Utilization of Graphical Method to Determinethe Characteristics of Desublimation Equilibrium Curve of Benzonitrile

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ABSTRACT: *The characteristics of the desublimation equilibrium curve of benzonitrile were determined by utilizing the so-called graphical method which was adapted from the one used by Lord Kelvin to estimate the absolute zero temperature. Experimental results which include the density values of benzonitrile at various pressures and temperatures were used to construct the density vs pressure (at constant temperatures) and density vs temperature curves (at constant pressures). Similar to the isotherms in the density vs pressure graphs which were revealed the existence of a critical point on the solid-liquid equilibrium curve in the previous studies, all the isobars in the density vs temperature graph at constant pressures were convened on a single point in the graphic at ρ= 1150 kg/m3 and T= 198 K, which points out the existence of a critical point on the solid-gas equilibrium curve of benzonitrile phase diagram. The projection of this point on the solid-gas equilibrium curve of the benzonitrile on the pressure axis of the phase diagram was the pressure value (P= 0.172 bar) of the critical point This critical point is thought to be the starting point of the desublimation equilibrium curve of benzonitrile due to the facts that it was identified by utilizing the graphical method which was developed from the one that was used for the determination of thermodynamically very important parameter, absolute zero temperature, and relevance of the use of this method with the axiomatic method which states that the previously defined basic concepts should be defined through the same concepts in the new situation because the new situation is a logical consequence of previously proven statements.*
KEY WARDS: *Phase diagram, benzonitrile, graphical method, critical point, desublimation, solid-gas equilibrium*

I. INTRODUCTION

Boiling or condensation, melting or freezing and sublimation and desublimation which are directly related with the pressure and temperature of the matter are accepted as the first order phase transitions (Figure 1). Solid and gas phases are represent the sublimation and desublimation processes according to the temperature and pressure. Sublimation and desublimation are not chemical changes and they refer to physical changes in the phase transition of a matter. In general, desublimation (or deposition) is a phase transition of a substance directly from the gas phase to the solid phase without passing through the intermediate liquid phase. Desublimation is an exothermic phase change that occurs at temperatures and pressures below a substance's triple point in its phase diagram [1]. Since desublimation is an exothermic phase change, it releases energy. This energy released can be calculated by adding the enthalpy of fusion and the enthalpy of vaporization and is known as the enthalpy of sublimation (also called heat of sublimation). The reverse process of desublimation is sublimation, in which a substance passes directly from a solid to a gas phase [2]. Since physical change from solid to gas requires the addition of energy to the substance, it is an example of endothermic changes [3, 4].
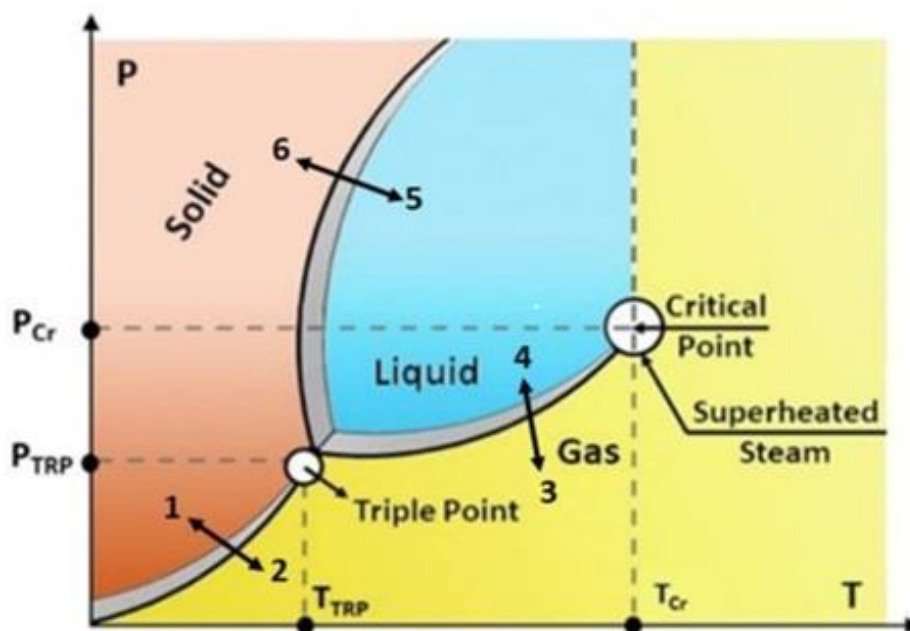

