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Effect of liquid phase on the triple point pressure of argon

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Abstract. We report here a systematic data analysis of the vapour pressure of argon at different amounts of the liquid phase to understand the thermodynamic behaviour of this inert gas around triple point. At the triple point plateau, the applied heat pulse melts a certain phase of solid argon into liquid and increases vapour pressure. It is observed that this vapour pressure attains the thermodynamic equilibrium pressure after a certain time interval. The exponential decay of the vapour pressure as a function of time at different fractions of the liquid phase shows two different features. In one region, the relexation time constant (τ) is low and is not varying with the liquid phase, while in the other region the value of τ increases with the amount of the liquid phase. Further, the peak pressure from the equilibrium pressure (ΔP_h), obtained from the fitting parameters, shows a dip at around 50% of the liquid phase. A qualitative physical interpretation has been given to explain these results.

Keywords. Argon triple point; pressure measurements; relaxation time; liquid phase.

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1. Introduction

In the triple point state, three phases namely, gas, liquid and solid of a pure substance are in thermodynamic equilibrium. Under this equilibrium state, a plot of temperatures or pressures as a function of the phase of sample melted (F) gives a well-defined representation of the melting curve. The melting of rare gas solid near the triple point has been widely used to understand the ordering and metastability during melting or freezing phenomenon (Mahato *et al* 1991). However, very little experimental work has so far been reported on the accurate measurement of pressure and the subsequent determination of thermodynamic behaviour of the system near triple point along the melting curve. It may be mentioned that the experimental method for the determination of triple point of the substance, which is gaseous at room temperature, requires cooling the gas at low temperature (Pavese 1978). The gas, while cooling, passes through its dew point and the liquid phase starts appearing. The vapour pressure decreases with temperature until the liquid begins to freeze. During this solidification process, the pressure and temperature remain constant. When it is completely solidified, the pressure in the vapour phase would once again fall following the sublimation curve. Therefore, the freezing curve consists of a curved region at the onset of freezing, followed by a flat region over which the bulk of transformation occurs, and finally a region of decrease in pressure and temperature as the freezing is completed. The flat region is known as the triple point plateau where both the liquid and solid phases are present. The pressure and temperature in this plateau region are defined to be constant (Landau and Lifshitz 1980). However, in practice, the pressure and temperature are found to have a characteristic dependence on the fraction of the liquid phases even when the best purity specified sample is used and great care is taken to maintain the adiabatic condition in the cryostat.

The triple point temperature or pressure is, therefore, obtained by using two methods [Pavese (1981); Bonhoure and Pello (1983)]. In the first method, the equilibrium points of the initial and final 15% of the curve are discarded and one then takes the mean of the remaining 70% of F. In the second method, one plots the temperature or pressure versus 100/F values between about five and two, extrapolates this part of the melting curve to 100/F = 1 (liquidus point) and defines this as the triple point. The second method is widely used and followed for the determination of the triple point pressure.

In our previous paper (Bandyopadhyay *et al* 1991), we have reported the measurement of the argon triple point pressure in a laboratory designed triple point cell. We have shown that from the study of 30 different equilibrium pressure points at different percentage liquid and solid phases, the triple point pressure is obtained as 68·8908 kPa with an uncertainty of pressure measurement of ± 1·0 Pa. This is in agreement with the earlier reported values by Pavese (1981) and Bonhoure and Pello (1983).

In the present paper, a systematic analysis of the experimentally obtained data is carried out with a view to understand the thermodynamical behaviour of the system near the triple point and to establish a qualitative explanation of the two methods explained earlier for the triple point.

2. Results and observations

The details of the experiment have already been published by Bandyopadhyay *et al* (1991). The piston gauge was operated in the absolute mode and the pressure was measured within an uncertainty of 10 ppm. The major correction to measure pressure comes from the aerostatic head correction which was estimated to be 9·2 Pa. The details of the uncertainty of the measurements showed that the pressure was measured within an uncertainty of 1 Pa.

