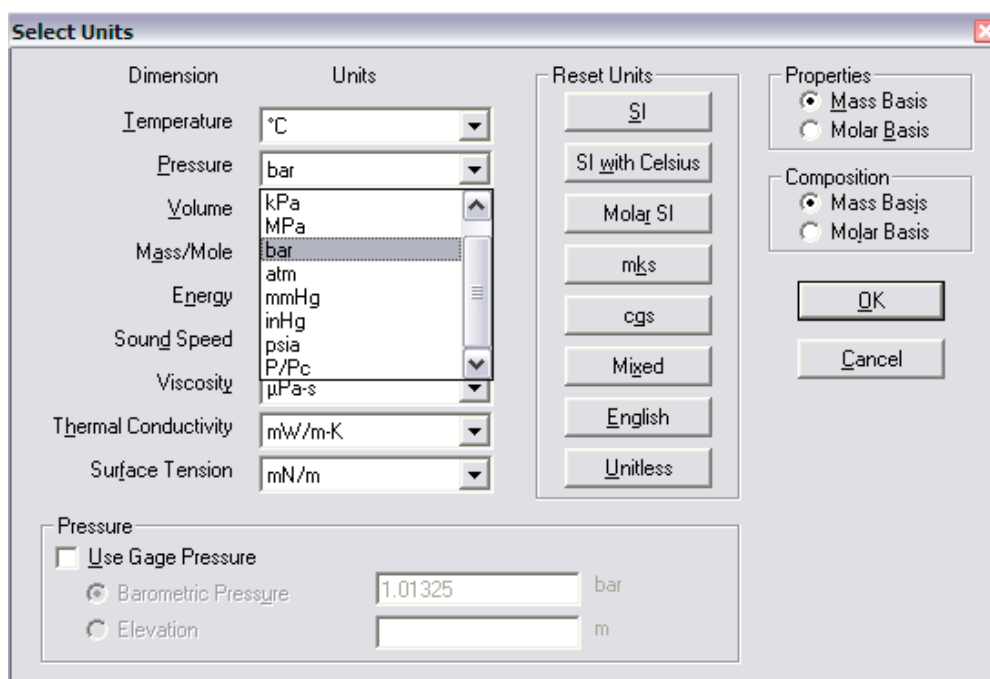



Figure 31: Switching pressure units by selecting Options – Units – bar.

Now let’s explore the density of the fluid methane at “Normal Conditions” and as we cool it colder and colder. View this in Figure 32. Normal Conditions are conditions that are set by various agencies. A common set of normal conditions are 0 C and 1.01325 bar. Note that the density at that normal condition is 0.71746 kg/m^3 .

For the rest of the computations, for ease of typing, let’s use 1 bar as the pressure and let’s make the gas colder and colder. Then observe the density as the fluid, methane gets colder. Observe this in Figure 32. At -50 C, the density is 0.8686 kg/m^3 . This makes sense. The fluid got colder so the density got higher. At -100 C, the density is 1.252 kg/m^3 . Again, this makes sense as the methane gas is getting colder. At -161 C the methane gas has a density of 1.7831 kg/m^3 .

Now look at what happens when the methane is cooled just one more degree to -162 C. The density increases from 1.7831 kg/m³ all the way up to 423.11 kg/m³. What happened between -161 and -162 C to cause the extreme jump in density? What happened is that the methane vapor became a liquid. At -161 C it is a vapor and at -162 C it is a liquid. Also note the very large drop in energy (enthalpy) between -161 C to -162 C. The enthalpy changed sharply from 511.98 kJ/kg to -1.8014 kJ/kg. Note also the large drop in entropy.

 3: methane: Specified state points

	Temperature (°C)	Pressure (bar)	Density (kg/m ³)	Enthalpy (kJ/kg)	Entropy (kJ/kg-K)
1	0.00000	1.0000	0.70805	854.83	6.4882
2	0.00000	1.0133	0.71746	854.82	6.4814
3	-50.00	1.0000	0.86860	747.59	6.0548
4	-100.00	1.0000	1.1252	642.22	5.5202
5	-150.00	1.0000	1.6091	536.02	4.7959
6	-157.00	1.0000	1.7152	520.79	4.6686
7	-158.00	1.0000	1.7316	518.59	4.6496
8	-159.00	1.0000	1.7484	516.40	4.6305
9	-160.00	1.0000	1.7656	514.19	4.6111
10	-161.00	1.0000	1.7831	511.98	4.5915
11	-162.00	1.0000	423.11	-1.8014	-0.016141
12	-163.00	1.0000	424.57	-5.2751	-0.047535
13	-164.00	1.0000	426.02	-8.7418	-0.079151
14					

Figure 32: Observation of what happens to methane as it is cooled. Note how it changes to a liquid between -161 C and -162 C when maintained at 1 bara.


2.8 Observing Saturation Temperature, Pressure and Density

Let's explore Methane at the saturation pressure and temperature. From the menu select "Calculate" and then select "Saturation Points". As shown in Figure 33, now you only need to input 1 intensive property and click enter to populate the table with data. This is because you have selected "saturated" properties and for each pressure below the critical pressure and above the triple point pressure, there is a corresponding saturation temperature. The same is true if you input pressure or any other intensive property.

For our work as shown in Figure 33, we have opted to input Temperature and then allowed REFPROP to calculate and display the saturated properties. The first temperature we put in is 0 C and we get an error! Why did we get an error? The error occurs because there is no saturated pressure associated with that temperature. 0 C is above the critical temperature. The very same thing occurs at -50 C. It is too warm to have a saturated condition.

Note that at -90 C, REFPROP displays a corresponding saturated pressure of 36.399 bara. That is a very high pressure. Note the liquid density is 261.66 kg/m³ and the vapor density is 72.271 kg/m³. This is close to the critical conditions.

As we make the methane colder the saturation pressure gets lower and lower and we note that the densities of the vapor and liquid diverge as we get further from the critical conditions (have a larger difference between them).

 6: methane: Saturation points (at equilibrium)

	Temperature (°C)	Pressure (bar)	Liquid Density (kg/m³)	Vapor Density (kg/m³)	Liquid Enthalpy (kJ/kg)	Vapor Enthalpy (kJ/kg)	Liquid Entropy (kJ/kg-K)	Vapor Entropy (kJ/kg-K)
1	0							
2	-50							
3	-90.000	36.399	261.66	72.271	306.71	521.52	2.0062	3.1791
4	-110.00	18.026	328.76	29.056	198.85	556.28	1.4209	3.6117
5	-130.00	7.5201	371.11	11.848	115.39	550.97	0.89560	3.9384
6	-150.00	2.3784	405.02	3.9877	40.694	528.60	0.34399	4.3058
7	-157.00	1.4439	415.73	2.5151	15.742	518.11	0.13731	4.4624
8	-158.00	1.3376	417.22	2.3442	12.216	516.52	0.10704	4.4866
9	-159.00	1.2373	418.71	2.1822	8.6978	514.91	0.076565	4.5112
10	-160.00	1.1429	420.18	2.0288	5.1885	513.28	0.045884	4.5363
11	-161.00	1.0542	421.65	1.8836	1.6874	511.63	0.014992	4.5620
12	-162.00	0.97079	423.11	1.7465	-1.8056	509.96	-0.016117	4.5882
13	-161.64	1.0000	422.59	1.7946	-0.55734	510.56	-0.0049665	4.5787
14								

Figure 33: Observation of what happens to methane as it is cooled along the saturation curve. On the last line a pressure of 1 bara was selected instead of a temperature.

In the same way you chose to look at the saturated conditions, you can also use REFPROP to create Iso Tables. An Iso Table is a table where one of the properties is kept constant and the other properties are varied. Under the menu “Calculate” tab you can select “Iso-property Tables” and then select any of the following:

Constant T (temperature)

Constant P (pressure)
 Constant (1/sv) (density)
 Constant sv (specific volume)
 Constant h (enthalpy)
 Constant s (entropy)

2.9 Plotting Graphs

There are many plots that can be made using REFPROP. Some graphs that can be plotted are: T-s, T-h, T-d, P-h, P-v, P-d etc.

Let's plot a Ph diagram. From the menu select "Plot", then "Ph diagram". You will need to adjust the parameters for the X and Y axis ranges and for the steps of the parameters until you have the correct range of properties desired. The the plot should look like that shown in Figure 34. Remember if you make the steps too close, the graph will become too cluttered and if you make the steps too big, there will not be enough data shown. We will not spend further time on plotting but rather focus on using REFPROP for analysis.

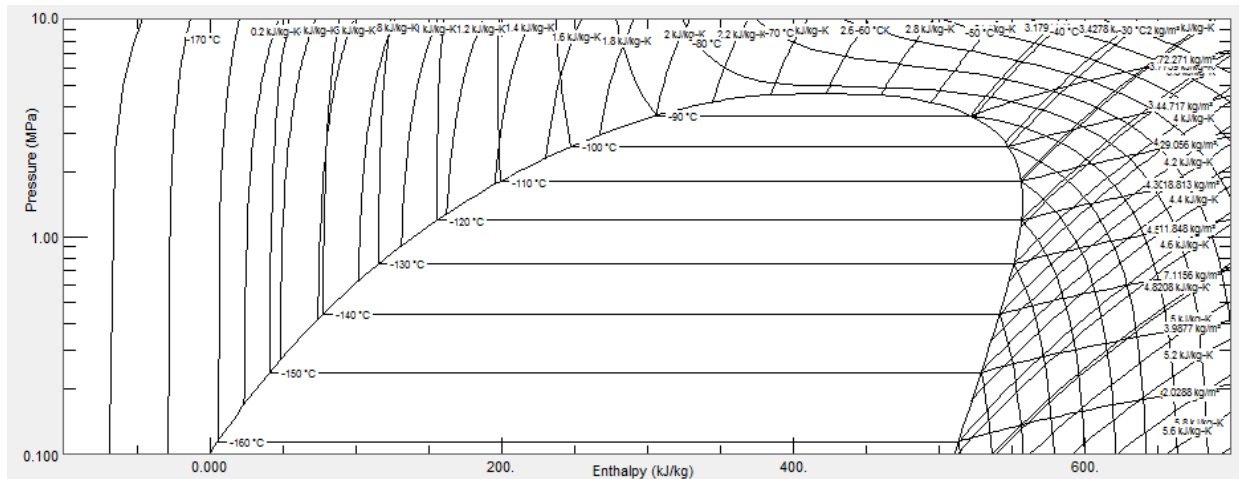


Figure 34: REFPROP plot of Ph diagram for methane (properties other than pressure and enthalpy can be plotted on a Ph diagram).

2.10 Changing Substance of the Fluid to a Mixture of Methane and Ethane

Whenever you open REFPROP the default substance is nitrogen. Unless you are using nitrogen for your analysis you will need to change the substance to that which you want to analyze. Earlier we had changed the substance from nitrogen to methane. Now we will change the substance to a mixture of methane and ethane. Methane and ethane are the two major components of natural gas.

To do this, on your menu select “Substance” as shown in Figure 35 and then select “Define New Mixture”.

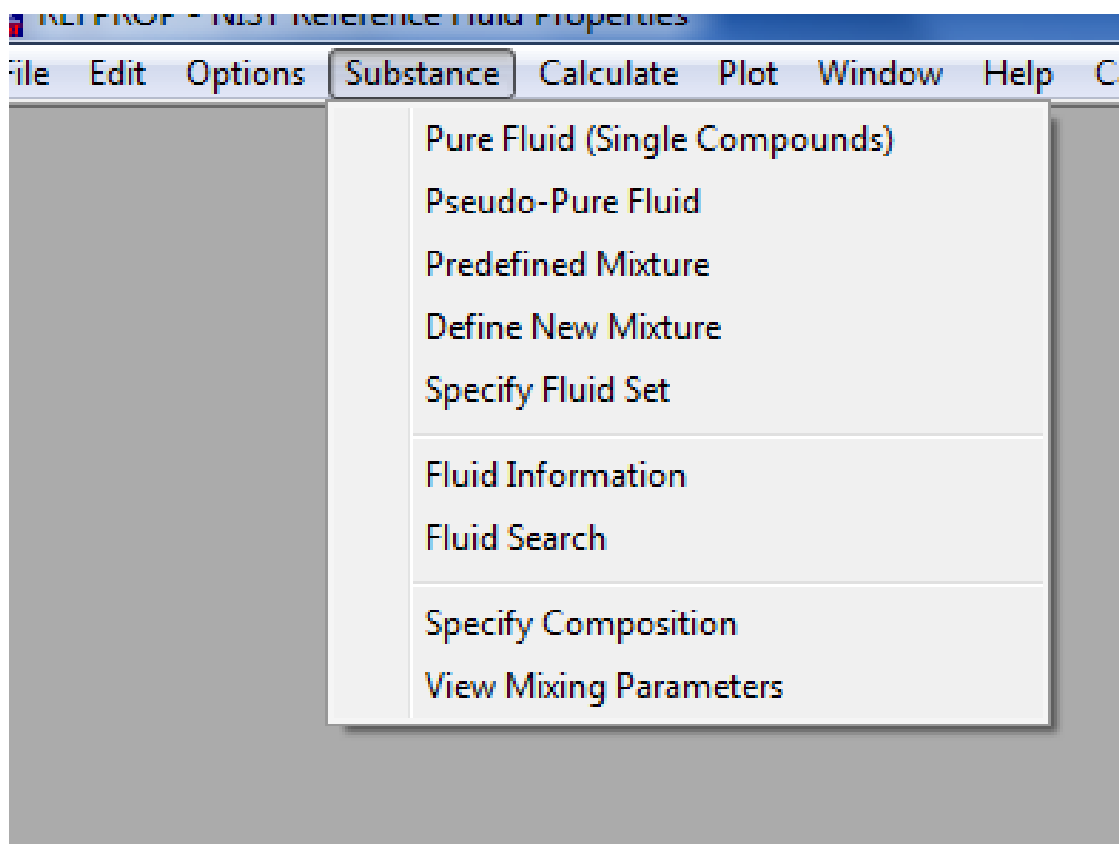


Figure 35: Menu selection of “Substance” and then “Define New Mixture”.

Once you have selected “Define New Mixture” and press enter, the screen shown in Figure 36 will display. Use this screen to select “methane” then depress the “add” button. Then select “Ethane” and then depress the “add” button. Then select the “OK” button.

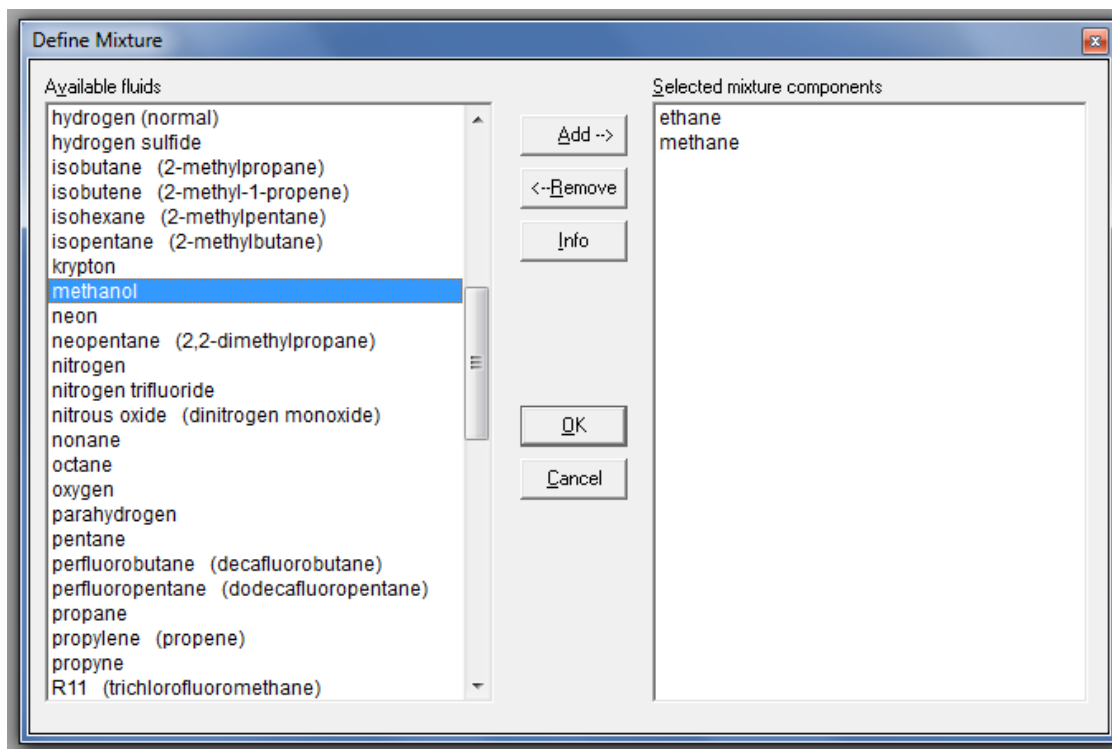


Figure 36: REFPROP menu of mixture components. This menu is used create mixtures for analysis.

After you select “ok” on the Figure 36 screen the screen shown in Figure 37 will appear. This screen gives the user the ability to specify the concentrations of the various components. Note, in this case we selected a mixture of only methane and ethane. We could have selected a mixture of many more components.

Take note that as shown in Figure 37, this is a 95% methane and 5% ethane mixture. Further note that this has been selected as a “**molar** mixture (Mole Fraction)”.

The components must = 1. Observe that the sum of components in Figure 37 shows as 0.55. This will change to 1.0000 after “ok” is depressed. Further, notice that ethane is shown first. Ethane is shown first only because it was selected first (See Figure 36).

Specify Mixture Composition

Mixture Name: ethane/methane

Components
Sum = 0.55000 Mole Fraction

ethane	0.05
methane	0.95

☐ Normalize composition to one

OK Copy Add Fluid
Cancel Paste Remove Fluid
Store

Figure 37: REFPROP screen that allows the user to input the concentration of the mixture components. Note, this is a mole fraction mixture.

Let's see how the mixture of methane ethane differs from a mixture of pure methane. As a high-level view, plot a Ph diagram. Using approximately the same parameters as used to develop the plot shown in Figure 34 plot a Ph diagram for the mixture of 95/5 methane ethane. This is shown in Figure 38.

Observe that the temperature lines between the saturated liquid line and the saturated vapor lines on Figure 34 are horizontal. Then note that the temperature lines of Figure 38 are sloped downward as the enthalpy is increased between the saturated liquid and saturated vapor lines. This is because the composition of the liquid and vapor are changing as the light hydrocarbon methane, preferentially boils off first as the mixture vaporizes.

It should also be noted that the constant temperature lines between the saturated liquid and vapor lines are shown as straight lines. These are not in fact straight lines, but are shown as

straight lines because the software has been instructed to connect these points and it does so use straight lines. In reality these are curved lines. This will be discussed and shown further in section 10.1.3 problem # 2.2.

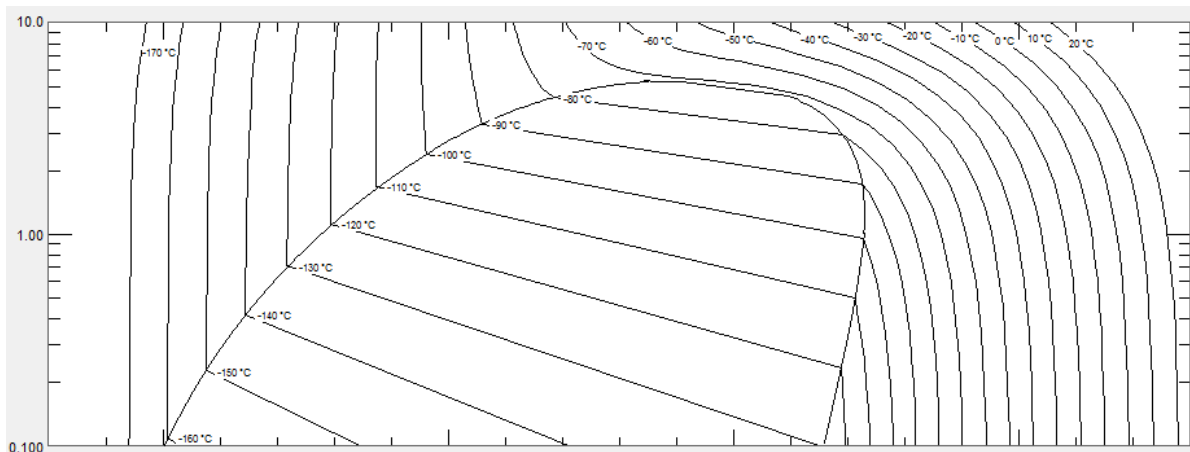


Figure 38: REFPROP Plot of Ph Diagram for a 95/5 methane ethane mixture.

Figure 39 is the same plot is shown with a constant pressure line drawn across the plot. Seeing the constant pressure line clearly brings attention to how the constant temperature line between the saturated liquid and vapor lines differs from a horizontal line.

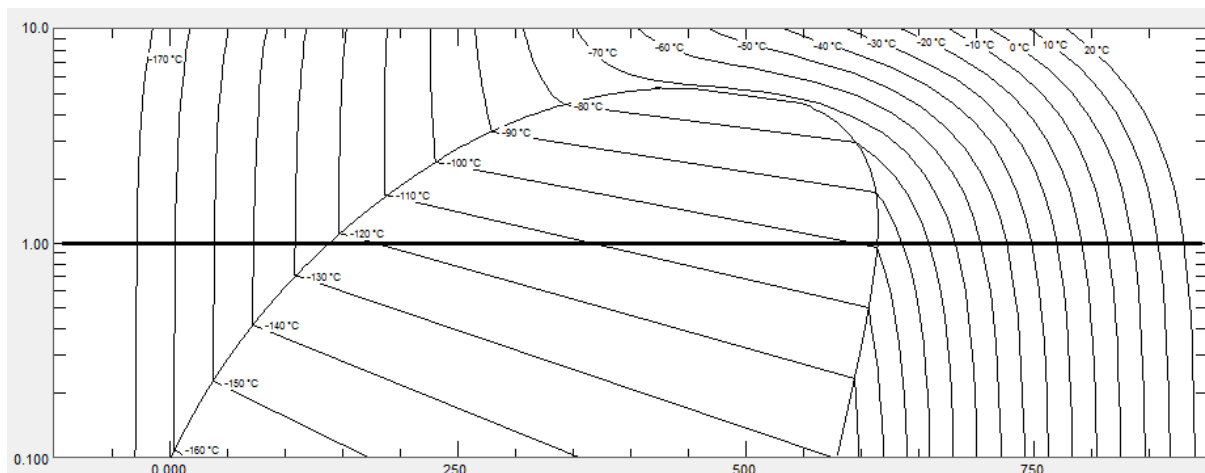


Figure 39: REFPROP plot of Ph diagram for a 95/5 methane ethane mixture with a horizontal line shown at 1 MPa.

Note how the mixture causes the boiling temperature to vary as heat is added and the composition changes. It should also be noted that the constant temperature lines between the saturated liquid and vapor lines are shown as straight lines. These are not in fact straight lines but are shown as straight lines only because the software has been instructed to connect these points and it does so use straight lines. This will be discussed further in section 10.1.3 problem # 2.2.

2.11 Changing the Properties Displayed

Select “Options” then “Properties” and then select the properties you want to display. In the bottom of the screen, you can choose to display “Bulk Properties Only” or both “Bulk and Liquid and Vapor Properties”. In Figure 40 we have chosen to display Temperature, Pressure, Density and Composition. Further we have selected to show both “Bulk” and “liquid and vapor Properties”.

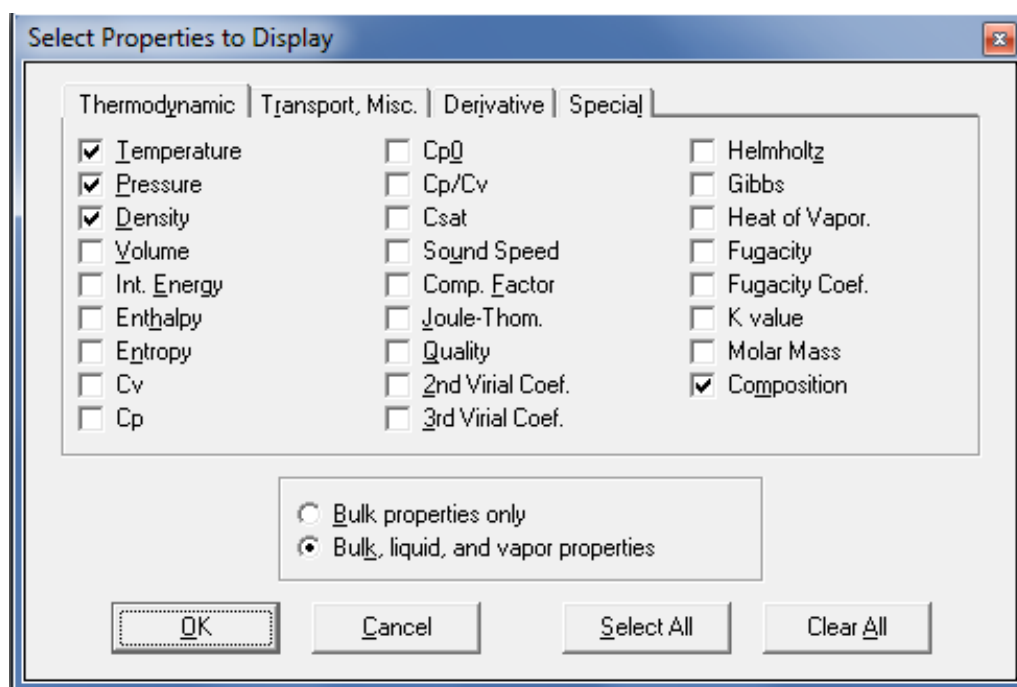


Figure 40: Screen for selection of which properties will be displayed.

We have already showed how a phase change of a mixture is shown on a Ph diagram. Now look at it via tabulated data. Select “Calculate”, then “Saturation Point (Bubble and Dew Points at Same Composition)”. Using the 95/5 methane ethane composition, the selection of Saturation Point (Bubble and Due Points.....) results in the display of the table shown in upper

portion of Figure 41. Take note, the vapor and liquid phase change temperature is different (the dew point is -99.395 C and the bubble point is -122.68 C).

In the lower portion of Figure 41 “Saturation Point at Equilibrium” was selected. Now if you put the pressure of 1MPa in the liquid column, the software designates the liquid as being at the 95/5 composition and the vapor composition is computed by the software as being at a composition of 99.856% methane and 0.14385 % ethane. The temperature of this phase change is -122.68 C.

Now if you put the pressure of 1MPa in the vapor column, the software designates the vapor as being at the 95/5 composition and the liquid composition is computed by the software as being at a composition of 63.163 % methane and 36.837 % ethane. The temperature of this phase change is -99.395 C.

39: methane/ethane: Saturation points (bubble and dew points at same composition) (0.95/0.05)										
	Liquid Phase Temperature (°C)	Vapor Phase Temperature (°C)	Liquid Phase Pressure (MPa)	Vapor Phase Pressure (MPa)	Liquid Phase Density (kg/m³)	Vapor Phase Density (kg/m³)	Liquid Phase Mole Frac. (methane)	Liquid Phase Mole Frac. (ethane)	Vapor Phase Mole Frac. (methane)	Vapor Phase Mole Frac. (ethane)
1	-122.68	-99.395	1.0000	1.0000	374.52	13.101	0.95000	0.050000	0.95000	0.050000
2										

40: methane/ethane: Saturation points (at equilibrium) (0.95/0.05)										
	Liquid Phase Temperature (°C)	Vapor Phase Temperature (°C)	Liquid Phase Pressure (MPa)	Vapor Phase Pressure (MPa)	Liquid Phase Density (kg/m³)	Vapor Phase Density (kg/m³)	Liquid Phase Mole Frac. (methane)	Liquid Phase Mole Frac. (ethane)	Vapor Phase Mole Frac. (methane)	Vapor Phase Mole Frac. (ethane)
1	-122.68	-122.68	1.0000	1.0000	374.52	15.482	0.95000	0.050000	0.99856	0.0014385
2	-99.395	-99.395	1.0000	1.0000	491.84	13.101	0.36837	0.63163	0.95000	0.050000
3										

Figure 41: REFPROP output for a 95/5 molar mixture of methane ethane.

Note: in the lower table if the pressure of 1 MPa is placed in the liquid phase pressure column, the program calculates based on the liquid being of a 95/5 composition (phase change temperature is -122.68 C). If the pressure of 1MPa is placed in the vapor phase pressure column, the program calculates based on the vapor being of a 95/5 composition (phase change temperature is -99.395 C). Take note, as highlighted above, the mixture is shown as a decimal value (0.95/0.05). This being shown as a fraction is a REFPROP indicator that this is a **molar** mixture.

2.12 Problem # 1.4 – Pressure at the Bottom of a Tank of LNG

What is the pressure at the bottom of a tank of liquid methane?

2.13 Solution # 1.4

It depends! It depends on the pressure at the top of the tank, the liquid density, the height of liquid in the tank and the local gravitational acceleration.


What is the pressure at the top of the tank? Assume 150 mbarg.

What is the height of liquid in the tank? Assume 30 meters.

What is the local gravitational acceleration? Assume 9.8 m/sec^2 .

Assume tank is well mixed liquid methane, thus, the temperature everywhere in the tank is the saturation temperature at 150 mbarg.

Use REFPROP to find density of liquid methane. Select “Substance” then “Pure Fluid” then “Methane”. Then select “Units” and select “SI with Celcius” and at the bottom select “Gauge Pressure”. Then on the main menu select “Calculate” and “Saturation Points”. Then put in 0.15 bar gauge pressure. Press enter and the table shown in Figure 42 is displayed. From this table, the density of the liquid can be read as 419.86 kg/m^3 . Since the density is largely a function of temperature and only very slightly a function of pressure, it is reasonable to use this density for computing the head pressure caused by the LNG.

 12: methane: Saturation points (at equilibrium) [Barometric pressure: 1.0133 bar]

	Temperature (°C)	Pressure (bar_g)	Liquid Density (kg/m³)	Vapor Density (kg/m³)	Liquid Enthalpy (kJ/kg)	Vapor Enthalpy (kJ/kg)	Liquid Entropy (kJ/kg-K)	Vapor Entropy (kJ/kg-K)
1	-159.78	0.15000	419.86	2.0619	5.9616	513.64	0.052667	4.5307
2								

Figure 42: REFPROP data for pure methane at saturation at 150 mbarg gauge pressure.

How much force pushes down on 1 m^3 of liquid methane? Assume $g = 9.8 \text{ m/sec}^2$. Then on the bottom of 1 cubic meter of liquid methane the force is $419.86 \text{ kg} \times 9.8 \text{ m/sec}^2 \text{ (sec}^2 \times \text{Newton)} / (\text{kg} \times \text{m}) = 4,114.63 \text{ N}$. Then on the bottom of a 1 m^2 column of liquid methane 30 meters high, the force would be $4,114.63 \text{ N/m} \times 30 \text{ m} = 123,439 \text{ N}$ ($123,439 \text{ N/m}^2$ since we had only selected a column of liquid 1 m^2 at the base). $123,439 \text{ N/m}^2 = 1.23439 \text{ barg}$. The pressure on the bottom of the tank would be 1.23439 barg (pressure due to the head of liquid) + 0.150 (pressure in the vapor space of the tank) barg = **1.38439 barg**. **(ANSWER)**

In the above computation, the head pressure of liquid, for a liquid that is of uniform density, is calculated as: **Head pressure = density x gravitational acceleration x height of liquid**. This is a convenient equation to remember. It is often remembered as: **pressure = density x g x h**. However, to find the total pressure at the bottom of the tank we must add the vapor space pressure to the head pressure caused by the height of liquid.

2.14 Change of Reference State for REFPROP

In Part 1 *“What Every Energy Engineer Needs to know about Thermodynamics and Liquefaction Systems Part 1”* a Ph diagram was used from a 1962 publication. If we wanted to duplicate that Ph diagram, how could we use REFPROP to plot that 1962 diagram and to duplicate and confirm the analyses done using that graph?

The way to duplicate that plot is to either use the same reference points for that chart in REFPROP or to select a set of properties and then input the enthalpy and entropy for that state into REFPROP.

Let’s do the latter. Read as carefully as possible, the enthalpy and entropy from the 1962 Ph diagram for some temperature and pressure.

Since the 1962 chart is in English terms, we first need to select “Options” then “Units” then “English” then enter. Select 60 F and 20 psia as a reference point. Read the chart by eye for 60-degree F and 20 psia. As accurate as possible the enthalpy is read to be -1534.5 Btu/lbm and the entropy is read to be 2.72 Btu/lbm R.

On REFPROP select “Options” then “Reference State” then select “Specify the Reference State Values” and input the data of: 60-degree F, 20 psia, $h = -1534.5$, and $s = 2.72$. This is shown in Figure 43.

Figure 43: REFPROP change of reference properties to replicate the 1962 Ph diagram used in book 1 of “LNG and Gas, An Operators Guide to Thermodynamics”.

The 1962 published Ph diagram is shown in Figure 44. The REFPROP reproduced Ph diagram is shown in Figure 45 and the plotting information used for the REFPROP plot is as shown in Figure 46.

For the next several problems this “Selected Reference State” will be used. If you want to convert back to the original reference state, which will produce the ASHRAE tables and plots, then select “Selected Reference State” and then select:

☐ Use the default reference state (the default state for this fluid is NBP)

Then select ok.

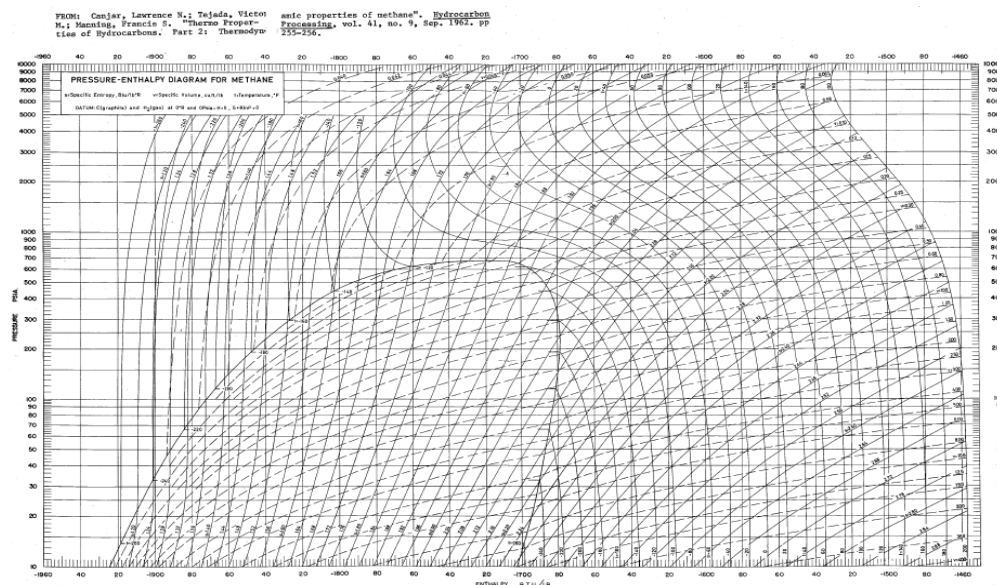


Figure 44: 1962 published Ph diagram for methane. After inputting the data displayed in Figures 45 and 46 REFPROP will compute values consistent with this chart.