Figure 1: Phase diagram of pure matter

Sublimation and desublimation processes are widely used in the chemical industry, especially in the production of explosives, in the lyophilization of frozen solutions, gels, suspensions and biological materials. The loss of minimum amount of products and the absence of solvents are the main advantages of use of sublimation is for purification processes. These processes make it possible to obtain high purity substances and create efficient equipment at minimal cost, which promises them in the production of pure materials for nuclear energy [5].

The density of any material, regardless of the state of aggregation, is one of the main physical characteristics [6]. It is the main element of physicochemical parameters that determine and characterize the composition and structure of its various products. Phase transition usually involves an abrupt change in the density of a substance, with the density of the vapor phase being always smaller than the density of the condensed phase in the event of vaporization and sublimation.

In this study, the characteristics and critical parameters of desublimation equilibrium curve will be determined by applying the axiomatic thermodynamic geometric method to the experimental density data of the benzonitrile in liquid and gas phases. In general, the axiomatic method is utilized for creating a mathematical theory in which some of the principles considered axiomatic are accepted (axioms) and the rest are completely logically deduced. According to the axiometric system proposed by D. Hilbert, the previously defined basic concepts should be defined through the same concepts in the new situation because the new situation is a logical consequence of previously proven statements [7, 8].

In this study, the graphical method which was utilized for the determination of the characteristics and critical parameters of desublimation equilibrium curve of the benzonitrile was adapted from the one that was used for the determination of absolute zero by Lord Kelvin. These adaptation and utilization approaches are coherent with the previously accepted, reliable axiomatic method that is relatively easy to apply and accepted by scientific community.

II. MATERIAL AND METHODS

As it is known very well, the absolute zero was determined by using a graphical method since it is not possible to determine it experimentally or theoretically. The absolute zero was determined by Lord Kelvin in 1840, after applying a graphical method to the gas phase of the substances [4]. The basis of the method applied by Lord Kelvin is shown in Figure 2. The physical significance and theoretical importance of the absolute temperature is not debatable.
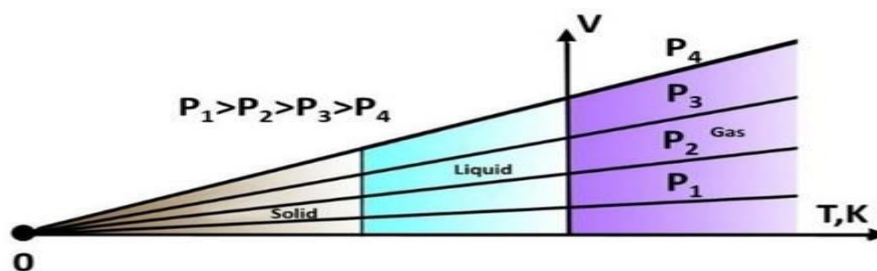
Figure 2: (V-T), P = const diagram

It was possible to determine the ionization and decomposition temperature of a pure substance just like the presence of absolute zero temperature with the application of the graphical method to the gas phase of the substances [9, 10]. Previous examinations showed that the point determined from the graphical method was ionization temperature for monatomic gases and the decomposition temperature for polyatomic gases. This demonstrated that the graphical method is an effective tool for identifying the critical points in the phase diagrams of the pure substances. Graphical method is the only method that determines all physical properties of pure substances at various pressures and temperatures. In addition, the results obtained with various studies have enabled the graphical method to be reliably included in scientific research methodology [11-14].

