STUDY OF METASTABLE STATES OF LIQUIDS AT HIGH PRESSURES

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Introduction

The measurement of phase changes of a fluid phase of matter at high temperatures and pressures [1,2] introduces a composite experimental problem and gains the increasing value in connection with the solution of scientific and engineering problems of physical chemistry. In this research some limits at which there exist metastable states at various pressures and temperatures are considered on an example of benzene.

Experiments

The experiments for analysis of phase changes of benzene were conducted on the installation, where the pressure in a system (within the limits of pressure variation from 0.1 up to 100 MPa) has been set through a dead-weight pressure gauge, which one is paired through the clip device to a measuring vessel, where the studied matter was chilled and was heated. Temperature of matter in a measuring vessel is measured through the thermoelectric couple of a chromel – koppel type. The thermoelectric couple is paired to the electronic self-recording potentiometer, graduated for measurement of temperature in limits of -50°C - +50°C. The vessel, insulated from environment and located in a refrigeration camber, is cooled by the vapors of fluid nitrogen, which one pass through the coil pipe of the special shape. The coil pipe has no contact with a surface of vessel. To prevent leakage of cold air, and also for an even distribution of cooling, all system is concluded in a safety casing.

For successful carrying out of experience, observance of following conditions is required: high cleanliness of investigated substance, slow constant rate of cooling (not exceeding 0.55 C°/min), high cleanliness of polishing on an internal surface of a vessel in which an investigated substance is placed, absence of mechanical pushes during the moment of carrying out of experience [4].

At cooling of clean benzene, as is known from the literature, the benzene should freeze at +5°C at atmospheric pressure. It is known that at the given pressure phase change occurs under certain strict temperature. However, at cooling of clean benzene a meta-stable state at first will derivate, as it is shown in a fig. 1 (at pressure of 50 MPa), that is the liquid is super cooled usually on 14 - 16 °C below than freezing temperature, then temperature is augmented by a jump up to freezing temperature t = 18.5°C and remains constant before full formation of a solid phase on all measuring vessel [3, 4].

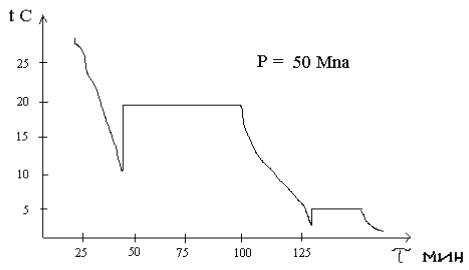

Figure 1.

At instantaneous increase of temperature, pressure in a system instantaneously drops also, which one is reset to initial value through a dead-weight pressure gauge.

Results and discussion

Results of experiments are characterized by the following: after full formation of a solid phase, at pressures above 15 MPa, and cooling progress, the discontinuous increase of temperature with simultaneous pressure drop is watched again and the segment is watched, where temperature remains constant. As it is shown in the Table 1, at pressure above 15 MPa, 2 phase changes are watched. With a pressure buildup, the value of transition temperatures are differing legibly, at pressure lower than 15 MPa, distinctions are watched poorly.

It follows from the data of the table 1 and fig. 2, the benzene has 3 crystalline states.

Table 1

P, atm.	ΔP	T_1°C	T_2°C	T_3°C	Δt_1	Δt_2
300	30.0	11.0	7.5	5.0	18.0	-
400	26.0	16.0	8.0	4.8	17.0	-
500	23.5	18.5	9.0	4.5	16.5	2.0
540	21.0	20.0	9.1	4.3	16.0	2.0
600	18.0	21.5	9.3	4.0	15.0	3.0
700	13.5	23.5	9.5	3.8	14.5	3.0
800	11.0	26.5	9.8	3.5	14.0	-
900	9.0	29.5	10.0	3.3	-	-
1000	8.0	33.0	10.2	3.0	12.0	2.5

Pressure drop at transitions shows, that the modifications of benzene differ from each other on volume basis of solid state. As shown in [2], at heating of a solid, since enough low temperatures, the discontinuous change of width and second moment NMR can be watched. In this case body not necessarily should test phase change in the thermodynamic sense. But for benzene such changes were watched at temperatures 90 – 120 K.

Conclusions

The investigation concerns an experimental study of phase change of benzene that is examined at different temperatures and pressure.

For an experimental research of phase changes of benzene new installation is used, which one is completely described in the article [4]. Ground obtained experimental data P-T charts are constructed and metastable states of benzene demonstrated. The researches were conducted up to values of pressure 1000 atm, where temperature was augmented up to 33 °C.

Also 3 crystalline forms of benzene were obtained at phase changes for the first time.

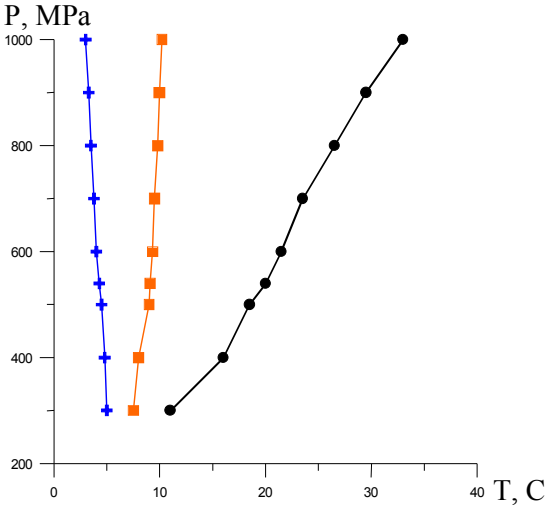

Figure 2.

References

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