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Temperature and Pressure Range of Liquid Phase

Beycan İBRAHİMOĞLU[1*], Şeyma ÖNAL[1]
[1] Department of Industrial Engineering, Ankara Science University, Ankara, Turkey
* Corresponding author: beycan.ibrahimoglu@ankarabilim.edu.tr

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Abstract

In physics, the liquid is one of the four main phases of the material, a fluid phase of the substance associated with the gas, the crystalline solid and the plasma. The interval of the liquid phase depends on the temperature between the triple point and the critical temperature range depending on the pressure between the triple point and the critical pressure. In our research, it is shown that critical pressure in literature is not actual critical value, it is only pressure value corresponding to the critical temperature. In order to investigate this situation, graph method at (P-ρ) T = const values were applied to liquid phase of many substances.

Keywords: liquid phase, temperature and pressure range of liquid phase, critical temperature, real critical pressure, graphical and graphical analytical geometry, ortho meta and para toluidine, Benzonitril.

1. Introduction

Liquid phase of matters is at the interval between solid and gas phases. Particles in the liquid phase have higher kinetic and potential energy. Although particles in the liquid phase are too close to each other, they don’t have regular position. It is generally accepted that the liquid phase of the substance has a single modification. In this respect, the liquid phase of the substance is not only a phase of that substance, but also a thermodynamic phase. (Quantum liquid and liquid crystals are the most important exceptions). The liquid phase of the pure substance is determined by temperature and pressure, and with the increase in temperature the difference between the liquid and gas at the critical point is completely lost in the (P-T) phase diagram. The temperature interval of liquid between critical temperature and triple point is displayed in Figure 1.

In this study, the classical (P-T) state diagram of the pure substance is predicted and the pressure and temperature range in the liquid phase (ρ-T) is investigated. The liquid phase is only available between Ttp and Tcr values depending on the temperature. Yet, the same approach does not apply to pressure because the liquid phase has only Ptr point which determines the interval of liquid phase depending on the pressure. The classical (P-T) state diagram (Pcr) is the pressure corresponding to the critical temperature, not the physical critical pressure value for that substance.

Critical state should characterize the situation at which the two phases of a substance are indistinguishable from each other. The critical point should characterize the endpoint of a phase equilibrium curve defined by critical pressure (Pcr), critical temperature (Tcr), and critical density (ρcr). The critical pressure defined in the literature does not characterize the boundary value for the phase change. The pressure and temperature values that cause the critical state should be referred to as critical pressure (Pcr) and critical (Tcr) temperature values.

Naturally, at the critical point, there is the critical density (ρcr) of the substance, or vice versa, the critical specific volume (vcr). This combination is called a critical point. In the critical case, the characteristics of a substance vary most unusually. The liquid phase determines the temperature range of the triple point and the critical temperature. As the temperature decreases, the liquid phase ends at the triple point and crystallization begins.

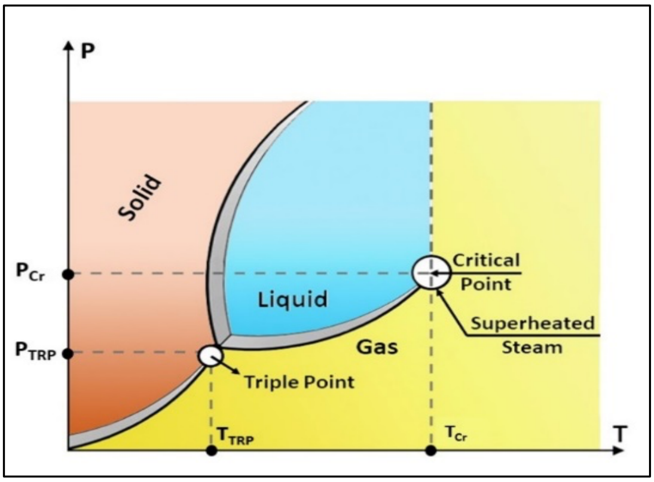

Figure 1: Triple point and critical point in the phase diagram.

