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Liquid-solid Equilibrium Position and Critical Point for Benzene

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Abstract

Using a specially constructed experimental apparatus, the freezing thermograms of benzene at increasingly higher constant pressures and temperatures were determined. The isotherm reversible freezing of liquid benzene, which metastabilizes irreversibly through super cooling and isentalpic transformation steps, is studied in detail. In addition to the temperature and pressure changes, it was determined that the step times decreased rapidly due to increasing pressure and temperature and reached zero. Where these quantities are zero, 356 K and 2230 bar are considered as the temperature and pressure of the critical point of the liquid-solid equilibrium line, respectively. The liquid-solid equilibrium line for the variation of pressure with temperature between this critical point and the triple point is precisely determined. A pressure-temperature phase diagram with the critical point and this test line is arranged for benzene. The irreversible metastabilization of liquid benzene has been studied thermodynamically. It has been determined that enthalpy, entropy, volume and internal energy changes and work done on the system decrease rapidly with temperature and pressure as they gradually increase and approach zero at critical values.

Keywords

Benzene, freezing, metastabilization, liquid-solid equilibrium, critical point, super cooling, isentalpic change

1. Introduction

The states of matter in which the variables such as temperature, pressure, density and composition are the same at every point are called phases. Possible phases are known as solid, liquid, gas and plasma. The gas phase that can liquefy or solidify at its temperature with a sufficiently high pressure applied on it is characterized as vapor. Other phases that can physically transform into each other are chemically transformed into plasma by an ionization reaction [1].

Stable phases become metastable at their specific temperatures and pressures than begin to transform into another metastable phase [1-4]. During isobaric and isothermic transformation, metastable phases with equal chemical potentials are in thermodynamic equilibrium [5-6]. The first derivatives of equal chemical potentials with respect to temperature and pressure are characterized as first-order phase transformations if they are different, and second-order phase transformations if they are the same. [7]. The other metastable phase formed at the end of phase transformation is stabilized by changing the temperature and/or pressure.

For nearly 200 years, the formation and position of phases of pure substances, the thermodynamic equilibria between them and the critical points where these equilibria terminate have been investigated [8-11]. The temperature and volume changes as well as heat exchanges of different substances on which pressure is increasingly applied are studied in detail [12-15]. However, there are no studies on the melting of solids under high pressure by heating. Conversely, no studies have been conducted on the freezing of liquids by cooling them as the pressure on them is gradually increased.

In classical phase diagrams, the triple point where solid, liquid and vapor are in equilibrium, the liquid-vapor equilibrium line and the critical point where it ends are precisely specified [16]. The formation of the supercritical fluid, which is claimed to exist above this critical point, is discussed [17-19]. These types of fluids are used as industrial solvents [20-22].

Studies on phase transformations have focused on benzene (C_6H_6), an aromatic hydrocarbon with planar symmetric molecules [23-25]. Depending on the pressure and temperature, a large number of solid phases related to benzene were observed to form [26-27]. The positions of these phases in the temperature-pressure diagram were determined [28-30]. Possible stacking of benzene molecules forming amorphous and crystalline solid phases is discussed [31-34].

The experimentally determined triple point, liquid-vapor equilibrium line and the critical point at which it terminates for benzene and other pure substances on which similar research has been carried out are given in the literature [14]. However, it is seen that the liquid-solid and solid-vapor equilibrium lines starting from the triple point are not fully determined. The critical points where these equilibrium lines terminate, often shown qualitatively, are not even indicated schematically.

Therefore, the aim of this study is to determine the possible freezing thermograms for benzene, as well as to determine the parameters related to metastabilization and isothermic freezing steps, thermodynamic investigation of metastabilization and determination of the critical point where it ends with the liquid-solid equilibrium line.

2. Material and method

The triple point (278.5 K and 0.048 bar), the liquid-vapor equilibrium and the critical point at which it terminates (562 K and 49 bar) are known with certainty for benzene, which has been studied extensively. In this study, liquid benzene with a mass purity of 99.5% and a density of 0.787 g/cm^3 under standard conditions was selected as the material. A specially designed and constructed experimental apparatus was used to determine the freezing thermograms of cooled liquids at increasingly higher and constant pressures and temperatures [35-37]. A certain pressure is applied to 10 mL of liquid benzene placed in the freezing cell of the device and its temperature is raised to a constant value by heating. The pressure and temperature of the system cooled at a constant rate of 0.85 K/s using liquid nitrogen vapor were measured with absolute errors of 0.1% and 0.20%, respectively. The experiments were repeated by varying the pressure between 1-2300 bar and temperature between 278.5-356.0 K. Freezing due to mechanical and electromagnetic environmental influences has been observed to occur in two different ways.

