

# Reservoir Fluids

## PETE 310

### Lab 2: Determination of the Vapor Pressure of Propane

#### Learning Objectives

When you complete this laboratory, you should be able to:

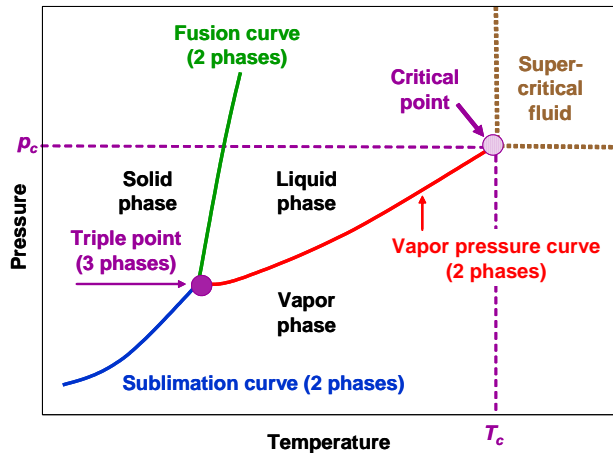
- Use closed-cell and sight-glass methods for collecting vapor-pressure data and explain the advantages and disadvantages of each.
- Determine and describe the phase behavior of a pure component as pressure or temperature change.
- Use the Clayperon equation to model the relationship between vapor pressure and heat of vaporization and explain the significance of that relationship.

#### Introduction

As oil and gas are produced from the reservoir, they are subjected to a series of pressure, temperature, and compositional changes. Such changes affect the volumetric and transport behavior of these reservoir fluids and, consequently, the produced oil and gas volumes. This behavior is used to identify the optimal recovery method (such as thermal, miscible, or chemical) and to design the recovery process.

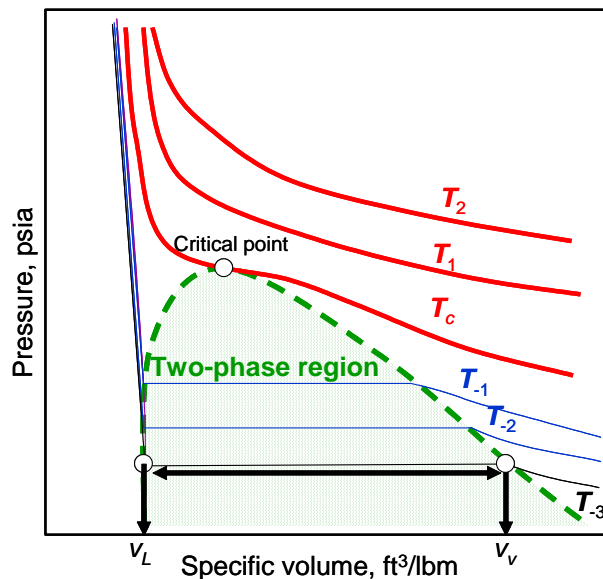
**Phase behavior.** A fluid *phase* is a portion of the system which has homogeneous intensive properties and is bounded by a physical surface. The phases—solid, liquid, and gas—are separated by interfaces where two phases may coexist when the substance is at equilibrium.

A *phase diagram* (**Fig. 1**) is a plot of pressure ( $p$  or  $\ln p$ ) against temperature ( $T$ ) that is commonly used to represent the various phases of a substance and the conditions under which each phase exists at equilibrium. Interface curves on the diagram indicate the pressure and temperature conditions that will cause a phase change: Along a curve, two (or three) phases may coexist at equilibrium; in other areas, except for the *triple point*, only one phase exists. At the triple-point temperature and triple-point pressure, three phases can coexist at equilibrium.



**Fig. 1—Phase diagram indicates pressure and temperature conditions under which a substance may change from one phase to another. Along the curves, two phases may coexist; all three exist at the triple point. Beyond the critical temperature and pressure, the substance becomes a supercritical fluid.**

At temperatures above the critical temperature,  $T_c$ , and pressures above the critical pressure,  $p_c$ , gas and liquid phases can no longer be distinguished. At  $T > T_c$  and  $p > p_c$  the substance is referred to as a *supercritical fluid*, which is a compressed gas that has the density of a liquid.