2. Critical Pressure

One of the thermodynamic parameters affecting the liquid phase of the substance is pressure. The critical pressure of a substance is the pressure required to liquefy a gas at its critical temperature [1,2]. In other words, the critical pressure indicates the pressure value at the temperature corresponding to the critical temperature. The critical pressure (vapor pressure at critical temperature) generally ranges from 40 to100 bar [27,31]. These approaches in various sources belong only to the pressure corresponding to the critical temperature and do not characterize the actual critical pressure of the liquid phase. The pressure range of the liquid phase is limited between the pressure corresponding to the triple point (Ptp) and the pressure corresponding to the critical temperature (Pcr) as shown in Figure 2. The pressure range between Ptr and Pcr cannot be the pressure dependent on boundary values for the phase change of the substance. In this case, the pressure range of the liquid phase boundary range Ptp and the pressure value corresponding to the critical temperature Pcr cannot determine the actual pressure range of the liquid phase.

In the diagram, the temperature at (Tcr) only characterizes the critical situation because the liquid phase from the point (Tcr) at the right (T2) terminates at the end of the gaseous phase and at the point (Tcr) at the left (T1) the liquid phase. However, the same situation cannot be considered valid for critical pressure. The pressures P1, P2 and P3 given in the figure 2 (left) represent the liquid phase at different values. The pressure P1 in the diagram represents the liquid phase at values lower than the critical pressure and the pressures P2 and P3 represent the liquid phase at higher than the critical pressure values. In the right side of the Figure 2, different pressure values are displayed in the critical temperature line. In this case (Pcr), it is clear that the critical pressure does not characterize a critical condition depending on the pressure. In other words, the critical pressure (Pcr) given in the diagram is the pressure corresponding to the temperature which completely eliminates the difference between the liquid and the gas phases. At the same time, the pressure values that completely eliminate the difference between the liquid and the gas phases do not have a critical value but correspond to the critical temperature. We can say that the only parameter representing the critical point is the critical temperature (Tcr).

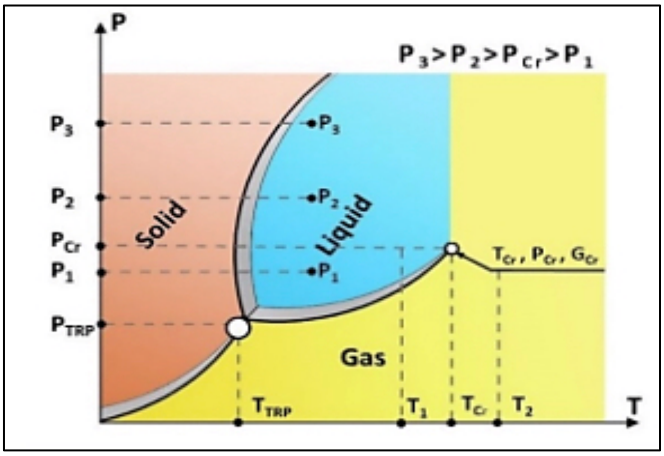

Figure 2: Determination of the pressure interval of the liquid phase.

3. Pressure Interval for the Liquid Phase

Our implementation of graphic-analytical system shows that critical temperature is a parameter that separates liquid and gas while critical pressure is a parameter that separates solid and liquid.

Currently, there is no explanation for the characteristic of the melting curve in high pressure. Inducted phase transition by pressure is discovered between solid phases. However, there are no results for phase transition between solid and liquid phases [13,14,16,19,20]. Some studies indicate the existence of critical pressure on the melting curve, as like critical temperature [32,33,34]. Moreover, it is described how to find the critical pressure on the melting line [4,6,7,8].

Percy Williams Bridgman has created experiments to measure physical effects under high pressure. In this scope, several experiments are done with benzene up to 1.25 GPa pressure, between 273K and 473K temperature. L.D. Landau indicates that “There are no finite point along the solid-liquid phases boundary curve, and the curve appears to continue infinitely” [17,18]. Except from these two Nobel-prize winning scientists, none of the studies have reported the existence of a fundamental point that completely eliminates the difference between the liquid-solid phases.