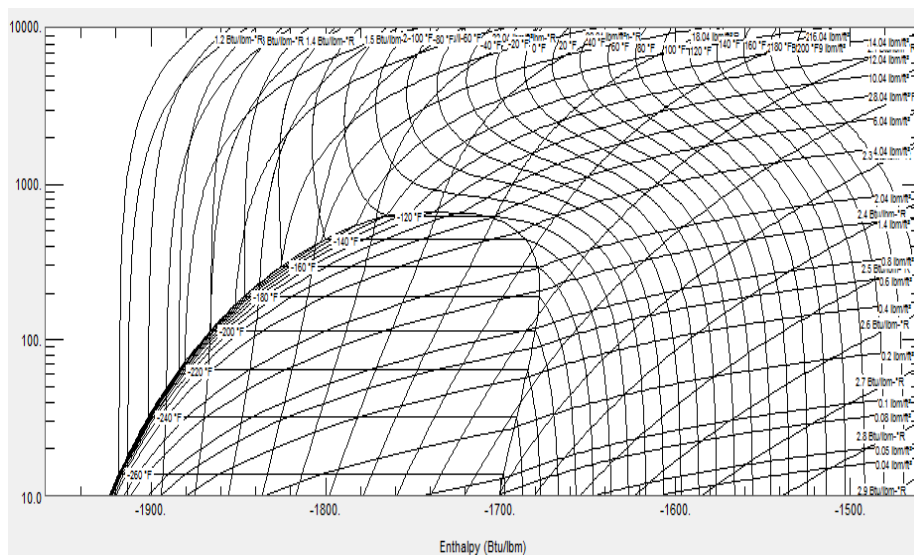


Figure 45: 1962 published Ph diagram duplicated by REFPROP.

Setup Pressure vs. Enthalpy Plot

Temperature (°F)	Density (lbm/ft³)	Entropy (Btu/lbm·°R)	Quality
From: -260	From: .04	From: 1.2	From: 0
To: 200	To: 25	To: 3	To: 1
Step: 20	Step: 2	Step: .1	Step: 0.25
<input type="checkbox"/> Show 2-phase	<input checked="" type="checkbox"/> Show 2-phase	<input checked="" type="checkbox"/> Show 2-phase	<input type="checkbox"/> Show 2-phase
Additional values	Additional values	Additional values	Additional values
	.05 .8		
	.08 1.4		
	.1		
	.2		
	.4		
	.6		

Axis scaling

x-Axis Range: -1960 to -1460 Btu/lbm Enthalpy

y-Axis Range: 10 to 10000 psia Pressure

Point spacing

☐ Coarse

☒ Medium

☐ Fine

☐ Very fine

Labels

☒ Include labels

☒ with units

☐ Unlabeled Lines

Options

☒ Draw saturation lines

☐ Draw melting line

☒ Connect saturation states

☐ Swap density for specific volume

☒ Add s and v lines at saturated temp.

OK Cancel Less

Figure 46: Input data for making the plot of Figure 45 using the Reference State Properties shown in Figure 43. Take note, to get to this screen, you must select Plot and then in the lower right hand corner you must select More. Then you need to input the ranges you want to plot.

2.15 Problem # 1.5 – Heat Needed to Vaporize High Pressure LNG (Invalid Properties)

How much heat must be added to a lbm of saturated liquid methane at 1,000 psia to vaporize it to 40-degree F?

2.16 Solution # 1.5

Use REFPROP. Select “methane”. Then select “Saturation Points”. Then input 1,000 psia. pressure and enter and you get an “ERROR message (See Figure 47)

What went wrong?

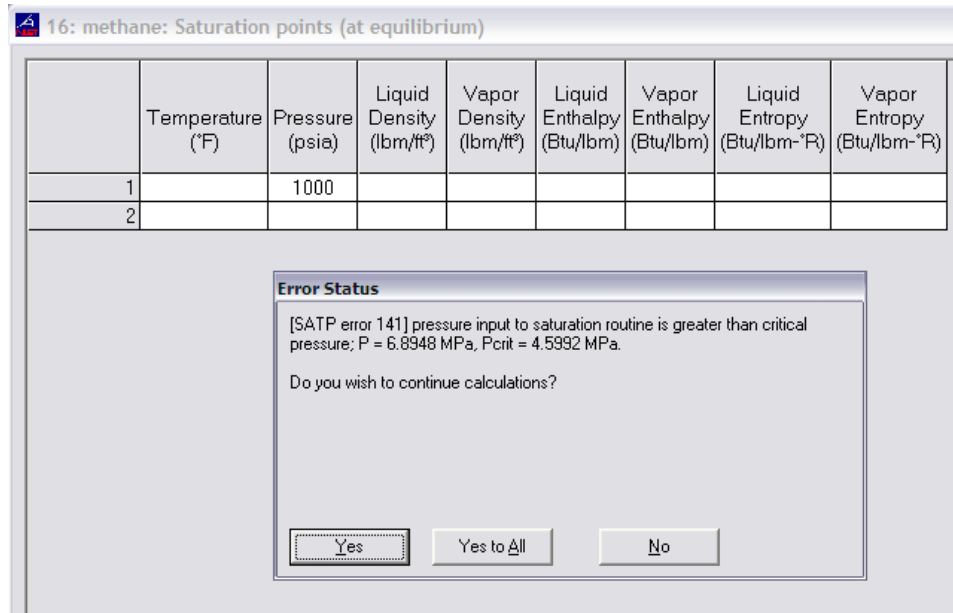


Figure 47: Error message displayed when 1000 psia is input into the saturated points table (1,000 psia is above the critical point pressure of methane).

What went wrong is that 1,000 psia is above the critical point, so there is no such thing as a saturated liquid at 1,000 psia for methane. This is because there is no liquid or vapor defined above the critical point. There is only fluid above the critical point. The words liquid and vapor imply a difference in density between the 2 phases. At the critical point the density of the liquid and the density of the vapor are exactly the same and at that point and at higher pressures the substance no longer exists as a vapor or a liquid but is called a fluid. Thus, a saturated liquid at 1,000 psia is undefined (impossible to be saturated at that pressure). The only way to continue with this problem is to give 2 intensive properties, such as pressure and temperature, to define the state of the fluid.

The critical point is shown as a single point at the top of the dome where the saturated liquid and saturated vapor lines meet and the densities of the liquid and vapor are equal as shown in Figures 48 and 49.

Also shown on Figure 49 is the horizontal line at 1,000 psia. Viewing this horizontal line and the saturation dome highlights why the error message was displayed when we tried to input saturated data at 1,000 psia.

22: methane: Saturation points (at equilibrium)

	Temperature (°F)	Pressure (psia)	Liquid Density (lbm/ft³)	Vapor Density (lbm/ft³)	Liquid Enthalpy (Btu/lbm)	Vapor Enthalpy (Btu/lbm)	Liquid Entropy (Btu/lbm-°R)	Vapor Entropy (Btu/lbm-°R)
2	-205.12	100.00	23.367	0.67982	-1870.5	-1680.9	1.3833	2.1284
3	-177.99	200.00	21.492	1.3608	-1844.3	-1677.6	1.4780	2.0698
4	-159.48	300.00	19.943	2.1177	-1824.5	-1678.8	1.5430	2.0284
5	-145.02	400.00	18.453	3.0049	-1807.1	-1682.9	1.5964	1.9913
6	-133.02	500.00	16.842	4.1263	-1790.2	-1690.1	1.6457	1.9523
7	-122.75	600.00	14.744	5.8116	-1771.2	-1703.1	1.6995	1.9017
8	-118.14	650.00	12.886	7.4811	-1757.0	-1717.0	1.7394	1.8565
9	-117.26	660.00	12.138	8.1965	-1751.9	-1723.0	1.7541	1.8383
10	-116.83	665.00	11.440	8.8872	-1747.2	-1728.7	1.7674	1.8214
11	-116.75	666.00	11.174	9.1546	-1745.5	-1730.9	1.7724	1.8150
12	-116.66	667.00	10.484	9.8356	-1740.8	-1736.1	1.7859	1.7995
13	-116.66	667.05	10.281	10.030	-1739.4	-1737.6	1.7901	1.7953
14	-116.66	667.05	10.229	10.081	-1739.0	-1738.0	1.7911	1.7942
15	-116.65	667.06	10.155	10.155	-1738.5	-1738.5	1.7927	1.7927
16								
17								

Figure 48: REFPROP used to show that the density of the vapor and the density of the liquid are identical at the critical point.

Note, that the critical point is between 667.058 and 667.059 but in the above table the value is rounded off to 667.06 psia. At this point all the intensive properties of the liquid and vapor converge to be the same value.

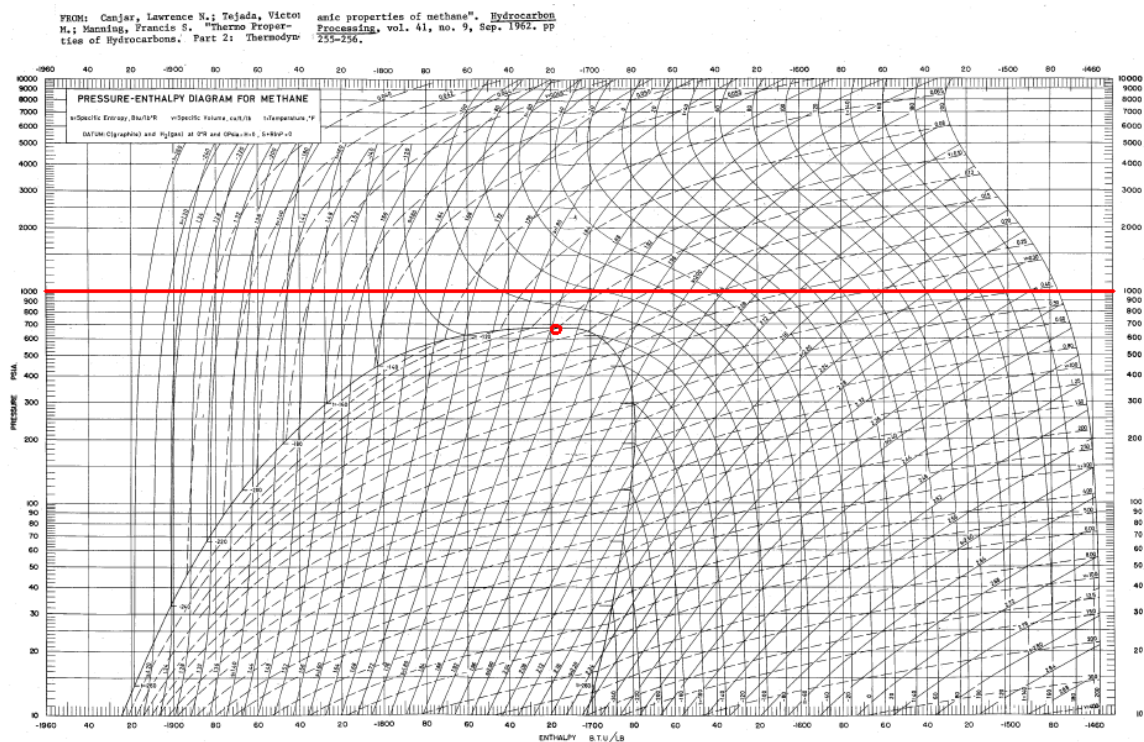


Figure 49: 1962 Published Ph diagram for methane showing the critical point as a single point at the top of the Ph diagram and the constant pressure line of 1,000 psia.

2.17 Problem # 1.5 Revised – Heat Needed to Vaporize High Pressure LNG

How much heat must be added to a lbm of liquid methane at 1,000 psia and -250 F to vaporize it (or should we say heat it – see below) to 40-degree F?


2.18 Solution # 1.5 Revised

Even though there is no liquid phase or vapor phase above the critical point, it is common jargon to say that the fluid at this pressure is vaporized when heated in a vaporizer. From a purely technical point of view, the fluid is heated and not really vaporized as vaporizing implies a phase change. However we can use the term vaporized since it is common industry jargon. Use REFPROP to solve this (keep in mind that we are still using the reference properties as shown in Figure 43) .

Methane at 1,000 psia and -250 F $h = -1905.9$ Btu/lbm (See Figure 50)

Methane at 1,000 psia and 40 F $h = -1580.1$ Btu/lbm (See Figure 50)

Subtract h_{before} from h_{after} and get **325.8 Btu/lbm (Answer)**

 17: methane: Specified state points

	Temperature (°F)	Pressure (psia)	Density (lbm/ft³)	Enthalpy (Btu/lbm)	Entropy (Btu/lbm-°R)
1	-250.00	1000.0	26.332	-1905.9	1.2022
2	40.000	1000.0	3.5108	-1580.1	2.1640
3	60.000	14.730	0.042457	-1534.8	2.7581
4					

Figure 50: Delta enthalpy for LNG heated from -250 F to 40 F at 1,000 psia. Also shown here is a standard cubic foot data using 60 F and 14.73 psia as the standard conditions. Remember, the properties of a standard cubic foot are dependent on what agency definition is used.

It needs to be noted that the reference state is still that of the 1962 chart. It does not matter what reference state is used for solving problems. This is because the absolute value of the enthalpy and entropy is not what matters, but the “change” in enthalpy and entropy is what matters. Regardless of the reference points, the delta (change of) enthalpy and entropy will remain unchanged when going from one state to another.

2.19 Problem # 1.6 – Methane Fuel Needed to Heat LNG Vaporizer Water

If we burn methane to provide the heat for vaporization, what percent of liquid methane must be used as fuel for the vaporizer? Assume the inlet and outlet conditions of problem “1.5 Revised” and a water bath vaporizer with an efficiency of 90%. Assume a standard cubic foot is defined at 60 F and 14.73 psia.

2.20 Solution # 1.6

The first thing we will need to do is to make few assumptions. Assume a standard cubic foot of methane has a heating value of 1,011 Btu/scf (close enough for our calculations (for more accurate calculations do a literature search look up)). Keep in mind that the heating value is based on a specific number of molecules of methane reacting with oxygen in air in a complete combustion. Thus, the heating value depends on the definition of a standard cubic foot (the properties of a scf). A standard cubic foot at 14.73 psia and 60 F has more molecules than a standard cubic foot at 14.7 psia and 60 F and a standard cubic foot at 14.7 psia and 60 F has more molecules than a standard cubic foot at 14.696 psia and 60 F.

Also assume the vaporizer is operating at its rated efficiency of 90%. At this efficiency we need to provide $(325.8 \text{ Btu/lbm})/0.9 = 362 \text{ Btu}$ of energy in the form of fuel for every lbm of LNG heated. The value of 325.8 Btu/lbm came from the solution of problem 1.5 Revised. Realize that the actual vaporizer efficiency is dependent on many parameters including tuning, weather, operating load, etc.

From Figure 50, it is seen that a standard cubic foot (scf) has a density of $0.042457 \text{ lbm/ft}^3$. A mass of methane converts to $1/0.042457 \text{ lbm/scf} = 23.55 \text{ scf/lbm}$ which when burned produces 23,812 Btu of energy per lbm ($23.55 \text{ scf/lbm} \times 1011 \text{ Btu/scf}$).

Percent of Liquid Methane used for heating is $(362/23,812) \times 100 = 1.5\%$ (ANSWER)

2.21 Problem # 1.7 – Does Methane Behave Like an Ideal Gas?

Does methane behave like an ideal gas?

2.22 Solution # 1.7

Answer..... It depends!

An ideal gas performs like $PV = NRT$.

For an Ideal Gas, enthalpy (h) is NOT a function of pressure (P).

Let's look at the Ph diagram (See Figure 51). In Figure 51 hold temperature fixed and increase pressure to see if enthalpy changes. We see that at low pressure and high temperature the enthalpy does not change as we increase the pressure while holding the temperature fixed. However, when we are near the top of the dome of the saturated vapor line, the enthalpy changes as we increase pressure while holding temperature fixed. This makes sense because a gas acts like an ideal gas when the molecule-to-molecule forces do not have a significant contribution to the pressure. That happens only when the molecules are far apart from each other, which corresponds to their being at low pressure and high temperature.

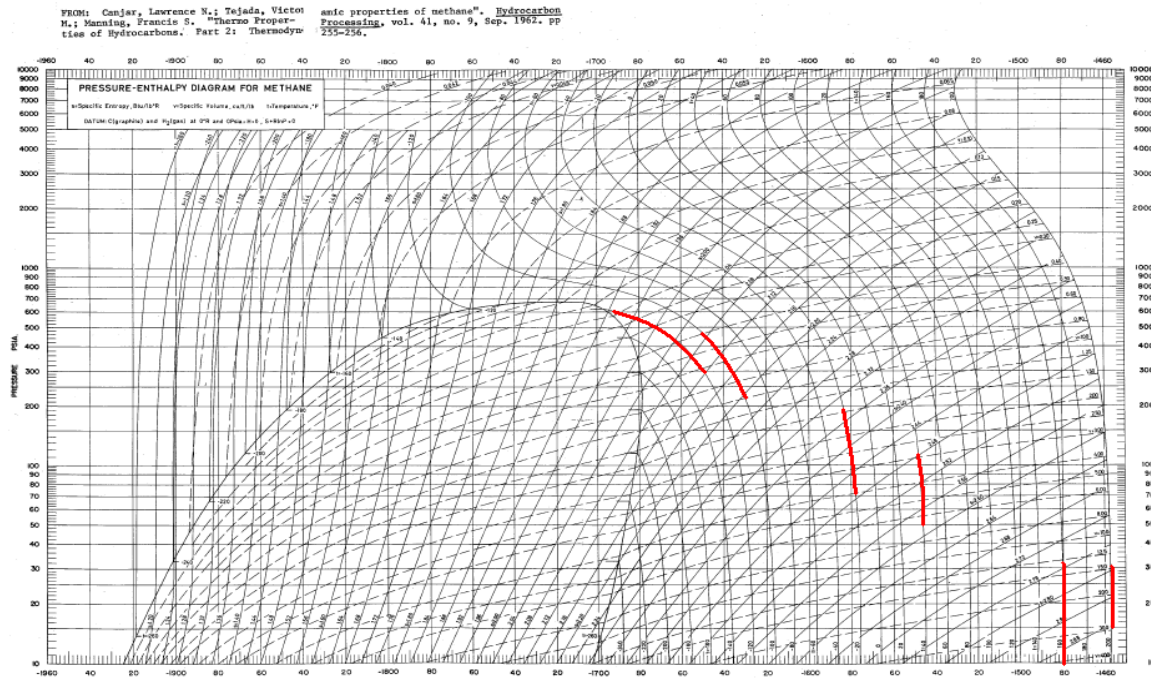



Figure 51: Ph Diagram showing that methane at low pressure and high temperature (shown highlighted at the lower right) acts like an ideal gas (its enthalpy is not a function of pressure, when the temperature is held constant). As shown highlighted in the middle of the diagram, methane acts like a non-ideal gas when the pressure is higher and the temperature is colder (its enthalpy is a function of pressure, when temperature is held constant)

Let's show this analytically using REFPROP. Let's analyze a vessel where we maintain the temperature constant and double the absolute pressure. First, we will do this at low pressure and high temperature and then we will do this at high pressure and low temperature.

Case 1: Methane maintained at 200 F is increased in pressure from 1 atm abs (0 gauge) to 2 atm abs.

Case 2: Methane maintained at -120 F is increased in pressure from 20 atm abs to 40 atm abs.

This is analyzed from data shown in Figure 52.

 20: methane: Specified state points

	Temperature (°F)	Pressure (atm)	Density (lbm/ft³)	Enthalpy (Btu/lbm)	Entropy (Btu/lbm-°R)
1	200.00	1.0000	0.033328	-1457.6	2.8898
2	200.00	2.0000	0.066706	-1457.9	2.8036
3	-120.00	20.000	1.5639	-1648.0	2.1271
4	-120.00	40.000	4.8238	-1689.6	1.9428
5					

Figure 52: Case 1 and case 2 analyzed to determine if methane acts like an ideal gas.

For ideal gas behavior, if we double the pressure the density should also double.

If volume and temperature are fixed and R is a constant, then $P = NC$ if the gas acts like an ideal gas (where $C = \text{const} = RT/V$ and N is the number of moles of the gas)

Using the data shown in Figure 52, with the volume and temperature constant, it is found that:

@ 200 F from 1 atm abs to 2 atm abs the error is 0.07% (the pressure is doubled and the density is almost exactly doubled, **thus the gas acts like an ideal gas**). Also note, the enthalpy changes only by about 0.02%.

@ -120 F from 20 atm abs to 40 atm abs, the error is 35% (54% if you divide by 2 x initial density) (the pressure is doubled and the density is not doubled, **thus the gas does NOT act like an ideal gas**). Also note, the enthalpy changes by about 2.5%.

Thus, methane acts like an **ideal gas** at “**RELATIVELY**” low pressures and “**RELATIVELY**” high temperatures and **NOT** as an ideal gas at “**RELATIVELY**” high pressure and “**RELATIVELY**” low temperatures (Answer).

IT IS CRITICALLY IMPORTANT TO REALIZE THAT THE WORD “RELATIVELY” IN THE ABOVE IS IMPORTANT. RELATIVE TO WHAT? RELATIVE TO THE PRESSURE ENTHALPY DOME FOR THAT PARTICULAR SUBSTANCE. THE CLOSER YOU ARE TO THE SATURATION DOME THE MORE THE FLUID DOES NOT ACT LIKE AN IDEAL GAS.

As an example, we showed that methane acts like an ideal gas at 200 F between 1 and 2 atm. Intuitively from that and our knowledge of the pressure enthalpy domes for various substances, we can also conclude that at 200 F between 1 and 2 atm, nitrogen also acts like an ideal gas. This is because at this temperature and pressure we are far away from the dome. How about water at 200 F between 1 and 2 atm? Does water act like an ideal gas at 200 F between 1 atm and 2 atm. Absolutely not! In fact water is a liquid at that temperature and pressure. However water at 2000 F between 1 and 2 atmosphere acts like an ideal gas.

In this discussion we have used extremes to make the point about being relatively close to the saturated dome. We said for nitrogen and methane we are very far away from the dome so at 1 to 2 atm nitrogen acts like an ideal gas. Then we talked about water and said, it is not even a gas at these properties. The other fluids we typically deal with in the gas industry fall somewhere in between. These gases such as ethane, propane, butane, pentane, hexane fall somewhere in between the extremes of nitrogen and water we stated above.

As you become more familiar with the characteristics of each gas you will eventually learn to know intuitively if you can treat the gas as an ideal gas. Often the answer will be determined by just how much error you are willing to accept. For example if you are doing an order of magnitude calculation, you may be willing to accept a 5-10% error. However, for a plant design, such an error would not be acceptable.

Before we leave the topic of a gas acting like an ideal gas, we need to discuss mixtures. We already stated that nitrogen and methane act like an ideal gas at 200 F between 1 and 2 atm. Intuitively we can also conclude that oxygen will also act like an ideal gas at these properties. How about air which is mostly nitrogen and oxygen. Well, dry air will act like an ideal gas at these properties also. However, air saturated with water vapor at these properties will not act as an ideal gas since it is mostly water vapor and very little air (at 200 F the vapor pressure of water is 11.5 psia).

Now let's use an example closer to our every day life. It is 100 F outside and the humidity is 100%. We know that we can treat dry air as an ideal gas at this pressure and temperature. Can we treat 100% humidity air as an ideal gas if it is held at 100 F and increased in pressure from 1 atm to 2 atm? The answer is NO. As we compress the air, the water vapor in the air will start to condense significantly changing the enthalpy of the fluid. About 1/2 of the water condenses out of the air as it is compressed from 1 atm to 2 atm. This changes the total enthalpy of the fluid by about 12% and the density differs from an ideal gas computation by about 3.5%.

Remember for an ideal gas, the fluid enthalpy is not a function of pressure and should remain constant at constant temperature. Also remember for an gas to act like an ideal gas it needs to follow the $PV=NRT$ relationship. Lastly, it is not acting like an ideal gas if it has phase change occurring during the process.

For comparison for the same process (1atm to 2 atm), for dry air, the enthalpy changes only about 0.07% (compared to 12% with 100% humid air) and the density differs from an ideal gas computation by only about 0.02% (compared to 3.5% with 100% humid air). Thus, dry air acts very much like an ideal gas and high humidity air does not.

Thus, mixtures that result in a phase change during a process can not be accurately modeled using the ideal gas formula.

2.23.Brain Teaser # 1.1 - Vessel Depressurized and Pressurized (Treat as an Ideal Gas)

A vessel containing 100 scf of methane maintained at 60 F is initially at 14.696 psig. The gas is maintained at 60 F while being depressurized to 0 psig. Approximately how much gas left the vessel?

After the vessel is depressurized, approximately how much gas must be added to bring the vessel to 29.392 psig and 60 F.

2.24 Solution to Brain Teaser # 1.1

A vessel containing 100 scf of Methane maintained at 60 F and at 14.696 psig is depressurized to 0 psig. Approximately how much gas left the vessel? **Approximately 50 scf was removed because at this pressure and temperature it acts nearly like an ideal gas and its absolute pressure was halved, so half of the original mass was removed.**

(ANSWER)

It is interesting to note here that a “scf” is treated as a mass measurement. That is because it is a mass measurement as it is a measure of a cubic foot at a specific pressure and temperature. Therefore, a scf is a measure of the mass of that substance as it is a cubic foot at a fixed state.

After the vessel is depressurized, approximately how much gas must be added to bring the vessel to 29.392 psig. Approximately 100 scf must be added, because at this pressure and temperature it acts nearly like an ideal gas. Thus if its absolute pressure is tripled from 1 atm abs to 3 atm abs, its mass is tripled from 50 scf to 150 scf. This is an **addition of 100 scf.**

(Answer)

2.25 Use REFPROP to Better Understand Critical Pressure and Density/Temperature Relationship

Using REFPROP select “Calculate” and then select “Saturation Points”. Put in a pressure of 100 psia. The rest of the table populates with values. At this saturation pressure we see a significant difference between the density of the saturated vapor and the saturated liquid (23.367 vs. 0.67982) lbm/ft³. As you put in higher and higher pressures, you will notice that the difference between the density of vapor and liquid becomes smaller. As the saturated liquid follows the saturated liquid line it becomes warmer and it expands becoming less and less dense. As the saturated vapor follows the saturated vapor line it experiences higher pressure and becomes denser. At the critical pressure the saturated liquid and saturated vapor lines converge to a single point which is the top of the Ph diagram dome. In Figure 53 this is seen as being just under 667.06 psia for methane. The critical pressure is found to be between 667.058 psia and 667.059. Due to the number of significant digits selected, the input data shown on Figure 53 has been rounded off by REFPROP.

Note that if you input a pressure that is higher than the critical pressure, such as 667.059 psia, as in line 16 of Figure 53, REFPROP will return an error message. That is because, as stated earlier in this work, you cannot define a saturated condition above the critical pressure.

22: methane: Saturation points (at equilibrium)

	Temperature (°F)	Pressure (psia)	Liquid Density (lbm/ft ³)	Vapor Density (lbm/ft ³)	Liquid Enthalpy (Btu/lbm)	Vapor Enthalpy (Btu/lbm)	Liquid Entropy (Btu/lbm-°R)	Vapor Entropy (Btu/lbm-°R)
2	-205.12	100.00	23.367	0.67982	-1870.5	-1680.9	1.3833	2.1284
3	-177.99	200.00	21.492	1.3608	-1844.3	-1677.6	1.4780	2.0698
4	-159.48	300.00	19.943	2.1177	-1824.5	-1678.8	1.5430	2.0284
5	-145.02	400.00	18.453	3.0049	-1807.1	-1682.9	1.5964	1.9913
6	-133.02	500.00	16.842	4.1263	-1790.2	-1690.1	1.6457	1.9523
7	-122.75	600.00	14.744	5.8116	-1771.2	-1703.1	1.6995	1.9017
8	-118.14	650.00	12.886	7.4811	-1757.0	-1717.0	1.7394	1.8565
9	-117.26	660.00	12.138	8.1965	-1751.9	-1723.0	1.7541	1.8383
10	-116.83	665.00	11.440	8.8872	-1747.2	-1728.7	1.7674	1.8214
11	-116.75	666.00	11.174	9.1546	-1745.5	-1730.9	1.7724	1.8150
12	-116.66	667.00	10.484	9.8356	-1740.8	-1736.1	1.7859	1.7995
13	-116.66	667.05	10.281	10.030	-1739.4	-1737.6	1.7901	1.7953
14	-116.66	667.05	10.229	10.081	-1739.0	-1738.0	1.7911	1.7942
15	-116.65	667.06	10.155	10.155	-1738.5	-1738.5	1.7927	1.7927
16		667.059						
17								

Figure 53: Analysis of saturated vapor density and saturated liquid density showing how they converge to 10.155 lbm/ft³ as the pressure increases to the critical point

2.26 Brain Teaser # 1.2 – A Solid Floating in Saturated Liquid Methane as it Heats Up

Part 1

A solid with a density of 12 lbm/ft^3 is floating on the top of saturated liquid methane in a vessel initially at 100 psia. Instrumentation is placed on the solid to determine its height from the bottom of the vessel and from the liquid-vapor interface.

The vessel is a vertical cylinder 30 feet high. Initially the liquid level is 15 feet from the bottom. The liquid and vapor in the vessel are slowly heated. Describe the location of the solid from the bottom of the vessel as the saturated mixture of methane liquid and vapor is heated. Also, describe how much of the floating solid is above the liquid-vapor interface. Assume the density of the solid does not significantly change as it is heated. Neglect any phase change between the liquid and vapor and use the density of the liquid to determine the location of the liquid-vapor interface. Assume the total volume of the vessel remains constant during the heating. Assume the density of the solid remains at 12 lbm/ft^3 during the heating. Assume the total volume of the solid is very small compared to the total volume of the methane (so that the displacement of the solid into the liquid will not cause a significant increase in the height of the liquid-vapor interface).

Part 2

Do the exact problem as above but this time the solid block has a density of 4 lbm/ft^3 .

Part 3

Would the results found in part 1 and part 2 be any different if the gravitational field of the location were 10% less than the gravitational acceleration at sea level?

Part 4

Would the results in part 1 and part 2 be any different if there was no gravitational field such as in outer space? What impact might this have on a fuel vessel on a on a space station?

2.27 Solution to Brain Teaser 1.2

Part 1 Solution

View Figure 53 to better understand what is happening in this problem. Initially the solid will be floating at a distance of 15 feet from the bottom of the vessel and the solid will be approximately $\frac{1}{2}$ submerged below the liquid vapor interface. At this pressure the density of the liquid is nearly twice that of the solid causing most of the buoyant force on the solid. Initially the density of the vapor is significantly small compared to the density of the solid (vapor

density is 6% that of the floating solid) so at the starting point, the vapor density causes only a small buoyant force on the solid.

As the liquid is heated, the solid will raise higher and higher in the vessel as the liquid level rises. The liquid level will rise as the liquid is heated because its density decreases causing the liquid to occupy more and more of the vessel's volume. When the vessel pressure reaches 660 psia, the height of the liquid-vapor interface will be approximately 28.9 feet above the bottom of the vessel. At this saturation pressure, the density of the liquid methane is 12.138 lbm/ft³. Since the solid is slightly lower in density (12 lbm/ft³) the solid will float with most of its volume below the liquid vapor interface. However, at this pressure the density of the vapor is significant, as it is approximately 68% that of the solid. Thus, the density of the vapor will cause a buoyant effect on the small portion of the solid that is above the liquid vapor interface causing the block to float slightly higher. Thus, the height of the solid is aligned with the liquid-vapor interface (28.9 feet above the bottom) with most of the solid being under the liquid-vapor interface and just a small portion being above the liquid-vapor interface.

As the saturated liquid-vapor methane is heated further, the density of the liquid drops below 12 lbm/ft³. When the density of the liquid methane drops below 12 lbm/ft³, the solid will drop to the very bottom of the vessel. This will occur at approximately 661.3 psia and -117.15 F.

The above is graphically shown in Figure 54 using data mostly from Figure 53. (Answer)

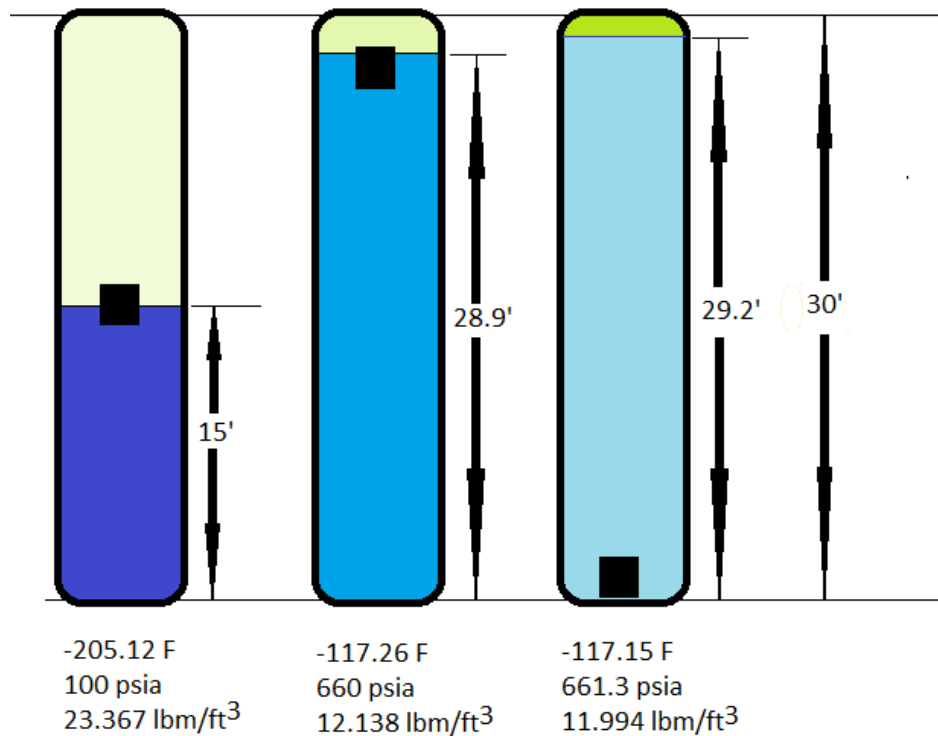


Figure 54: Liquid density relationship as a vessel of saturated methane is heated. Note, the density of the liquid decreases as it is heated. Density of the solid is 12 lbm/ft³. Most of the above data is from Figure 53.