3. Results and discussion

3.1 Possible freezing ways

Freezing thermograms showing the variation of temperature (T) with time (t) were constructed using the experimental data. Accordingly, benzene was found to freeze in two different ways. The thermograms of these spontaneous freezings are shown schematically in Figure 1 and Figure 2, respectively. In experiments conducted under standard environmental conditions, it has been determined that freezing usually occurs in the first way. In contrast, it was found that the second way of freezing occurred more frequently in studies conducted at night and at times when mechanical and electromagnetic environmental influences were less. The dots and lines in the freezing thermograms are described in detail in the captions. In this study, only the second way of freezing was evaluated in detail.

3.2 Freezing parameters and critical point for liquid-solid equilibrium

The measured parameters for second way freezing at increasingly higher pressures and temperatures are given in Table 1. As pressure and temperature increase, ΔT, Δp, t_1, t_2, t_3 and t decrease rapidly and reach zero. As an example, the graphs for the variation of isothermic freezing time with pressure (t_3-p) and temperature (t_3-T) are given in Figure 3 and Figure 4, respectively. Freezing is assumed to terminate at the pressure and temperature where the freezing parameters are zero. In other words, the liquid phase in these conditions remains unfrozen or solidifies completely. This position, with a pressure of 2230 bar and a temperature of 356 K, is defined as the critical point of the liquid-solid equilibrium for benzene. This critical point is also considered to be the position where the freezing of benzene from the first type transforms into the second type. The fact that benzene has crystalline as well as amorphous solid phases supports this possibility.

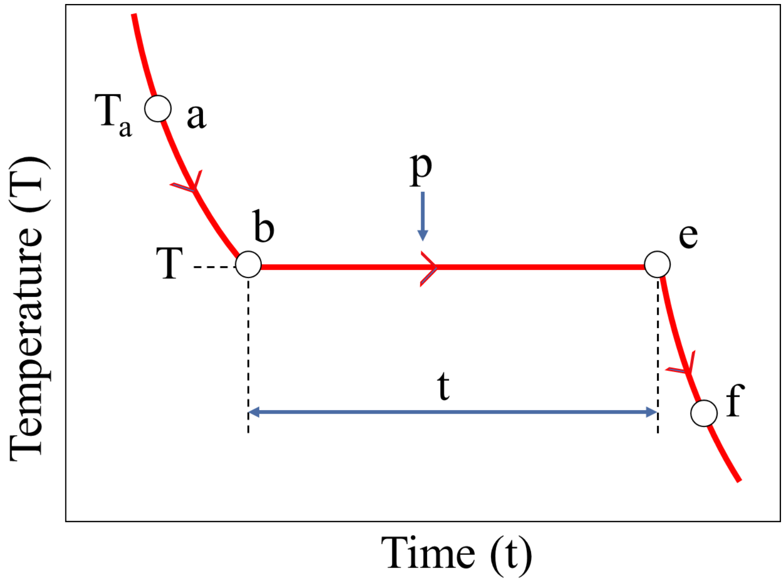

Figure 1. Freezing through metastable liquid formed via reversible way [a: stable liquid with temperature T_a and pressure p, ab: isobaric reversible cooling of stable liquid, b: metastable liquid, e: metastable solid, T: freezing temperature, be: isothermic and isobaric reversible freezing, t: freezing time, ef: stabilization of metastable solid, f: stable solid].