As discussed, the realization of a triple point was carried out by first freezing the sample in the solid form; then a series of measured heat pulses were applied. As the triple point cell was maintained in an adiabatic condition, the heat pulse would melt a given amount of the solid phase and disturb thermodynamic equilibrium condition. One of this melting plateau is shown in figure 1. It can be seen from this figure that as soon as the melting procedure starts, the vapour pressure increases with the heat pulse depending upon the amount of liquid phase. However, as the heat pulse is interrupted, the vapour pressure decays with time and attains the equilibrium starting pressure. The time, which the vapour pressure takes to attain this equilibrium pressure value, is also found to be dependent on the amount of liquid phase. We have reported three plateaux in the different solid and liquid fractions. However, the first run is shown where a small increment of the liquid phase has been studied and 14 different peaks from 20 to 84·5% liquid phase have been considered. The second and third run are essentially of same nature and are not taken for discussion here.

In order to analyse these results, in particular the decay of the vapour pressure

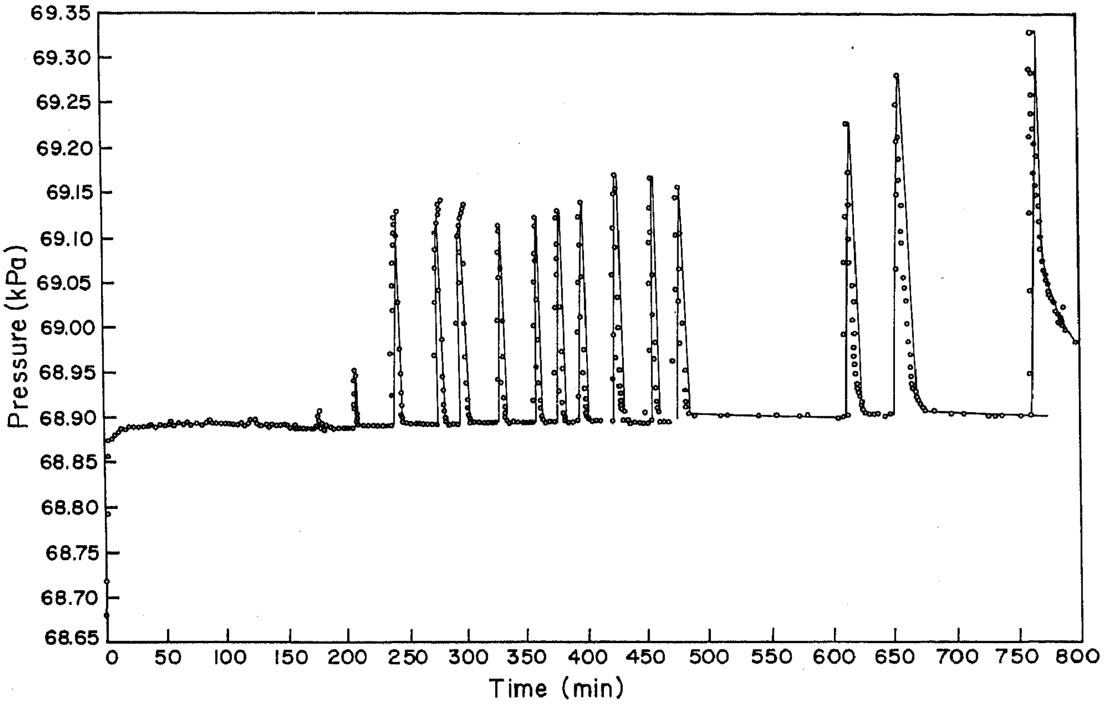

Figure 1. Observations of argon triple point pressure at various percentages of liquid phase.

with time, an attempt has been made to fit this vapour pressure with time by an expression,

$$\Delta P(t) = P_{\mathrm{eq}} \exp(A - B(t - t_b)) \tag{1}$$

where $\Delta P(t) = P(t) - P_{\mathrm{eq}}$, $P(t)$ is the pressure at time t, P_{eq} is the equilibrium pressure, t_b is the time at the beginning of the experiment, A and B are the constants. Redefining $\Delta P(t)$ at $t = t_b$ as ΔP_h, that is, peak height, (1) can be written as,