Part 2 Solution

In part 2 the block is much lighter. Therefore, initially it will be floating on the top of the liquid vapor interface. The block has a density that is approximately about 1/6th that of the liquid. Thus, due to the liquid density alone about 1/6th of the block will be below the liquid vapor interface. However, because the density of the block is so much lighter, the density of the vapor does have much more of a significant effect on how much of the block is above the liquid vapor interface. At the initial conditions the vapor density is 17% that of the solid density. Thus, the vapor will cause a significant buoyant force on the solid. The combination of the buoyant force due to the liquid and the vapor will result in the block floating on the liquid vapor interface with about only 1/7th of the solid below the liquid vapor interface.

As the liquid is heated, the solid will raise higher and higher in the vessel as the liquid level rises. The liquid level will rise as the liquid is heated because its density decreases causing the liquid to occupy more and more of the vessel's volume. When the vessel pressure reaches 490 psia, the height of the liquid-vapor interface will be approximately 20.598 feet above the

bottom of the vessel. At this saturation pressure, the density of the liquid methane is 17.016 lbm/ft³ and the density of the vapor methane is 3.998 lbm/ft³. Since the density of the solid (4 lbm/ft³) is much lighter than that of the liquid methane and only slightly higher than that of the vapor methane, the solid will float on top of the liquid-vapor interface. At this saturation pressure because the vapor methane is almost the same density of the solid, the solid will be floating almost fully above the liquid-vapor interface.

As the saturated liquid-vapor methane is heated further, the density of the vapor increases above 4 lbm/ft³. When the density of the vapor methane raises to above 4 lbm/ft³, the solid will rise to the very top of the vessel. This will occur at approximately 491.2 psia and -134.11 F with a liquid-vapor interface of approximately 20.603 feet above the bottom of the vessel.

Take note, that it makes little sense to give the height in 3 significant figures while using the word approximately. The significant digits are used only to show that we are right at the point where the buoyancy force just balances the weight of the solid.

The above is graphically shown in Figure 55 using data from Figure 53. and Figure 56.

(ANSWER)

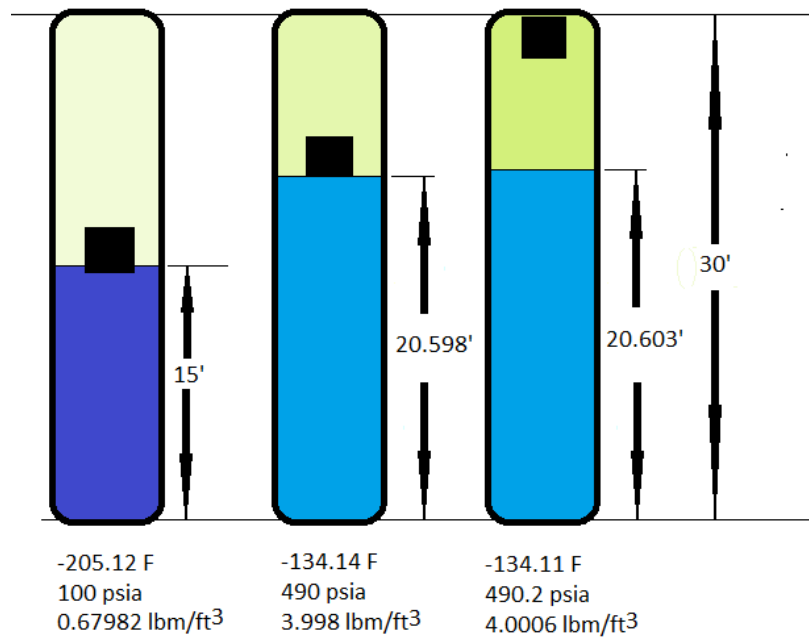


Figure 55: Vapor density relationship as a vessel of saturated methane is heated. Note, the density of the vapor increases as it is heated. Density of the solid is 4 lbm/ft³. Most of the above data is from Figure 53 and Figure 56

2: methane: Saturation points (at equilibrium)

	Temperature (°F)	Pressure (psia)	Liquid Density (lbm/ft³)	Vapor Density (lbm/ft³)	Liquid Enthalpy (Btu/lbm)	Vapor Enthalpy (Btu/lbm)	Liquid Entropy (Btu/lbm·°R)	Vapor Entropy (Btu/lbm·°R)
1	-138.77	450.00	17.677	3.5255	118.54	231.26	0.44091	0.79215
2	-136.42	470.00	17.352	3.7544	121.92	229.75	0.45072	0.78431
3	-135.27	480.00	17.185	3.8742	123.61	228.94	0.45563	0.78030
4	-134.14	490.00	17.016	3.9980	125.32	228.08	0.46056	0.77621
5	-134.02	491.00	16.999	4.0107	125.49	227.99	0.46105	0.77580
6								
7								
8	-134.07	490.60	17.005	4.0056	125.42	228.02	0.46085	0.77596
9	-134.08	490.50	17.007	4.0043	125.41	228.03	0.46080	0.77600
10	-134.10	490.30	17.011	4.0018	125.37	228.05	0.46070	0.77609
11	-134.11	490.20	17.012	4.0006	125.36	228.06	0.46065	0.77613
12	-134.12	490.10	17.014	3.9993	125.34	228.07	0.46060	0.77617
13								

Figure 56: Additional REFPROP data needed for computation of buoyancy shown in Figure 55

Part 3 Solution

The results shown in parts 1 and 2 would not be any different if the gravitational field was 10% less as long as there is a gravitational field. This is because the field is applied to all masses uniformly. Thus, in a lower gravitational field the weight of the solid may be less, but the buoyant force is also proportionally less.


Part 4 Solution

The results shown in parts 1 and 2 would be drastically different if there was no gravitational field. A gravitational field is the reason there is a liquid-vapor interface. If there was no gravitational field, the fluid and vapor and solid would be floating randomly within the vessel regardless of the saturation pressure and temperature.

On a space station unless there is a created acceleration field, it would be difficult to measure the amount of fuel in the container (you can have a level gauge in a tank where vapor and liquid are randomly floating and you cannot put a float device in place). Also, unless there is a created acceleration field, it would be difficult to draw liquid fuel from the container since the liquid does not lay on the bottom of the tank but instead is dispersed with the vapor. As for the solid, it could be anywhere in the tank and may be blocking the fuel outlet port.

2.28 Switching Back to the REFPROP Reference State

Let's switch the "Reference State" back to the default REFPROP reference state by selecting "Options" and then selecting "Reference States" and then selecting the "Use Default Reference State"

 Use the default reference state (the default state for this fluid is NBP)

then selecting "ok."

2.29 Using REFPROP to Better Understand Fill Induced Rollover

Fill induced rollover occurs after stratification occurs due to filling a different density LNG into an existing LNG inventory without mixing. If a high-density LNG is placed under a light layer of LNG or if a light layer of LNG is placed over a denser layer of LNG, stratification may occur. Once stratification occurs, the lower layer has no significant way to release heat gained from outside the tank and the lower layer becomes warmer. As the lower layer warms, it becomes less dense. This is shown in the following pictures.

Under normal circumstances, circulation currents caused by heat influx carry warmer liquid to the surface, where evaporation takes place. A full tank circulation pattern provides natural formation of boiloff at the surface as shown in Figure 57 below.

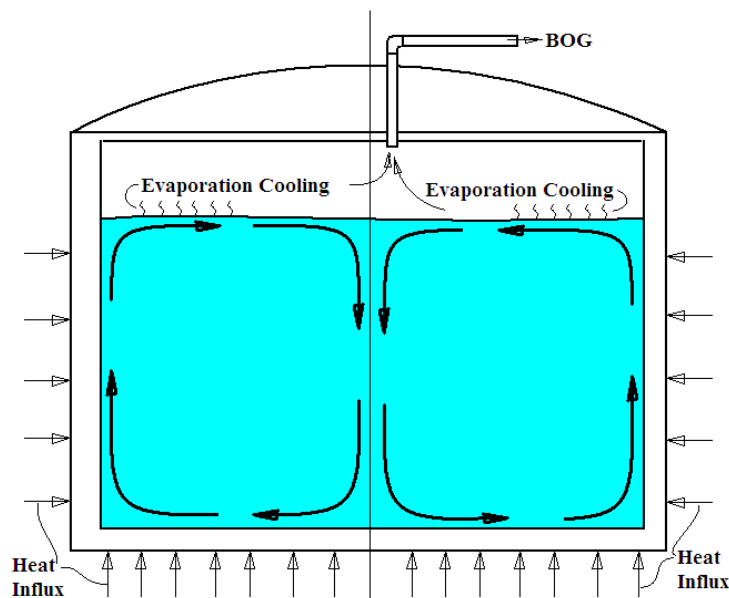


Figure 57: Non-stratified LNG tank. Natural convection keeps the entire tank at approximately the same temperature as evaporation cooled LNG at the surface is circulated throughout the entire tank.

If a lower density LNG is loaded over a denser LNG or if a denser LNG is loaded under a lower density LNG stratification can occur. Stratification can also automatically occur if the LNG contains a high concentration of nitrogen. A stratified tank is shown in Figure 58.

In a stratified tank, the upper layer remains cold as it has evaporative cooling occurring at the LNG surface and that cold LNG is circulated within the upper stratum of LNG. However, the lower layer gains heat and has no place to release that heat and thus, the lower layer warms up. As the lower layer warms up, it expands and its density drops. Once the lower layer density becomes close to that of the top layer, the two layers mix and a very large amount of boil off is generated. This is shown in Figure 59:

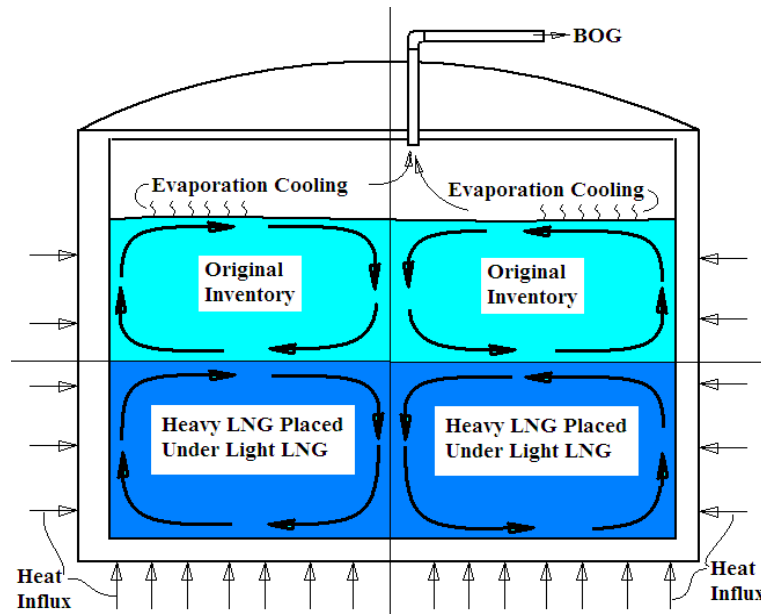


Figure 58: One of several types of stratification whereby a denser LNG is placed under a less dense LNG inventory.

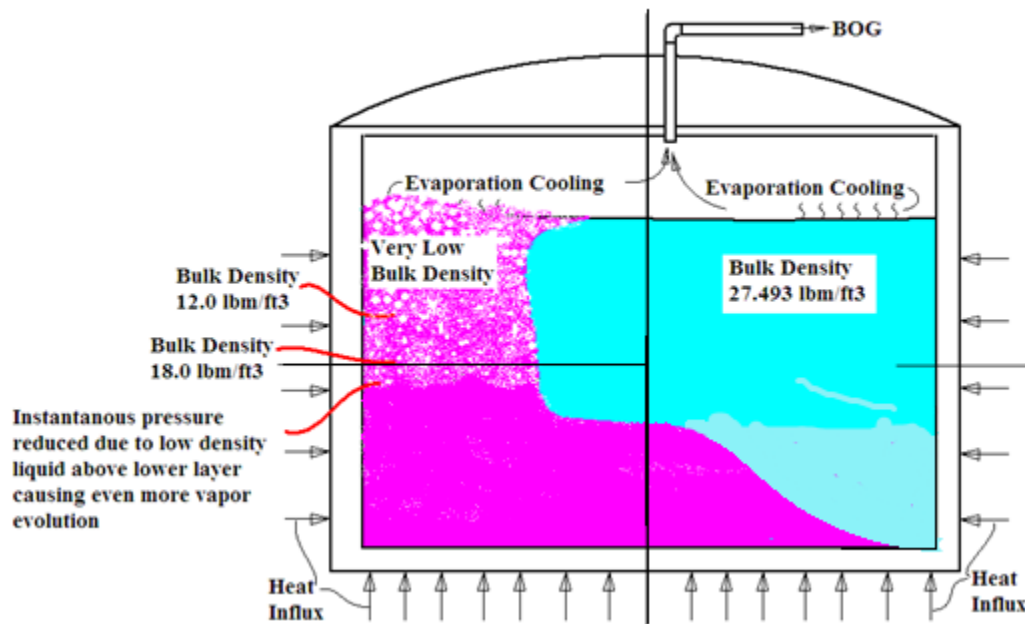


Figure 59: LNG tank rollover. It is not known whether the inventories actually flip as depicted above or the layers just mix. In either case, the end result of high boil off rates occurs. Source: Self-made.

To explore how rollover occurs, let's create a stratification by placing a 95/5 methane ethane mix under pure liquid methane at a saturation pressure of 15.5 psia. Figure 60 shows the density of saturated liquid methane at 15.5 psia as being 26.307 lbm/ft³.

5: methane: Saturation points (at equilibrium)

	Temperature (°F)	Pressure (psia)	Liquid Density (lbm/ft³)	Vapor Density (lbm/ft³)	Liquid Enthalpy (Btu/lbm)	Vapor Enthalpy (Btu/lbm)	Liquid Entropy (Btu/lbm·°R)	Vapor Entropy (Btu/lbm·°R)
1	-257.50	15.500	26.307	0.11908	0.97869	220.23	0.0048269	1.0893
2								

Figure 60: REFPROP showing the saturated density of liquid methane at 15.5 psia as 26.307 lbm/ft³.

With the liquid methane in the tank inject a 95/5 methane ethane “MASS” mix of LNG beneath the layer of liquid methane. Then use REFPROP to determine the density of the lower layer of the 95/5 LNG as it warms up. The saturated liquid density is used for this analysis because the density of the LNG is a strong function of temperature and only a very weak function of

pressure. Thus, the temperature dominates the change in density. The density of the 95/5 mix as it warms is shown in Figure 61.

Take note, in this problem we chose a 95/5 mixture based on mass, not moles. The molecular weight of methane is ~ 16 and the molecular weight of ethane is ~30.

Using the mass mixture means that 95% of the mass of the mixture is methane and 5% of the mass of the mixture is ethane. We could have used either a mole mixture or a mass mixture for this problem. In this problem a mass mixture was used, just to exercise the use of both **molar** and mass mixtures. A 95/5 methane ethane mass mixture approximately a 97.33/2.67 **molar** methane ethane mixture. A 97/3 methane **molar** mixture is analyzed later in this work (see Figure 99).

Take note, that when using a mass mixture, the screen display will show the mixture proportions as a whole number fraction (5/95 or 95/5 depending on the order of components). When using a **molar** mixture, the screen display will show the mixture in decimal values (i.e. 0.5/0.95 or 0.95/0.5 depending on the order of components). The 5/95 display showing that this is a “MASS” mixture of the display is highlighted in Figure 61.

6: ethane/methane: Saturation points (at equilibrium) (5/95)

	Liquid Phase Temperature (°F)	Vapor Phase Temperature (°F)	Liquid Phase Pressure (psia)	Vapor Phase Pressure (psia)	Liquid Phase Density (lbm/ft³)	Vapor Phase Density (lbm/ft³)
1	-256.87	-256.87	15.500	15.500	26.778	0.11867
2	-254.13	-254.13	17.500	17.500	26.640	0.13265
3	-251.62	-251.62	19.500	19.500	26.513	0.14651
4	-249.29	-249.29	21.500	21.500	26.394	0.16027
5	-247.13	-247.13	23.500	23.500	26.283	0.17394
6						

Figure 61: REFROP display of density as the temperature of the lower layer warms up. Note, this is a mass mixture and not a molar mixture. The telltale that this is a mass mixture is that the composition is shown in whole numbers 5/95 (circled above).

IT IS CRITICALLY IMPORTANT THAT THE USER OF REFPROP BE CAREFUL TO ASSURE THE CORRECT MIXTURE PARAMETER (MOLAR OR MASS) IS USED. A VERY COMMON MISTAKE IS TO USE A MASS MIXTURE WHEN A MOLAR MIXTURE WAS NEEDED FOR THE PROBLEM (OR VICE VERSA).

As can be seen in Figures 61 and 62, as the lower layer of LNG warms, it becomes less and less dense. Eventually the bottom layer becomes light enough to mix with the upper layer. Once the lower layer LNG mixes with the upper layer and is exposed to the lower pressure at the top of the tank, a large amount of boil off is generated.

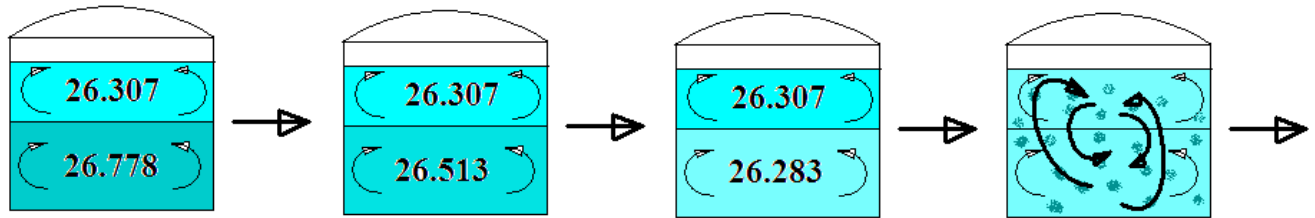


Figure 62: Depiction of a fill induced rollover using data from Figures 60 and 61. Note the unstable condition that exists in the 3rd tank from the left.

In Figures 60 and 61 saturated conditions were used for the analysis. An alternate to this would have been to use “Specific State Points” to find the density. If “Specific State Points” were used, one could select 23.5 psia as the pressure of the lower liquid and then increase the temperature using the temperatures given in Figure 61. The results would be nearly identical because as stated earlier, the LNG density is largely a function of temperature and not of pressure. The use of “Specific State Points” is very slightly more accurate, but the conclusion by using the saturated temperature and pressure is the same. This will be discussed in more detail later in this book.


2.30 Learner Exercise # 1.1 – Hail Formation on a Summer Day

Use REFPROP to explain how hail may be formed on a summer day.

2.31 Learner Exercise Solution # 1.1

Air at 1 atm and 20 C is driven up to a high elevation (18,000 ft.) where the air pressure is approximately ½ atm.

As the air rises it expands with a nearly adiabatic isentropic expansion (nearly constant entropy). This is shown in Figure 63 where a constant entropy expansion of dry air changed in temperature from 20 C to -32.762 C. Take note the entropy is kept at 6.8433 kJ/kg K while the pressure is reduced in pressure to 0.5 atm.


 2: Air: Specified state points (75.57/1.2691/23.16)

	Temperature (°C)	Pressure (atm)	Density (kg/m³)	Enthalpy (kJ/kg)	Entropy (kJ/kg-K)
1	20.000	1.0000	1.2043	293.41	6.8433
2	-32.762	0.50000	0.73445	240.52	6.8433
3					

Figure 63: Constant entropy expansion of air from 1 atmosphere to 1/2 atmosphere. Note: this is on a mass basis.

Can you see how this condition might cause hail if moisture had been in the air? Moisture in the air would condense, coalesce, and then freeze into balls of ice. The weight of the balls of ice, overcomes the upward force due to the upward velocity of the air and the hail formed falls to the ground. Wow – hail in the middle of the summer!

Something settle needs to be pointed out here! In the above hail production analysis, we used a predefined mixture of dry air for a substance! Of course, the air would need to have water vapor in it in order to make ice, but aside from that, take note of the air composition. It shows as the air mixture as being 75.57% nitrogen, 1.2691% argon and 23.16% oxygen. How can that be as we have always been taught that air is ~ 79% nitrogen and 21% oxygen. The reason that the reading is shown as 75.57% nitrogen, 1.2691% argon and 23.16% oxygen is because we left the parameters as a mass measurement. If we change it to a **molar** (volume type measurement) the very same air composition would read as shown in Figure 64 below. As shown, now the composition on a volume or **molar** basis is shown as being ~ 79% nitrogen and ~ 21% oxygen.

 2: Air (dry): Specified state points (0.7812/0.0092/0.2096)

	Temperature (°C)	Pressure (atm)	Density (kg/m³)	Enthalpy (kJ/kg)	Entropy (kJ/kg-K)
1	20.000	1.0000	1.2043	293.41	6.8433
2	-32.762	0.50000	0.73445	240.52	6.8433
3					

Figure 64: Constant entropy expansion of air from 1 atmosphere to 1/2 atmosphere. Note: this is on a molar basis. Note also that the values in the table are the same as the values of Figure 63.

Applying REFPROP to LNG Plant Operations

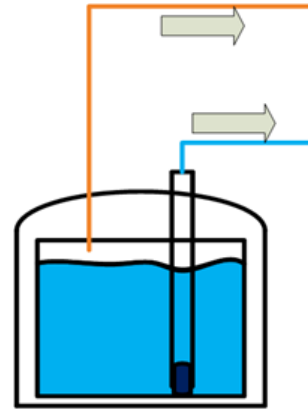
In this section we will evaluate plant equipment and use REFPROP to better understand thermodynamically, how this equipment operates.

1. Typical types of plant analysis

The thermodynamic analyses that can be performed in an LNG plant are almost limitless. It is suggested that the learner closely follow the plant's mass energy balance and use REFPROP to analyze each piece of equipment. In doing this the engineer will gain a keen sense of how closely the plant performs to the design basis and how closely the analysis can predict physical plant performance. Further, by doing this type of analysis the operator can become familiar with the limitations of the field measurements and the effects of heat transfer and pressure drops.

The ideal solutions can be modeled by constant property steady state, steady flow analysis and then adjusted for real life deviations from these modeled processes.

Some of the equipment that the learner may want to analyze includes pumps, compressors, turbines, heat exchangers, vaporizers, desuperheaters, recondensers and JT valves.



1.1 Problem # 2.1 - In-Tank Pump Analysis

An LNG plant is designed to operate with 1 in-tank pump operating at 1 Bscf/day. Use REFPROP to confirm the pump manufacturer's data scaled up to 1 Bscf/day. The pump manufacturer's data is as shown below.

- 555 hp
- 78% efficiency
- 8,045 gallon per minute (gpm)
- 452 feet of head
- The pump manufactures use the worst case of very dense LNG for these ratings. Thus, all the above is at SG. = 0.47 or LNG with a density of 29.328 lbm/ft³.

1.2 Solution # 2.1

To scale the manufacturer's data up to 1 Bscf/d at the LNG density used by the manufacturer, the following is calculated. See REFPROP data in Figure 65 and 66.

- 1 Bscf/d = 41,666,666 scf/hr.
- On REFPROP use “Substance” then “Define New Mixture” to put in a mixture of 84% methane, 13% ethane and 3% propane to match the worst case data used by the pump manufacturer.
- LNG at a **molar** composition of 84% methane, 13% ethane and 3% propane gives us a saturated liquid density at 15.5 psia of 29.321 lbm/ft³ (or 3.92 lbm/gallon). This mixture was selected by trial and error in order to arrive at a mixture that closely matched the pump manufacturer’s density of 29.328 lbm/ft³. This mix is considered close enough to the target density.
- This same composition at 60 F and 14.696 psia makes a scf have a mass of 0.049438 lbm/scf (Figure 65). Note, different agencies use different values for standard temperature and pressure (STP). It is unknown what the pump manufacturer used as STP, so for this analysis STP was selected as being 60 F and 14.696 psia.
- Our mass flow rate is 41,666,666 scf/hr. x 0.049438 lbm/scf = 2,059,917 lbm/hr. = 8,758 gallons/min
- Find the saturated liquid enthalpy (the liquid in the tank) and make that the pump inlet enthalpy. Assume the tank vapor pressure is 15.5 psia. (See Figure 65)
- Then pump the liquid in an isentropic pump from the inlet conditions to the outlet pressure. The outlet pressure can be computed by the feet of head the pump produces (manufacturer’s data).
- From the isentropic pumping the ideal power required (Δh) is found (See Figure 66). This is then adjusted to find the actual power required by using the manufacturer’s data on efficiency.
- The flow rate and power values from the manufacturer’s data need to be scaled up to 1 Bscf/day. Assume a linear scaling for this analysis.

6: methane/ethane/propane: Saturation points (at equilibrium) (0.84/0.13/0.03)										
	Liquid Phase Temperature (°F)	Vapor Phase Temperature (°F)	Liquid Phase Pressure (psia)	Vapor Phase Pressure (psia)	Liquid Phase Density (lbm/ft³)	Vapor Phase Density (lbm/ft³)	Liquid Phase Enthalpy (Btu/lbm)	Vapor Phase Enthalpy (Btu/lbm)	Liquid Phase Entropy (Btu/lbm-°R)	Vapor Phase Entropy (Btu/lbm-°R)
1	-254.06	-254.06	15.500	15.500	29.321	0.11688	-15.076	222.02	-0.0058081	1.0982
2										

7: methane/ethane/propane: Specified state points (0.84/0.13/0.03)									
	Mole Frac. (methane)	Mole Frac. (ethane)	Mole Frac. (propane)	Temperature (°F)	Pressure (psia)	Density (lbm/ft³)	Enthalpy (Btu/lbm)	Entropy (Btu/lbm-°R)	
1	0.84000	0.13000	0.030000	60.000	14.696	0.049438	352.82	1.4059	
2									

Figure 65. Properties of the 84/13/3 LNG mixture at saturated and standard conditions. Note the close match of the saturated density to that used by the pump manufacturer.

7: methane/ethane/propane: Specified state points (0.84/0.13/0.03)									
	Mole Frac. (methane)	Mole Frac. (ethane)	Mole Frac. (propane)	Temperature (°F)	Pressure (psia)	Density (lbm/ft³)	Enthalpy (Btu/lbm)	Entropy (Btu/lbm-°R)	
1	0.84000	0.13000	0.030000	60.000	14.696	0.049438	352.82	1.4059	
2	0.84000	0.13000	0.030000	-254.06	15.500	29.321	-15.076	-0.0058081	
3	0.84000	0.13000	0.030000	-253.80	107.53	29.340	-14.495	-0.0058081	
4									

Figure 66: Properties of the 84/13/3 LNG mixture at standard conditions and across an “adiabatic isentropic” pump (entropy is kept constant, lines 2 and 3).

Use a linear relationship to scale up the manufacturer’s data to 1 BCF/day (factor 8,758 gpm / 8045 gpm = 1.08863).

- 555 hp x 1.08863 = 604 hp
- 78% eff
- 8,045 gpm x 1.08863 = 8,758 gpm for a Bscf/d
- 452 feet of head = 92 psi pressure increase (452 ft x (29.328 lbf/ft³)/144in²/ft²) @sea level where g= 32.174 ft/sec²

- All the above at SG.= 0.47 or LNG with a density of 29.328 lb/ft³

Our REFPROP computation should come close to 604 hp for this LNG composition. Let's do the computation.

Take note that the isentropic pump increase in enthalpy is (15.076 – 14.495)Btu/lbm = 0.581 Btu/lbm (See Figure 66).

Thus, at 78% efficiency the pump requires 0.7449 Btu/lbm pumped ((0.581/0.78)Btu/lbm).

The horsepower required to drive the pump is computed as follows:

- Flow rate x enthalpy increase x hp conversion = horsepower
- 2,059,917 lbm/hr x 0.7449 Btu/lbm x 0.000393 hp-hr/Btu = 603 hp (See page 779 of the pocket reference to find the conversion of Btu/hr to hp.
- Manufacturer's data = 604 hp
- Our Computed data = 603 hp
- **Computation Confirmed.** (ANSWER)

1.3 Problem # 2.2 – Properties and BOG Composition from an LNG Mixture (Tx and Ph diagrams)

LNG in a tank has a **molar** composition of 95% methane 4% ethane and 1% nitrogen.

- What is its boiling temperature? (tank vapor pressure 15.5 psia)
- What is the composition of the boil off vapor in volume (**molar**)?
- What is the LNG density?

What would the density and temperature of the LNG be if the mixture were 96% methane and 4% ethane and what would the boil off composition be?

- Plot the Tx diagram @ 15.5 psia and Ph diagram for the 96/4 **molar** LNG mixture.

1.4 Solution # 2.2

See Figure 67.

- **Boiling temp for 95/4/1 methane, ethane, nitrogen mixture is -262.3 F (ANSWER)**
- **Boil off is 22.98% N₂, 77.01% CH₄, .005% C₂H₆ (ANSWER)**
- **LNG density is 27.453 lbm/ft³ (ANSWER)**

5: methane/ethane/nitrogen: Saturation points (at equilibrium) (0.95/0.04/0.01)

	Liquid Phase Temperature (°F)	Vapor Phase Temperature (°F)	Liquid Phase Pressure (psia)	Vapor Phase Pressure (psia)	Liquid Phase Density (lbm/ft³)	Vapor Phase Density (lbm/ft³)	Liquid Phase Mole Frac. (methane)	Liquid Phase Mole Frac. (ethane)	Liquid Phase Mole Frac. (nitrogen)	Vapor Phase Mole Frac. (methane)	Vapor Phase Mole Frac. (ethane)	Vapor Phase Mole Frac. (nitrogen)
1	-262.30	-262.30	15.500	15.500	27.453	0.14268	0.95000	0.040000	0.010000	0.77014	0.000054915	0.22981
2												

Figure 67: Properties of the 95/4/1 LNG mixture at saturated conditions at 15.5 psia.

Now switch to an LNG **molar** mixture of 96% methane and 4% ethane. See Figure 68 which shows the following data:

- **Boiling temp is –256.59 F** (ANSWER)
- **Boil off is 0% N₂, 99.99% CH₄, 0.0089% C₂H₆ (Answer)**
- **LNG density is 26.993 lbm/ft³ (Answer)**

Why such a change as compared to the 95/4/1 LNG mixture?

The reason there was such a change is because 1 % nitrogen significantly reduces the saturation temperature of the LNG. It also significantly changes the boil off concentration and the density as shown in Figure 68.

6: methane/ethane/nitrogen: Saturation points (at equilibrium) (0.96/0.04/0)

	Liquid Phase Temperature (°F)	Vapor Phase Temperature (°F)	Liquid Phase Pressure (psia)	Vapor Phase Pressure (psia)	Liquid Phase Density (lbm/ft³)	Vapor Phase Density (lbm/ft³)	Liquid Phase Mole Frac. (methane)	Liquid Phase Mole Frac. (ethane)	Liquid Phase Mole Frac. (nitrogen)	Vapor Phase Mole Frac. (methane)	Vapor Phase Mole Frac. (ethane)	Vapor Phase Mole Frac. (nitrogen)
1	-256.59	-256.59	15.500	15.500	26.993	0.11849	0.96000	0.040000	0.00000	0.99991	0.000089415	0.00000
2												

Figure 68: Properties of the 96/4 LNG mixture at saturated conditions at 15.5 psia.

Next on the REFPROP menu select “Plot” then select “Tx diagram”. The Tx diagram is a plot of the dew point and bubble point that spans the full range of mixture compositions. This is shown in Figure 69. In Figure 69 the upper line is the dew point line and the lower line is the bubble point line. These lines span all composition mixtures of methane and ethane.

For the Tx diagram shown in Figure 69 the **molar** concentration selected was 96% methane and 4% ethane. If you had selected any other concentration of methane ethane (say 50%/50%) you would have gotten the exact same diagram as shown in Figure 69. That is because a Tx

diagram is a plot of the equilibrium relationships for all mixtures of two pure substances. A Tx diagram can be made only for binary mixtures. For mixtures of more than 2 components the composition relationship cannot be shown on an xy plot. For a single pure substance, the dew point and bubble point would overlay each other as a horizontal line. For a Tx plot, you must select a particular pressure. In this example we selected 15.5 psia. Note, this pressure is shown on the right side of the plot's dew point line.

Since the Tx diagram is valid for all mixtures of the two components, let's exercise how to use this diagram for a 95/5 mixture of methane and ethane.

If you have a liquid of 95% methane and 5% ethane (molar), you draw a vertical line starting at the bottom of the chart until it hits the bubble point line. Then draw a horizontal line until it hits the dew point line. Where the horizontal line meets the dew point line depicts the concentration of the vapor produced. This is shown in Figure 70. In Figure 70 a vertical line down to the X axis shows that the vapor is 99.99% methane. You can read the vapor composition on either the top or bottom X axis but it is shown as being read on the bottom line only for ease of reading the value. However, it is the reading of the methane concentration of the vapor.

If you have a vapor of 95% methane and 5% ethane, you draw a vertical line starting at the top of the chart until it hits the dew point line. Then draw a horizontal line until it hits the bubble point line. Where the horizontal line meets the bubble point line depicts the concentration of the condensed liquid produced. This is shown in Figure 71. In Figure 71 a vertical line down to the X axis shows that the liquid is 10.4% methane. You can read the liquid composition on either the top or bottom X axis but it is shown as being read on the bottom line only for ease of reading the value. Note, it is the reading of the methane concentration of the liquid (10.4%).

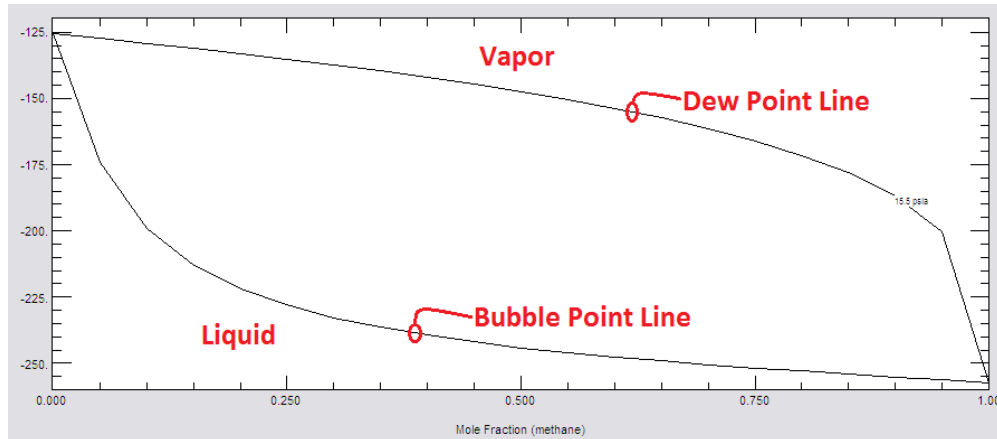


Figure 69: T-x diagram for all methane ethane LNG mixtures.