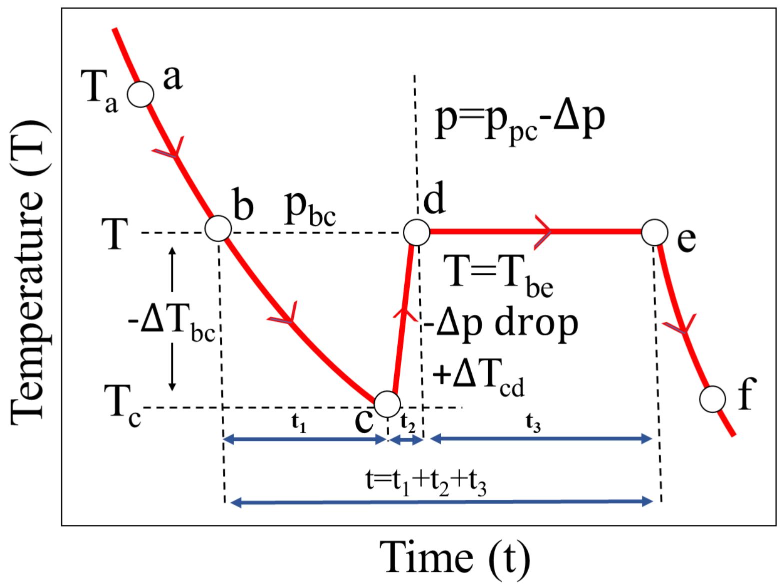

Figure 2. Freezing through metastable liquid formed via irreversible way, [ab: isobaric reversible cooling of a stable liquid, bc: isobaric irreversible super cooling of a stable liquid, -ΔT: temperature drop during super cooling, cd: adiabatic and reversible (isentalpic) change of super cooled liquid, ΔT= (-ΔT): isentalpic temperature rise, −Δp: isentalpic pressure drop, bcd: metastable fluid formation, de: isothermic ($T = T_{be}$) and isobaric ($p= p_{bc}-\Delta p$) freezing, e: metastable solid, f: stable solid, $t_1+t_2+t_3=t$: step times and total duration].

Table 1. Variations with pressure and temperature of the experimental parameters defined in Figure 2 for freezing over irreversible metastable liquid formation

p_{bc}/bar	T/K	T_c/K	-ΔT/K	p/bar	−Δp/bar	t_1/s	t_2/s	t_3/s	t/s
1.01	278.5	258.5	20.0	-	-	160.0	6.0	260.0	426.0
101.3	279.0	267.0	13.0	68.9	32.8	131.0	3.0	210.0	343.0
202.7	280.0	270.0	10.0	175.3	27.8	112.0	2.5	180.0	294.0
304.0	282.8	274.6	8.2	280.7	23.6	97.0	2.0	155.0	254.0
405.3	284.8	277.8	7.0	385.0	20.5	85.0	2.0	135.0	222.0
506.6	286.7	280.7	6.0	488.9	17.9	72.0	2.0	115.0	189.0
608.0	289.5	284.5	5.0	592.8	15.4	61.0	1.5	97.0	159.0
709.3	291.2	287.2	4.0	696.1	13.4	53.0	1.5	85.0	139.0
810.6	294.8	291.2	3.6	798.9	11.9	44.0	1.5	70.0	115.0
911.9	297.0	293.8	3.3	902.3	9.7	37.0	1.5	60.0	98.0
1013.3	299.5	296.6	2.9	1005.1	8.3	31.0	1.0	50.0	82.0
1114.6	302.5	300.1	2.4	1107.8	6.9	25.0	1.0	40.0	66.0
1215.9	305.3	303.3	2.0	1210.3	5.3	22.0	1.0	35.0	58.0
1317.2	308.0	306.2	1.8	1313.0	4.3	18.0	1.0	30.0	49.0
1418.6	312.2	310.7	1.5	1414.9	3.8	16.0	1.0	25.0	42.0
1519.9	315.5	314.3	1.1	1517.0	2.9	12.0	1.0	19.0	32.0
1621.2	320.1	319.2	0.9	1619.3	1.9	8.0	1.0	14.0	23.0
1722.5	324.0	332.3	0.7	1721.3	1.2	6.0	0.5	10.0	16.0
1823.9	328.0	327.5	0.5	1923.2	0.7	4.0	0.5	6.0	10.0
1925.2	333.5	333.2	0.3	1925.0	0.2	2.0	0.5	4.0	6.0
2026.5	340.5	340.4	0.1	2026.4	0.1	1.0	0.5	2.0	3.0
2127.8	347.0	347.0	0.0	2127.8	0.0	0.5	0.0	1.0	1.0
2229.2	356.0	356.0	0.0	2229.2	0.0	0.0	0.0	0.0	0.0