**Fig. 2—Another approach to a phase diagram shows how pressure stabilizes in the two-phase region where gas and liquid exist in equilibrium.**

Another approach to the phase diagram (**Fig. 2**) shows that fluids exhibit stabilized pressure when they cross the two-phase region at a given temperature. In this diagram, the curve or *isotherm* that represents each temperature becomes completely flat in the region between the point dewpoint,  $V_L$ , where the volume ( $V$ ) of the fluid is completely a liquid ( $L$ ) and the bubblepoint,  $V_v$ , where it is completely a vapor ( $v$ ). Note that the length of the two-phase region

of each isotherm depends on the temperature of the fluid, and the behavior is apparent only below the critical point.

The shaded area under the skewed bell curve on Fig. 2 is the fluid's *saturation envelope*. Its shape depends on interpretation of the points  $V_L$  and  $V_v$  along each of the isotherms. Developing the curve that describes the saturation envelope depends on collecting data along enough isotherms to define its shape and ensuring that the points  $V_L$  and  $V_v$  are at the same pressure.

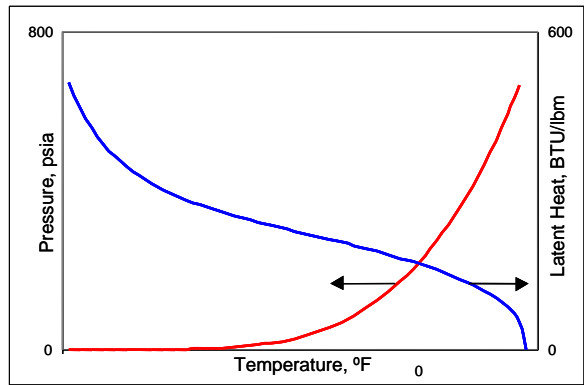
**Cox Charts and Latent Heat.** Developing the graph of the saturation envelope can be extremely time consuming unless you know the critical point, which you can read you're your textbook (page 492...) and the vapor pressure range (p and T) which you can get from the Cox charts (from your textbook again). The Clausius-Clayperon equation relates the heat of vaporization, or latent heat ( $\Delta H_v$ ), to the slope of the vapor pressure curve as indicated in the following equation

$$\Delta H_v = T\Delta V \frac{dP_v}{dT} \dots\dots\dots (1)$$

Where  $\Delta V$  is the difference between molar volume of gas minus molar volume of the saturated liquid. The units are expressed in BTU/lb-mol or Cal/mol.

In this exercise, you will develop curves to show the relationship between latent heat and pressure across a range of temperatures. Industrial uses of latent heat include heat exchangers, cooling systems, and steam injection processes. In petroleum engineering, latent heat is particularly important for enhanced oil recovery (EOR) using steam.

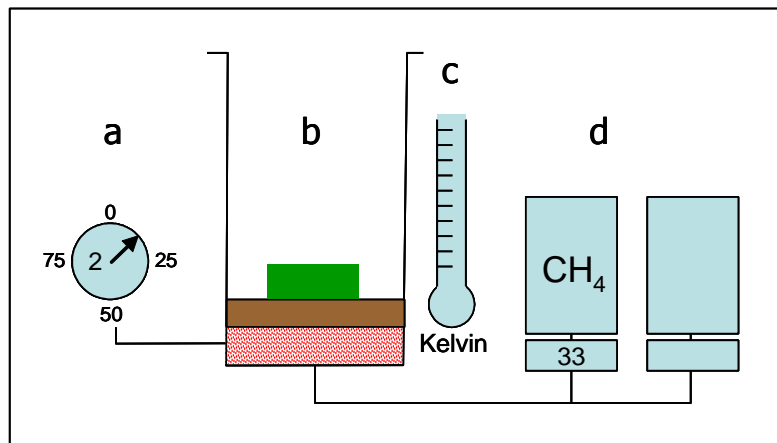
The heat of vaporization is not constant; this phenomenon must be accounted for in modeling the behavior of fluids during thermal recovery processes or in other cases where the vaporization of liquids is critical. As shown in **Fig. 3**, your graph of  $\Delta H_v$  indicates that this decreases with pressure and becomes zero at the critical point.



**Fig. 3—The curve of latent heat illustrates it decreases as it approaches the critical point.**

**The Virtual Cell.** You will be using a virtual PVT cell (**Fig. 4**) for this experiment. You will charge the cell with an amount of propane from a cylinder (in a gas phase), then change the temperature or pressure to force propane toward a phase change. Because the software (Simulation of Phase Behavior, or SOPE) attempts to make the experiment as

realistic as possible, you'll find that you can increase the pressure too high and explode the cell.