In high pressure ($\sim 10^{12}$), electron shells of atoms are deformed and internal energy rapidly increases. The bond between electron shells and atom weakens and the matter commodificates [12, 24, 25, 26]. In this situation, the bonds become irrelevant and the matter acts as electron gas with high density ($\sim 10^9$ kg/ m^3) [23]. Difference between liquid and gas disappears when the pressure reaches at 10^2 and 10^3 atm. Between 10^3 and 10^5 atm, the difference between liquid and solid disappears. When the pressure reaches at 10^6 atm, metallic bond appears. At higher pressure, unregular conglomerates of atomic nucleus and plasma alike electrons are seen [12,24,25,26]. According to investigations in the several studies, the difference between liquid and solid phase can disappear, especially between 10^3 and 10^5 atm pressure. Thus, new method is created, apart from the studies that have been done to date.

4. Implementation of Graphic – Analytic System to the Gas and Liquid

Geometrical methods are implemented on the graphics in a wide scope like physics, mathematics, astronomy, chemistry and etc. By applying the graphical system to the thermodynamic parameters of the gas phase substances such as temperature, pressure, volume and density, it is possible to obtain information about the fundamental parameters of that matter. Furthermore, it is possible to obtain more important information by applying the graphical-analytical geometry system to the gas and liquid phases of substances [3-12].

William Kelvin experimented with the gas phase of the substance by using geometry in the pressure temperature diagram and revealed the absolute temperature (T = 0K) in the solid phase of the substance.

All isochores are intersected in the single point named as absolute zero. Similar geometrical methods are applied to the density temperature diagram of gas-phased matter and all isobars intersected at the same point. It is observed that special intersection point is decomposition or ionization temperature of matters [3,5-12].

The different decomposition or ionization energies of the gases cause isobars to accumulate at different points on the temperature axis in the direction in which the temperature increases. The decomposition temperature values for various gases are given in Table 1 and Xenon gas density temperature diagram as exemplified in Figure 3 [21,22].

In other studies, the pressure value corresponding to the critical temperature of the gases is determined by applying geometry to the gases in the volume temperature diagram. By the same method, the boiling temperature and the critical temperature of the material are determined by the pressure viscosity diagram. In addition, the freezing temperature and the triple point temperature are determined in the pressure density diagram depending on the pressure.

Table 1: Decomposition temperatures for various matters.

Gas	**Temperature from geometrical approach [K]**	**Temperature from References [K]**
Oxygen	2550	2573 [12]
Argon	2920	-
Air	2690	-
Nitrogen	3700	3573 [19]
Flore	3000	-
Carbon Dioxide	2223	2273 [19]
Xenon	2500	

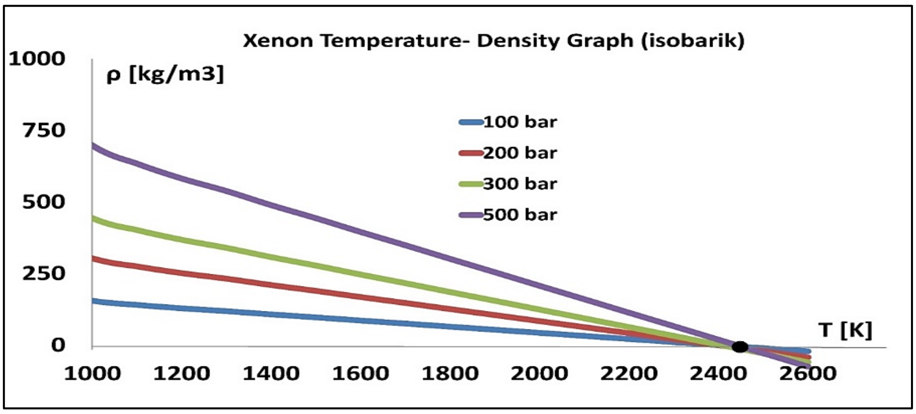

Figure 3: Temperature Density Graph of Xenon.

All these studies are done for the gas phase of the matter. Other studies on the liquid phase of matter bring up a unique point [11,29]. Geometrical methods are applied on the pressure density diagrams which are created with experimental data of various liquid matters at high pressure and temperature. Geometrical methods display all isotherms in the pressure density diagram intersect in the single point. As an example, o-Toluidine, m-Xylene and benzonitrile are displayed in the Figures 4,5 and 6. Value for the intersection point for other matters are given in the Table 2.