It is possible to adapt the graphical method to the solid-liquid phase transitions of a pure substance. The aim is to see if there exist an intersection point for the isotherms in the (ρ-T) P=const diagram of the liquids. In other words the postulates that are under investigation now are:
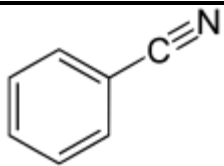
$$\left(\frac{\partial \rho}{\partial T}\right)_P = constant \tag{1}$$

i.   There exists a temperature where density of the fluid is zero for all pressures.

In this study, the characteristics of the desublimation equilibrium curve were specified by using the experimental results related to the density values of the benzonitrile at various pressures and temperatures which were obtained in a previously designed experimental set-up. The information about the set-up and its working principles were given in the previous studies [15-17].

Benzonitrile is a member of benzenes and a nitriles. Used as a specialty solvent and to produce other chemicals [18]. The basic properties of the benzonitrile (C6H5(CN)) which was used during the experimental studies are given in the Table 1.

Table 1: Basic properties of benzonitrile used in the experiments

Chemical Structure	
Triple Point (Tttp)	260 K
Critical Point Temperature (Tc)	700 K
Critical Point Pressure (Pc)	43 bar

III. RESULTS AND DISCUSSIONS

The density values of the benzonitrile which were obtained from the experiments performed at high pressures and temperatures are given in Table 2.

Table 2: Experimental density values of benzonitrile at high pressures and temperatures

T(K) \ P (MPa)	298	323	348	373	398	423	448	473	498	523
0.1	1001.2	980.1	957.5	935.8	911.8	885.1	859.8	832.6	-	-

5	1004.2	982.8	962.1	940.9	917.4	893.8	866.8	842.3	816.5	791.2
10	1006.2	985.9	965.4	944.1	922.1	899.7	874.8	852.3	826.3	804.8
20	1010.8	990.9	969.9	949.8	927.6	907.1	884.8	862.2	839.6	818.2
30	1016.2	996.6	977.4	957.0	936.2	915.5	893.6	874.0	853.0	832.5
40	1020.2	1001.4	981.3	963.6	943.6	923.7	903.2	883.1	863.1	844.8
50	1022.6	1005.1	987.5	969.9	950.1	930.1	913.0	893.2	874.2	861.8

The graphical method was applied to the experimental data (Table 2) in Figure 3 and it was observed the all the isobars in the graphic were convened on a single point at the desublimation (solid-gas) equilibrium curve of benzonitrile (T=198 K and ρ=1150 kg/m3).
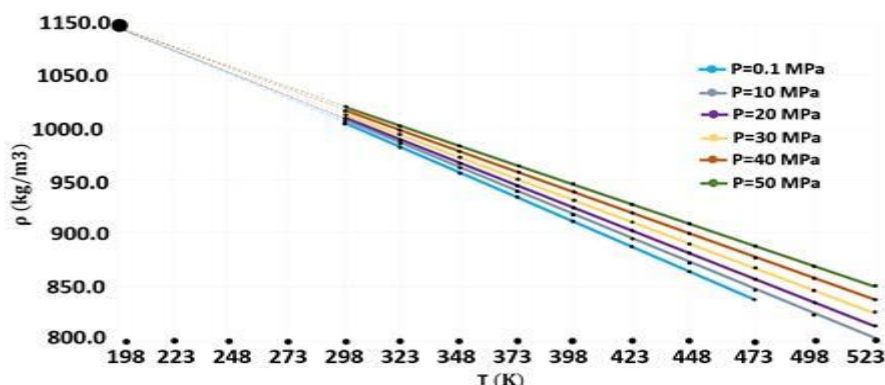

Figure 3:Applicationofthegraphicalmethodtotheisobars in (ρ-T) P=const graph of benzonitrile

The projection of a point detected on the solid-gas equilibrium curve on the pressure axis shows the pressure value of that point. The pressure value of the critical point which is thought to be the starting point of the desublimation equilibrium curve was found to be 0.172 bar by the projection of the point on the pressure axis.

