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Study of the freezing temperature of benzoic acid as a standard reference material in thermometry

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Measurements of the liquidus temperature of 99.97% pure benzoic acid by using platinum resistance thermometer has been carried out. The average value is found to be 122.358 ± 0.005° C. A laboratory technique for the purification of benzoic acid to be used as a standard reference material for thermometric and calorimetric work is also described.

1. Introduction

The aim of this study is to find some reproducible fixed points in the vicinity of 100° C insensitive to variations in barometric pressure to replace the boiling point of water. Benzoic acid is one of these, it has a freezing temperature of 122.3° C and possesses the properties required for a thermometric standard of which the more important are; sufficiently large latent heat at the change of phase, adequate velocity of crystallization, existence in only one crystalline form at temperatures near freezing point, and stability under conditions of use.

In 1945 Schwab and Wichers [1] carried out research work on the freezing and triple point of benzoic acid and gave a value of 122.37° C for its triple point.

The international temperature scale of 1968 listed the triple point of benzoic acid as one of the secondary reference points 122.37° C [2] as given by Schwab and Wichers. In 1985 Vaughan and Butler [3] studied the triple point of benzoic acid and gave a value of 122.365 ± 0.005° C.

Benzoic acid as a fixed point in now needed for calibration of thermometers used in sterilization units. Sterilization at 121° C is required for several materials especially intravenous drip feeds which unless properly sterilized at this temperature can have fatal consequences for patients, however these feeds are based on glucose and if heated to a temperature much higher than 121° C they begin to discolour. It is essential to manufacturers, therefore, that these products should be sterilized at precisely that temperature. The triple point of benzoic acid which is assigned a temperature of 122.37° C being quite close to 121° C, is very convenient for the calibration of thermometers used for this purpose.

In the present work we have used entrainer sublimation to purify benzoic acid. This technique is simpler and more efficient than the fractional freezing technique which was developed by Shwab and Wichers [4] and later used by Vaughan and Butler.

2. Experimental work

2.1. Purification of benzoic acid by the entrainer sublimation technique

This technique is similar in principle to that previously described by Uskov and Oleinik [5]. The apparatus used is shown in Fig. 1. About 1 kg of benzoic acid of 99.85% purity is melted in the sublimation flask (1) and its temperature is adjusted to be about 140° C. At that temperature the vapour pressure of benzoic acid is about 15 mm Hg. The pressure in the system is regulated at about 25 mm Hg by means of the vacuum pump. The needle valve (6) is used to regulate the rate of flow of the entrainer gas which is dry air. The temperature of the crystallizer is regulated at 70–80° C by means of the heater (2) and is measured by the thermometer (14). At a temperature of around 70–80° C the vapour pressure of benzoic acid drops to 0.3 mm Hg and crystallization occurs. The heater around the neck of the distillation flask is switched on during the experiment to prevent the sublimed acid from condensing in the neck and subsequently blocking it. The main bulk of benzoic acid vapour condensed as large needles in the first zone of the crystallizers (1), in the second zone (11) condensation took place as smaller crystals, while on the sintered glass disc (11) some powder grains condensed. The sintered glass disc is used to prevent the benzoic acid powder from being swept out with the gases to the vacuum pump. Most of the mineral and slightly evaporating organic impurities either remained or were charred in the sublimation flask. Impurities that were easy to evaporate were evaporated and pumped out. The sublimation process stopped when 25% of the main bulk remained in the sublimation flask.

2.2. Filling of the benzoic acid cell

The freezing point cell used in the present work is similar to the usual water triple point cell. The cell as shown in Fig. 2 is made of pyrex glass, cylindrical in shape 4 cm in diameter and about 25 cm long. A thermometer well 8 mm in diameter extends nearly the length of the cell. The cell is filled with the benzoic acid through the bottom side tube. The volume of the molten acid is so as to leave a free space of about 50 ml in the cell. The benzoic acid cell after being filled is placed inside the furnace and the acid is allowed to melt completely. The cell containing the molten acid is then evacuated on the vacuum line to about 0.1 torr. Under this reduced pressure the air and water vapour

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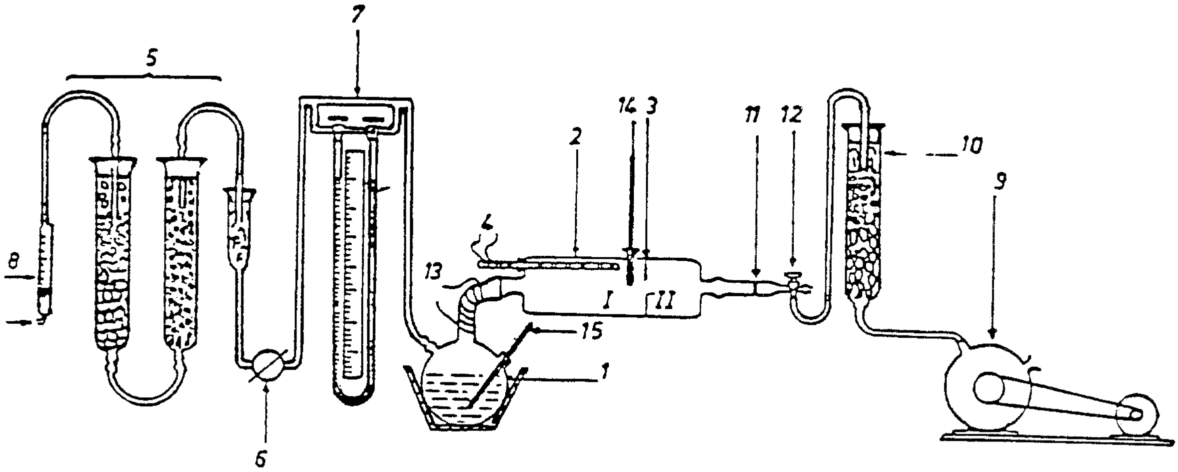