**Fig. 4—The virtual PVT cell simulates testing of pure gases or mixtures in the charged cell (b). Here, the cell has been charged with 33 millimoles of methane from one of the cylinders (d). The second cylinder could be charged with a second gas. The pressure gauge (a) measures pressure in bar and the thermometer (c) measures temperature in Kelvin.**

In this lab, you will use two approaches to the exercise. In the first, you will replicate the test using a closed cell, where you must determine the dewpoint and bubblepoint by reducing pressure within the cell; in the second, you will replicate the test in a sight-glass cell, where the dewpoint and bubblepoint will be clearly visible, but adjusting the temperature within the cell.

## Learning Activities

- Use both variable volume and fixed volume (also called sight-glass) methods to construct and interpret graphs indicating the PVT behavior of a pure substance.
- Evaluate and graph the heat of vaporization of propane from the experimental data and the Clapeyron equation.

## Tools

- Cox Charts
- Excel spread sheets
- Evaluation of derivatives (numerical and analytical)
- Unit conversion (from any online conversion site) for example <http://www.digitaldutch.com/unitconverter/>

## Procedures

The three figures that you develop and interpret will illustrate your ability to operate both closed-cell and sight-glass experiments.

### Part 1— Variable Volume Cell Expansion

In this part of the experiment you will determine gas and liquid specific volumes and vapor pressure. You will collect data to define vapor pressure curves by lowering the pressure in the cell under stabilized temperatures. Remember that in a real lab, the process of stabilizing temperatures can take more than 4 hours. Since you will be reducing pressure, you need to watch for changes in volume.

1. Use the Cox charts from your textbook to determine the range and spacing of temperatures for propane testing; you will need to have about 5 different temperatures sufficiently spaced to give a fairly good portion of the vapor-pressure curve.
2. Set the temperature of the cell at one of the desired values.
3. Set the weights in the piston such that the pressure in the PVT cell is higher than the critical pressure of propane.
4. Charge the PVT cell with propane to about 30% of the total cell volume. The propane you are using is extremely pure. Record the amount of propane charged into the cell in moles and convert this quantity to mass. You will use this to determine the specific volume.
5. Starting from the liquid phase, start a series of isothermal expansions by reducing the weights on the piston.
6. Record all pressure and cell volume readings. (Corrections from pressure and thermal expansions are taken into account automatically by the program installed in the virtual PVT cell).
7. Plot a diagram of pressure vs. specific volume (gas & liquid) for each temperature and estimate the vapor pressure for each one of the temperatures used with an accuracy of at least 0.1 bar.

### Part 2—Fixed Volume Experiment (Also Called Sight Glass Method)

In this part of the experiment, you will decrease the temperature in the cell. You will be able to observe the changes in pressure as temperature changes, but the volume will remain fixed.

1. Charge a certain amount of propane into the PVT cell and bring it to supercritical conditions. The pressure and the temperature should be both about 10 to 20% higher than the critical point.
2. Once the fluid reaches the critical state, lock the volume of the cell. Now you cannot control the pressure of the system by adding/subtracting weights because the volume is fixed, but you can change the temperature of the cell.
3. Lower the temperature of the cell gradually and observe the fluid behavior inside the cell (at some temperature you will have two phases). Use temperature decrements of 5°C and go as low as you can until you freeze the sample. The total volume of the cell is fixed and constant (we know that!), but the proportions of liquid and gas change. **For every temperature, record the following:**

- The pressure and the temperature of the cell.
- The percents of gas and liquid volumes indicated in parenthesis to the right of the gas and molar volumes.
- The gas and molar volumes in  $\text{cm}^3/\text{mol}$  (the digital output from the PVT cell does not tell you which is which; you will have to figure that out). You will need these volumes to evaluate heat of vaporization.

Plot  $p$  vs  $T$  from your experiments and overlap the vapor pressure points from Table 1.

Table 1—Experimental Data for Propane <sup>1</sup>

Temperature (F)	Pressure (psia)	Vapor Density (lbm/ft <sup>3</sup> )	Liquid Density (lbm/ft <sup>3</sup> )
60	107.72	1.0018	31.634
70	124.92	1.1622	31.115
80	144.05	1.3437	30.576
90	165.25	1.549	30.014
100	188.65	1.7815	29.427
110	214.38	2.0457	28.811
120	242.6	2.347	28.16
130	273.46	2.6924	27.467
140	307.11	3.0916	26.722
150	343.74	3.5581	25.912
160	383.55	4.1123	25.016
170	426.76	4.7866	24.001
180	473.65	5.64	22.805
190	524.57	6.8012	21.296
200	580.04	8.7064	19.021