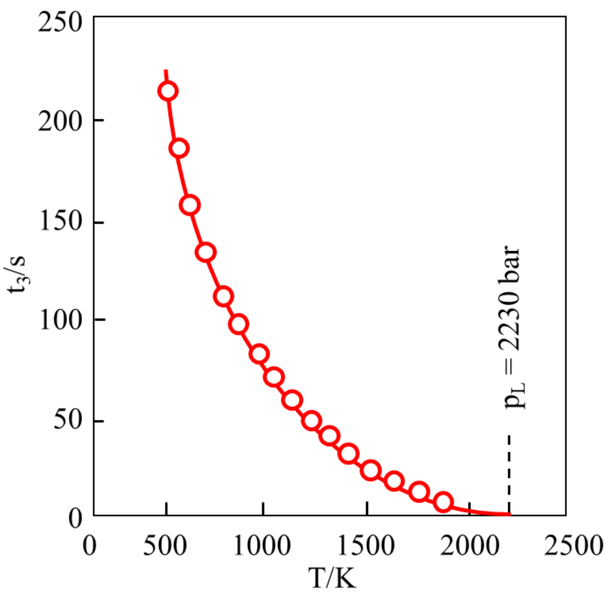

Figure 3. Freezing time of metastable liquid formed irreversibly decreases rapidly with increasing pressure and reaches zero at 2230 bar.

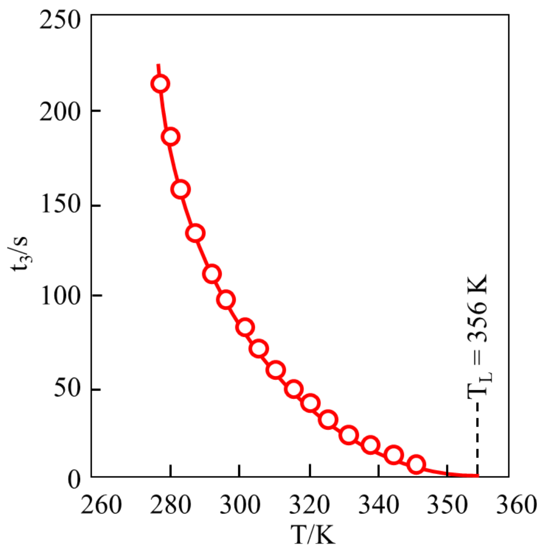

Figure 4. The freezing time of the irreversibly formed metastable liquid decreases rapidly with increasing temperature and reaches zero at 356 K.

3.3 Pressure-temperature (p-T) phase diagram

A possible p-T diagram for benzene is given in Figure 8. The triple point (J), liquid-vapor equilibrium line (JK) is drawn with experimental data from the literature [14]. The solid-vapor equilibrium line (JM) and its critical point (M), whose locations are not known from the literature, are shown qualitatively. The liquid-solid equilibrium line (JL) and its critical point (L) were determined for the first time in this study. The equilibrium lines JK, JL and JM delimit the positions of the solid, liquid and gas phases up to the critical points K, L and M. There are no boundaries between the possible phases after these critical points. Just above the critical point K, a supercritical fluid with high dissolving power is formed [19].

Plasma specific phase diagrams do not include a special position for plasma. The plasma formed by the ionization reaction is mixed with other phases. The composition of the plasma, which is a mixture of molecules, atoms, ions and electrons, and its fraction in the mixture varies depending on temperature and pressure. The high dissolving power of supercritical fluid can be attributed to plasma formation [2].

For a physical system with pressure p, temperature T, P phases and C components in each phase, the degrees of freedom F, which is equal to the number of independent variables, is calculated from the following relation (formula) F=(C+2)-P. According to this relation known as Gibbs' phase rule, the degrees of freedom of the one-phase, two-phase and three-phase systems shown in Figure 5 are calculated as 2, 1 and 0, respectively.

Plasma formed by ionization of solid, liquid and gas phases contain new components. These components are bound to the phase in which they are formed by the chemical reactions written about ionization. In other words, the same number of chemical equations can be written for the R components formed. In this case, it is assumed that the number of components that increase the degrees of freedom and the number of chemical equations that decrease the degrees of freedom are equal to each other, so that the degrees of freedom do not change during plasma formation.