By applying the geometrical method to the pressure density diagram of liquid phased matter, the point where all the isotherms are collected on the pressure axis also shows a certain pressure value on the liquid-solid phase boundary curve of that matter. The pressure value shows a difference for each substance. It can be seen in the Figures 4,5 and 6 that the presence of this base point on which the isotherms are collected on the pressure axis indicates that there is also a special case on the liquid solid phase (such as the absolute temperature, decomposition or ionization points determined by the geometrical method in the gas phase). This special point is different for all matters as critical temperature is different for all matters. With the application of the geometrical method, it is possible to say that both points on the liquid-solid and liquid-gas boundary curves characterize a critical situation. As a result of our investigations, we consider this point on the liquid-solid boundary curve as the critical pressure of the liquid phase.

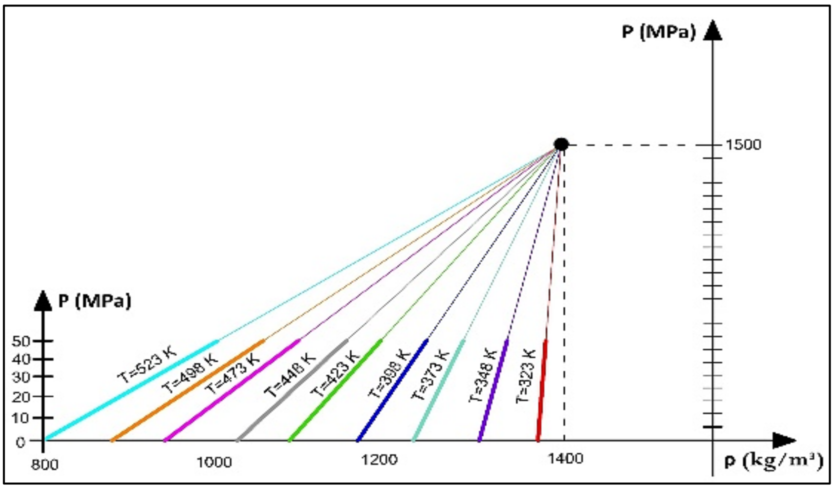

Figure 4: Isotherms of o-Toloidne in the Pressure Density diagram.

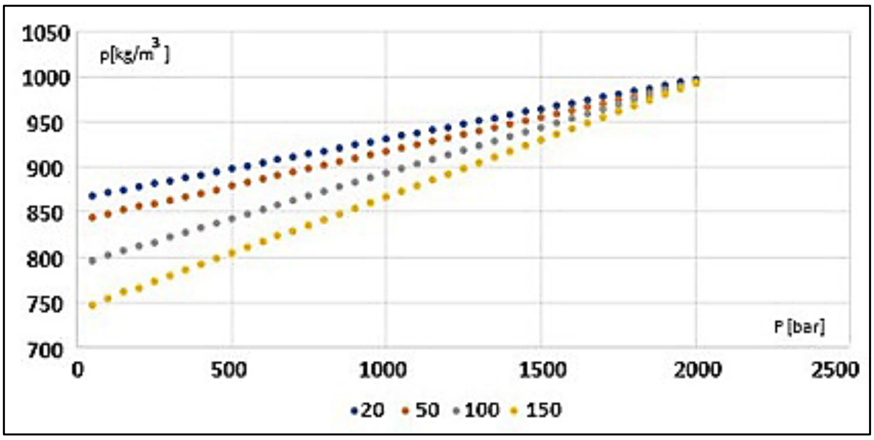

Figure 5: Isotherms of M-Xylene in the Pressure Density diagram.