(ANSWER)

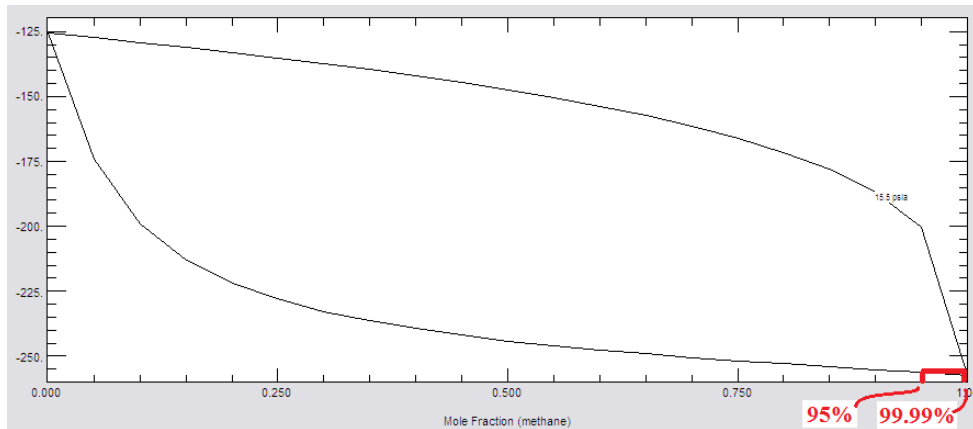


Figure 70: T-x diagram for all methane ethane LNG mixtures. This shows that a 95/5 LNG mixture would produce boil off in excess of 99.99% methane concentration.

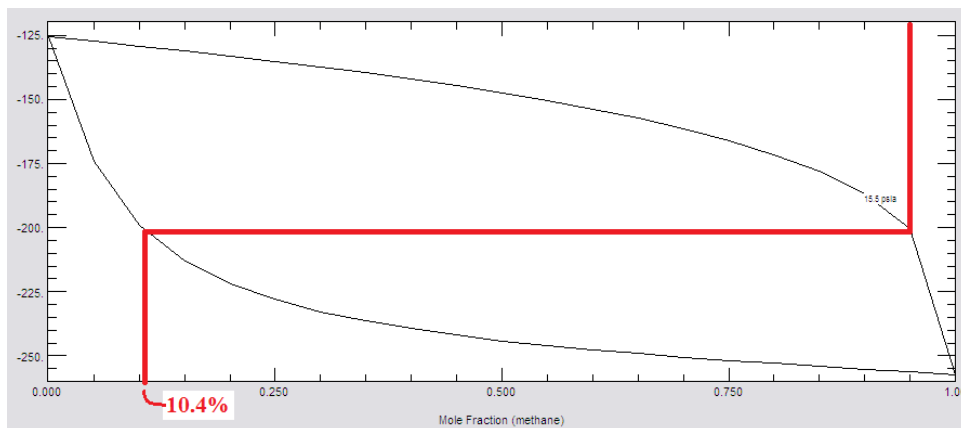


Figure 71: T-x diagram for all methane ethane LNG mixtures. This shows that a 95/5 mix of vapor would condense to produce LNG with a methane content of approximately 10.4%.

For those who want to duplicate the plot shown in Figure 69 the range data for this plot is shown in Figure 72. Take note that we selected 15.5 psia as the saturation pressure.

Figure 72: Input data for producing the Tx diagram shown in Figure 69

If your screen does not look as large as this, you may not have selected more on the earlier screen.

The diagram as shown in Figure 69 was made using a **molar** mixture of methane and ethane defined in that order. If you had chosen the very same mixture but had input ethane first, the resulting plot would be as shown in Figure 73. It is the reverse of the chart shown in Figure 69. Look closely at what is different. Look at the X axis. In figure 69, the X axis is the mole fraction of methane and in figure 73 the X axis is the mole fraction of ethane. This explains why the graphs look reversed. However, either graph will render the very same results.

Although the graphs are nice for a quick visual representation of the relationship between dew and bubble points and concentrations, it is much more accurate to have REFPROP calculate the actual values. This is done by selecting “Calculate” and then “Saturation Points at Equilibrium” for analytical work.

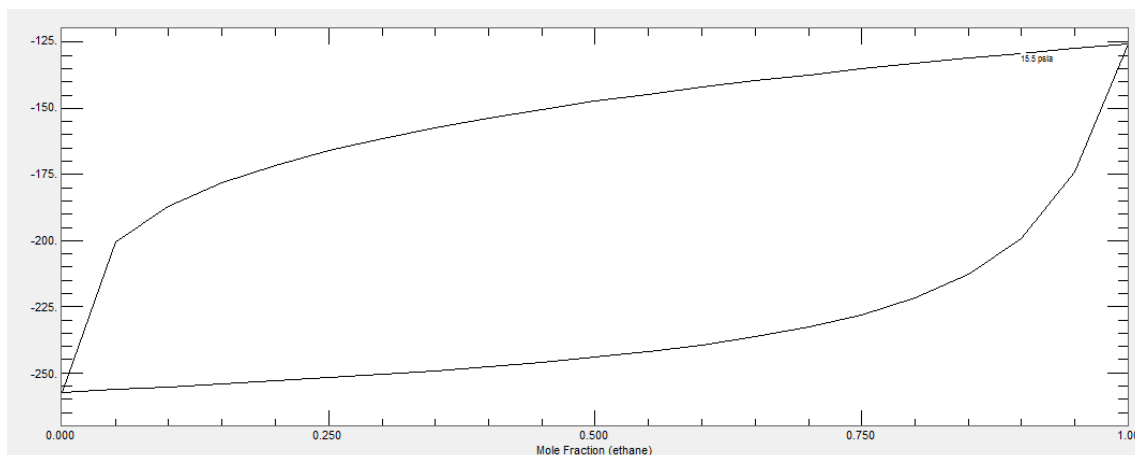


Figure 73: Tx diagram for all ethane methane LNG mixtures.

Take note, this is a reverse image of the graph shown in Figure 69. However, the X axis here is mole fraction of ethane while the X axis of Figure 69 is mole fraction of methane.

Next on the REFPROP menu select “Plot” and then Ph Diagram. Adjust the parameters until you get the plot shown in Figure 74.

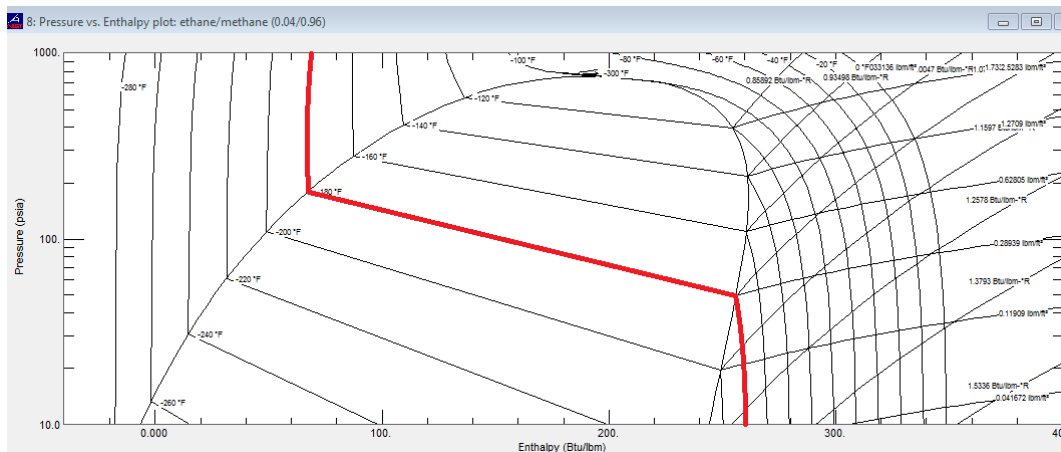


Figure 74: Ph Diagram for 96/4 methane ethane LNG mixture.

Note, the change of phase does not occur at a constant temperature and constant composition. Instead, the temperature and composition changes as the LNG converts to vapor. In this figure the constant temperature line of -180 F has been highlighted. Note, the lines under the dome are shown by the software as straight lines “only” because the computer has been instructed to connect the saturated and liquid temperature lines. If the software was instructed to compute these lines, they would have been curved lines. (ANSWER)

For those who want to duplicate the plot shown in Figure 74 the data ranges for this plot are shown in Figure 75.

Setup Pressure vs. Enthalpy Plot

Temperature (°F)	Density (lbm/ft³)	Entropy (Btu/lbm·R)	Quality
From: -300	From: 1	From: -0.2	From: 0
To: 7	To: 40	To: 2	To: 1
Step: 20	Step: 1	Step: 0.2	Step: 0.25
<input type="checkbox"/> Show 2-phase	<input type="checkbox"/> Show 2-phase	<input type="checkbox"/> Show 2-phase	
Additional values	Additional values	Additional values	Additional values

Axis scaling
 x-Axis Range: -40 to 400 Btu/lbm Enthalpy
 y-Axis Range: 10 to 1000 psia Pressure

Point spacing
☐ Coarse
☒ Medium
☐ Fine
☐ Very fine

Labels
☒ Include labels
☒ with units
☐ Unlabeled Lines

Options
☒ Draw saturation lines
☐ Draw melting line
☒ Connect saturation states
☐ Swap density for specific volume
☒ Add s and v lines at saturated temp.
☐ Skip critical region calculations

OK Cancel Less

Figure 75: Data ranges used to plot the Ph diagram in Figure 74.

If your screen does not look as large as this, you may not have selected more on the earlier screen. For the production of the diagram of Figure 74, either the “more” or the “less” of the above display can be used.

As stated in Figure 74 the lines within the dome are shown as straight lines only because the software has been instructed to connect the temperature points between the saturated liquid and saturated vapor lines and does so with straight lines. They are not in fact, straight lines! If you want to view the actual contour of these lines you will need to check the box that reads “show 2 phases” as checked and highlighted by a circle in Figure 76. In Figure 76, to avoid graph clutter only the temperature lines were plotted as shown in Figure 77.

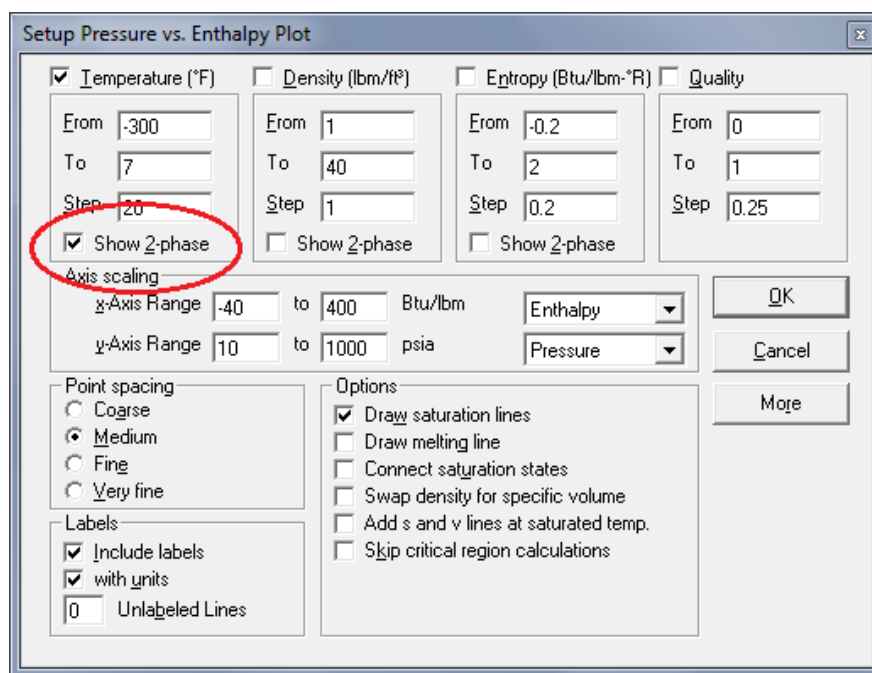


Figure 76: Data ranges used to plot the Ph diagram in Figure 77. Note, that the “Show 2 phase” box has been selected.

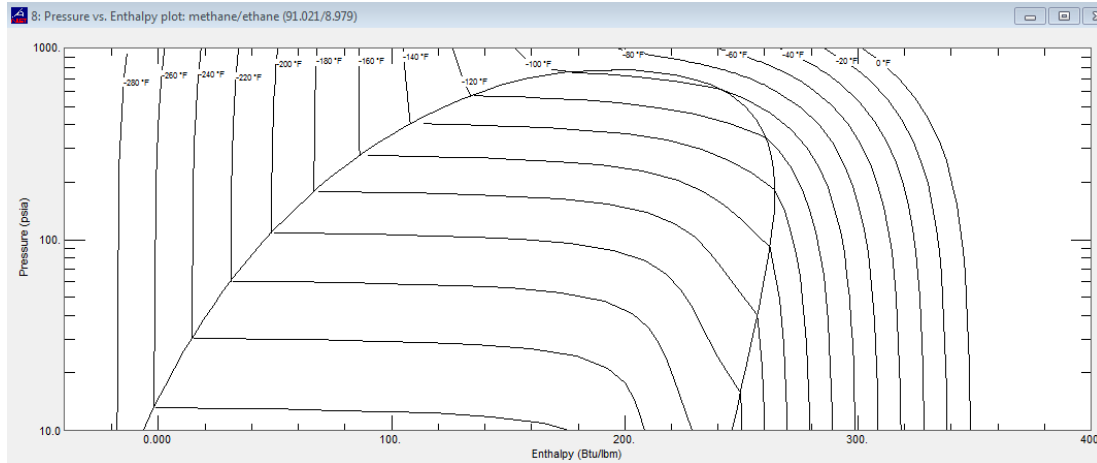


Figure 77: Ph diagram resulting from data input of Figure 76.

Note, temperature lines within the dome for a mixture are curved. This is the actual computed values of temperature/pressure vs. enthalpy.

1.5 Problem # 2.3 – Recondenser Operation Analyzed via Ph Diagram

- You have -254 F and 100 psia LNG entering a condenser operating at 65 psia (JT valve at the inlet).
- You have -130 F vapor entering the same vessel
- How much vapor can you condense if your LNG flow rate into the condenser is 100,000 lbm/hr. and the LNG leaving the condenser is -227 F.
- Use the 1962 Published Ph Diagram to solve this problem. Later we will duplicate this work using the REFPROP software.
- Take note, the term “condenser” and “recondenser” are used interchangeably.
- Use methane for this analysis. Assume SSSF conditions for this analysis.

1.6 Solution # 2.3

What do the pictures in Figure 78 have in common? Some people think they are both magic! (ANSWER). We can not explain the image on the left, but the operation of the recondenser on the right can be clearly explained by thermodynamic analysis.



Figure 78: Some people do not understand how a recombiner works.

It is not magic. Superheated vapor goes in and subcooled liquid goes in. Then slightly subcooled LNG leaves the recombiner.

As shown in Figure 79 the in-tank pump produces subcooled LNG. This subcooled LNG is sprayed in intimate contact with superheated vapor which is condensed. The subcooled LNG becomes less subcooled as it cools down and then condenses the originally superheated vapor.

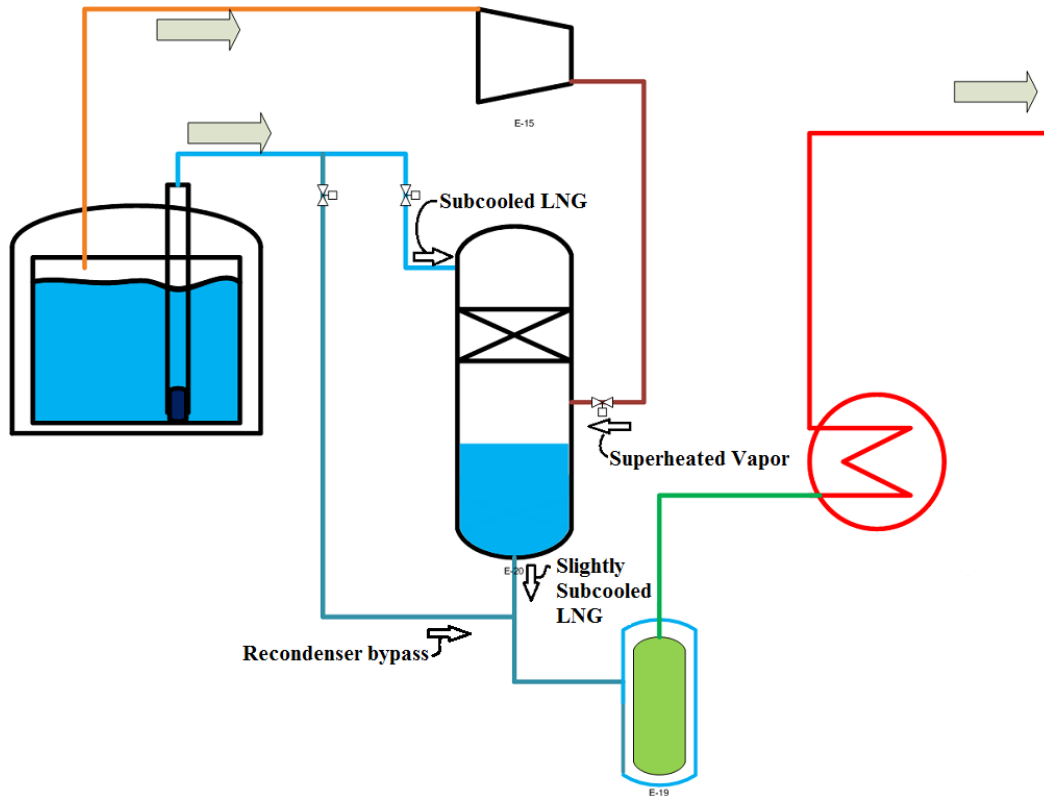


Figure 79: Some people do not understand how a recondenser works.

It is not magic. Superheated vapor goes in and subcooled liquid goes in. Then slightly subcooled LNG leaves the recondenser.

A good way to understand the operation of a recondenser is to picture a room filled with superheated or saturated steam at or above 212 F. If 50 F water (subcooled) were to be sprayed into that steam, the steam would condense and collect on the floor of the room. The water would heat somewhat (perhaps raise in temperature to 70 F) and become less subcooled. The total mass leaving the room would be the sum of the water sprayed and the water condensed. This is shown in Figure 80.

In order for a recondenser to work, the LNG injected into the recondenser needs to be subcooled. If in Figure 81 the water sprayed is at the saturation temperature, then NO condensing would be taking place.



Figure 80: Cold water sprayed on steam condenses the steam.



Figure 81: If the water sprayed is not subcooled, then NO condensation would take place.

Figure 82 is a review of the parameters of the pressure enthalpy diagram. Figure 83 shows how the outlet of the in-tank pump provides subcooled LNG which is used to condense boil off vapor in the recondenser.

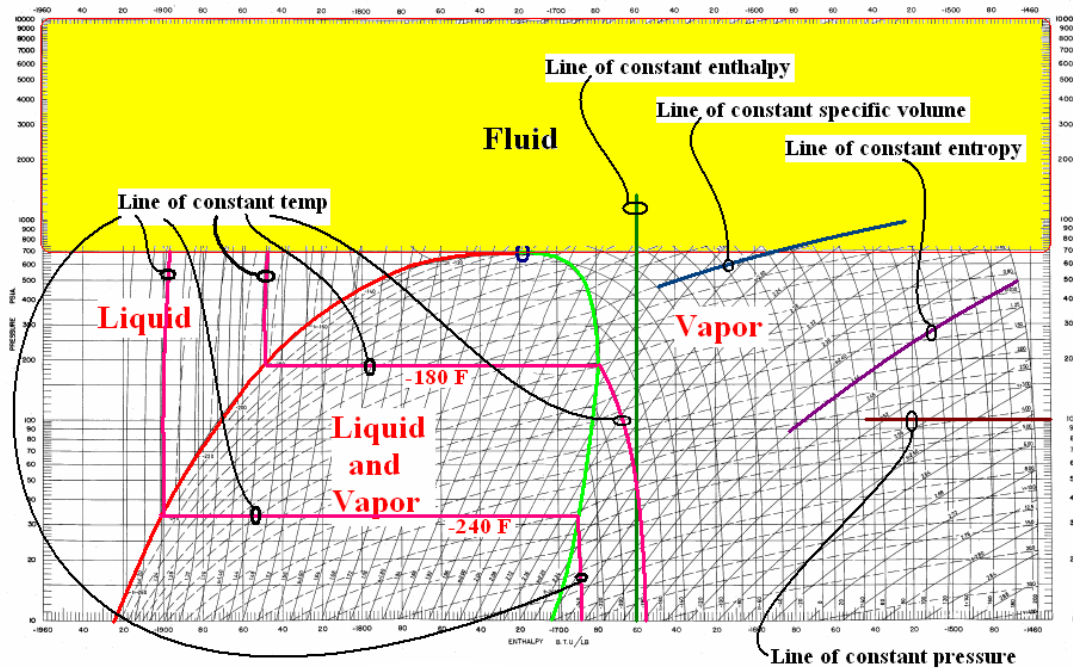


Figure 82: Review of the pressure enthalpy diagram.

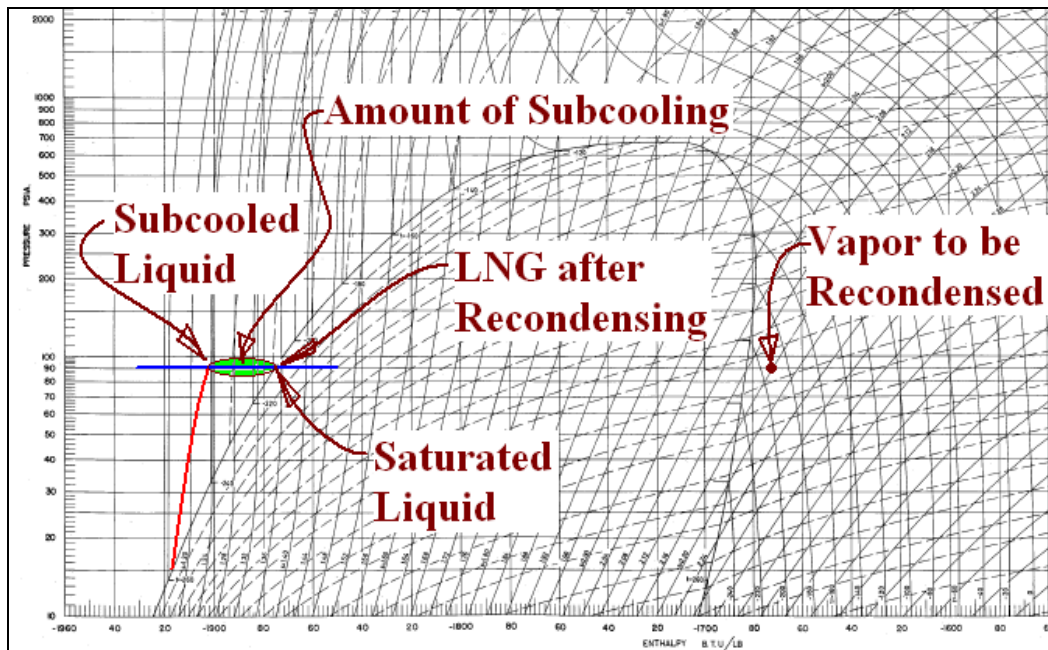


Figure 83: Pressure enthalpy diagram showing the output of the in-tank pump is subcooled LNG which is used to condense boil off vapor in the recombiner.

This drawing shows the maximum amount of recondensing. In actual condensers, the LNG leaving is subcooled.

Figure 84 is a close up view of the pressure enthalpy diagram showing the inlet to the in-tank pump (point 23), the outlet of the 1st stage pump (point 25), the inlet of the LNG to the Recondenser (point 26 – having the same enthalpy as point 25), the outlet of the recondenser (point 27), and the inlet of the 2nd stage pump (point 28 which is a mixture of the outlet of the recondenser and the recondenser by-pass).

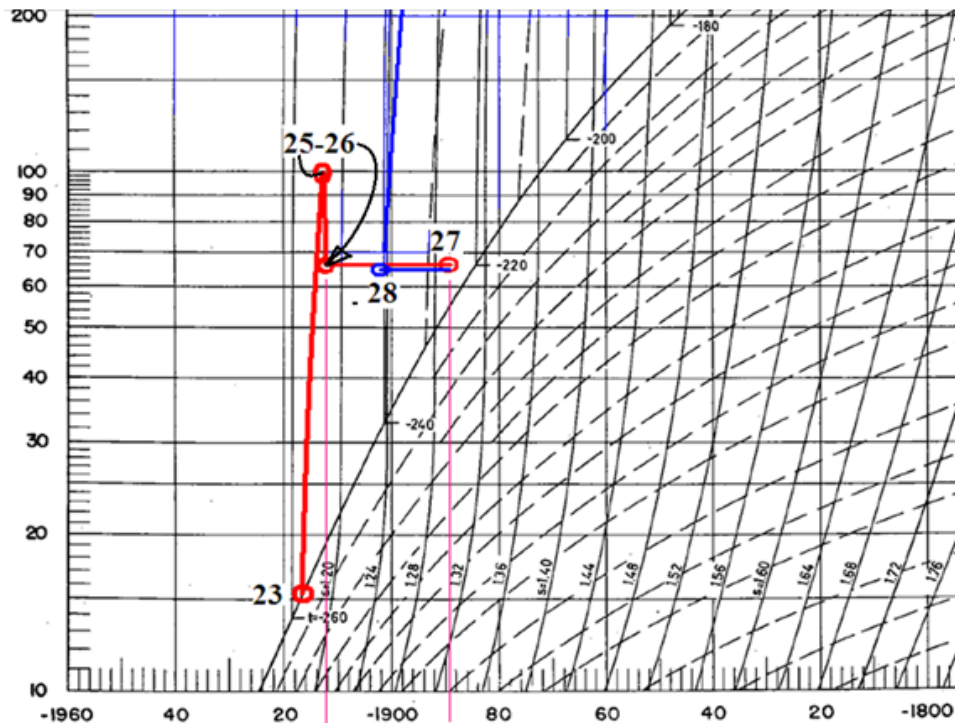


Figure 84: Ph diagram showing liquid flows into and out of the recondenser.

Per the mass-energy balance the LNG flow into the recondenser is 100,000 lb/hr (assume recondenser inlet LNG to be -254 F and 100 psia and outlet to be -227 F and 65 psia). How much heat was absorbed in an hour going from point 26 to 27? Point 26 is read on the chart to be at an enthalpy of -1912 Btu/lbm (identical enthalpy as point 25) and point 27 is read on the chart to be at an enthalpy of -1889.5. $100,000 \text{ lbm/hr} \times (1912 - 1889.5) \text{ Btu/lbm} = 2,250,000 \text{ Btu/hr}$ which can be used to condense vapor. How much vapor (@-130 F) can that heat removal condense?

Let's again look at the Ph diagram. Look at point 22 which shows vapor into the recondenser (See Figure 85).

T= -130 F and P= 65 psia. The enthalpy is = -1636 Btu/lbm.

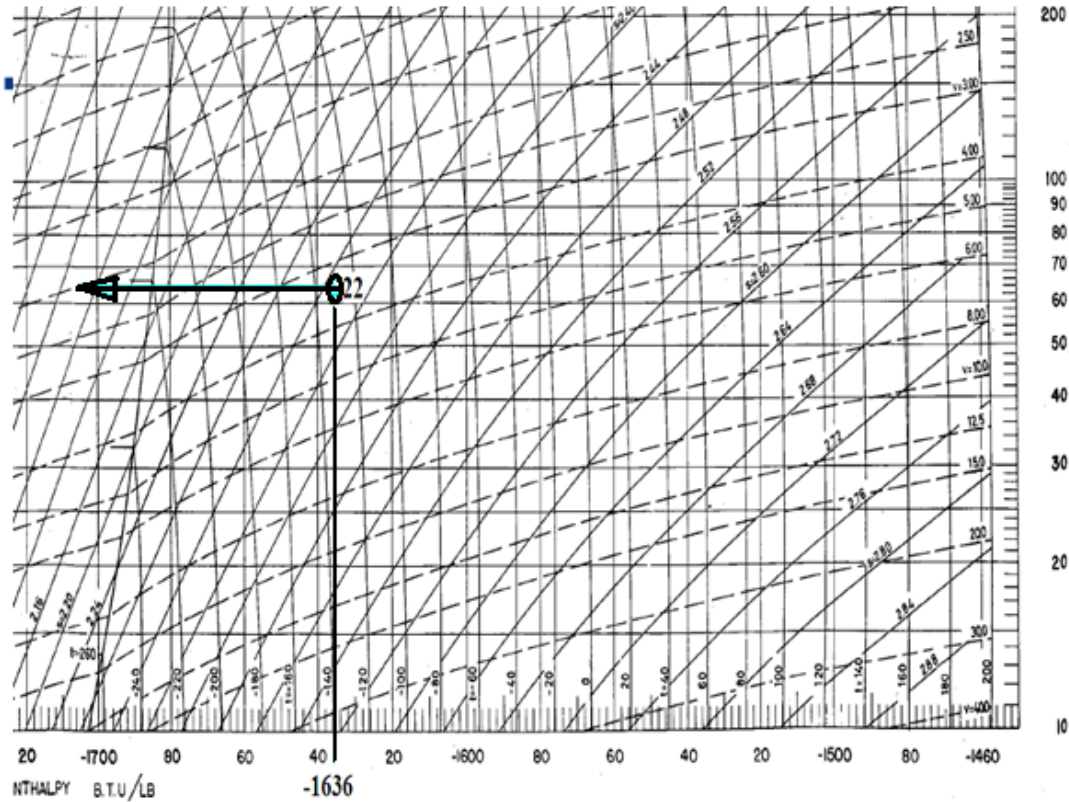


Figure 85: Ph Diagram showing vapor flow into the recondenser.

Per the Ph diagram, each lbm of vapor is condensed to point 27 conditions (65 psia and -227 F) would require $(1889.5 \text{ Btu/lbm} - 1636 \text{ Btu/lbm}) = 253.5 \text{ Btu/lbm}$.

- We have available 2,250,000 Btu/hr for condensing vapor.
- Thus, we can condense 8,876 lbm/hr of vapor per hour $((2,250,000 \text{ Btu/hr})/253.5 \text{ Btu/lbm})$ (ANSWER)
- This means 108,876 lbm/hr of LNG (slightly subcooled) leaves the condenser. (ANSWER)

1.7 Problem # 2.3.1 – Recondenser Operation Analyzed via REFPROP (Same problem as 2.3 but now we will use REFPROP to solve)

- You have -254 F and 100 psia LNG entering a condenser operating at 65 psia
- You have -130 F vapor entering the same vessel

- How much Vapor can you condense if your LNG flow rate into the condenser is 100,000 lbm/hr. and the LNG leaving the condenser is -227 F.
- For this exercise we will continue to use the default REFPROP reference state. If you have not already reset back to the default reference state do so by selecting “Options” and then selecting “Reference State” and then selecting “Use Default Reference State” and then selecting “Ok”.
- Use REFPROP to solve this problem. Earlier we used a Ph diagram to solve this problem.
- Use methane for the analysis and assume SSSF conditions.

1.8 Solution # 2.3.1

This is the exact same problem as problem # 2.3, however, this time you are asked to use REFPROP instead of the published Ph diagram to solve the problem. You will note that using the default reference state will result in very different enthalpy values, but with the same delta enthalpy values.

Figure 86 shows the recondenser process on the Ph diagram and Figure 87 shows the liquid and vapor data for flows in and out of the recondenser.

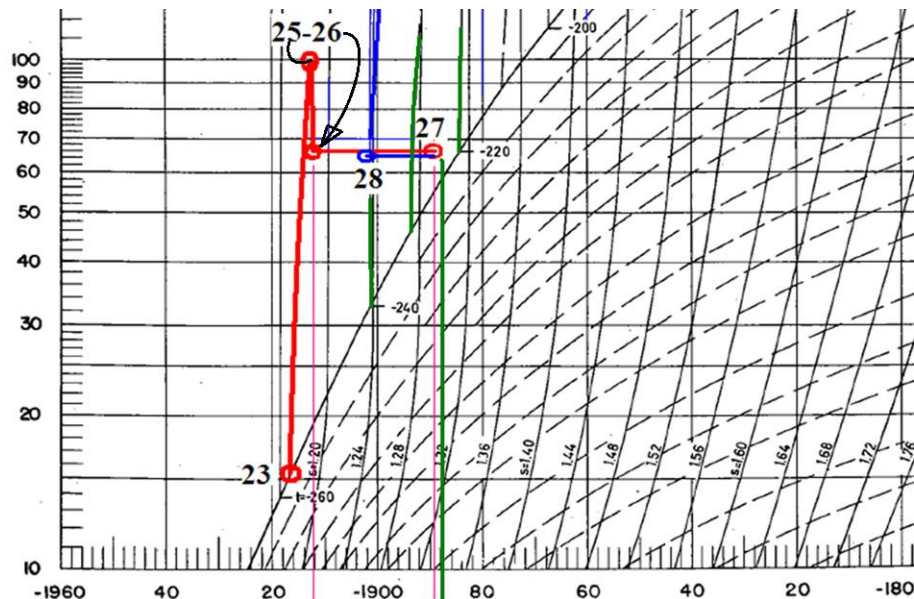



Figure 86: Ph diagram showing liquid flows into and out of the recondenser.

 **1: methane: Specified state points**

	Temperature (°F)	Pressure (psia)	Density (lbm/ft³)	Enthalpy (Btu/lbm)	Entropy (Btu/lbm-°R)
1	-254.00	100.00	26.164	4.2550	0.017969
2	-253.82	65.000	26.140	4.2550	0.019174
3	-227.00	65.000	24.683	27.113	0.12351
4	-130.00	65.000	0.30624	281.82	1.1547
5					

Figure 87: REFPROP data showing liquid and vapor flows into and out of the recondenser.