3.4 Thermodynamics of irreversible metastabilization of liquid benzene

According to the fundamental laws of thermodynamics, the following equation is derived between internal energy (U), enthalpy (H), free internal energy (U: Helmholtz energy), free enthalpy (G: Gibbs energy), entropy (S), volume (V), pressure (p) and temperature (T)

$$G=H-TS=U+pV-TS=A+pV \tag{1}$$

The quantities p, T, V and S of a system whose absolute value can be measured are characterized as state variables. On the other hand, quantities such as U, H, A and G, whose absolute value cannot be measured but whose change can be measured, are called state functions. On the other hand, the quantities V and S, which are mostly used by measuring their variations in addition to their absolute values, are also evaluated as state functions.

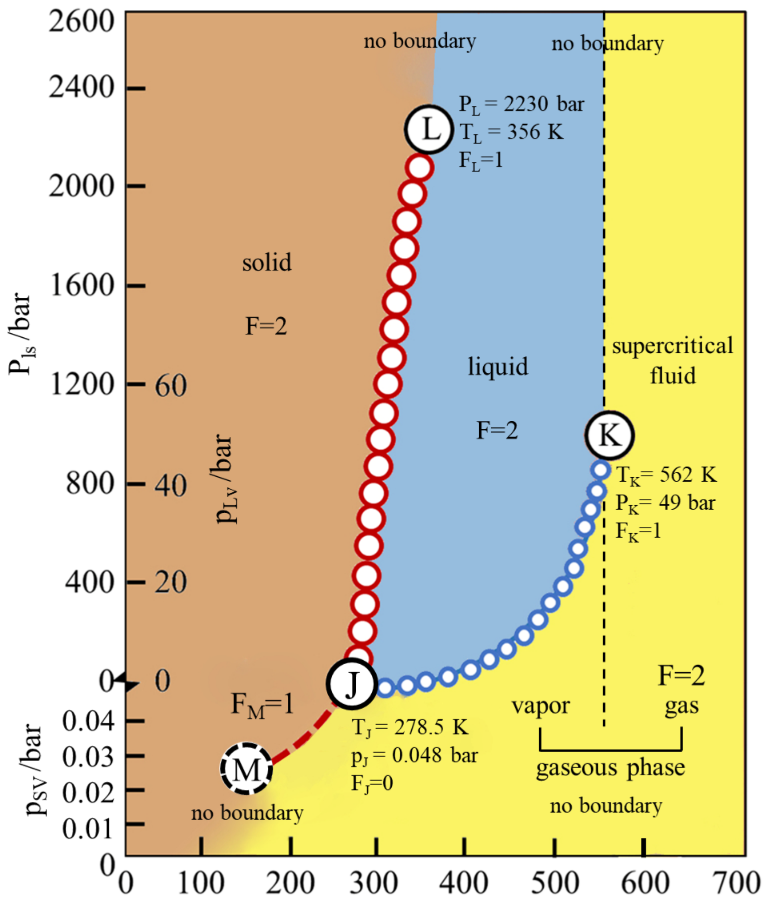

Figure 5. Pressure-temperature (p-T) phase diagram of benzene (J: triple point, JK: liquid-vapor equilibrium line, K: critical point of liquid-vapor equilibrium. JL: liquid-solid equilibrium line with its critical point, determined for the first time in this study. JM: Solid-vapor equilibrium line and critical point (M), shown qualitatively, Psv: Vapor pressure of solid, p: vapor pressure of liquid, Pls: applied pressure on the liquid-solid equilibrium, F: degree of freedom.

Changes in the state functions depend only on the initial and final state of the system. In other words, it does not depend on the way between these two states. Accordingly, the changes in ΔH, ΔG, ΔS, ΔV and ΔU along the irreversible (bcd) and reversible (bd) ways for the metastabilization of benzene shown in Figure 2 must be the same. In steps where temperature and pressure remain constant, these changes are zero. The same result emerges from the equal effects of changing temperature and pressure in opposite directions. Considering these situations, the following assessments were made in turn.