- Plot  $\log p$  vs.  $1/T$  (absolute temperature) (saturation points only)
- Plot saturation pressures versus liquid and gas molar volumes indicating the saturation envelope
- Plot the vapor pressure curve for  $\text{C}_3\text{H}_8$  ( $p$  vs  $T$ ) and fit a trend line to represent the vapor pressure as a function of temperature.
- Determine the slope of the vapor pressure at each temperature using the derivative of the trend line estimated in Step 6, you will need this to determine the heat of vaporization.
- Using the saturated gas and molar volumes from Step 5 above, estimate the heat of vaporization for all temperatures using the Clapeyron equation (some conversions will be required).
- Plot the heats of vaporization versus pressure obtained using the Clapeyron equation

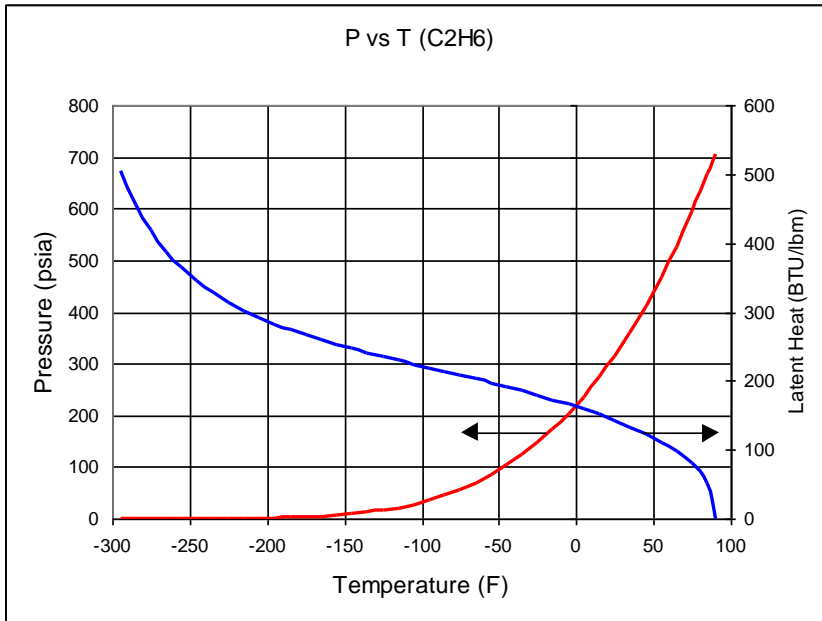
## References

- Data from NIST Standard Reference Database 69 - March 2003 Release: NIST Chemistry WebBook <http://webbook.nist.gov/chemistry/>

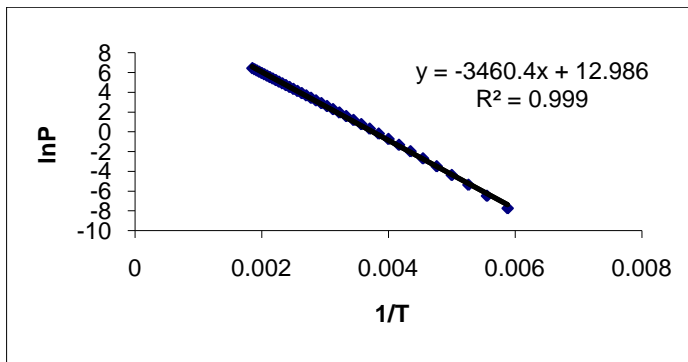
## Appendix A: Formatting graphs

When plotting make sure you use the proper units, label the axes, and write an interpretative caption for your graph. Graphs should be properly labeled!

The following is a good example of a graph that is properly labeled.



The following graph is not a good example of a professionally well presented result – Why?



## **Appendix B: Reports**

**Your report should contain the following elements:**

A brief abstract telling problem, solution, value of this work, telling which tests you used and why you chose them. Include an evaluation of your success in applying the methods.

Conclusions

A brief introduction

Methods used, including selection of temperatures and rationale for this selection.

In developing your conclusions,  
Answer the following questions:

What can you say about procedure 1 and procedure 2?

Which one is easier to use?

How did the Cox charts help you to design this experiment?

How do your experimental results compare with those published for propane?

Headings for your report may follow this pattern (with some flexibility in discussion sections):

Abstract

1. Conclusions
2. Introductions
3. Isothermal Expansions
4. Heat of vaporization
5. Comparison of methods
6. Nomenclature
7. References