- Delta enthalpy liquid, $\Delta h = 22.858 \text{ Btu/lbm}$ ($27.113 - 4.2550$)
- Heat removed from the injected LNG = $100,000 \text{ lbm/hr} \times (22.858 \text{ Btu/lbm}) = 2,285,800 \text{ Btu/hr}$.
- Delta enthalpy vapor to liquid = 254.707 Btu/lbm ($281.82 - 27.113$)
- Condensed vapor = $(2,285,800 \text{ Btu/hr}) / (254.707 \text{ Btu/lbm}) = 8,974 \text{ lbm/hr}$. (Answer)
 - Note, this answer is approx. 1% different than our graphical result. This is due to the inaccuracy of chart reading and round off.
- This means $108,974 \text{ lbm/hr}$ of LNG (slightly subcooled) leaves the condenser. (Answer)
- Check the answer by doing a 1st law of thermodynamics energy balance around the entire recondenser (energy in = energy out for SSSF process). Check: $100,000 \text{ lbm/hr} \times 4.255 \text{ Btu/lbm} + 8974 \text{ lbm/hr} \times 281.82 \text{ Btu/lbm} = 108,974 \text{ lbm/hr} \times 27.113 \text{ Btu/lbm}$
- Check: $425,500 \text{ Btu/hr} + 2,529,053 \text{ Btu/hr} = 2,954,612 \text{ Btu/hr}$.
- $2,954,553 \text{ Btu/hr} = 2,954,612 \text{ Btu/hr}$. Check! (an error of 0.002% is due to round off)

1.9 Problem # 2.4 – Explaining 2nd Stage Pump Fluid Enthalpy Change

- You are examining your 2nd stage pump. The pump curve shows that you are putting in shaft work of 2800 hp for the present flow rate.
- You check the temperature and pressure of the flow and you find the delta enthalpy to be $7,920,000 \text{ Btu/hr}$. ($\Delta h \times \text{flowrate}$).
- Using your pocket reference book page 779 this comes to $7,920,000 \text{ Btu/hr} \times 0.000393 \text{ hp-hr/Btu}$ which is 3113 hp.
- Explain to the director of operations why there is a discrepancy.

110 Solution # 2.4

- What happened to the motor heat?
- The motor is 90% efficient. This means only 90% of the electrical input gets converted shaft work. The remainder of the energy (inefficiency) goes into heating the LNG just as if you had a heater in the LNG. Thus, the measured temperature increase came from both shaft work and motor heat.
- $3,113 \text{ hp} \times 0.90 = 2,801 \text{ hp}$ (This matches the pump curve work so this is viable reason why the numbers do not match). (Answer)
- Could another possible reason that the values don't match? Could it be because the temperature sensors could be wrong?
- Look at REFPROP (75% eff pump) and investigate how much error is caused by just 1 F error in the temperature reading? (See data shown in Figure 88)
- 6.6 % error is caused by a temperature reading error of only 1 deg F! That is 13.2285 Btu/lbm vs. 12.4105 Btu/lbm of energy added to the fluid. 6.6% of 3,144 hp is an error of 208 hp!
- Thus another possible reason for the values don't match is because the temperature sensors could be slightly wrong. However, the inefficiency is clearly a reason and the temperature sensor issue was explored just to show the learner how sensitive the findings are to field data. (Answer)



2: methane: Specified state points

	Temperature (°F)	Pressure (psia)	Density (lbm/ft³)	Enthalpy (Btu/lbm)	Entropy (Btu/lbm-°R)
1	-255.00	75.000	26.204	3.3145	0.014247
2	-250.67	1400.0	26.516	12.622	0.014247
3	-246.87	1400.0	26.338	15.725	0.028963
4	-245.87	1400.0	26.291	16.543	0.032798
5					

Figure 88: REFPROP data showing how an error of 1 F in sensor data (line 3 vs. 4) can change the pump power calculation by 6.6% (delta h due to 1 F difference in temperature).

1.11 Problem # 2.5 – Analyzing Heat Gain During LNG Circulation to Offshore then to the 2nd Stage Pump

A 2nd stage pumps can seize if we do not provide LNG with sufficient subcooling.

- Assuming that the feed to the 2nd stage pumps comes from the return line from offshore, at what rate do we need to circulate LNG offshore and back in order to provide various subcooling temperatures at the inlet to the 2nd stage pump?
- Use liquid methane for order of magnitude answers. Assume SSSF conditions.
- Assume booster pump outlet (in-tank pump) is at 90 psia and -255F and the pressure drop across circulation piping to 2nd stage pumps is 15 psig

1.12 Solution # 2.5

- Assume your piping from booster pump to the 2nd stage pump is a total of 4 miles of “on average” 32” diameter pipe with 6” of insulation. That is approx. 21,000 feet of pipe with a exterior surface area (32”+12” = 44” dia, A/lin ft. = $\pi(44/12)$) of 11.5 sq.ft. per linear foot of pipe.
- Assume a heat leak of 8.5 Btu/sq.ft.-hr (based on exterior pipe area)
- That means that 21,000 feet of 32” pipe adds (21,000 lin ft x 11.5 sq ft/lin ft x 8.5 Btu/hr-ft²) = 2,052,750 Btu/hr.
- The volume of a 32” pipe is 5.585 cu. ft./ lin ft. ($\pi(16/12)^2$ /lin ft)
- From the above data, the table in Figure 89 can be populated.

Flow rate	Flow rate	Volumetric Flow	Fluid Velocity	Round Trip Time
GPM	lbm/hr.	ft ³ /hr.	ft./hr.	hours
500	105,117	4010	718	29.2
1,000	210,234	8021	1436	14.6
1,500	315,351	12031	2154	9.7
2,000	420,468	16042	2872	7.3
2,500	525,585	20052	3590	5.8
3,000	630,702	24062	4308	4.9

Figure 89: Calculation data for various circulation flows, velocities, and hours to make one circulation.

Using the data shown in Figures 89, REFPROP is used as shown in Figure 90 to determine the temperature of the LNG entering the 2nd stage pumps. This data is further shown in Figure 91.



1: methane: Specified state points

	Temperature (°F)	Pressure (psia)	Density (lbm/ft³)	Enthalpy (Btu/lbm)	Entropy (Btu/lbm-°R)
1	-255.00	90.000	26.211	3.3781	0.014040
2	-231.89	75.000	24.967	22.906	0.10491
3	-243.31	75.000	25.593	13.142	0.060940
4	-247.16	75.000	25.797	9.8875	0.045761
5	-249.09	75.000	25.899	8.2601	0.038068
6	-250.26	75.000	25.959	7.2837	0.033418
7	-251.03	75.000	26.000	6.6328	0.030304
8					

Figure 90: REFPROP data using energy input into the LNG and data from Figure 89 and the final pressure of 75 psia. Example line 3 computes from $((2,052,750 \text{ Btu/hr})/210,234 \text{ lbm/hr}) = 9.76 \text{ Btu/lbm}$. Inlet enthalpy + 9.76 Btu/lbm = $(3.3781 + 9.764) \text{ Btu/lbm} = 13.142 \text{ Btu/lbm}$.

Flow rate	Flow rate	Heat Added/lbm	Circulation Loop Inlet Temperature	Return Temperature
GPM	lbm/hr	Btu/lbm	Deg F	Deg F
500	105,117	19.5	-255	-232
1,000	210,234	9.8	-255	-243
1,500	315,351	6.5	-255	-247
2,000	420,468	4.9	-255	-249
2,500	525,585	3.9	-255	-250
3,000	630,702	3.3	-255	-251

Figure 91: Data showing increase in enthalpy per lbm, start and return temperature. Based on data from Figure 90. (ANSWER)


1.13 Problem # 2.6 – Horsepower of 2nd Stage Pumps

How much horsepower does a XYZ second stage pump require at design conditions?

1.14 Solution 2.6

Look at the Mass/Energy Balance and read the inlet and outlet state conditions (pressure and temperature). Use liquid methane for the analysis.

- Then use REFPROP to determine the change in enthalpy.
- Then multiply the delta h by the mass flow rate and get an answer in Btu/hr
- Use the black book pocket reference conversion factor (page 779), or any other conversion factor reference, to convert this to hp.
- Then adjust for heat gained via motor losses (use motor efficiency).

 **1: methane: Specified state points**

	Temperature (°F)	Pressure (psia)	Density (lbm/ft³)	Enthalpy (Btu/lbm)	Entropy (Btu/lbm-°R)
1	-241.20	64.630	25.474	14.893	0.069340
2	-230.50	1415.4	25.559	29.257	0.089725
3					

Figure 92: REFPROP enthalpy data using pressure and temperature data from a mass energy balance (Line 1 = pump inlet, Line 2 = pump outlet).

- The pump puts 14.364 Btu of energy into each lbm (See Figure 92 and subtract pump inlet enthalpy from pump outlet enthalpy) $((29.257 - 14.893) \text{ Btu/lbm})$.
- The pumps are moving 1,658,680 lbm/hr (from mass energy balance), therefore the pumps are adding 23,825,280 Btu/hr to the flow $(1,658,680 \text{ lbm/hr} \times 14.364 \text{ Btu/lbm})$
- Using the little black book pocket reference (page 779), or an other conversion factor reference, we multiply $23,825,280 \text{ Btu/hr} \times 0.000393 \text{ hp-hr/Btu} = 9,363 \text{ hp}$.
- The mass energy balance states that 3 pumps are being used to pump this flow. These 3 pumps require 9,363 hp or 3,121 hp each.
- This seems high and compared to the pump curve which shows about 2,800 hp. Think about why?

- The fluid appears to have picked up approx. 3,121 hp of energy yet we think the shaft hp is about 2,800 hp.
- Where did the extra energy come from?
- If the motor is only 90% efficient, then only 90% of the 3,121 hp gets to the shaft for pumping and the rest just heats the fluid
- **$3,121 \times 0.9 = 2,809$ shaft horsepower (this matches well the pump curve for this pump (2800 hp)).** (ANSWER)

1.15 Problem # 2.7 – Compressor Power and Temperature Changes with Gas Composition Change

How much horsepower is required and what is the temperature outlet if an 80% efficient gas compressor compresses 5 MMscf/d of pure methane or a mix of 80% methane and 20% nitrogen from 60 F and 25 psia to 80 psia (like in the first stage of a BOG to pipeline compressor). Assume STP is 60 F and 14.696 psia. Assume SSSF conditions.

1.16 Solution # 2.7

Mass Flow Rate Analysis

3: methane: Specified state points						
	Temperature (°F)	Pressure (psia)	Density (lbm/ft³)	Enthalpy (Btu/lbm)	Entropy (Btu/lbm-°R)	
1	60.000	14.696	0.042359	382.45	1.5781	
2						


1: methane/nitrogen: Specified state points (0.8/0.2)						
	Temperature (°F)	Pressure (psia)	Density (lbm/ft³)	Enthalpy (Btu/lbm)	Entropy (Btu/lbm-°R)	
1	60.000	14.696	0.048659	305.38	1.6465	
2						

Figure 93: REFPROP data showing standard conditions of pure methane and an 80/20 mix of methane nitrogen.

- For pure methane, the mass flow is $[(5,000,000 \text{ scf/d})/(24 \text{ hr/d})] \times (0.042359 \text{ lbm/cu.ft.}) = 8,825 \text{ lbm/hr.}$
- For 80% methane with 20% nitrogen, (see Figure 93) the mass flow is $(5,000,000 \text{ SDF/d})/(24\text{hr/day})] \times (0.048659 \text{ lbm/cu.ft.}) = 10,137 \text{ lbm/hr}$ This is 14.9% more mass compressed as compared to the pure methane case (interesting).

Analysis of Compression Using 100% Methane


- Use REFPROP and use the inlet conditions of 60 F and 25 psia and an outlet pressure of 80 psia to determine the power required per lbm.
- First we will analyse an isentropic compression. Take note that the entropy was held constant and thus, for the outlet conditions we defined the same entropy as the inlet along with the outlet pressure of 80 psia (See the REFPROP results in Figure 94)
- This isentropic compression would have required 85.49 Btu/lbm (delta enthalpy) and the outlet temperature would be 216 F

 **3: methane: Specified state points**

	Temperature (°F)	Pressure (psia)	Density (lbm/ft³)	Enthalpy (Btu/lbm)	Entropy (Btu/lbm-°R)
1	60.000	14.696	0.042359	382.45	1.5781
2					
3	60.000	25.000	0.072158	382.13	1.5119
4	215.71	80.000	0.17771	467.62	1.5119

Figure 94: REFPROP data showing constant entropy compression of pure methane from 25 psia to 80 psia (enthalpy increase is $467.62 - 382.13 = 85.49 \text{ Btu/lbm}$).

- Assuming an 80% efficiency of the compressor tells us that the real enthalpy increase should be $((85.49 \text{ Btu/lbm})/0.8)$ which is 106.86 Btu/lbm.
- Thus, the outlet properties should be a pressure of 80 psia and an enthalpy of 488.99 $(382.13 + 106.86) \text{ Btu/lbm}$.
- Plug this into REFPROP (See Figure 95) and it shows that the real work in is 106.86 Btu/lbm and the real temperature is 252 F.

 3: methane: Specified state points

	Temperature (°F)	Pressure (psia)	Density (lbm/ft³)	Enthalpy (Btu/lbm)	Entropy (Btu/lbm-°R)
1	60.000	14.696	0.042359	382.45	1.5781
2					
3	60.000	25.000	0.072158	382.13	1.5119
4	215.71	80.000	0.17771	467.62	1.5119
5					
6	251.52	80.000	0.16862	488.99	1.5427
7					


Figure 95: REFPROP data showing real world compression of pure methane from 25 psia to 80 psia (enthalpy increase is = 106.86 Btu/lbm).

- **The outlet temperature has already been found to be 252 F.** (ANSWER)
- Work required is mass flow rate x energy added to each lbm.
 - Work in = 8,825 lbm/hr x 106.86 Btu/lbm = 943,040 Btu/hr
 - Look up the conversion on page 779 of black book pocket reference.
 - **Horsepower required is 370 hp.** (ANSWER)

Analysis of Compression Using an 80/20 mix of methane and nitrogen

Now let's do the same exercise using a mixture of 80% methane and 20% nitrogen. In REFPROP select "Substance" and then "Define New Mixture". Then select an 80/20 **molar** mixture of methane and nitrogen.

Caution, if you do not select a **molar** mixture, your answers will be different than that shown in the following:

 1: methane/nitrogen: Specified state points (0.8/0.2)

	Temperature (°F)	Pressure (psia)	Density (lbm/ft³)	Enthalpy (Btu/lbm)	Entropy (Btu/lbm-°R)
1	60.000	14.696	0.048659	305.38	1.6465
2					
3	60.000	25.000	0.082867	305.15	1.5889
4	223.08	80.000	0.20175	380.00	1.5889
5					
6	260.95	80.000	0.19101	398.71	1.6156
7					

Figure 96: REFPROP data showing constant entropy compression of an 80/20 mix of methane and nitrogen from 25 psia to 80 psia (enthalpy increase is $380 - 305.15 = 74.85$ Btu/lbm). Then in line 6 the real-world compression is shown by increasing the enthalpy by 93.56 Btu/lbm ($(74.85 \text{ Btu/lbm})/0.8$).

- See Figure 96. If you did not get the same numbers make sure you are specifying a “molar” mixture.
- From Figure 96 it can be seen that the isentropic compression requires 74.85 Btu/lbm ($380 - 305.15$)Btu/lbm.
- Assuming an 80% efficiency tells us that the real enthalpy increase should be $(74.85/0.8)$ Btu/lbm which is 93.56 Btu/lbm.
- Thus our outlet properties should be a pressure of 80 psia and an enthalpy of 398.71 ($305.15 + 93.56$) Btu/lbm.
- Plug this into REFPROP (See Figure 96) and it shows the real work in is 93.56 Btu/lbm and the **real temperature out is 261 F.**

(ANSWER)

Comparing the compression of pure methane to a 80/20 mixture methane nitrogen shows:

- Energy per lbm is less for the mixture (93.56 vs. 106.86)Btu/lbm. This is a 12.4% decrease in in power required for each lbm of the 80/20 mix as compared to pure methane.
- However to move the same volume the compressor needs to move more lbms because the 80/20 mixture of gas is denser at the inlet than the 100% methane case! Thus, to move the same volume of the 80/20 mixture (in scf/hr) it is necessary to move 14.9%

more mass (look at the density difference between the inlet of pure methane and that of the 80/20 mixture).

- Outlet temperature of the 80/20 mixture has already been found to be 261 F.
- Work required for the 80/20 mixture is mass flow rate x energy added to each lbm.
 - 10,137 lbm/hr x 93.56 Btu/lbm = 948,418 Btu/hr.
 - Look up the conversion on page 779 of black book pocket reference.
 - **Horsepower required is 373 hp (this is reasonable). (ANSWER)**

Summary

- Thus, the power to compress the same volume of boil off would be almost the same:
 - **Methane hp required is 370 (ANSWER)**
 - **80/20 mix hp required is 373 (ANSWER)**
- **The temperature of the of the compressed gas would be higher for the 80/20 mixture as compared to the pure methane mixture.**
 - **Methane 252 F (ANSWER)**
 - **80/20 Mixture 261 F (ANSWER)**
- Note both fluids are compressed at the same volume flow rate of 5 MMscf/d but the mass flow rates are significantly different.
 - **Methane 8,825 lbm/hr**
 - **80/20 Mixture 10,137 lbm/hr**

1.17 Problem # 2.8 – Heat Delivered to Water Bath Vaporizers (Similar to Problem # 1.5)

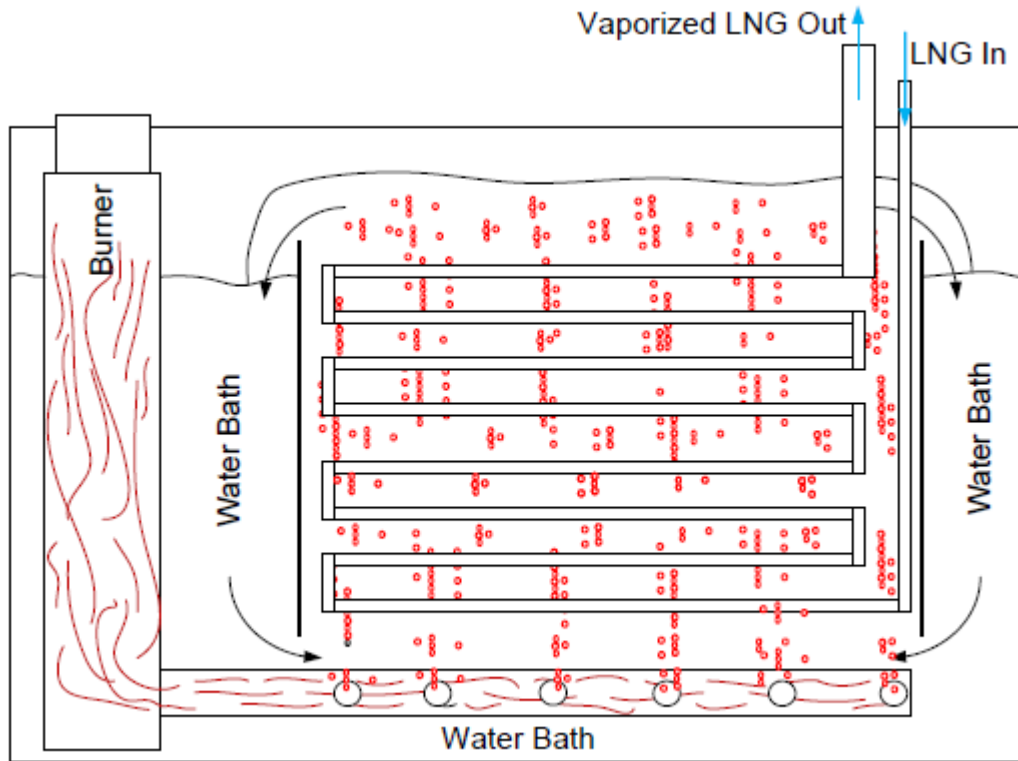



Figure 97: Submerged combustion vaporizer
Source: Self made

How much heat must be delivered to the 90% efficient vaporizers. This is similar to problem 1.5 but with actual plant parameters. Use liquid methane for the analysis.

1.18 Solution # 2.8

- Via mass energy balance, the vaporizer is designed to take 1,618,240 lbm/hr. at -230.4 F and 1417.08 psia and heat it to 39.7 F at an outlet pressure of 1268.39 psia. REFPROP is used to determine the increase in enthalpy of the LNG (technically it is not a liquid but methane fluid – see earlier discussion on fluids over the critical pressure). (See Figure 98)

 **4: methane: Specified state points**

	Temperature (°F)	Pressure (psia)	Density (lbm/ft³)	Enthalpy (Btu/lbm)	Entropy (Btu/lbm-°R)
1	-230.40	1417.1	25.555	29.347	0.090063
2	39.700	1268.4	4.6418	326.99	0.93874
3					

Figure 98: REFPROP data showing heating of pure methane LNG from vaporizer inlet conditions to vaporizer outlet conditions.

- Heat delivered per lbm is 297.6 Btu/lbm (326.99 – 29.347) Btu/lbm
- Why is this lower than the amount we normally calculate when comparing saturated liquid methane at 1 atm to ambient temperature? It is because we normally calculate it from a colder starting temperature (-260 F) and a lower pressure (1 atmosphere).
- The total heat into the LNG for these vaporizers (above case shown in Figure 98) is 1,618,240 lbm/hr. x 297.6 Btu/lbm = 481,657,808 Btu/hr. into the LNG.
- If these vaporizers are 90% efficient, then the burners need to deliver ((481,657,808 Btu/lbm) /0.9) = **535,175,342 Btu/hr. into the vaporizer** (ANSWER).

2. Detailed Use of REFPROP to Better Understand Rollover (Fill and Nitrogen Induced)

2.1 Fill Induced Rollover

- A mixture of dense LNG (97% methane and 3% ethane **molar** mixture (see Figure 100)) is placed under a layer of light LNG (100% methane (see Figure 99)).
 - Both fluids are at saturation temperature of methane at 15.5 psia (-257.5 F)
 - Stratification occurs
 - The bottom layer, unable to cool, gets less and less dense as it heats up.

2: methane: Saturation points (at equilibrium)				
	Temperature (°F)	Pressure (psia)	Liquid Density (lbm/ft³)	Vapor Density (lbm/ft³)
1	-257.50	15.500	26.307	0.1
2				

Figure 99: REFPROP data showing pure methane LNG saturated density as 26.307 lbm/ft³.

6: methane/ethane: Specified state points (0.97/0.03)					
	Temperature (°F)	Pressure (psia)	Density (lbm/ft³)	Enthalpy (Btu/lbm)	Entropy (Btu/lbm·°R)
1	-257.50	24.630	26.862	0.44395	0.0018596
2	-255.00	24.630	26.736	2.4833	0.011885
3	-252.00	24.630	26.584	4.9381	0.023792
4	-250.00	24.630	26.481	6.5795	0.031658
5	-247.00	24.630	26.326	9.0490	0.043353
6	-246.60	24.630	26.306	9.3790	0.044903

Figure 100: REFPROP data showing density of a 97/3 molar mix of methane ethane at various temperatures as it heats up under a head pressure of liquid. The pressure of 26.306 psia was selected as being due to 50' of the upper top layer of pure methane LNG + tank vapor pressure of 15.5 psia.

This had been shown earlier in this book using saturated temperatures of the LNG (see Figure 61). Take note that in this example (Figure 100) we are using “Specified State Points” using a 97/3 molar mixture and in the earlier analysis a 95/5 mass mixture was used for analysis. As can be seen the 97/3 molar and the 95/5 mass mixtures gives nearly the same result since these are close to the same composition. Also, the use of saturated temperatures or specified state points will result in the same findings. This is because the density is a strong function of temperature and a weak function of pressure. The end result of Figure 62 is the same as shown in Figure 101. Rollover results after stratification.

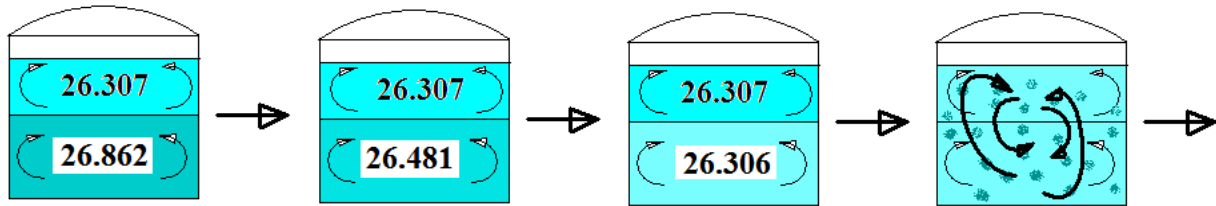


Figure 101: REFPROP data used to depict rollover.

Let's discuss the phenomenon of rollover in a little more detail and use REFPROP to better understand it. In a well-mixed tank of LNG, the temperature and density across the entire tank is nearly uniform. That is because the tank is continuously mixing as shown in Figure 102.

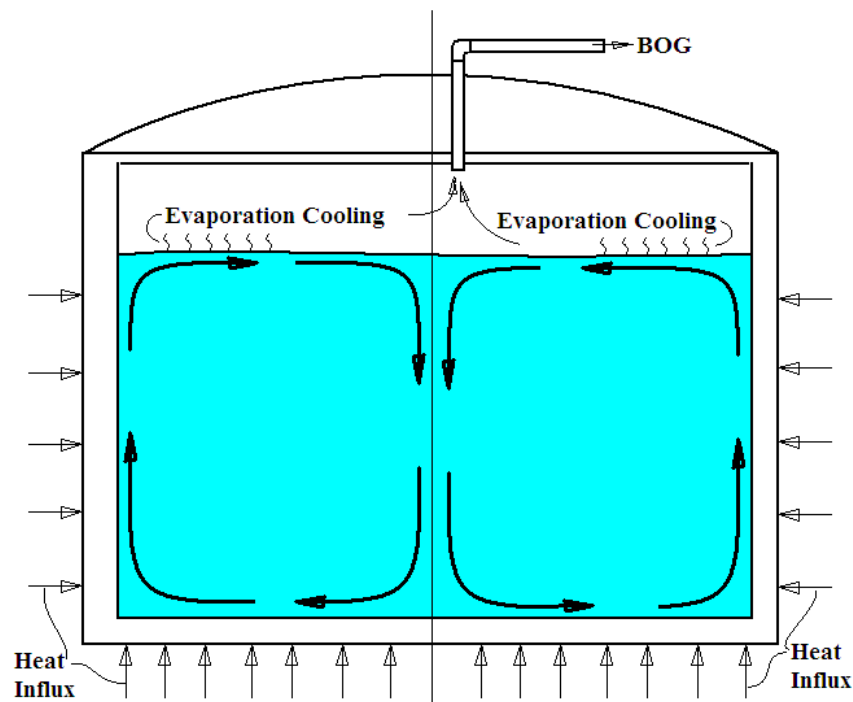


Figure 102: A well-mixed LNG tank.

If a heavy layer (denser layer) of LNG is placed under the light LNG, stratification may occur. This is shown in Figure 103.

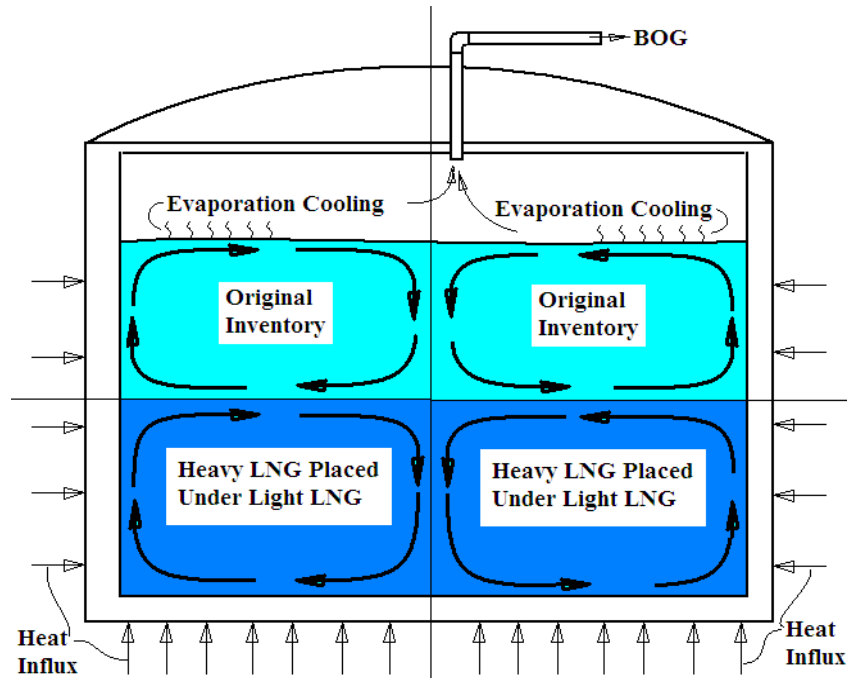


Figure 103: A stratified LNG tank caused by injecting denser LNG under light LNG. The very same type of stratification may occur if light LNG is placed over a denser layer of LNG. This is shown in Figure 104.

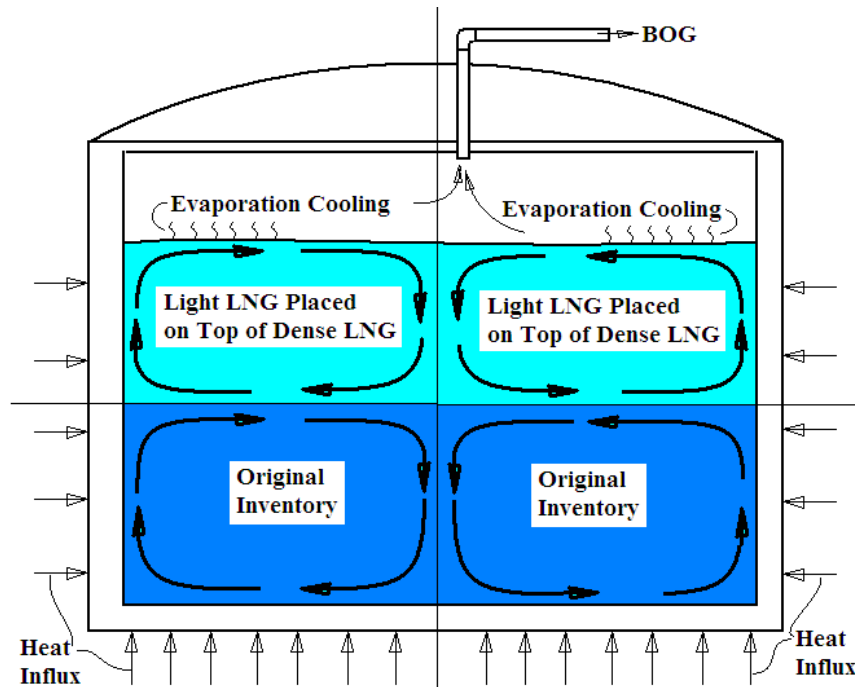


Figure 104: A stratified LNG tank caused by injecting less dense LNG on top of dense LNG.

Regardless of how the stratification was caused, via the mechanism of Figure 103 or Figure 104, the lower layer of the stratified LNG will warm up and become less dense as shown in Figure 105.

In addition, in real world conditions, the upper layer would typically be a mixture of hydrocarbons which becomes heavier over time. This is called “weathering”, whereby light hydrocarbons preferentially outgas from the LNG causing the LNG to become denser.

The increase in density of the top layer, and the decrease in density of the bottom layer, eventually causes an unstable condition in the tank resulting in rapid mixing of the 2 LNG layers.

The density changing of both layers is shown in Figure 105.

It should also be noted, that stratification layering is not limited to only 2 layers. Stratification can occur with many layers in an LNG tank.

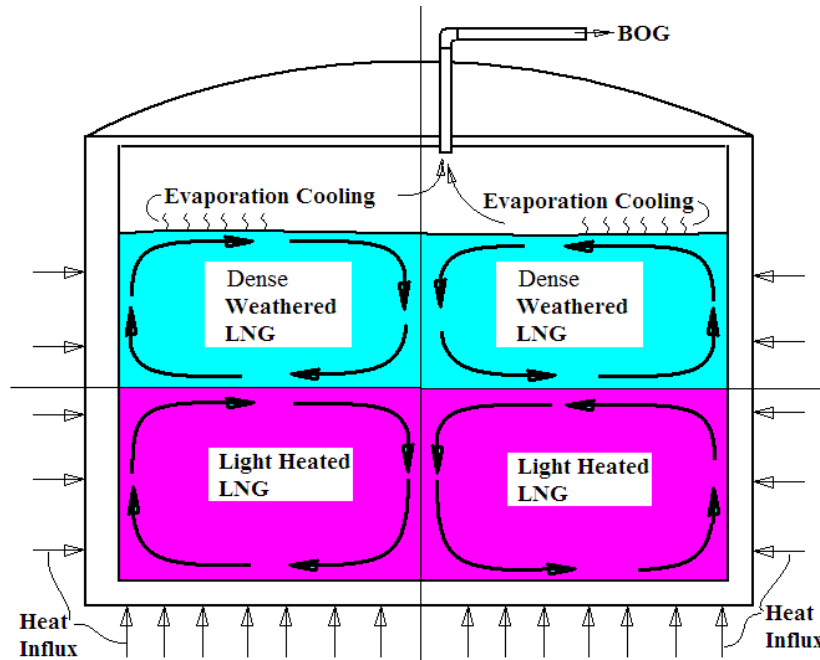


Figure 105: A stratified LNG tank is shown with the top layer becoming denser as the bottom layer becomes less dense.

Once the density of the bottom layer is near that of the top layer, mixing occurs. It is uncertain if the mixing occurs as a layer flip flop mixing as shown in Figure 106 or as a sudden random mixing or as a return to symmetrical mixing as shown in Figure 101 and then Figure 102.

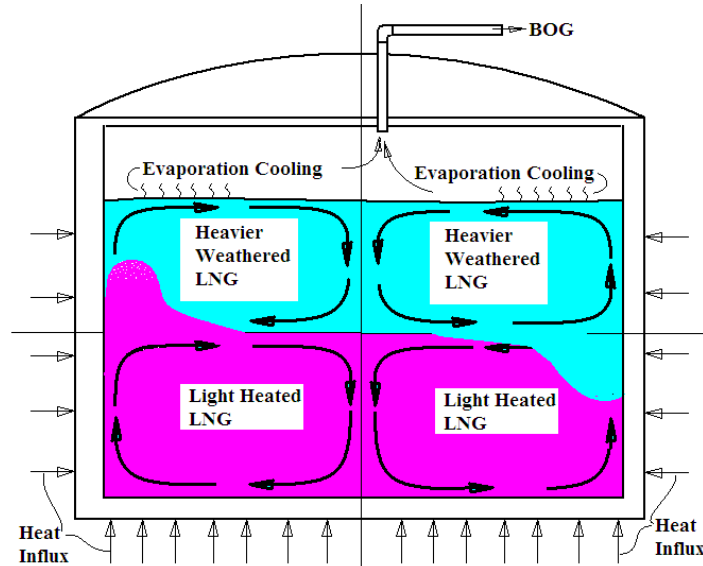


Figure 106: A rollover occurring depicted as a flip flop of the bottom and top layers. It is uncertain if the rollover occurs as a flip flop, or as a random mixing or as a return to the symmetrical mixing shown in Figure 102.