Moreover, the starting point of the solid-gas equilibrium curve was also determined theoretically as 0.172 bar, by using the following equation:

$$Ps = Tsx\frac{P_{TRP}}{T_{TRP}} \tag{2}$$

where,

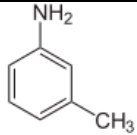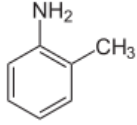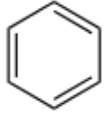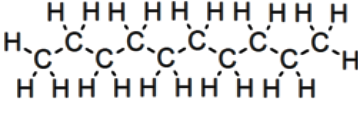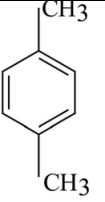P_S: Pressure value at the starting point of solid-gas equilibrium curve,

T_S: Temperature value at the starting point of solid-gas equilibrium curve,

P_{TRP}: Pressure value at the triple point,

T_{TRP}: Temperature value at the triple point.

The same methodology was also applied to various hydrocarbons with different chemical structures and it was seen that each point specific to certain hydrocarbon where isobars accumulate in the studies utilizing the graphical method shows the presence of a critical point on the solid-gas equilibrium curves of each hydrocarbon (Table 4) [19]. These points are thought to be the starting point of the desublimation equilibrium curve for each hydrocarbon regardless of its chemical structure of the aliphatic or aromatic hydrocarbons with different pendant groups.

Table 4. Critical temperature and density values obtained by the utilization of graphical method on various hydrocarbons

Hydrocarbon	Chemical Structure	Critical Density [kg /m3]	Critical Temperature [K]
m- Toluidine		1085	178
o- Toluidine		1115	153
Benzonitrile		1055	160
n-Decane		839	140
p-Xylene		990	120

Finally, the (P-T) phase diagram of the benzonitrile (Figure 4) was constructed by using the critical parameters which were determined by applying the graphical method to the experimental data for various pressure and temperature values. Since the lines or the surfaces corresponding to the interrelation between the parameters determining the phase equilibrium are usually depicted by using sets of points of various sizes, drawing the phase diagram in detail is only possible using the geometric graphical method. The construction of phase diagrams in this way is a visual representation of all possible phase transformations for a particular substance.

The desublimation equilibrium curve tends to zero pressure and temperature values, that is, a point towards the beginning of the coordinate system of the phase diagram [20] which means that each substance has a starting and ending point of the solid-gas equilibrium curve and these points are different for each substance.

The desublimation equilibirium curve in the phase diagram was formed by taking into account that the triple point on the (P-T) phase diagram represents the minimum pressure that a substance can be in the liquid form. Below this pressure, when the temperature drops below the solid phase level, the substance goes directly to the gas phase. First degree phase transition occurs with heat absorption and an increase in specific volume [21, 22]. On the solid-gas equilibrium curve the "$\Delta G = \Delta H - T\Delta S = 0$" equality is valid and the following Clausius – Clapeyron relation can be used to characterize the equilibrium curve:

$$\frac{dP}{dT} = \frac{L}{T(v_{gas} - v_{solid})} \tag{3}$$

where,

$\frac{dP}{dT}$: Slope of the tangent line to the solid-gas equilibrium curve at any point