$$\Delta P(t) = \Delta P_h \exp(-(t - t_b)/\tau) \tag{2}$$

where τ is the relaxation time. As can be seen that $\Delta P_h = P_{\mathrm{eq}} \exp A$ and $\tau = 1/B$. The experimentally obtained 14 different peaks of the vapour pressure, which decay with time, for different liquid phases have been analysed with (2). Figure 2 shows the plot of $\ln \Delta P(t)$ versus $(t - t_b)$ at different liquid phases. As can be seen, with the change of the liquid phases a systematic change in the slope as well as the intercept has been observed. The best fitted value of the slope, which essentially represents $(1/\tau)$, has been plotted with the liquid phase (F) and shown in figure 3. It is clear that there are two distinct regions. In the first region, decay is rapid and as a result τ is low. However, in the second region the decay is sluggish and τ is changing with the liquid phase. Figure 4 shows the plot of ΔP_h as a function of liquid phase (F). This figure shows, except for the first point of 20% of the liquid phase, ΔP_h has an unusual dip at around 50% of the liquid phase and then it starts increasing.

At this moment we do not have enough theoretical understanding of these results. However, a qualitative model has been suggested based on the experimental results. It can be assumed that as soon as the heat pulse is applied, a part of the heat which entered the sample melts some of the solids and a part of it simply heats the liquid

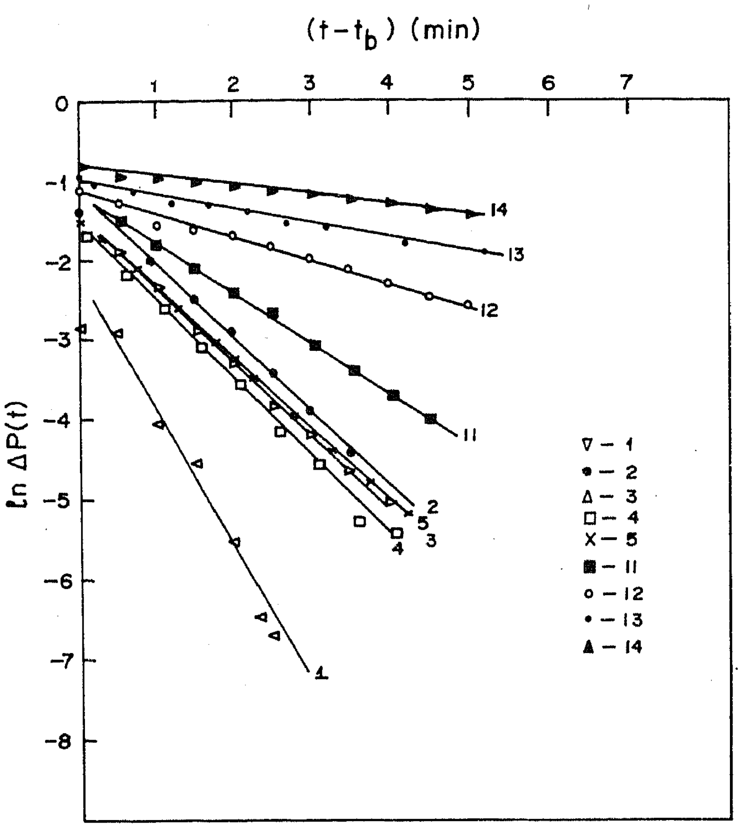

Figure 2. In $P(t)$ versus $(t-t_b)$ plot at the various percentages of liquid phase.