Since there is an adiobatic and reversible, i.e. isenthalpic, change along the cd in Figure 2, $\Delta H_{cd} = 0$ is taken. According to this,

$$\Delta H_{bd} = \Delta H_{bc} + \Delta H_{cd} = \Delta H_{bc} + 0 = \Delta H \tag{2}$$

The enthalpy of metastabilization is equal to the enthalpy of isobaric super cooling of liquid benzene as shown above. The temperature dependence of the molar heat of heating of liquid benzene, which is assumed to be independent of pressure, is taken from the literature as follows

$$C_p/JK^{-1}\,mol^{-1} = 66.908 + 0.2316T \tag{3}$$

(Oliver et al 1947[38]] Enthalpy changes are calculated from the following relation and given in Table 2

$$\Delta H = \Delta H_{bc} = \int_{Tb}^{Tc} C_p\,dT \tag{4}$$

Ethropy changes ΔH, defined as the ratio of reversible heat exchange ($Q_{bd} = \Delta H_{bd}$) to temperature ($T = T_{bd}$), are calculated from the following relation and given in Table 2

$$\Delta S = \Delta H / T \tag{5}$$

Free enthalpy varies with temperature and pressure. By combining the exact differential of this state function with thermodynamic relations, the following relation is found

$$G = f(T,p) \tag{6}$$

$$dG = (\partial G/\partial T)_p\, dT + (\partial G/\partial p)_T \tag{7}$$

$$dG = -SdT + Vdp \tag{8}$$

For an incident where temperature and pressure vary byΔT and Δp, respectively, the entropy volume and free enthalpy will vary by ΔS, ΔV, ΔG, respectively, so the following equation can be written

$$\Delta G = -\Delta S\ .\ \Delta T + \Delta V.\ \Delta p \tag{9}$$

The free enthalpy change along the reversible way (bd) where temperature and pressure remain constant will be zero ($\Delta G_{bd} = 0$). On the other hand, the sum of the free enthalpy changes along the bc and cd steps of the irreversible way (bcd) between the same boundaries must also be zero. This is due to the fact that the free enthalpy changes in opposite directions with temperature and pressure. Accordingly, when$\Delta G = 0$, the last relation becomes t he Clapeyron equation, which is usually written as follows

$$\Delta p/\Delta T = \Delta S/\Delta V \tag{10}$$

Since the pressure drop during super cooling leads to a pressure drop during isenthalpic change, the ratio $\Delta p/\Delta T(-\Delta p/-\Delta T)$ has a plus sign. The ΔV values calculated from the final relation using the experimental data and the ΔS change calculated above are given in Table 2.

Table 2. Thermodynamic quantities for the irreversible metastabilization of liquid benzene [p and T: pressure and temperature of the metastable fluid, ΔH: enthalpy change, ΔS: entropy change, ΔV: volume change, w = mechanical work, ΔU: internal energy change]

p/bar	T/K	$-\Delta H$/J mol^{-1}	$-\Delta S$/JK^{-1}mol^{-1}	$-\Delta V$/cm^{3}mol^{-1}	w/J mol^{-1}	$-\Delta U$/J mol^{-1}
101.3	279.0	1628.53	5.837	0.231	2.37	1626.1
202.7	280.0	1305.98	4.664	0.168	3.45	1302.5
304.0	282.8	1077.93	3.811	0.132	4.07	1073.8
405.3	284.8	924.40	3.246	0.111	4.54	919.8
506.6	286.7	795.68	2.775	0.093	4.76	790.9
608.0	289.5	650.13	2.246	0.073	4.50	645.6
709.3	291.2	535.55	1.839	0.055	4.04	531.51
810.6	294.8	485.16	1.646	0.050	4.13	481.0
911.9	297.0	439.72	1.481	0.050	4.56	435.22
1013.3	299.5	394.22	1.316	0.046	4.76	389.49
1114.6	302.5	382.05	1.084	0.038	4.24	377.81
1215.9	305.3	274.77	0.900	0.032	3.89	270.88
1317.2	308.0	248.45	0.807	0.034	4.48	243.97
1418.6	312.2	208.56	0.668	0.026	3.83	204.73
1519.9	315.5	161.12	0.511	0.019	2.89	158.23
1621.2	320.1	126.85	0.396	0.019	2.99	123.77
1722.5	324.0	99.31	0.307	0.018	3.10	96.21
1823.9	328.0	71.41	0.218	0.016	2.92	68.49
1925.2	333.5	43.23	0.130	0.019	3.66	39.57
2026.5	340.5	14.493	0.043	0.004	0.91	13.68

Knowing the pressure (p) applied on the system and the volume change ΔV, the mechanical work is calculated from the following relation and given in Table 2

$$w = -p\Delta V \tag{11}$$

In the last relation, a minus sign is used so that the work given to the system has a plus sign.