Another phenomenon that may occur is that of the rising LNG beginning to boil before it reaches the surface. This might occur in the event of a flip flop rollover. In this case it is likely at the rollover will be accelerated as the bulk density of the rising fluid causes a rapid convective current upward through the upper layer. This is shown in Figure 107.

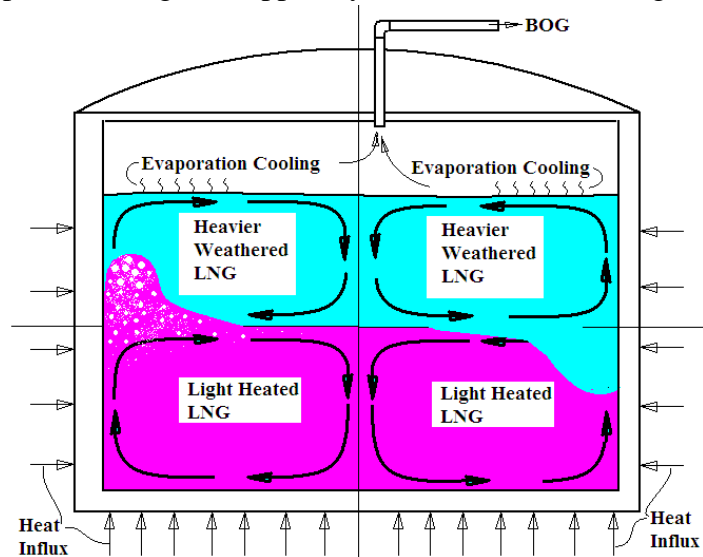


Figure 107: A stratified bubbling rising lower layer may accelerate the rollover as the bulk density of the rising fluid would be greatly reduced with its conversion to vapor.

Another phenomenon that can occur is that the lower layer starts to boil even before the density of the lower liquid becomes lighter than the upper layer. This can happen as the lower layer reaches its bubble point. This phenomenon can cause the “bulk fluid” of the lower layer to penetrate the upper layer even before the liquid portion of the lower layer becomes lighter than the upper layer. This is shown in Figure 108.

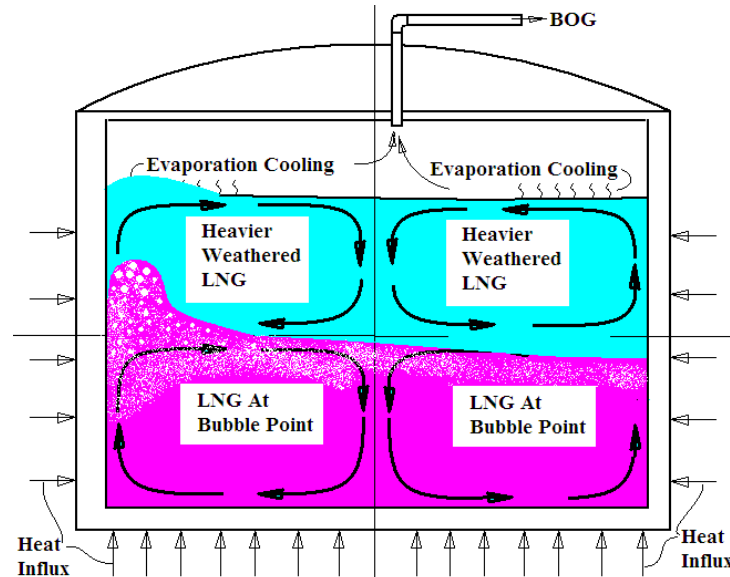


Figure 108: A boiling lower layer can cause the breakdown of stratification even before the lower layer can fully warm to achieve a density less than the upper layer.

Let's use REFPROP to depict the motion of fluid in a well-mixed tank. Assume for modeling purposes that the LNG rising up the side of the tank increases in temperature by 1 F. Using REFPROP we can show how the density changes create convection currents of a well-mixed tank. This is shown in Figure 109. Take note that, as modeled, after the LNG preferentially boils off methane, the density of the remaining LNG (27.178 lbm/ft³) is greater than the bulk density of (27.161 to 27.165 lbm/ft³). As you will see in the next section, this is the opposite of what happens when there is a significant concentration of nitrogen in the LNG.

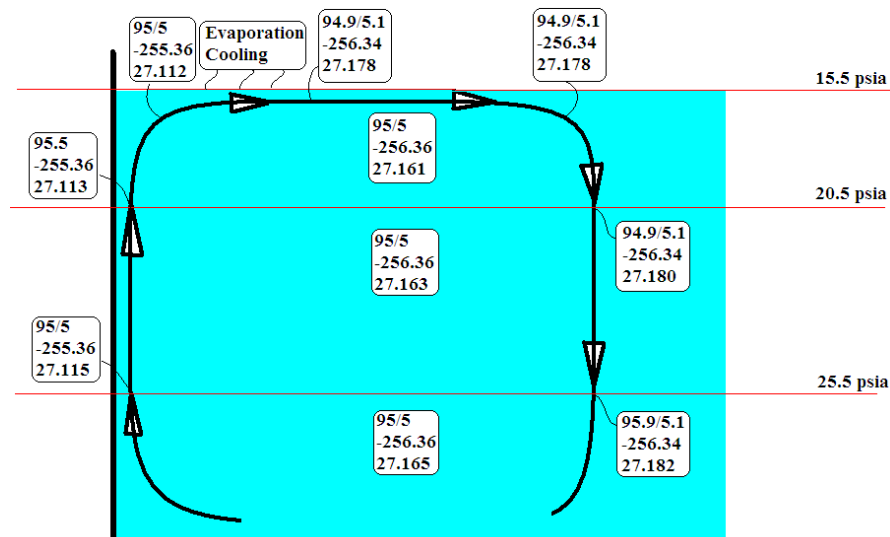


Figure 109: A well-mixed tank modeled by using data from REFPROP to show the temperature and density of the moving fluids. In each of the data boxes the top number is the composition of the mixture, the center number is the temperature of the mixture and the bottom number is the density of the mixture. All density data is from REFPROP.

2.2 Nitrogen Induced Rollover

Another phenomenon that can occur is that of a nitrogen induced rollover. Well mixed LNG containing 1 % or more of nitrogen has been known to self-stratify. This self-stratification is due to the preferential boil off of nitrogen from the LNG. In the case of nitrogen preferential boil off, the LNG becomes lighter instead of heavier when the boil off occurs at the surface of the LNG. This happens for 2 reasons. The first reason is that nitrogen is typically heavier in density than the LNG mixture. Thus, the outgassing of nitrogen would typically lower the density of LNG just because of the density of N_2 (MW =28). The 2nd reason is that as nitrogen boils off of the LNG the saturation temperature increases. The higher temperature causes the LNG to expand thereby becoming less dense.

A crude attempt was made at modeling this using REFPROP as shown in Figure 110. This modeling is by no means an accurate model of the real-world case, but it does show the concept. As can be seen the density of the LNG after evaporating results in a density (27.581 lbm/ft³) which is lighter than the bulk density (27.626 to 27.630 lbm/ft³). Thus, the LNG remaining after the preferential boil off of nitrogen is lighter instead of heavier than the bulk tank density. This is the opposite result that occurred in Figure 109.

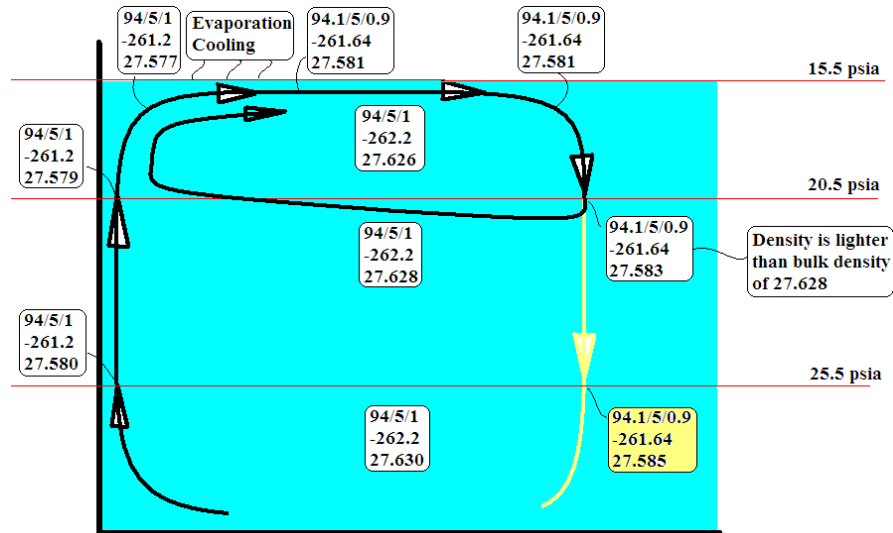


Figure 110: A modeling of the initiation of nitrogen induced stratification.

Once the self-stratification starts, as can be seen in the modeling shown in Figure 111, the upper stratified layer becomes more well defined and stronger layered once the flow recirculates within its own layer. As modeled in Figure 111, this is because the upper layer becomes even more devoid of nitrogen as it recirculates within its own cell. This reinforces the stratification.

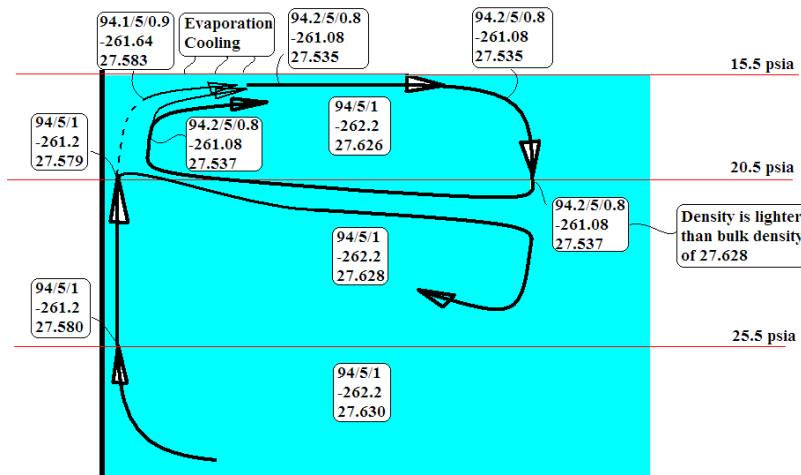


Figure 111: A modeling of the nitrogen induced stratification as the upper layer recirculates within itself.

Once the upper layer is fully formed, the lower layer can no longer be cooled by the surface evaporation and the lower layer begins to circulate within itself and heats up. This heating up can result in one of two rollover initiators. These are 1) the lower layer can become less dense

and cause the layers to mix due to density changes (this is shown in Figure 112 after the lower layer has warmed up) or 2) the lower layer can reach its saturation temperature (its bubble point) and begin to boil causing the layers to mix. In either case, this nitrogen induced rollover can occur. If after the rollover occurs there is still sufficient nitrogen in the LNG to cause self-stratification again, a second and third or more stratifications and subsequent rollovers may occur.

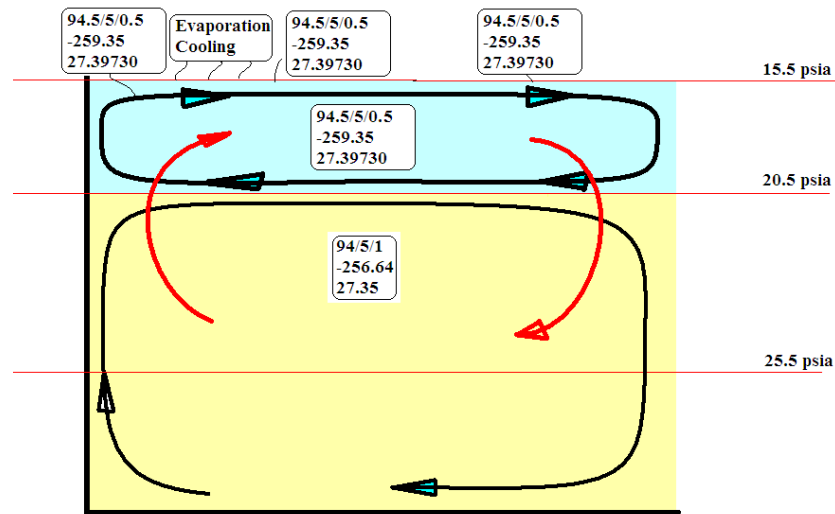


Figure 112: A stratified tank after a prolonged period of stratification has a warmed up lower layer. As shown exaggerated in this figure, the lower layer can become less dense than the upper layer resulting in a rollover.

A review of a nitrogen induced rollover is as follows:

- A well-mixed tank of LNG with a relatively high nitrogen content.
- Nitrogen is preferentially off-gassed at the surface of the liquid.
- The loss of nitrogen at the liquid surface increases the LNG saturation temperature. This and the fact that nitrogen is typically heavier than LNG results in a reduction of density of the top most layer of the LNG.
- The reduction of density at the surface of the LNG causes the tank's natural continuous mixing of LNG to stop and stratification occurs.
- This nitrogen induced stratification then causes a subsequent rollover.
- This typically becomes a more significant concern when the N₂ concentration is 1% or higher

In Figure 113 a conceptual plot of the density of a tank of 89/10/1 methane ethane nitrogen LNG mix is compared to a density plot of a tank of 90/10 methane ethane LNG mix. This modeling was created using REFPROP and is based on some assumptions thought to be

reasonable. In this conceptual analysis both tanks are considered to be fully mixed by forced convection. Although this is conceptual in nature, it mimics the difference in density behavior reported in published rollover literature. The LNG with the nitrogen in it initially becomes less dense over time as the nitrogen is depleted. Then after much of the nitrogen is depleted, the LNG becomes denser over time. The LNG without the nitrogen content becomes denser over time and continues to become denser over time.

In making Figure 113 because in the **90/10 mix** there is not a significant change in the composition of the LNG and its boil off, iteration was not considered necessary. Thus, for this analysis the total mass of the initial LNG was considered as if it was a fixed mass with a growing control volume as the liquid was converted to gas. The entire mix was analyzed as a fixed mass system with the total enthalpy being increased by 2 Btu/lbm per time increment. This is shown in Figure 116.

In making Figure 113 because for the 89/10/1 mix there is a significant change in the composition of the LNG and its boil off. Thus, iteration was considered necessary. For this analysis the boil off gas was removed after each increase in enthalpy and the new composition and properties of the remaining liquid were used for the next analysis in an iterative fashion. This is shown in Figures 114 and 115.

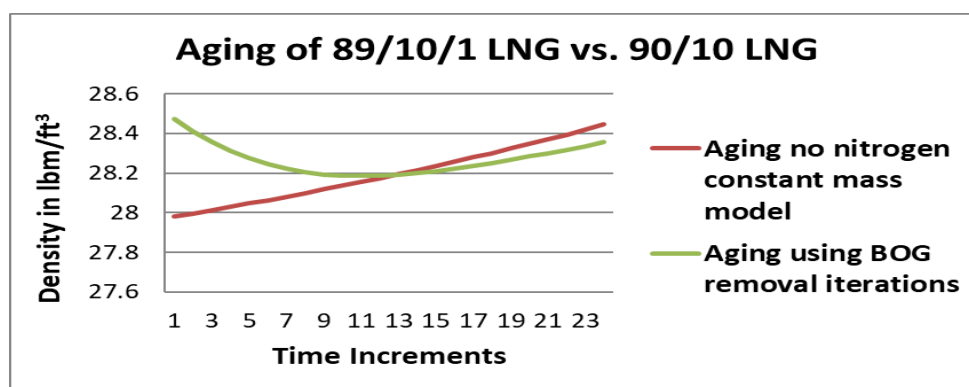


Figure 113: A density plot over time of a continuously mixed tank of 89/10/1 methane, ethane, nitrogen mix as compared to a density plot over time of a tank of 90/10 methane ethane LNG mix.

For those who may want to duplicate this analysis, a small number of the REFPROP iterations are shown in Figures 114 and 115 for the LNG containing nitrogen. In each iteration the LNG in the in the tank was changed to correspond to the change in composition in the fluid from the earlier iteration. In each step, the enthalpy of the remaining liquid was put in place of the total

enthalpy. Then the enthalpy was increased by 2 Btu/lbm. This in effect mimics the real world as it accounted for the continuous removal of boil off from the tank.

1: methane/ethane/nitrogen: Saturation points (at equilibrium) (0.89/0.1/0.01)														
	Liquid Phase Temperature (°F)	Vapor Phase Temperature (°F)	Liquid Phase Pressure (psia)	Vapor Phase Pressure (psia)	Liquid Phase Density (lbm/ft³)	Vapor Phase Density (lbm/ft³)	Liquid Phase Enthalpy (Btu/lbm)	Vapor Phase Enthalpy (Btu/lbm)	Liquid Phase Mole Frac. (methane)	Liquid Phase Mole Frac. (ethane)	Liquid Phase Mole Frac. (nitrogen)	Vapor Phase Mole Frac. (methane)	Vapor Phase Mole Frac. (ethane)	Vapor Phase Mole Frac. (nitrogen)
1	-261.74	-261.74	15.500	15.500	28.472	0.14438	-14.386	154.15	0.89000	0.10000	0.010000	0.74504	0.25496	0.00001
2														
2: methane/ethane/nitrogen: Specified state points (0.89/0.1/0.01)														
	Temperature (°F)	Pressure (psia)	Density (lbm/ft³)	Liquid Phase Density (lbm/ft³)	Vapor Phase Density (lbm/ft³)	Enthalpy (Btu/lbm)	Liquid Phase Enthalpy (Btu/lbm)	Vapor Phase Enthalpy (Btu/lbm)	Mole Frac. (methane)	Mole Frac. (ethane)	Mole Frac. (nitrogen)	Liquid Phase Mole Frac. (methane)	Liquid Phase Mole Frac. (ethane)	Liquid Phase Mole Frac. (nitrogen)
1	-261.74	15.500	28.472	28.472	Subcooled	-14.386	-14.386	Subcooled	0.89000	0.10000	0.010000	0.89000	0.10000	0.010000
2	-260.78	15.500	11.240	28.411	0.14075	-12.386	-13.720	161.68	0.89000	0.10000	0.010000	0.89080	0.10072	0.0084778
3														
3: methane/ethane/nitrogen: Specified state points (0.8908/0.10072/0.0084778)														
	Temperature (°F)	Pressure (psia)	Density (lbm/ft³)	Liquid Phase Density (lbm/ft³)	Vapor Phase Density (lbm/ft³)	Enthalpy (Btu/lbm)	Liquid Phase Enthalpy (Btu/lbm)	Vapor Phase Enthalpy (Btu/lbm)	Mole Frac. (methane)	Mole Frac. (ethane)	Mole Frac. (nitrogen)	Liquid Phase Mole Frac. (methane)	Liquid Phase Mole Frac. (ethane)	Liquid Phase Mole Frac. (nitrogen)
1	-260.78	15.500	28.405	28.411	0.14075	-13.720	-13.720	161.68	0.89080	0.10072	0.0084778	0.89080	0.10072	0.0084776
2	-259.92	15.500	10.970	28.358	0.13740	-11.720	-13.125	169.00	0.89080	0.10072	0.0084778	0.89141	0.10147	0.0071227
3														
4: methane/ethane/nitrogen: Specified state points (0.89141/0.10147/0.0071227)														
	Temperature (°F)	Pressure (psia)	Density (lbm/ft³)	Liquid Phase Density (lbm/ft³)	Vapor Phase Density (lbm/ft³)	Enthalpy (Btu/lbm)	Liquid Phase Enthalpy (Btu/lbm)	Vapor Phase Enthalpy (Btu/lbm)	Mole Frac. (methane)	Mole Frac. (ethane)	Mole Frac. (nitrogen)	Liquid Phase Mole Frac. (methane)	Liquid Phase Mole Frac. (ethane)	Liquid Phase Mole Frac. (nitrogen)
1	-259.92	15.500	28.345	28.358	0.13740	-13.125	-13.125	169.00	0.89141	0.10147	0.0071227	0.89141	0.10147	0.0071223
2	-259.15	15.500	10.709	28.313	0.13436	-11.125	-12.603	175.99	0.89141	0.10147	0.0071227	0.89182	0.10225	0.0059299
3														

Figure 114: A modeling of the density changes of an 89/10/1 methane ethane nitrogen LNG mix. In each iteration the liquid enthalpy from the earlier iteration becomes the total enthalpy of the next iteration which is then increased by 2 Btu/lbm. Figure 115 shows how the data is transferred to the next iteration table and how the enthalpy is increased.

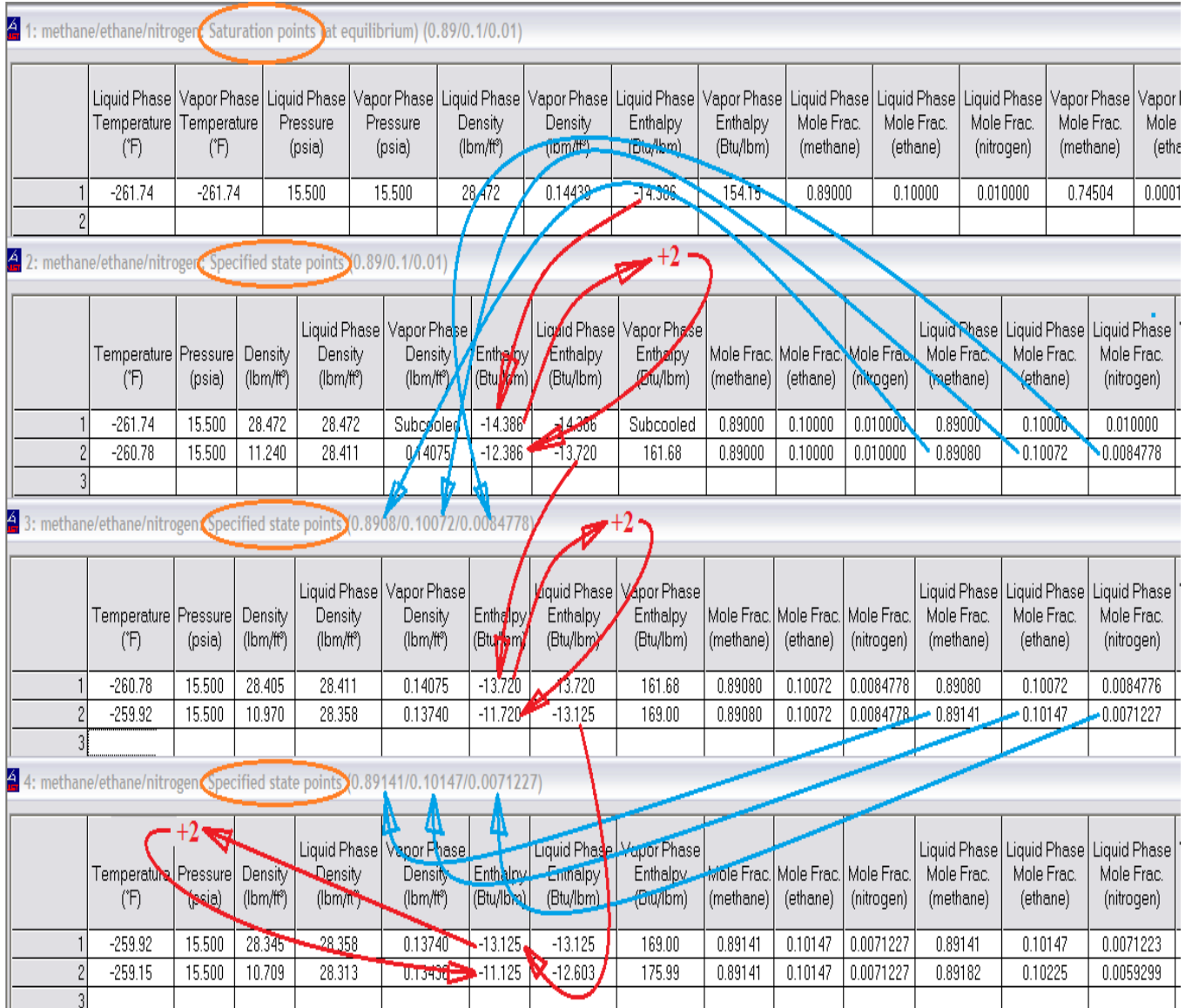


Figure 115: A modeling of the density changes of an 89/10/1 methane ethane nitrogen LNG mix. In each iteration the liquid enthalpy from the earlier iteration becomes the total enthalpy of the next iteration which is then increased by 2 Btu/lbm.

3: methane/ethane: Specified state points (0.9/0.1)

	Mole Frac. (methane)	Mole Frac. (ethane)	Liquid Phase Mole Frac. (methane)	Liquid Phase Mole Frac. (ethane)	Vapor Phase Mole Frac. (methane)	Vapor Phase Mole Frac. (ethane)	Temperature (°F)	Pressure (psia)	Density (lbm/ft³)	Liquid Phase Density (lbm/ft³)	Vapor Phase Density (lbm/ft³)	Enthalpy (Btu/lbm)	Liquid Phase Enthalpy (Btu/lbm)
1	0.90000	0.10000	0.90000	0.10000	0.99977	0.00022858	-255.24	15.500	27.955	27.981	0.11763	0.94064	0.93972
2	0.90000	0.10000	0.89901	0.10099	0.99977	0.00023096	-255.21	15.500	8.8814	27.997	0.11761	2.9407	0.83713
3	0.90000	0.10000	0.89799	0.10201	0.99977	0.00023339	-255.19	15.500	5.2791	28.013	0.11760	4.9407	0.73272
4	0.90000	0.10000	0.89696	0.10304	0.99976	0.00023587	-255.17	15.500	3.7554	28.030	0.11758	6.9412	0.62634
5	0.90000	0.10000	0.89590	0.10410	0.99976	0.00023841	-255.14	15.500	2.9144	28.047	0.11757	8.9407	0.51801
6	0.90000	0.10000	0.89482	0.10518	0.99976	0.00024100	-255.12	15.500	2.3811	28.064	0.11755	10.941	0.40761
7	0.90000	0.10000	0.89372	0.10628	0.99976	0.00024365	-255.10	15.500	2.0127	28.082	0.11754	12.940	0.29510
8	0.90000	0.10000	0.89260	0.10740	0.99975	0.00024636	-255.07	15.500	1.7429	28.100	0.11752	14.941	0.18040
9	0.90000	0.10000	0.89145	0.10855	0.99975	0.00024913	-255.04	15.500	1.5369	28.118	0.11750	16.941	0.063470
10	0.90000	0.10000	0.89028	0.10972	0.99975	0.00025196	-255.02	15.500	1.3744	28.137	0.11749	18.941	-0.055758
11	0.90000	0.10000	0.88909	0.11091	0.99975	0.00025486	-254.99	15.500	1.2430	28.156	0.11747	20.941	-0.17735
12	0.90000	0.10000	0.88786	0.11214	0.99974	0.00025783	-254.96	15.500	1.1345	28.175	0.11745	22.941	-0.30141
13	0.90000	0.10000	0.88661	0.11339	0.99974	0.00026087	-254.94	15.500	1.0434	28.195	0.11744	24.941	-0.42796
14	0.90000	0.10000	0.88534	0.11466	0.99974	0.00026398	-254.91	15.500	0.96583	28.215	0.11742	26.941	-0.55709
15	0.90000	0.10000	0.88403	0.11597	0.99973	0.00026717	-254.88	15.500	0.89898	28.236	0.11740	28.941	-0.68889
16	0.90000	0.10000	0.88269	0.11731	0.99973	0.00027043	-254.85	15.500	0.84078	28.257	0.11738	30.941	-0.82344
17	0.90000	0.10000	0.88133	0.11867	0.99973	0.00027378	-254.82	15.500	0.78965	28.279	0.11736	32.940	-0.96082
18	0.90000	0.10000	0.87993	0.12007	0.99972	0.00027721	-254.79	15.500	0.74435	28.301	0.11734	34.941	-1.1012
19	0.90000	0.10000	0.87849	0.12151	0.99972	0.00028074	-254.75	15.500	0.70398	28.324	0.11732	36.941	-1.2445
20	0.90000	0.10000	0.87703	0.12297	0.99972	0.00028435	-254.72	15.500	0.66774	28.347	0.11730	38.941	-1.3910
21	0.90000	0.10000	0.87552	0.12448	0.99971	0.00028806	-254.69	15.500	0.63505	28.370	0.11728	40.941	-1.5406
22	0.90000	0.10000	0.87398	0.12602	0.99971	0.00029186	-254.65	15.500	0.60540	28.395	0.11726	42.941	-1.6936
23	0.90000	0.10000	0.87241	0.12759	0.99970	0.00029578	-254.62	15.500	0.57839	28.419	0.11724	44.941	-1.8501
24	0.90000	0.10000	0.87079	0.12921	0.99970	0.00029979	-254.58	15.500	0.55368	28.445	0.11721	46.941	-2.0101
25													

Figure 116: A modeling of the density changes of a 90/10 methane ethane LNG mix. Because there is not a significant change in the composition of the LNG and its boil off, iteration was deemed not necessary. Instead, the total enthalpy in each step is just increased by 2 Btu/lbm.

As mentioned earlier, the lower layer of a stratified tank may reach its boiling point before the density of the lower layer becomes lighter than the upper layer. This is shown in Figure 117.

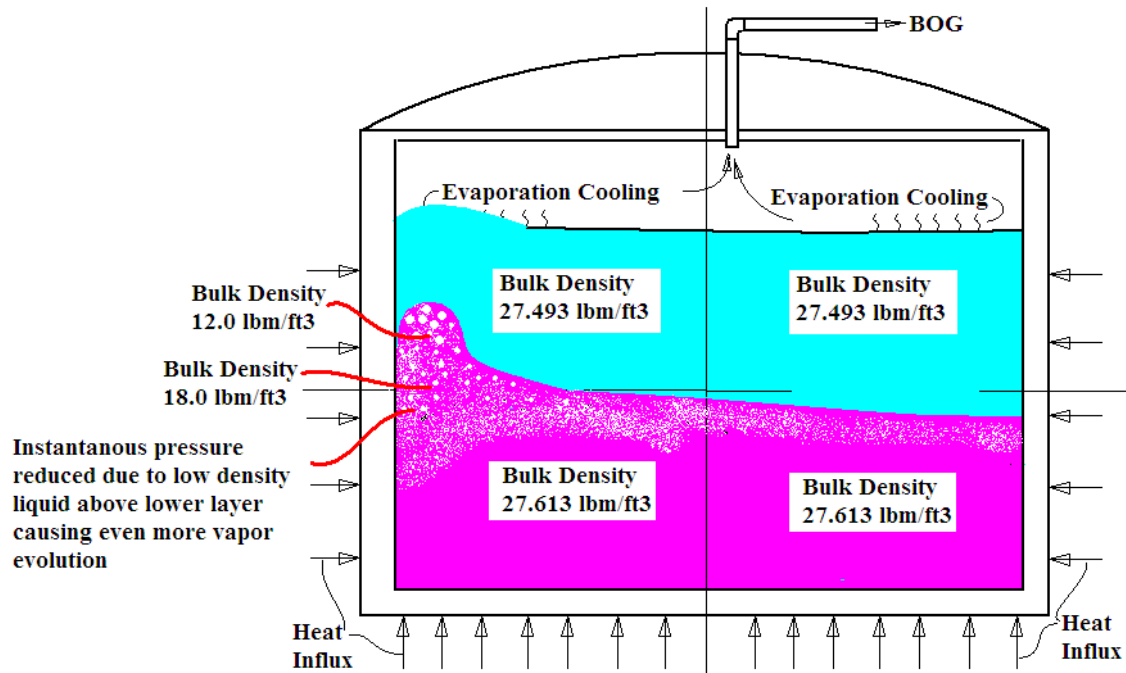


Figure 117: A conceptual drawing of how the lower layer may begin to boil even before its density becomes lighter than the upper layer. This would cause a penetration of the upper layer by lower layer fluid as the bulk density of the lower layer drops due to vapor bubbles. Take note that as the lower layer rises, it vaporizes even more because as it rises it experiences a lower pressure.

Figure 118 shows the effect nitrogen has on the saturation temperature. In this figure, a mix of methane ethane and nitrogen is analyzed using REFPROP and showing how nitrogen in the mixture impacts the bubble point of the mixture. It is interesting to note how a mixture with 1.5% nitrogen at 22.5 psia has approximately the same bubble point temperature a mixture without nitrogen at 15.5 psia. This shows how a lower layer can start to boil even though it is under a pressure caused by a higher layer of LNG.

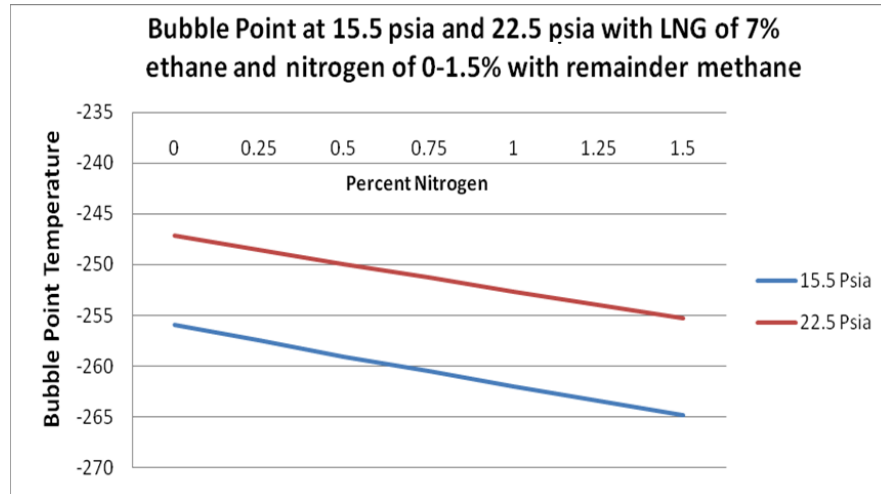


Figure 118: Graph showing the effect of nitrogen on bubble point on LNG mixtures at a pressure of 15.5 psia and 22.5 psia.

Figure 119 shows pictorially how a mixture of 93/7 methane ethane at 15.5 psia has approximately the same bubble point as the lower layer of a 91.5/7/1.5 methane ethane nitrogen mixture at 22.5 psia. Take note that as the lower layer warms up, even slightly, it can start to boil even under a head pressure of 7 psig.