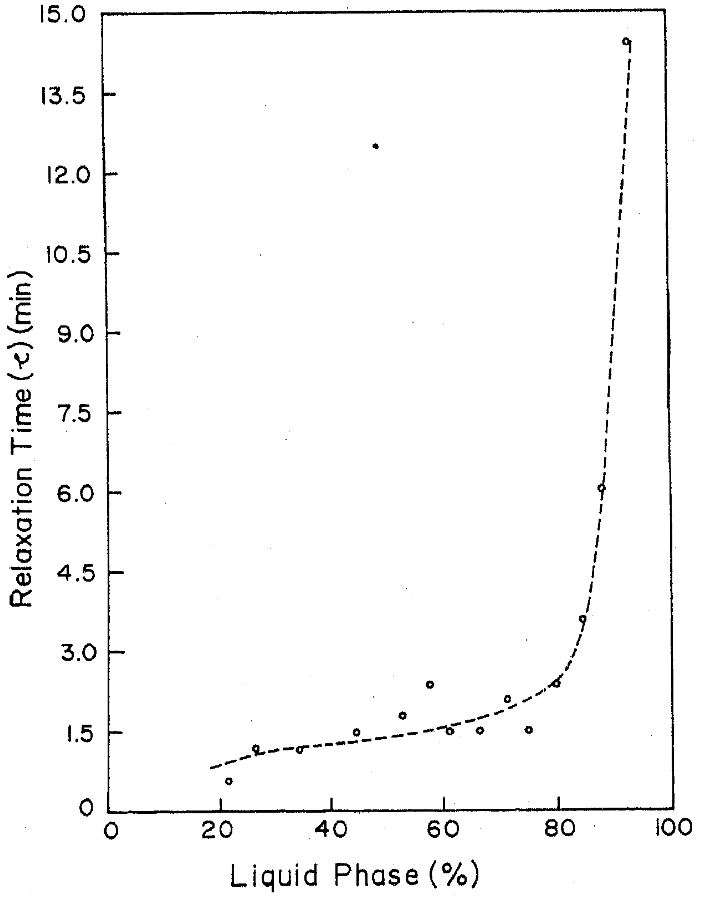

Figure 3. The calculated relaxation time (τ) at the various percentages of liquid phase.

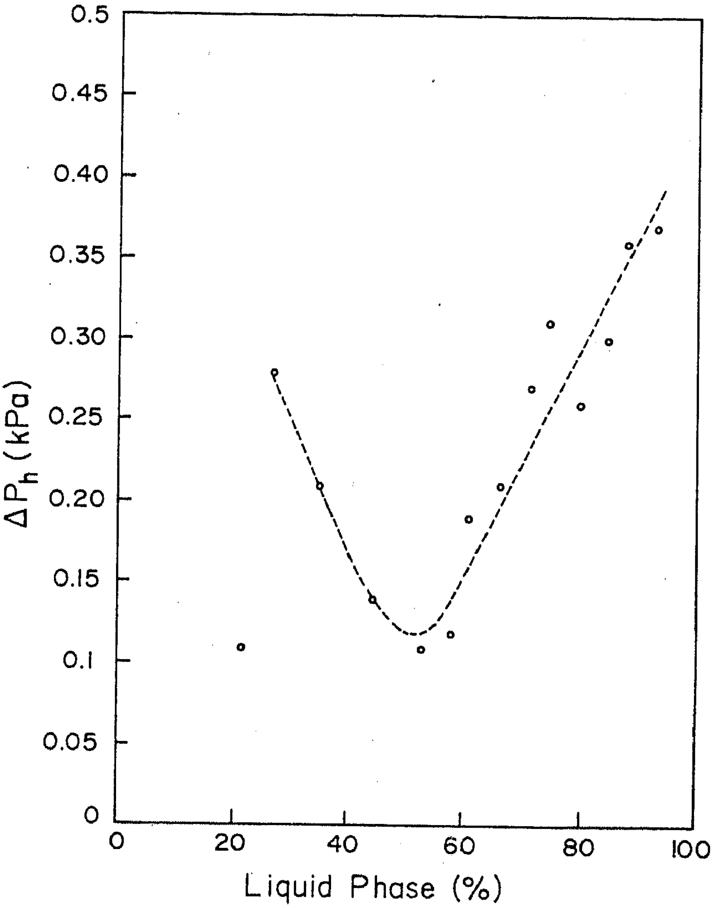

Figure 4. The calculated difference in pressure (ΔP_h) from the expression $P_{\mathrm{eq}}\exp A$ at the various percentages of liquid phase.

portion considerably above the triple point. As a result, during melting because of this overheating of the liquid, the vapour pressure increases. However, the increase in vapour pressure represents an average vapour pressure between the overheated liquid and the melting solid. It has been reported (Ancsin 1973) that the melting usually commences around those impurity centres which weaken the crystal lattice (lower the melting point), this could happen if the melting proceeded very slowly and if the heat conductivity of the sample is high. But, the heat conductivity of most of the cryogenic substances is very low, the melting always starts from the vicinity of the heater, no matter where the impurity within the sample is located. If the heating of a melting sample is interrupted and if the sample is well insulated from the environment (adiabatic experimental conditions), the overheated liquid cools, releasing some of its heat content into the solid portion of the sample and thus melting some more solid. At first only that solid will melt which is in direct contact with the overheated liquid, no matter what its purity. As the temperature distribution of the sample approaches uniformity, some regions which are relatively pure but were melted during heating due to their proximity either to the heater or to the overheated liquid regions, will begin to refreeze. On the other hand, impure regions that were not near such local heat sources and did not melt during heating, would begin to melt. These processes of overheating and recrystallization depend on the thermal diffusivity of the substance. Therefore, if the thermal conductivity of the solid state differs considerably from the liquid state, there seems to be a change in the relaxation time with the change of phase percentage.