Since the enthalpy change (ΔH) and mechanical work (w) are known, the internal energy changes (ΔU) are calculated from the following relation and given in Table 2.

$$\Delta U = \Delta H - w \tag{12}$$

The calculated ΔH, ΔS, ΔV and ΔU quantities related to the metastabilization thermodynamics of liquid benzene gradually decrease with temperature and pressure in the reversible way and approach zero. Examples of -ΔH =f(p) and -ΔH =f(T) graphs are given in Figure 6 and Figure 7.

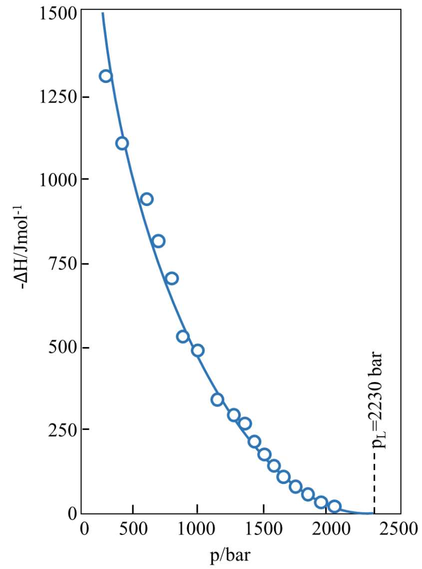

Figure 6. The enthalpy of irreversible formation of metastable benzene decreases exponentially with pressure and approaches zero at a critical pressure of 2230 bar.

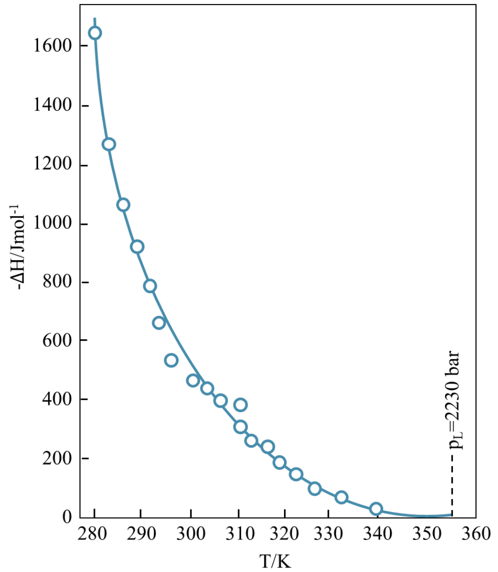

Figure 7. The enthalpy of irreversible formation of metastable benzene decreases exponentially with temperature and approaches zero at the critical temperature of 356 K.

The pressure and temperature at which they approach zero are 2230 bar and 356 K, respectively. These quantities indicate the critical point of the liquid-solid equilibrium line for benzene.

4. Conclusions

The conclusions reached in this study are listed below.

1) A specially designed experimental apparatus was used to study the freezing of liquids under increasing pressure and temperature.
2) Freezing thermograms of liquid benzene taken as material were determined under different conditions.
3) Stable liquid cooled at constant rate is observed to freeze reversibly or irreversibly by becoming metastable.
4) More detailed irreversible metastabilization is observed to increase as mechanical and electromagnetic environmental effects decrease.
5) Freezing thermograms through irreversible metastabilization were evaluated in detail.
6) By evaluating the relationships between freezing parameters in this way, the liquid-solid equilibrium curve and critical point in the pressure-temperature phase diagram of benzene were determined for the first time.
7) A method for the thermodynamics of irreversible metastabilization is proposed for the first time.
8) A method for determining liquid-solid equilibrium curves and critical points for all pure substances in the same way has been proposed.

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