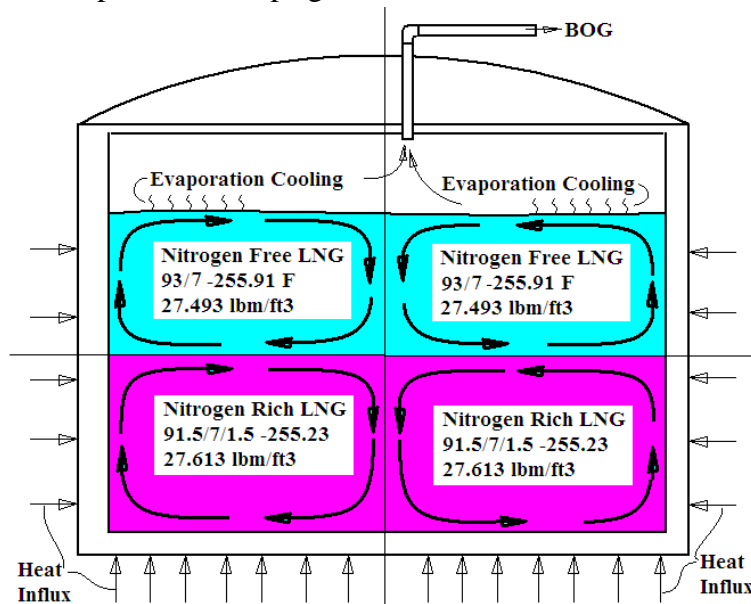


Figure 119: Conceptual picture showing the effect of nitrogen on bubble point on LNG mixtures at a pressure of 15.5 psia and 22.5 psia. In this picture, the lower layer is at its bubble point and if it is slightly heated, it starts to boil.

Figure 120 shows conceptually how a boiling lower layer can impact the bulk density of the lower layer causing it to boil up through the upper layer.

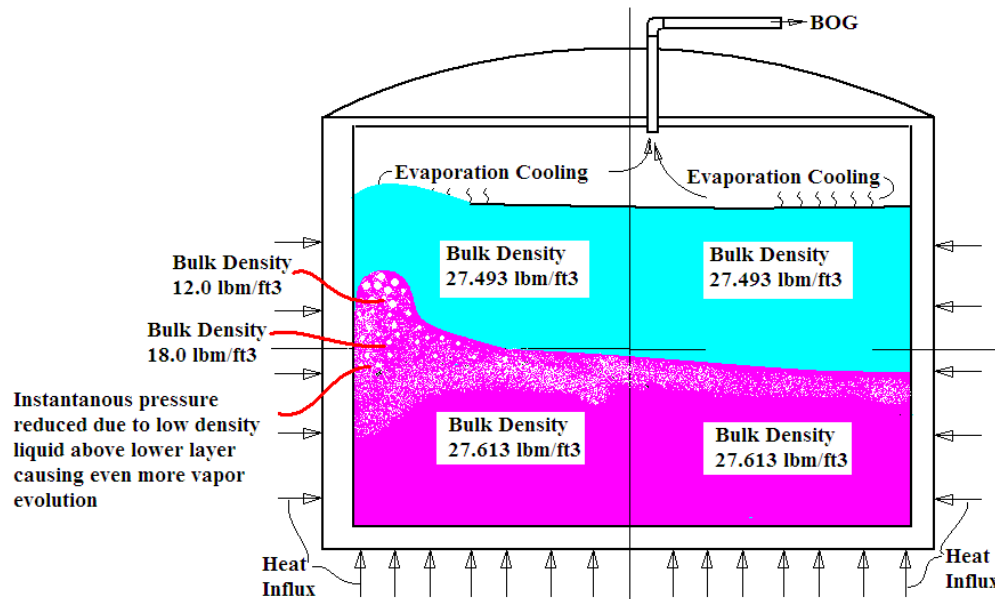


Figure 120: Conceptual picture showing the effect of nitrogen on bubble point on LNG mixtures at a pressure or 15.5 psia and 22.5 psia.

Take note that once the LNG begins to boil, the bulk density of the fluid with a small number of bubbles becomes significantly lower.

Figures 118, 119, and 120 raise a concept that has not been discussed in the literature searched. That concept is a postulation that as bubbles rise through a column of liquid, they can cause the liquid above the lower layer to have a lessened bulk density. Conceptually, one could postulate how this might cause a violent mixing rollover event as shown in Figure 121.

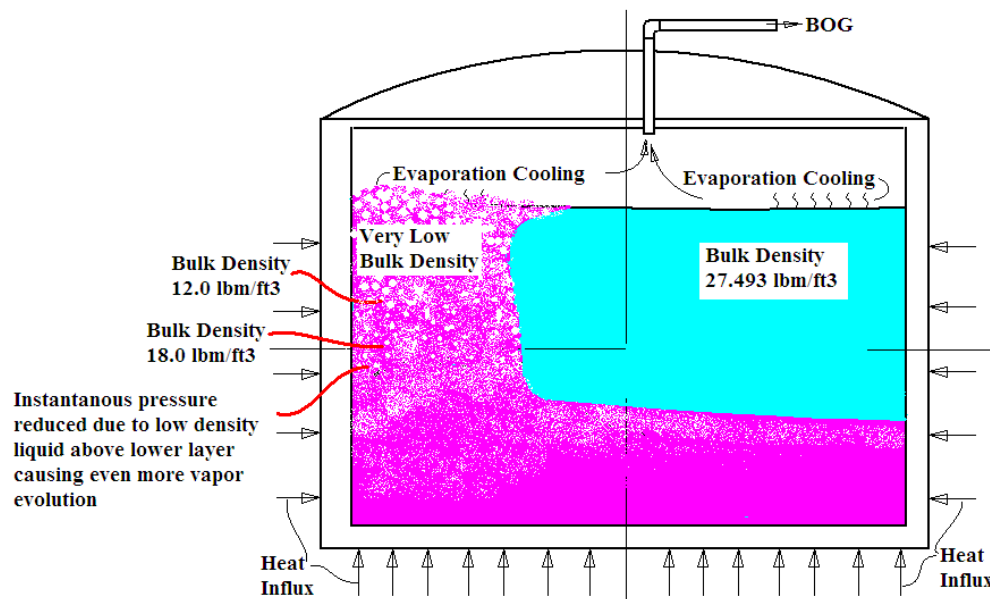


Figure 121: Conceptual picture showing the effect of nitrogen on bubble point of the lower layer causing bubbling of lower layer.

Take note that once the LNG begins to boil, the bulk density of the fluid with a small number of bubbles becomes significantly lower. One could postulate that this could cause a very violent bubble through the upper layer which is accelerated due to the significantly lowered bulk density of the LNG column.

Two prominent rollover events found in the literature are:

- LA Spezia 1971 – Vapor generation over-pressurized the tank – Vapor generation was estimated at 184 to 245 normal boil off (this was a fill induced rollover).
- Parrington 1993 – As best as can be determined from the literature, the vapor generation was approximated similar in quantity as in LA Spezia (no data on over-pressurization) (This was a nitrogen induced rollover)

As a result of these events:

- NFPA-59A requires a tank venting capability of 3% of tank inventory in a 24-hour period (approximately 60 times normal Boil Off)
- New Tanks are typically designed to relieve 100-300 times the normal boil off rate.

It should be noted that in addition to stratification and rollover concerns, nitrogen rich LNG also poses the following concerns (partial list):

- N₂ lowers the saturation temperature of the LNG (what temperature is your LNG tank rated to legally accept?)
 - 93/7 mixture at 15.5 psia sat temp is -255.91 F
 - 92/7/1 mixture at 15.5 psia sat temp is -262 F
 - The tank may be rated for only -260 F
- N₂ hinders or even reverses normal LNG aging densification
- N₂ lessens NPSHA for the same temperature LNG
- N₂ lowers the bubble point of LNG
- N₂ increases the density of LNG
- N₂ decreases the heating value of LNG
- N₂ may cause end use interchangeability issues
- N₂ LNG can cause very significant N₂ concentrations in boil off. This can be very hard to manage as the plant switches from use of boil off to vaporized LNG for fuel gas. For instance, the boil off may contain 20% nitrogen and the vaporized LNG may contain only 1% nitrogen. If a plant boiler is operating on boil off and then switches to vaporized fuel gas, the switch may not be well tolerated by the end use equipment. This is also true if the boil off is sent to a line that feeds local customers.

Reinforcement Exercises

The following exercises are intended to sharpen your skills in the use of REFPROP for solving thermodynamic analysis.

1. Problem # 3.1- Analysis of a Positive Displacement Air Compressor

A single stage positive displacement adiabatic air compressor rated at STP compresses 200 scfm air with 75% efficiency. The electric motor is 90% efficient. The air inlet is at sea level and ranges from 0 F to 60 F. The outlet pressure is 100 psig.

- Motors are available in 20 hp increments. Estimate the minimum size (hp) motor needed to drive this compressor
- Is the motor load more or less at cold temperature inlet vs. high temperature inlet?
- Assume efficiencies to remain constant across varying conditions.

2. Solution # 3.1

2.1 Analysis at 60 F inlet temperature

- Air density at STP = 0.076341 lbm/ft³ (See Figure 122)
- Mass Flow rate at 60 F inlet air temperature = 200 ft³/min x 0.076341 lbm/ft³ = 15.2682 lbm/min
- Isentropic compression to 100 psig (delta enthalpy = (223.94 – 124.31) = 99.63 Btu/lbm (See Figure 122).



1: Air: Specified state points (75.57/1.2691/23.16)

	Temperature (°F)	Pressure (psia)	Density (lbm/ft ³)	Enthalpy (Btu/lbm)	Entropy (Btu/lbm-°R)
1	60.000	14.696	0.076341	124.31	1.6319
2	470.62	114.70	0.33175	223.94	1.6319
3					

Figure 122: Properties of air at STP and isentropic compression to 100 psig. Note, that the pressure of 114.696 psia was rounded off by the software to 114.70 due to the number of digits displayed. The number of digits displayed can be changed by selecting “Options”, then “Preferences” and then changing the numbers in the lower left-hand corner of the display.

Ideal work/min = 99.63 Btu/lbm x 15.2682 lbm/min = 1521.171 Btu/min

Actual work/min = (1521.171 Btu/min)/0.75 = 2028.22769 Btu/min

Black book pocket reference page 779 1 Btu/min = 0.02358 hp

Actual work = 2028.22769 Btu/min x 0.02358 hp-min = 47.826 hp

Motor efficiency = 90% (so what... still need 47.826 shaft hp). This data was given in the problem but not needed for the answer. Do not be fooled by excess data.

Motor size needed = 60 hp.

(ANSWER)


At 60 F the compressor draws in 200 scfm.

At 60 F the compressor draws in 200 acfm.

At 60 F the compressor draws in 15.2682 lbm/min

2.2 Analysis at 0 F inlet temperature

At 0 F the density is 0.086344 lbm/ft³ (The density increased!) (See Figure 123).

 1: Air: Specified state points (75.57/1.2691/23.16)

	Temperature (°F)	Pressure (psia)	Density (lbm/ft ³)	Enthalpy (Btu/lbm)	Entropy (Btu/lbm-°R)
1	0.00000	14.696	0.086344	109.88	1.6024
2	365.68	114.70	0.37406	198.07	1.6024
3					

Figure 123: Properties of air at 1 atm and 0 F and isentropic compression to 100 psig.

- Mass Flow rate at 0 F inlet temperature = 200 ft³/min x 0.086344 lbm/ft³ = 17.2688 lbm/min (13% increase)
- Isentropic compression to 100 psig (delta enthalpy = (198.07 – 109.88) = 88.19 Btu/lbm (11.5% less!)
- Ideal work/min = 88.19 Btu/lbm x 17.2688 lbm/min = 1522.9355 Btu/min
- Actual work/min = (1522.9355 Btu/min)/0.75 = 2030.581 Btu/min
- Black book pocket reference page 779 1 Btu/min = 0.02358 hp
- Actual work = 2030.581 Btu/min x 0.02358 hp-min = 47.881 hp
- Motor efficiency = 90% (so what... still need 47.881 shaft hp)
- **Motor size needed = 60 hp**

(ANSWER)

- With 0 F inlet air the compressor compresses 13 % more air with almost no additional power needed. With a 60 F inlet the shaft work was 47.826 hp and with a 0 F inlet the shaft work needed was 47.881 hp.


(ANSWER)

3. Problem # 3.2 – Analysis of a BOG Compressor with Varied Inlet Pressures

- A single stage positive displacement boils off gas compressor is operating with an inlet pressure of 7 psig at 60 F and an outlet pressure of 100 psig. The inlet pressure is increased to 12 psig.
 - What impact might you expect in the motor load in % change in load?
 - Assume the BOG is pure methane
 - Assume the compressor uses reed valves and the outlet pressure is maintained at 100 psig. Make a statement regarding if the machine was set up to deliver pressure based on a compression ratio instead of having a fixed outlet pressure and a reed valve configuration.

4. Solution # 3.2

- Per Figure 124 the density at 7 psig = 0.062594 lbm/ft³
- Density at 12 psig = 0.07707 lbm/ft³
- Isentropic work from 7 psig to 100 psig = (511.90 - 382.23) = 129.67 Btu/lbm

 2: methane: Specified state points

	Temperature (°F)	Pressure (psia)	Density (lbm/ft ³)	Enthalpy (Btu/lbm)	Entropy (Btu/lbm-°R)
1	60.000	21.696	0.062594	382.23	1.5296
2	60.000	26.696	0.077070	382.08	1.5037
3	289.74	114.70	0.22943	511.90	1.5296
4	258.92	114.70	0.23949	492.89	1.5037
5					

Figure 124: Specific state points at 60 F at 7 psig and 12 psig with isentropic compression from each state to 100 psig.

- Isentropic work from 12 psig to 100 psig = (492.89 - 382.08) = 110.81 Btu/lbm (14.5% decrease)

- Mass flow rate (7 to 100 psig) = density x (volumetric displacement/min) = ((0.062594 lbm/ft³) (volumetric displacement/min)) in lbm/min
- Mass flow rate (12 to 100 psig) = density x (volumetric displacement/min) = ((0.07707 lbm/ft³) (volumetric displacement/min)) in lbm/min
- Work (7 to 100 psig) = flow rate x work per lbm
- Work (7 to 100 psig) = (0.062594 lbm/ft³) (volumetric displacement/min) in lbm/min x 129.67 Btu/lbm = 8.11656 Btu/min x (coefficient of volumetric displacement/min)
- Work (12 to 100 psig) = flow rate x work per lbm
- Work (12 to 100 psig) = (0.07707 lbm/ft³) (volumetric displacement/min) in lbm/min x 110.81 Btu/lbm = 8.540 Btu/min (coefficient of volumetric displacement/min)
(increase of 5.2% hp required when the inlet pressure is increased from 7 psig to 12 psig) (Answer)
- Look at the temperature change. The higher inlet pressure resulted in a lower outlet temperature. This is because the compression ratio is less. Then where did the additional power requirement come from. It was caused because by increasing the inlet pressure, you are increasing the mass throughput of the compressor.
- In the above the term (volumetric displacement/min) was used. In much of the literature, you will see the term ACFM used. ACFM stands for actual cubic feet per minute. If this occurred at standard conditions it would be SCFM or standard cubic feet per minute.
- Ponder this. What if this was the first stage of a 4-stage compressor compressing up to 1,400 psig. Each stage would be pumping the increased mass caused by increasing the inlet pressure. However, the follow-on stages would not get the benefit of the lower compression ratio and thus would see a greater power requirement and a greater pin loading.
- **Note: this compressor used a reed valve and the outlet pressure was maintained at 100 psig. However, if this compressor used a fixed compression ratio to determine outlet pressure, the outlet pressure and temperature and the power required would have been significantly higher. It is important to realize that the inlet density at 60 F is a linear function of the absolute pressure. I.e., if the absolute pressure is doubled the density is doubled.**


5. Problem # 3.3 – Boiler Feed Water Pump Analysis and Boiler Heat Input Analysis

A 300 hp (shaft power delivered) adiabatic boiler feed water pump that is 80% efficient pumps water from 20 psia and 150 F to 600 psia.

- How many GPM are pumped?
- What is the temperature of the outlet water?
- How much heat per hour must be added to the outlet water to bring it to a temperature 600 F and 550 psia?

6. Solution # 3.3

- Isentropic pump of water from 20 psia (150 F) to 600 psia
- Calculate the isentropic work required $(119.86 - 118.11) \text{ Btu/lbm} = 1.75 \text{ Btu/lbm}$
- Calculate the actual work required $1.75/0.8 = 2.1875 \text{ Btu/lbm}$
- Figure 125 shows the properties for an isentropic and real-world pump


 3: water: Specified state points

	Temperature (°F)	Pressure (psia)	Density (lbm/ft³)	Enthalpy (Btu/lbm)	Entropy (Btu/lbm-°R)
1	150.00	20.000	61.196	118.11	0.21522
2	150.33	600.00	61.299	119.86	0.21522
3	150.77	600.00	61.291	120.30	0.21593
4					

Figure 125: Specific state points from 20 psia to 600 psia isentropic and real-world pump.

- Find new properties at actual outlet conditions (Line 3)
- $H_p (\text{shaft}) = \text{energy input per lbm} \times \text{flow rate (lbm/hr.)} \times \text{conversion factor}$
- $300 \text{ hp} = 2.1875 \text{ Btu/lbm} \times \text{flow rate} \times 0.02358 \text{ hp-min/Btu}$ (reference book page p779)
- $\text{Flow rate} = 300 \text{ hp} / (2.1875 \text{ Btu/lbm} \times 0.02358 \text{ hp-min/Btu})$
- $\text{Flow rate} = 5,816.07 \text{ lbm/min}$
- $(5,816.07 \text{ lbm/min}) / (61.196 \text{ lbm/ft}^3) = 95.04 \text{ ft}^3/\text{min}$
- $1 \text{ ft}^3 = 7.48052 \text{ gallon}$
- **$95.04 \text{ ft}^3/\text{min} = 710.949 \text{ gpm}$** (ANSWER)
- **Per Figure 125 the Temperature at the pump outlet is 150.77 F** (ANSWER)
- Delta enthalpy from the outlet of the feed water pump to the final state in the boiler will determine how much heat is added.
- Note, that the boiler pressure is lower than the pump outlet pressure (constant h valve at the boiler inlet).
- Assume piping is perfectly insulated

- Hourly flow rate is 5,816.07 lbm/min x 60 min/hr. = 348,964 lbm/hr.
- Per Figure 3.5, $\Delta h = (1295.2 - 120.3) \text{ Btu/lbm} = 1174.9 \text{ Btu/lbm}$
- **Total heat in = 348,964 lbm/hr. x 1174.9 Btu/lbm = 409,997,803.6 Btu/hr.**
(ANSWER)

 3: water: Specified state points

	Temperature (°F)	Pressure (psia)	Density (lbm/ft³)	Enthalpy (Btu/lbm)	Entropy (Btu/lbm-°R)
1	150.00	20.000	61.196	118.11	0.21522
2	150.33	600.00	61.299	119.86	0.21522
3	150.77	600.00	61.291	120.30	0.21593
4	600.00	550.00	0.95891	1295.2	1.5464
5					


Figure 126: Specific state points showing the heat required to raise the temperature and phase of the boiler water feed to 600 F and 550 psia.

7. Problem # 3.4 – Recondenser Analysis at Varied Outlet Temperature

- An adiabatic recondenser is fed 10,000 scf of methane vapor at -140 F and 65 psig.
 - How much liquid at -245 F and 65 psig must be fed into the recondenser to hold the liquid level fixed and the outlet temperature at -230 F.
 - If the recondenser outlet is allowed to raise in temperature to -225 F, how much liquid at -245 F and 65 psig must be fed into the recondenser to maintain the level fixed?
 - Use methane for all your calculations. Use SSSF conditions.

8. Solution # 3.4

- Mass of vapor into recondenser = 10,000 scf x 0.042359 lbm/ft³ = 423.59 lbm of vapor
- Heat removed from the vapor (-140 F to -230 F) = (275.44 – 24.558) Btu/lbm x 423.59 lbm = 250.882 x 423.59 = 106,271.106 Btu. (See Figure 127)

 4: methane: Specified state points

	Temperature (°F)	Pressure (psia)	Density (lbm/ft³)	Enthalpy (Btu/lbm)	Entropy (Btu/lbm-°R)
1	60.000	14.696	0.042359	382.45	1.5781
2	-140.00	79.696	0.39270	275.44	1.1109
3	-245.00	79.696	25.685	11.731	0.054235
4	-230.00	79.696	24.863	24.558	0.11198
5	-225.00	79.696	24.576	28.909	0.13072
6					

Figure 127: Specific state points showing various recondenser parameters.

- Heat added to LNG (-245 F to -230 F) = $(24.558 - 11.731) \text{ Btu/lbm} \times \text{"X"} \text{ lbm} = 106,271.106 \text{ Btu}$
- $X = 106,271.106 \text{ Btu} / 12.827 \text{ Btu/lbm}$
- **X = 8,284.954 lbm of LNG (equivalent to 195,589 scf) (Approx. 19.6 units of liquid to 1 unit of vapor). (Answer)**
- Now change the outlet temperature from -230 F to -225 F.
 - Heat removed from the vapor (-140 F to -225 F) = $(275.44 - 28.909) \text{ Btu/lbm} \times 423.59 \text{ lbm} = 246.531 \times 423.59 = 104,428.07 \text{ Btu}$
 - Heat added to LNG (-245 F to -225 F) = $(28.909 - 11.731) \text{ Btu/lbm} \times \text{"X"} \text{ lbm} = 104,428.07 \text{ Btu}$
 - $X = 104,428.07 \text{ Btu} / 17.178 \text{ Btu/lbm}$
 - **X = 6,079.18 lbm of LNG (equivalent to 143,516 scf) (Approx. 14.4 units of liquid to 1 unit of vapor) (Answer) (Note, units can be either scf or lbm)**
 - 2,205.774 lbm less liquid (Approx. 27% less) is needed to condense the vapor at an outlet temperature of -225 F as compared to -230 F.
 - Take note, in this problem units were not given as a rate. That is the flow input was not stated in scf/m or lbm/hr. etc. There was no need to do this as we worked with a fixed mass of vapor and then computed the fixed mass of liquid needed to condense the vapor. The very same problem could have been set up as a rate problem.

9. Problem # 3.5 – Flash Outlet Compositions with Varied LNG Composition

- An LNG with a composition of 1% nitrogen, 90% methane and 9% ethane at a temperature of -250 F and a pressure of 65 psig is pressure dropped (flushed) across a valve to 15.5 psia.
 - What is the composition of the LNG downstream of the valve.
 - At saturated conditions at 15.5 psia, what is the density of LNG if the composition is 1/90/9 nitrogen methane ethane and what is the liquid density at saturated conditions at 15.5 psia of the outlet of the above flash valve?

10. Solution # 3.5

8: methane/ethane/nitrogen: Specified state points (0.9/0.09/0.01)

	Temperature (°F)	Pressure (psia)	Density (lbm/ft³)	Liquid Phase Density (lbm/ft³)	Vapor Phase Density (lbm/ft³)	Enthalpy (Btu/lbm)	Liquid Phase Enthalpy (Btu/lbm)	Vapor Phase Enthalpy (Btu/lbm)
1	-250.00	79.696	27.745	27.745	Subcooled	-3.9020	-3.9020	Subcooled
2	-258.70	15.500	3.0918	28.126	0.13190	-3.9020	-11.281	182.14
3								

0.09/0.01

Molar Mass	Liquid Phase Molar Mass	Vapor Phase Molar Mass	Mole Frac. (methane)	Mole Frac. (ethane)	Mole Frac. (nitrogen)	Liquid Phase Mole Frac. (methane)	Liquid Phase Mole Frac. (ethane)	Liquid Phase Mole Frac. (nitrogen)	Vapor Phase Mole Frac. (methane)	Vapor Phase Mole Frac. (ethane)	Vapor Phase Mole Frac. (nitrogen)
17.425	17.425	Subcooled	0.90000	0.090000	0.010000	0.90000	0.090000	0.010000	Subcooled	Subcooled	Subcooled
17.425	17.415	17.688	0.90000	0.090000	0.010000	0.90146	0.093508	0.0050320	0.86262	0.00016190	0.13721

Figure 128: Specific state points for LNG through a JT valve from -250 F from 65 psig to 15.5 psia.

The pressure drop across a valve is a constant enthalpy process. This is shown in Figure 128 as a process at a constant enthalpy of -3.902 Btu/lbm.

Per Figure 128, the composition of the LNG downstream of the valve is 90.146 % methane, 9.3508 % ethane, 0.5032 % nitrogen (read from chart). (ANSWER)

9: methane/ethane/nitrogen: Saturation points (at equilibrium) (0.9/0.09/0.01)

	Liquid Phase Temperature (°F)	Vapor Phase Temperature (°F)	Liquid Phase Pressure (psia)	Vapor Phase Pressure (psia)	Liquid Phase Density (lbm/ft³)	Vapor Phase Density (lbm/ft³)	Liquid Phase Enthalpy (Btu/lbm)	Vapor Phase Enthalpy (Btu/lbm)
1	-261.82	-261.82	15.500	15.500	28.305	0.14408	-13.362	155.02
2								

Figure 129: Properties of LNG downstream of the JT valve.

The density of the saturated liquid at a composition of 90/9/1 methane ethane nitrogen = 28.305 lbm/ft³ (per Figure 129). The density of LNG at outlet of the valve = 28.126 lbm/ft³ (per Figure 128). (ANSWER)

In reading the density of the LNG at the outlet of the JT valve, be careful to read the “liquid” density and not the total density as the total density is a mixture of liquid and vapor.

Just as a piece of added information, it is interesting to note that the density at the inlet of the JT valve = 27.745 lbm/ft³ (per Figure 128)

11. Problem # 3.6 – Flow Velocity Downstream of a JT Valve

In the following (see Figure 130 for fluid properties), the velocity before the JT valve is 1.5 ft./sec.

- What is the specific volume ratio from the inlet to the outlet of the JT valve?
- What is the velocity downstream of the valve?
- What % of the outlet volume is vapor?
- What % of outlet mass is vapor?

8: methane/ethane/nitrogen: Specified state points (0.9/0.09/0.01)

	Temperature (°F)	Pressure (psia)	Density (lbm/ft³)	Liquid Phase Density (lbm/ft³)	Vapor Phase Density (lbm/ft³)	Enthalpy (Btu/lbm)	Liquid Phase Enthalpy (Btu/lbm)	Vapor Phase Enthalpy (Btu/lbm)
1	-250.00	79.696	27.745	27.745	Subcooled	-3.9020	-3.9020	Subcooled
2	-258.70	15.500	3.0918	28.126	0.13190	-3.9020	-11.281	182.14
3								

0.09/0.01

Molar Mass	Liquid Phase Molar Mass	Vapor Phase Molar Mass	Mole Frac. (methane)	Mole Frac. (ethane)	Mole Frac. (nitrogen)	Liquid Phase Mole Frac. (methane)	Liquid Phase Mole Frac. (ethane)	Liquid Phase Mole Frac. (nitrogen)	Vapor Phase Mole Frac. (methane)	Vapor Phase Mole Frac. (ethane)	Vapor Phase Mole Frac. (nitrogen)
17.425	17.425	Subcooled	0.90000	0.090000	0.010000	0.90000	0.090000	0.010000	Subcooled	Subcooled	Subcooled
17.425	17.415	17.688	0.90000	0.090000	0.010000	0.90146	0.093508	0.0050320	0.86262	0.00016190	0.13721

Figure 130: Properties of an LNG mix before and after a JT valve. Line 1 shows properties before the JT valve. Line 2 shows properties after the JT valve.

12. Solution # 3.6

Inlet specific volume is $(1/27.745) = 0.0364253$ cu.ft./lbm

Outlet specific volume is $(1/3.0918) = 0.323436$ cu.ft./lbm

Specific volume ratio is $0.323436/0.0364253 = 8.9737$ (ANSWER)

Velocity at the outlet = inlet velocity x specific volume ratio = 1.5 ft./sec x $8.973713.46$ ft./sec (ANSWER)

- $Mass_{Total} = Mass_{Vapor} + M_{Liquid}$
- $Density_{Total} = \text{density of vapor} \times \text{fraction volume of vapor} + \text{density of liquid} \times \text{fraction volume of liquid}$
- Density of liquid = 28.126 lbm/ft³ (See Figure 130)
- Density of vapor = 0.13190 lbm/ft³ (See Figure 130)
- Let "X" = volume fraction of vapor
- $Density_{Total} = 3.0918$ lbm/ft³ = $(X (0.13190 \text{ lbm/ft}^3) + (1-X) (28.126 \text{ lbm/ft}^3))$
- $3.0918 = 0.13190X + 28.126 - 28.126X$
- $3.0918 - 28.126 = (0.1319 - 28.126) X$
- $25.0342 = 27.9941X$
- $X = 0.89427 = 89.427\%$

- **89.427% of outlet volume is vapor.** (ANSWER)

Find the percent of mass that is vapor.

- For each ft³ 89.427% is vapor and the mass of that vapor is:
 - $0.89.427 \times 0.13190 \text{ lbm/ft}^3 = 0.117954 \text{ lbm of vapor/ft}^3$
 - Mass of vapor/total mass x 100 = percent of outlet mass that is made up of vapor
- $(0.117954 \text{ lbm/ft}^3) / (3.0918 \text{ total mass/ft}^3) = 0.03815 = 3.815\%$
- **3.815% of outlet mass is vapor.** (ANSWER)

Another method to find the percent of mass that is vapor is to do an enthalpy balance as follows:

- Enthalpy = Mass of vapor x h of vapor + Mass of liquid x h of liquid
- Let X = mass fraction of vapor
- $-3.902 \text{ Btu/lbm} = X (182.14 \text{ Btu/lbm}) + (1-X) (-11.281 \text{ Btu/lbm})$
- $-3.902 = 182.14 X - 11.281 + 11.281 X$
- $-3.902 + 11.281 = (182.14 + 11.281) X$
- $7.379 = 193.421X$
- $X = 0.03815 = 3.815\%$
- **3.815% of outlet mass is vapor.** (ANSWER)

13. Problem #3.7 – Compressor Power and Temperatures Changes with Composition Change

A refrigeration compressor was designed to operate on a mixture of 50% ethane and 50% nitrogen. It is being tested with nitrogen only. What can the operator expect regarding mass flowrate, horsepower requirements, and outlet temperature?

Compute the differences in flowrates and how much horsepower is required and what is the outlet temperature if an 80% efficient gas compressor compresses pure nitrogen “OR” a mix of 50% ethane and 50% nitrogen from 75 F and 32 psia to 152 psia. Assume STP is 60 F and 14.696 psia. Assume a volumetric flowrate of 5 MMscf/d.

14. Solution # 3.7**14.1 Mass Flow Rate Analysis**

Properties of fluids for mass flowrate computations are shown in Figure 131.

1: nitrogen: Specified state points					
	Temperature (°F)	Pressure (psia)	Density (lbm/ft³)	Enthalpy (Btu/lbm)	Entropy (Btu/lbm-°R)
1	60.000	14.696	0.073841	128.82	1.6257
2					

2: ethane/nitrogen: Specified state points (0.5/0.5)					
	Temperature (°F)	Pressure (psia)	Density (lbm/ft³)	Enthalpy (Btu/lbm)	Entropy (Btu/lbm-°R)
1	60.000	14.696	0.076776	207.31	1.2452
2					


Figure 131: REFPROP data showing standard conditions of pure nitrogen and a 50/50 ethane nitrogen mix.

- Pure nitrogen the mass flow is $[(5,000,000 \text{ scf/d})/(24 \text{ hr/d})] \times (0.073841 \text{ lbm/scf}) = 15,384 \text{ lbm/hr. (Answer)}$
- 50% ethane with 50% nitrogen mass flow is $(5,000,000 \text{ scf/d})/(24\text{hr/day}) \times (0.076776 \text{ lbm/scf}) = 15,995 \text{ lbm/hr. (Answer)}$
 - The 50/50 mix results in almost 4% more mass compressed as compared to the pure nitrogen case (interesting).

14.2 Analysis of Compression Using Nitrogen

- Use REFPROP and use the inlet conditions of 75 F and 32 psia and an outlet pressure of 152 psia to determine the power required per lbm.


- First we will analyse an isentropic compression. Take note that the entropy was held constant and thus, for the outlet conditions we defined the same entropy as the inlet conditions along with the outlet pressure of 152 psia (See the REFPROP results in Figure 132)
- This isentropic compression would have required 74.49 Btu/lbm (delta enthalpy) and the outlet temperature would be 373.92 F

 3: nitrogen: Specified state points

	Temperature (°F)	Pressure (psia)	Density (lbm/ft³)	Enthalpy (Btu/lbm)	Entropy (Btu/lbm-°R)
1	60.000	14.696	0.073841	128.82	1.6257
2	75.000	32.000	0.15630	132.44	1.5773
3	373.92	152.00	0.47411	206.93	1.5773
4					

Figure 132: REFPROP data showing constant entropy compression of pure nitrogen from 32 psia to 152 psia (enthalpy increase is $206.93 - 132.44 = 74.49$ Btu/lbm).

- Assuming an 80% efficiency of the compressor tells us that the real enthalpy increase should be $(74.49 \text{ Btu/lbm}/0.8)$ which is 93.11 Btu/lbm
- Thus the outlet properties should be a pressure of 152 psia and an enthalpy of 225.55 $(132.44 + 93.11)$ Btu/lbm
- Plug this into REFPROP (See Figure 133) and it shows that the real work in is 93.11 Btu/lbm and the real temperature is 447.47 F

 3: nitrogen: Specified state points


	Temperature (°F)	Pressure (psia)	Density (lbm/ft³)	Enthalpy (Btu/lbm)	Entropy (Btu/lbm-°R)
1	60.000	14.696	0.073841	128.82	1.6257
2	75.000	32.000	0.15630	132.44	1.5773
3	373.92	152.00	0.47411	206.93	1.5773
4					
5	447.47	152.00	0.43554	225.55	1.5987
6					

Figure 133: REFPROP data showing real world compression of pure nitrogen from 32 psia to 152 psia (enthalpy increase is = 93.11 Btu/lbm).

- **The outlet temperature for pure nitrogen is found to be 447 F. (Answer)**
- Work required is mass flow rate x energy added to each lbm
 - Work in = 15,384 lbm/hr x 93.11 Btu/lbm = 1,432,404 Btu/hr
 - Look up the conversion on page 779 of black book pocket reference.
 - **Horsepower required for nitrogen compression is 562.9 hp. (Answer) based on 5,000,000 scf/d**

14.3 Analysis of Compression Using a 50/50 mix of ethane and nitrogen

Now let's do the same exercise using a mixture of 50% ethane and 50% nitrogen. In REFPROP select "Substance" and then "Define New Mixture". Then select an 50/50 mixture of ethane and nitrogen.