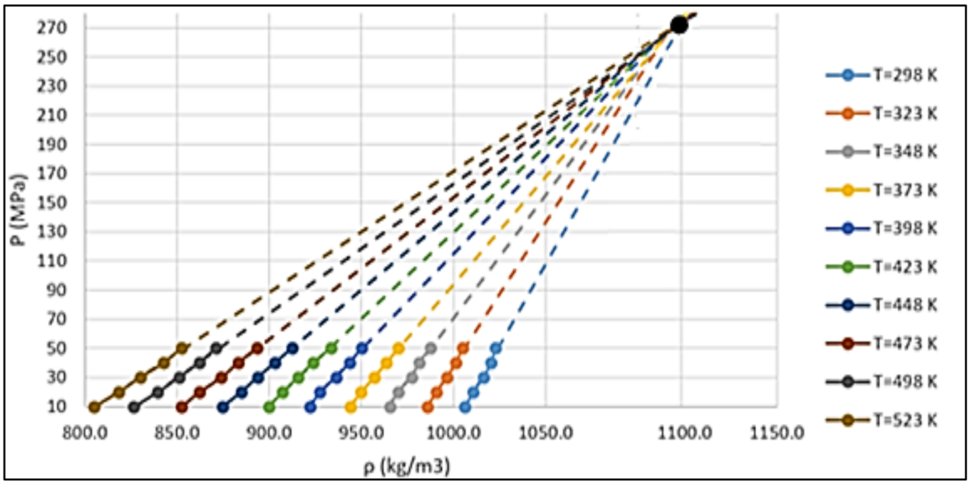

Figure 6: Point where the isotherms of benzonitrile, at p-ρ, T = constant dependency, intersect on the P axis (P = 270 MPa and density ρ = 1100 kg / m3).

Table 2: Critical pressure value for various matters.

Material	Chemical Name of Matter	Critical Pressure [MPa]	Density [kg /m3]
N Dekan	$C_{10}H_{22}$	130	0,83
N Nonan	C_9H_{20}	150	0,82
N Ksilen	C_8H_{10}	200	0,99
O Ksilen	C_8H_{10}	205	1000
O-toloudin	C_7H_9N	150	1400
M-toloudin	C_7H_9N	140	1450
P-ntoloudin	C_7H_9N	200	1100
Benzonitril	C_7H_5N	270	10
Benzen	C_6H_6	210	1200

Critical pressure which is found by geometrical methods from the pressure density diagram is displayed on the phase diagram in Figure 7.

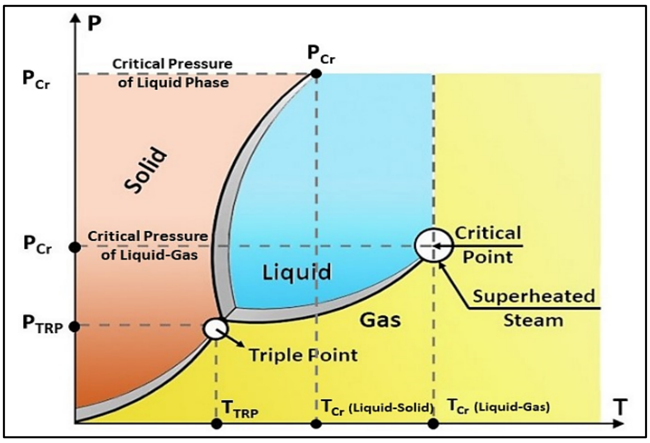

Figure 7: Critical pressure in the phase diagram.

5. Conclusion

Geometrical studies on the graphs are effective tools to solve problems. These applications provide visuality for problems and help to achieve a different approach. Thus, it is applied to solve scientific problems in different fields. It also applied to the physical diagrams of the matters in the light of previous studies. Absolute zero is found when geometrical method is applied on the pressure temperature diagram.

This study implements a similar methodology to the pressure density graphs. Geometrical approach on the density temperature graphs of various matters show that all isotherms intersect in the single point. As a result, this special point coincides with the ionization and decomposition temperature of the matter.

In addition, all isotherms in the density pressure diagram intersect on the pressure axis ($\rho=0$). According to our studies, this point is located on the liquid-solid boundary curve in the phase diagram. Since this point provides the characterizations of the critical point, it is evaluated as the critical pressure of matter. Similar to critical temperature, this point is specific for each matter. Interval for liquid phase should be limited by both temperature and pressure. It is possible to apply geometry on the physical diagrams of matters to determine important parameters such as freezing and boiling temperatures of the matters at high pressures and temperature without setting up experiments. This method provides fast, cheap and accurate solutions for problems related to the phase transitions.

Acknowledgments

Experimental Determination of Dynamic Viscosity and Density of Benzonitrile, Ortho, Meta and Para Toluidine Under High Pressure and Temperature were taken as the main references due to the thesis of the author. To determine the densities and dynamic viscosities benzonitrile, ortho, meta and para toluidine, a special and combined experimental set up was designed and experiments were conducted under high pressure and temperature [4,6,7,28].

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