T: Temperature

L: Heat of sublimation

v_{gas}: specific volume of gas on the solid-gas equilibrium curve

v_{solid}: specific volume of the solid phase

The specific volume of the gas on the solid-gas equilibrium curve is generally several orders of magnitude higher than the specific volume of the solid phase. According to this relation the slopes of the tangent lines to the solid-gas equilibrium curve at any point are always greater than zero and as a result of this the solid-gas equilibrium curve in the (P-T) phase diagram has a positive slope.
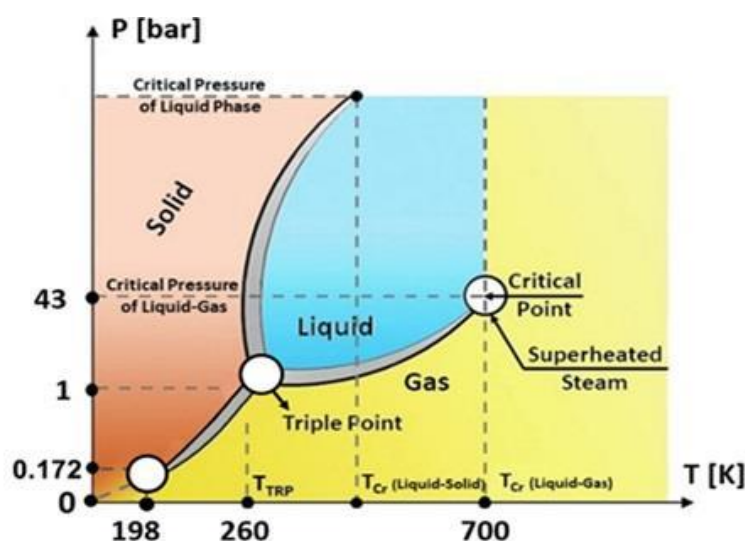

Figure 4: (P-T) phase diagram of benzonitrile

IV. CONCLUSIONS AND RECOMMENDATIONS

The essence of geometrical thermodynamics is not only the depiction of the state of thermodynamic systems using geometric images. These geometric images are not the target itself, but the subject of the research. Since geometric images have a certain physical meaning and depict real relationships between material's properties, their presence also leads to the same geometric positions with a specific physical meaning, that is, they express certain laws of nature. Therefore, on the one hand, it can be said that geometrical thermodynamics creates geometric images, which are a kind of "geometric story" about transformations in nature; on the other hand, based on the general laws of thermodynamics, unlike ordinary analytical methods, it establishes certain physical laws using geometrical methods. Therefore it is very important to utilize the axiomatic method, which is a method for creating a mathematical theory in which some of the principles considered axiomatic are accepted (axioms) and the rest are completely logically deduced, during the application of geometrical thermodynamics to the parameters that are thermodynamically important. By applying this method to thermodynamic parameters, it was possible to determine the equilibrium curves and critical points of all phases and to improve the details of (P-T) phase diagrams.

In this study, the critical point (starting point) on the desublimation equilibrium curve was determined with the application of the graphical method, which was adapted from the one that was used by Lord Kelvin to estimate the absolute zero temperature by using the axiomatic method principles, in the (ρ -T) P=const graphs that are constructed based on the experimental test results of the benzonitrile. These findings were compared with the ones which belong to various hydrocarbons and the results exhibited the suitability of the use of graphical method for the determination of the critical points of these different substances with various chemical structures.

According to the results of the graphical method, critical density (ρcr) is the starting point of the solid-gas and other equilibrium curve. The (P-T) phase diagram of the benzonitrile was constructed by using these critical parameters and the desublimation equilibrium curve was drawn by taking into account that below the triple point this curve tends to a point through the starting point of the coordinate system of the phase diagram

(zero pressure and temperature) and the solid-gas equilibrium curve, which is first order transition, has a positive slope due to the fact that specific volume of the gas phase is always greater than that of the solid phase. Besides the studies which are present in the literature, the existence and correctness of the critical pressure on the solid-liquid equilibrium curve and critical density which were determined by the graphical method in this study depend on the following two important reasons:

It is not possible to determine the absolute zero temperature which is a very important thermodynamic parameter either experimentally or theoretically. However, the only method for determining the absolute zero temperature was the geometrical thermodynamics. Therefore it can be said that, as a result of applying the same thermodynamic parameters (pressure, temperature and density) and a method which was adapted from the one that was used for the determination of absolute zero temperature, the results of this study, critical points indicating the starting points of the solid-liquid and solid-gas equilibrium curves, are real and correct.
According to the axiomatic geometrical thermodynamic system, the basic concepts described earlier should be defined in the new situation through the same concepts because the new situation is a logical consequence of previously proven statements.

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