It may be mentioned here that the thermal conductivity of argon in the various states, is as follows: 5·19 mW/mK at 90 K when it is in the gaseous state, 125 mW/mK at 85 K when it is in the liquid state, and 310 mW/mK at 77 K when it is in the solid state and the specific heat at 100 K is 0·287 J/gK (AIP Handbook, 3rd ed.). As can be seen the thermal conductivity in the liquid phase is very low compared to the solid phase. Moreover, the latent heat of fusion of argon is 1·188 kJ/mol while the latent heat of vaporization is 6·506 kJ/mol (AIP Handbook, 3rd ed.). Therefore, as discussed in figure 3, the first region represents the dominance of the solid phase which results in high thermal diffusivity. However, as the solid phase decreases and liquid phase increases, the processes of melting and solidification of the pure region and melting of the impure region, increase substantially. As a result, there seems to be a sluggish decay that represents a low thermal diffusivity and this can be seen in figure 3. It may be mentioned here that τ represents an average effect. Therefore, its slow variation with the liquid phase up to a limit of roughly 80% of the liquid phase, seems to be indicative of the presence of low impurity in the sample. The steep increase in τ after 80% of the liquid phase is obviously because of the low thermal diffusivity of the liquid phase as mentioned above. It may be mentioned here that oxygen has a higher thermal conductivity than argon and it has already been reported that the temperature stabilization of oxygen is much faster than argon (Ancsin 1973).

Further, the relaxation time of reaching the equilibrium pressure typically depends on the heat conductivity and the specific heat. τ is defined as $\tau = r^2 C_p/K$ where r is the radius, C_p is the specific heat and K is the thermal conductivity of the specimen. The density of argon at 83 K is 4·034 mg/cc and since we are measuring the vapour pressure, the estimated τ is found to be 10 s. It can be seen (figure 3) that τ obtained from the experiment varies from 30 to 90 s up to 80% of the liquid phase. Therefore, comparing the nature of simplistic approximation, the agreement seems to be reasonable.

The fitted peak pressure, that is, the increase in vapour from the equilibrium pressure, goes through a broad minimum at around 50% of the liquid phase, followed by a gradual increase with the liquid phase as shown in figure 4. This unusual minimum in the peak pressure at nearly 50% of the liquid phase is difficult to explain. However, based on our above arguments, it may be said that the cooling of the overheated liquid by the solid phase and the warming of the sample by the warmer vapour are always very active in the triple point plateau. As these processes are opposite in nature, at that percentage of liquid phase, this minimum is essentially representing close balancing of each other. This is further evident from the fact that after that percentage of liquid phase (50%), the peak pressure increases gradually with the liquid phase. The increase is mostly due to the gentle overheating of the liquid phase by the sample vapour. It may be added here that ΔP_h values at small F may be affected by the instrumental problem. If the time constant of the instrument is larger than the time needed for the solid to warm up, it would result in a low value of ΔP_h.

Therefore, the observed slow variation of the relaxation time with liquid phase up to a limit 80% followed by a steep increase and the peak pressure (ΔP_h) which shows an usual minimum at 50% of the liquid phase, can be explained from our model. It is further shown that the presence of impurity always influence the relaxation time or the time at which it attains the equilibrium pressure. The slow variation up to at least 80% of the liquid phase indicates that the level of impurity centres in the sample is extremely low. Further, it is interesting to note that the method of determining the triple point which has earlier been reported by Pavese (1981) and Bonhoure and Pello 1983, really takes the region of the melting plateau where the relaxation time is reasonably constant and where the increase in pressure (ΔP_h) is systematic across the minimum. Therefore, our explanation, although qualitative, certainly shows the reason of the successful operation of the two procedures as discussed by Pavese (1981) and Bonhoure and Pello (1983).

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