 4: ethane/nitrogen: Specified state points (0.5/0.5)

	Temperature (°F)	Pressure (psia)	Density (lbm/ft³)	Enthalpy (Btu/lbm)	Entropy (Btu/lbm-°R)
1	60.000	14.696	0.076776	207.31	1.2452
2					
3	75.000	32.000	0.16300	211.88	1.2009
4	261.43	152.00	0.57544	278.05	1.2009
5					
6	302.58	152.00	0.54314	294.59	1.2232
7					

Figure 134: REFPROP data showing constant entropy compression of a 50/50 mix of ethane and nitrogen from 32 psia to 152 psia (enthalpy increase is $278.05 - 211.88 = 66.17$ Btu/lbm). Then in line 6 the real-world compression is shown by increasing the enthalpy to 82.71 Btu/lbm ($(66.17 \text{ Btu/lbm})/0.8$).

- See Figure 134. If you did not get the same numbers make sure you are specifying a “**molar**” mixture.
- From Figure 134 it can be seen that the isentropic compression requires 66.17 Btu/lbm ($278.05 - 211.88$)Btu/lbm
- Assuming an 80% efficiency tells us that the real enthalpy increase should be $(66.17/0.8)$ Btu/lbm which is 82.71 Btu/lbm
- Thus the outlet properties should be a pressure of 152 psia and an enthalpy of 294.59 ($211.88 + 82.71$) Btu/lbm
- Plug this into REFPROP (See Figure 134) and it shows the real work in is 82.71 Btu/lbm and the **real temperature is 302.58 F**. **(ANSWER)**

Comparing the compression of pure methane and a 50/50 mixture ethane nitrogen shows:

- Compression energy per lbm is more for pure nitrogen than for the 50/50 (93.11 vs. 82.71)Btu/lbm. This is a 12.6% increase in power required for each lbm of the nitrogen as compared to 50/50 mix of ethane/nitrogen.
- However to move the same volume the compressor needs to move more lbms for the mixture because the 50/50 mixture of gas is denser at the inlet than the 100% nitrogen case! Thus, to move the same volume (5MMscf/hr) it is necessary to move almost 4% more mass (look at the density difference between the inlet of pure nitrogen and the 50/50 mixture)
- The outlet temperature for the 50/50 mixture has already been found to be 302.58 F

- The work required is mass flow rate x energy added to each lbm
 - $15,995 \text{ lbm/hr} \times 82.71 \text{ Btu/lbm} = 1,322,946 \text{ Btu/hr}$
 - Look up the conversion on page 779 of black book pocket reference.
 - **Horsepower required for the 50/50 mixture is 519.9 hp (this is reasonable).**
(ANSWER)

14.4 Summary

- Thus, the power to compress 5,000,000 scf/d of gas would be:
 - Nitrogen Hp required is 563 (ANSWER) (8.3% more than the 50/50 mix)
 - 50/50 ethane/nitrogen mix Hp required is 520 (ANSWER)
- The temperature of the of the compressed gas would be higher for pure nitrogen.
 - Nitrogen 447 F (ANSWER)
 - 50/50 ethane/nitrogen mix 303 F (ANSWER)
- Note, both fluids are compressed at the same volume flow rate of 5 MMscf/d but the mass flow rates are different (15,384 blm/hr for nitrogen vs. 15,995 lbm/hr for a 50/50 mix of ethane and nitrogen).

15. Problem #3.8 – Theoretically Estimate the Relationship between Height of Liquid in an LNG Tank and Boil Off Production

15.1 Assumptions:

- 1) Only heat leak below the liquid line results in an energy increase into the LNG so only heat transfer below the liquid line results in phase change from LNG to boil off. The premise is that any heat leak into the vapor space heats the vapor which itself is rising to the top of the tank where it is removed and thus this heat leak does not cause any phase change of the LNG. Some radiation from the warmer tank roof to the LNG will exist but for this analysis we will consider this negligible compared to the wall and floor heat leak.
- 2) The heat leak per unit area into the bottom of the tank is the same as the heat leak per unit area through the side of the tank. Probably not true but good for this theoretical analysis.
- 3) The inner tank is 200' in diameter and 120 feet high.

16. Solution # 3.8

Heat into the LNG = $Q = \text{Area} \times \text{Heat Leak per unit area}$ Since Heat Leak per unit area is constant, call it C

Then $Q = C (\text{Area})$

Area of bottom of the tank = $\pi r^2 = 3.14 (10000) = 31,400 \text{ sq. ft.}$

Full tank area of side of tank. = $\pi D \times \text{Height} = 3.14 \times 200 \times 120 = 75,360 \text{ sq. ft.}$

Total wetted area of tank when tank is full = 106,760 sq.ft.

Volume of the full tank = $31,400 \text{ ft}^2 \times 120 \text{ ft.} = 3,768,000 \text{ ft}^3$ of liquid approximately equals 2.261 Bscf. This size tank when full would create 1.13 MMscfd of boil off vapor per day based on a boil off rate of 0.05% full tank boil off per day (normal design).

Equation of a line $Y = mx + b$

$Y = \text{boil off}$, $x = \text{height of tank}$

At $x = 120'$ $\text{BOG} = 1.13 \text{ MMscfd}$

Let's postulate that at $x = 0'$ (bottom just barely covered) the BOG produced = $31,400/106,760 \times (1.13 \text{ MMSCFD}) = 0.3325 \text{ MMscfd}$.

$Y = m x + b$

At $x = 120 \text{ ft.}$ $Y = 1.13 \text{ MMscfd}$

At $x = 0 \text{ ft.}$ $Y = 0.3325 \text{ MMscfd}$

Make 2 equations with 2 unknowns.

$Y = mx + b$

Equation #1 $1.13 \text{ MMscfd} = m (120 \text{ ft.}) + b$

Equation #2 $0.3325 \text{ MMscfd} = 0 + b$

$b = 0.3325 \text{ MMscfd}$ (from equation #2)

Substitute the value of b into equation #1.

$1.13 \text{ MMscfd} = m 120 \text{ ft.} + 0.3325 \text{ MMscfd}$

$$m = (1.13 - 0.3325) \text{ MMscfd}/120 \text{ ft.} = 0.00664583 \text{ MMscfd}/\text{ft.}$$

Final equation is:

Boil off for this tank in MMscfd = $(0.00664583 \text{ MMscfd}/\text{ft.}) \times x + 0.3325 \text{ MMscfd}$ (where x is the number of feet of LNG in the tank)

Thus,

If the tank is full:

$$\begin{aligned} \text{Boil off} &= 0.00664583 \text{ MMscfd}/\text{ft.} (120 \text{ ft.}) + 0.3325 \text{ MMscfd} = (0.797499 + 0.3325) \text{ MMscfd} \\ &= 1.13 \text{ MMscfd} \end{aligned}$$

If the tank is nearly empty:

$$\text{Boil off} = 0.00664583 \text{ MMscfd}/\text{ft.} (0 \text{ ft.}) + 0.3325 \text{ MMscfd} = 0 + 0.3325 \text{ MMscfd} = 0.3325 \text{ MMscfd}$$

If the tank is half full:

$$\text{Boil off} = 0.00664583 (60) + 0.3325 = 0.3987498 + 0.3325 = 0.7312 \text{ MMscfd}$$

Of course, the equation would be different for every different configuration of tank. In reality some radiation from the warmer tank roof would occur when the tank is nearly empty and the roof tends to be relatively warm. Also, it is unlikely that the heat resistance is the same on the bottom of the tank as the side of the tank.


17. Problem #3.9 – Theoretically Estimate how much vapor is produced, due to the saturated pressure drop, when a well-mixed tank is dropped in pressure by 0.5 psig.

0.5 psig is approximately 13.85” of WC or 1.02” of mercury. Assume the tank contents settle out long enough for all of the LNG to reach the new saturation temperature.

18. Solution # 3.9

For simplicity, use liquid methane for the analysis. Assume the initial tank pressure is 16 psia and that the pressure is lowered to 15.5 psia. The tank is assumed to be perfectly insulated to assure the change of phase is due to the pressure change only. Assume the initial quantity of liquid methane in the tank is equivalent to 1 Bscf of methane. Assume the liquid methane in the tank is fully mixed to assure it is all at the saturated temperature.

Use REFPROP to determine initial mass of liquid methane. Then determine the enthalpy of the liquid methane before pressure let down and after pressure let down.


 6: methane: Specified state points

	Temperature (°F)	Pressure (psia)	Density (lbm/ft³)	Enthalpy (Btu/lbm)	Entropy (Btu/lbm-°R)
1	60.000	14.696	0.042359	382.45	1.5781
2					

Figure 135: Standard temperature and pressure for pure methane.

Initial mass of liquid methane is 1 Bscf x 0.042359 lbm/scf = 42,359,000 lbm of liquid methane.

As the saturated liquid methane is decreased in pressure and the bulk of the liquid cools. That cooling is the result of a change of phase of liquid methane to vapor methane.

 8: methane: Saturation points (at equilibrium)

	Temperature (°F)	Pressure (psia)	Liquid Density (lbm/ft³)	Vapor Density (lbm/ft³)	Liquid Enthalpy (Btu/lbm)	Vapor Enthalpy (Btu/lbm)	Liquid Entropy (Btu/lbm-°R)	Vapor Entropy (Btu/lbm-°R)
1	-256.79	16.000	26.272	0.12260	1.5685	220.51	0.0077217	1.0869
2	-257.50	15.500	26.307	0.11908	0.97869	220.23	0.0048269	1.0893
3								

Figure 136: Standard temperature and pressure for pure methane.

The initial total enthalpy at 16 psia of the tank of liquid methane is the mass of liquid methane times its specific enthalpy.

This is equal to 42,359,000 lbm x 1.5685 Btu/lbm = 66,440,091.5 Btu (See Figure 135)

The cooling of the liquid during the pressure reduction is due to the change of phase of some of the liquid to vapor. Designate the mass of vapor changed from liquid to vapor as “X”.

Initial enthalpy of liquid = final enthalpy of liquid + heat removed by evaporation

$$66,440,091.5 \text{ Btu} = (42,359,000 - X) 0.97869 + X (\text{heat of vaporization})$$

For the heat of vaporization use the average between 16 psia and 15.5 psia. Heat of vaporization is the difference between the saturated vapor enthalpy and the liquid enthalpy.

At 16 psia the heat of vaporization is $(220.51 - 1.5685) \text{ Btu/lbm} = 218.9415$

At 15.5 psia the heat of vaporization is $(220.23 - 0.97869) \text{ Btu/lbm} = 219.25131$

Average heat of vaporization = $((218.9415 + 219.25131) \text{ Btu/lbm}) / 2 = 219.0964 \text{ Btu/lbm}$

$$66,440,091.5 \text{ Btu} = (42,359,000 - X) \text{lbm} \times 0.97869 \text{ Btu/lbm} + X \text{lbm} (219.0964 \text{ Btu/lbm})$$

Cancel out units from each side of the equations.

$$66,440,091.5 = (42,359,000 - X) \times 0.97869 + X (219.0964)$$

$$66,440,091.5 = 41,456,329.71 - 0.97869 X + 219.0964 X$$

$$24,983,761.79 = 218.11771 X$$

$$X = 114,542.564 \text{ lbm of liquid methane vaporized.}$$

114,542.564 lbm of liquid methane is 2,704,090 scf of methane vaporized. (Answer)

2.7% of the liquid methane vaporized due to the pressure drop.

19. Brain Teaser # 3.1. How cold would a drop of liquid methane get as it free falls in a tank filled with nitrogen at atmospheric pressure?

20. Solution Brain Teaser # 3.1

You might be tempted to say -260 F but ponder this:

- A well-insulated pot of water at 1 atm and 212 F has saturated steam at 212 F passing over it at a high velocity. What temperature is the water after a period of time? The water remains at 212 F because the water vapor pressure of the saturated water and the water vapor pressure of the saturated steam are equal. Remember evaporation is an equilibrium process where the flow is in the direction to the lower concentration driven by vapor pressure.
- A well-insulated pot of water at 1 atm and 212 F has dry nitrogen at 212 F passing over it at a high velocity. What temperature is the water after a period of time? The water gets much colder than 212 F because the water vapor pressure of the saturated water is high and the water vapor pressure of the dry nitrogen is zero. Remember evaporation is an equilibrium process where the flow is in the direction to the lower concentration driven by vapor pressure.
- On a hot dry day, you perspire and your body is cooled by the evaporating sweat. However, on a day of the same temperature when there is high humidity, you perspire and your sweat does not sufficiently evaporate to cool you down.
- If you leave a glass of water out in the shade all day long and if the ambient temperature remains constant for the entire day and if the humidity is less than 100%, why is the water cooler than the air temperature? Because the water is constantly evaporating as the water vapor pressure in the water is greater than water vapor pressure in air.
- In the above the term vapor pressure is used. A more correct term is partial pressure. According to Dalton's law, the evaporating liquid will behave as if the gas above it was at a pressure equivalent to the number of molecules "of that substance". This means that if I have a **molar** mixture of 1/3 methane and 2/3 nitrogen at a pressure of 15 psia over a well-insulated beaker of liquid methane, the methane would cool as if it was at a saturation pressure of 5 psia. Keep in mind that the vapor needs to be blown over the liquid at a significantly high velocity in order to wipe away the layer of pure methane vapor directly over the liquid methane and the heat leak into the liquid needs to be less than the heat removed by evaporation. If the velocity is not significantly high, then the vapor directly over the beaker would become rich in methane and its partial pressure

would approach 15 psia at the liquid surface. Without a velocity, diffusion would be the only means of evaporating the liquid.

- Let's do some mental experiments. In each of these experiments the extremes of taking the concept to the limit is illustrated. In each of these mental experiments neglect the heat transfer from the gas stream to the liquid.
 - Have a well-insulated very tall, narrow vessel half filled with liquid methane and have a high velocity mixture of 1/3 methane, and 2/3 nitrogen blow across the mouth of the vessel. This is shown in Figure 137. Estimate the temperature of the liquid methane after equilibrium is achieved. Based on a very tall tower the vapor above the liquid that is 100% methane, the partial pressure of the methane vapor above the liquid is estimated to be 15 psia and thus the liquid is vaporizing at -258 F. Diffusion up the tube is the only means of evaporating the liquid. The heat transfer into the liquid may be higher than the heat removal by evaporation due to diffusion. In this case the difference between evaporation heat removal and heat leak into the fluid would cause the liquid would slowly boil at -258 F.

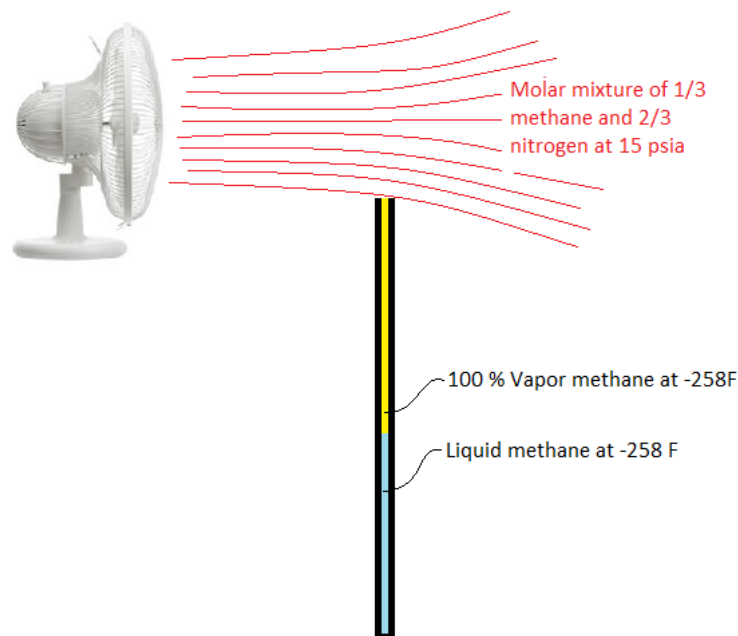


Figure 137: A very narrow column of methane vapor above the liquid methane isolates it from the methane vapor pressure of the fluid stream at the top of the vessel.

Thus, the liquid methane sees a vapor pressure of 15 psia of methane at the liquid vapor interface. Thus, the saturated temperature of the liquid methane is -258 F which is associated with a saturation pressure of 15 psia. In this case, diffusion up the long tube is the only means of evaporation. The excess heat in causes the liquid in the tube to slowly boil, disabling the diffusion mechanism by the constant flow of boil off gas up the tube. Thus, the boiling occurs at a saturated temperature and pressure of 15 psia and -258 F.

- Next have a well-insulated very short, wide vessel filled with liquid methane and have a high velocity mixture of 1/3 methane, and 2/3 nitrogen at 15 psia blow across the mouth of the vessel. This is shown in Figure 138. Estimate the temperature of the liquid methane after equilibrium is achieved. Based on the vapor above the liquid being immediately replaced with a mixture of 1/3 methane, and 2/3 nitrogen, the partial pressure of the methane vapor above the liquid is estimated to be 5 psia and thus, the liquid is vaporizing at -279 F. Here, the heat removed by evaporation is much greater than the heat into the liquid through the well-insulated vessel walls.

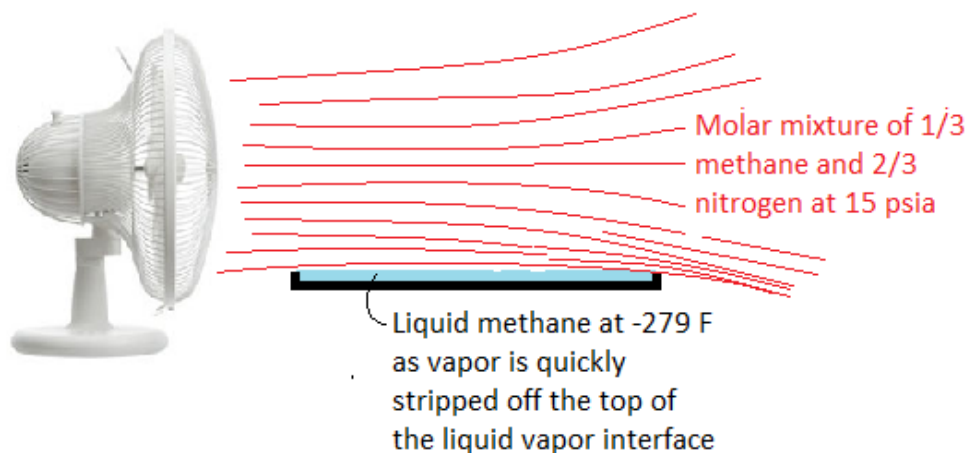


Figure 138: The liquid methane in the shallow pan cools to approach the temperature associated with the partial pressure of methane in the high velocity vapor stream across the top of the liquid vapor interface.

Thus, the saturated temperature of the liquid methane is approximately -279 F which is associated with a saturation pressure of 5 psia. The evaporation heat removal is much higher than the heat leak into the liquid methane. Note: This presumes no heat transfer from the nitrogen into the liquid methane.

- What other phenomenon would occur as the methane nitrogen vapor is blown across the liquid methane. Some of the nitrogen would condense into the liquid

methane. This is because initially the vapor pressure of the nitrogen in the pure liquid methane is zero. Thus, eventually the liquid methane would contain a few percent of nitrogen.

- In the above mental exercise, the extremes were taken to the limit. Presuming the vessel was very well insulated, in reality the liquid in Figure 137 may be a little colder than -258 F (if the evaporation due to diffusion is greater than the heat flux into the fluid via conduction through the walls of the vessel) and the liquid in Figure 138 would be somewhat warmer than -279 (as, even with high velocity stream, the laminar sub boundary layer at the liquid interface is 100% methane). This is because there is always a concentration gradient between the two fluids. In particular in the case of Figure 138, the very top layer of molecules of vapor above the liquid would be the pure methane within the laminar sub boundary layer of the gas that has just been evaporated. However, the concentration gradient between that layer of pure methane and the methane nitrogen mix is very high (but not infinitely high). Thus, as the vapor velocity increases, the liquid temperature approaches but never fully reaches the -279 F temperature.
- Also, for our mental exercise we postulated that the vessel was very well insulated and we neglected the heat transfer from the gas blowing over the top of the vessel to the liquid. If the heat transfer into the liquid is greater than the evaporative cooling, then boiling will occur at a temperature associated with the total pressure in the room. This is because the fluid on top of the liquid will always be 100% methane and the boiling that is occurring below the liquid line is occurring at the room's total pressure with only 100% pure methane in the liquid and vapor form.

Thus, in conclusion, if evaporative cooling is greater than the heat leak into the liquid, the temperature of the liquid will approach that associated with the partial pressure of the methane above it. This was shown in Figure 3.17. On the other hand, if the evaporative cooling is less than the heat leak into the liquid, the temperature of the liquid will approach that of the boiling point associated with the total pressure above the methane. This was shown in Figure 3.16. Also, many cases of steady state heat balances can occur somewhere between these two extremes.

A good analogy one could have would be a large pot of water at steady state at 160 F simmering on a stove with a low flame. It may be 90 F outside. The evaporative cooling is equal to that of the heat input. Thus, the temperature of the water is somewhere in between the boiling point at 1 atm (212 F) and the vapor pressure saturation point

(perhaps 70 F). If the flame is shut off, the eventual temperature of the water becomes 70 F. If the flame is raised, the eventual temperature of the water becomes 212 F. If the flame remains the same and a fan is placed over the pot, the water temperature may drop to 130 F.

- Although it is not discussed in this learning, it should be noted that as the nitrogen is blown across the liquid methane, some of the nitrogen will liquefy into the liquid methane. This would result in the composition of the liquid methane becoming liquid methane with a small amount of liquid nitrogen.
- So going back to our initial question, what is the potential temperature of a drop of liquid methane as it falls in a tank of pure nitrogen gas as shown in Figure 139. In the extreme limit from a theoretical perspective, one could expect the drop of liquid methane to approach a temperature of -296 F. This is approximately the triple point temperature of methane. **Note: This presumes no heat transfer from the nitrogen into the liquid droplet.**

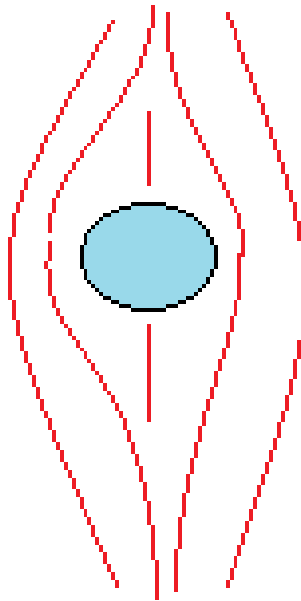



Figure 139: A droplet of pure liquid methane free falls in a tank filled with very cold pure nitrogen.

The droplet rapidly cools and approaches a temperature of -296 F. This very low temperature is approached because the partial pressure of methane in the tank is zero and the high velocity of the nitrogen around the falling droplet strips the methane vapor from the surface of the liquid

methane leaving a very high concentration gradient between pure methane and pure nitrogen. Also some of the nitrogen will start to liquefy into the droplet. Thus, if the droplet survives to the bottom of the tank, it will have a liquid concentration of both liquid methane and liquid nitrogen.

- Theoretically, in the extreme case, the droplet of liquid methane can decrease in temperature down to near its triple point temperature of approximately -296 F. In reality the real terminal temperature of the liquid methane drop lies somewhere between that of Figure 137 and Figure 139. Factors that enter into the actual temperature include:
 - The temperature of the surrounding vapor
 - The condensation of the nitrogen into the liquid methane droplet
 - The droplet mass, surface area, terminal velocity, and the time the liquid is falling before it either totally evaporates or hits the floor of the tank.
 - The real initial composition of the droplet. In our study above we used pure liquid methane for simplicity. An LNG droplet would change composition (weathers) as it evaporates.
- So, although we have not definitively stated the final temperature of the droplet of liquid methane, we have postulated that it would be something colder than saturated liquid methane temperature at 15 psia. For this reason, some LNG tank designers will NOT allow LNG tanks to be cooled down with LNG if the tank is initially filled with nitrogen. Typically, they require the tank to contain at least 80% methane before allowing LNG to be sprayed into the tank. This is to assure that the partial pressure of methane is sufficient to assure that the methane raining down on the tank floor is not colder than approximately -260 F. This precaution is taken to avoid exposing the tank material to temperatures colder than its design (typically -260 F). The data for the above postulations is shown in Figure 140.

 1: methane: Saturation points (at equilibrium)

	Temperature (°F)	Pressure (psia)	Liquid Density (lbm/ft³)	Vapor Density (lbm/ft³)	Liquid Enthalpy (Btu/lbm)	Vapor Enthalpy (Btu/lbm)	Liquid Entropy (Btu/lbm-°R)	Vapor Entropy (Btu/lbm-°R)
1	-258.22	15.000	26.344	0.11555	0.37465	219.94	0.0018512	1.0918
2	-279.62	5.0000	27.396	0.042222	-17.284	210.92	-0.090441	1.1770
3	-296.39	1.7000	28.183	0.015684	-30.874	203.26	-0.16953	1.2644
4								

Figure 140: Various saturation temperatures for pure methane.

Although the pressure above a vessel of liquid methane may be 15 psia, if the vapor above the vessel is only 1/3 methane then the methane vapor partial pressure and associated temperature is the same as if the vessel were at 5 psia of pure methane vapor over the liquid methane.

Figures 141 and 142 show a typical nozzle and nozzle configuration for spraying LNG into LNG tanks. Typically, there are 8 such nozzles in a tank that are used to cool down the tank. For the reasons stated above, these nozzles are not used unless the tank has at least 80% methane in it.



Figure 141: Typical type of nozzle that is used to spray LNG into an LNG tank to cool it down during commissioning.

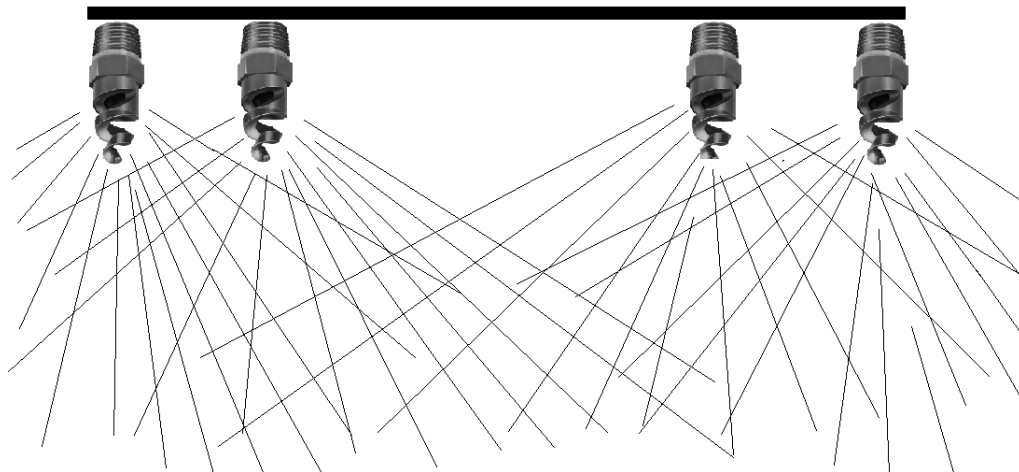


Figure 142: Multiple nozzles are (typically a minimum of 8 nozzles) used to cool down an LNG tank during commissioning.

21. Brain Teaser # 3.2. If you mix 1 lbm of water at 40 F with 1 lbm of water at 200 F, at constant pressure what would you expect the new properties of T, h, s and density to be? Would it be the average of the properties of the 2 initial substances?

22. Solution Brain Teaser # 3.2

We might be tempted to say “of course it would be the average of the properties of the 2 initial substances”. However, as we investigate this, we will find that for enthalpy it is exactly the average. For most of the other properties it is very close to the average. But for entropy difference from the average is greater. Also, we learn from the 2nd law of thermodynamics that if there is a “NET” change in entropy it will always be a positive number (never negative).

View Figure 143. The input for line 3 of that table is the enthalpy which we know by the 1st law of thermodynamics, for mixing water of 1 lbm with 1 lbm, is exactly the average of the 2 initial enthalpy values [$h_{\text{outlet}} = (h_{40} + h_{200})/2$] which is 88.16507943 and the pressure which is 14.696.

Note also that I increased the number of significant digits displayed to 10 in order to evaluate small differences in the values. This is done by selecting “Options” then “Preferences” then, in the lower left-hand corner of the screen you, increase the number of digits displayed. This may be even more than the convergence accuracy of the software, but it was selected to allow us to make a comparison with little influence from round off.

Also, note that I chose to display a new term that we have not used before. That term is Cp, which is the specific heat at constant pressure. This term was added by selecting “Options” then “Properties” and then selecting Cp. This term was selected to help explain some of the following.

5: water: Specified state points

	Temperature (°F)	Pressure (psia)	Density (lbm/ft³)	Enthalpy (Btu/lbm)	Entropy (Btu/lbm-°R)	Cp (Btu/lbm-°R)
1	40.00000000	14.69599999	62.42628423	8.080839263	0.01621503754	1.005349945
2	200.0000000	14.69600000	60.12072422	168.2493196	0.2942830108	1.005845567
3	120.0697873	14.69600000	61.71105512	88.16507944	0.1648827588	0.9992945659
4						

Figure 143: REFPROP output showing the results of adding 1 lbm of 40 F water to 1 lbm of 200 F water.

The input data is the initial pressures and temperatures and the final pressure and enthalpy. The final enthalpy is the average of the two input enthalpy values via the 1st law of thermodynamics a 1 lbm to 1 lbm water mixture.

Here are our findings:

- 1) The final specific enthalpy of the mixture is exactly the average of the enthalpy of each lbm of water before the mixing. This is due to the 1st law of thermodynamics. Energy in = Energy out. (Answer)**
- Although the pressure shown in line 1 was input as 14.696, the software showed back 14.69599999. That round off in the last digits is nothing more than the software algorithms converging on answers within some degree of defined accuracy. Thus, the last digits in the pressure data are an accepted output error which considered trivial. The same occurred with the last digit on the input of the final enthalpy (3 was typed in and 4 was displayed).
- 3) The final temperature is close to the average of 40 F and 200 F but it is not exact. It differs from the average by a small amount. The reason for that is because the specific heat of water changes as its temperature changes. Take note of that in the Cp column. However, it is very close to the average and thus, for an estimate, one could use the average of the 2 temperatures. (ANSWER).** However, that is true for this particular problem and may not be the case in many other mixing problems. For instance, if we mixed steam and water, we certainly could not have used the average temperature for an estimate.
- 4) The final density is close to the average of 40 F and 200 F specific volume but it is not exact. It differs from the average by a small amount. The reason for that is twofold. First, is because the density is a function of temperature and it may or may not be a straight-line function within this range. Second, even if the function were a straight-line relationship, as shown in 3 above, the temperature is not the**

exact average of the two initial temperatures. However, it is close to the average and thus, for an estimate, one could use the average of the 2 densities. (ANSWER). However, that is true for this particular problem and may not be the case in many other mixing problems. For instance, if we mixed steam and water, we certainly could not have used the average density for an estimate.

- 5) The final specific entropy is not close to the average of the entropy of the 40 F and 200 F specific entropy. The average of the 40 F and 200 F entropy is 0.155249024 and the actual entropy via Figure 143 is 0.1648827588. It is important to notice that the actual final entropy is significantly greater than the average of the 40 F and 200 F entropy. Since, it is not very close to the average, one could not use the average of the 2 input entropy values as an estimate for the output entropy, for this particular example. (Answer). The difference between the averaged value and the actual value is approximately 5.8%. The positive increase in “NET” entropy is due to the process being irreversible. You cannot make the water separate back into 1 lbm of 40 F water and 1 lbm of 200 F water without the use of even more energy and an even additional “NET” increase of entropy.

23. Advanced Discussion

The 2nd law of thermodynamics requires that “NO” processes cannot result in a “NET” reduction of entropy. In all real world processes the “NET” entropy change is always zero or positive. In the above example the final difference is relatively small but it is positive.

However, consider an example where a lbm of steam condenses from a vapor at 212 F to a liquid at 212 F by transferring heat to the environment which is at 90 F.

- 1) The difference in entropy of the fluid is (see Figure 144) -1.445 Btu/lbm R. The change of entropy of the environment is given by the equation: $[\Delta S_{\text{environment}} = \text{Heat Transferred} / T_{\text{environment absolute}}] = (970.728 \text{ Btu/lbm}) / 550 \text{ R} = 1.76496 \text{ Btu/lbm R}$
 - a. The sum of the change of the entropy of the system (the lbm of water that changed from saturated vapor to saturated water) and the change of entropy of the environment is $[(1.76496 \text{ Btu/lbm R}) + (-1.445 \text{ Btu/lbm R})] = +0.31996 \text{ Btu/lbm R}$. This is a very significant “positive” increase in entropy.
 - b. This tells us that in the world as we know it, processes are resulting in a continual “NET” increase in entropy. Day by day, minute by minute, in the trillions of processes taking place each moment on earth, entropy is

increasing. This raises an engineering and a philosophical question... how did our world or universe ever start off with such a low entropy? **The discussion explaining this is beyond the scope of this course. However, it is stated in order to leave the learner with a hunger to continue learning in this field.**

4: water: Saturation points (at equilibrium)

	Temperature (°F)	Pressure (psia)	Liquid Density (lbm/ft³)	Vapor Density (lbm/ft³)	Liquid Enthalpy (Btu/lbm)	Vapor Enthalpy (Btu/lbm)	Liquid Entropy (Btu/lbm-°R)	Vapor Entropy (Btu/lbm-°R)
1	212.0000000	14.70943680	59.82777681	0.03734252019	180.3296111	1151.057790	0.3124309611	1.757676660
2								

Figure 144: REFPROP output showing the results of condensing 1 lbm of steam at saturated conditions.

Conclusion

In this publication, we have used the conservation of mass and the first law of thermodynamics to understand the basics of liquid methane, methane gas, LNG mixtures and its BOG. It is understood for the reasons stated earlier that the analyses were simplified with the intent of teaching concepts. As you—the engineers of our LNG and propane plants—exercise the concepts described herein, it is hoped that you will gain a hunger for a deeper understanding of thermodynamic concepts.

From this point on, I encourage you to see everything in your day-to-day life with an understanding of thermodynamics:

- As you make a cup of coffee, you are transferring heat (increasing the enthalpy of the water) and to some extent changing phase.
- As that cup of coffee cools, it is transferring heat to the surroundings (its enthalpy is dropping), and its temperature is dropping.
- When you press on the accelerator of your car, there are so many processes that are taking place, each of which has its own thermodynamic phenomenon associated with it.
- When you turn on a methanol or an LNG pump, realize that you are increasing the enthalpy of the fluid as you add work energy to that fluid. As that fluid then flows through the plant piping, realize that, as it gains or loses heat, the fluid is changing in enthalpy. As you vaporize LNG to send gas out to your customers, realize that you are changing phase (if it is sub critical) and then warming the vapor to an acceptable temperature or if you are above the critical point that you are heating a fluid that does not have liquid and vapor phases.
 - Our LNG and propane plants are essential to our industry's future. Your skill and ability in managing these assets is a critical part of the future. This publication ends with appreciation of you for your technical ability and your dedication to excellence. You are our industry's greatest asset.