Figure 1 The apparatus used in purification of benzoic acid (see text for key).

dissolved in the acid bubbles off. The importance of drying benzoic acid stems from the fact that liquid benzoic acid saturated at a temperature near its freezing point, with air having a partial pressure of 5 mm of water vapour, contains about 0.06 mol % of dissolved water. This amount of water depresses the freezing temperature by between 0.04 and 0.05° C. It is therefore necessary to dry the acid in the cell quite thoroughly to avoid excessive depression of the freezing temperature in the cell. After 1 h of pumping, air freed from water vapour and CO_2, by passing through a trap containing phosphorous pentoxide and sodium hydroxide followed by a condenser immersed in solid CO_2 (−40° C) to freeze any remaining moisture, is introduced in the cell under one atmosphere pressure. The side tube is then flame-sealed. Any benzoic acid in the vicinity of the sealing arm is vaporized before sealing.

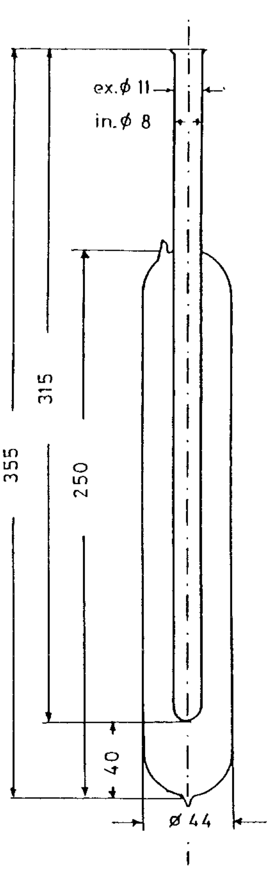

Figure 2 The benzoic acid cell. (All dimensions in mm)

2.3. Procedure for realization of the fixed point

It was found [1, 4] that the best way to realize the freezing point of an organic compound is by the "mush" method (i.e. by partial crystallization of the undercooled liquid). Benzoic acid supercools several degrees below its freezing point and is, therefore, suitable for the mush method. The cell is placed in an oven at about 135° C and when all the solid has melted the cell is removed from the oven and placed in the furnace which is adjusted to a temperature 2° C below the melting point of the acid. After about 15 min temperature measurements are begun, benzoic acid supercools about 10° C before the nucleation of the solid begins. When the acid starts to supercool, the cell is taken out of the furnace and given a slight shake until a mush of fine needle-like crystals appears throughout the liquid. The cell is then returned to the furnace. This operation results in the rapid nucleation and growth of a mantle of solid benzoic acid which releases sufficient latent heat to quickly raise the melt to its liquidus temperature.

The furnace used for the realization of the freezing temperature is similar in design to that described previously by McAllan and Ammar [6]. In this furnace the temperature uniformity along the central silica tube is achieved by non-uniform main heater winding and two separate top and bottom heaters. To avoid fluctuations due to power variations, a stabilized power supply was used and regulated separately in each of the three heaters by means of variacs. With this furnace the maximum temperature gradient in the zone occupied by the cell is within 0.01° C such a gradient may affect the temperature of benzoic acid by about 0.001° C which is within the experimental error.

The furnace power is adjusted to give a freezing plateau lasting for about 3 h. This gives about 30 min of stable plateau between the end of recalescence and the temperature depression which occurs in the latter part of the freeze.

2.4. Temperature measurement

For temperature measurement a standard platinum

TABLE I Physical and thermal properties of benzoic acid [7]

Property	Value
Latent heat of fusion	$33.586\,\mathrm{cal\,g^{-1}}$
Density of solid at the freezing temperature	$1.27\,\mathrm{g\,cm^{-3}}$
Specific heat at 20° C	$0.287\,\mathrm{cal\,g^{-1}\,K^{-1}}$
The pressure coefficient of the freezing temperature $(\Delta T/\Delta P)V$	$0.039°\,\mathrm{C\,atm^{-1}}$
Effect of hydrostatic pressure of liquid benzoic acid on the freezing temperature	$0.000\,040\,\mathrm{K\,cm^{-1}}$ depth of liquid benzoic acid
The change in volume of the acid on freezing	$-0.138\,\mathrm{cm^3\,g^{-1}}$
The density of liquid benzoic acid on freezing	$1.08\,\mathrm{g\,cm^{-3}}$

reistance thermometer was used. The thermometer has a resistance of 25Ω at ice point and was calibrated at the triple point of water and, the freezing points of zinc and tin. Measurement of the thermometer resistance has been made to an accuracy of 10 μΩ with a special a.c. thermometer bridge supplied by Tinsley. The thermometer resistance was corrected for the heating effect of the electric current. Before each freezing experiment the resistance of the platinum resistance therometer was determined at the triple point of water.

3. Results and discussion

Table I gives the physical and thermal properties of benzoic acid. As given in the table, the change in volume of the acid on melting is $0.38\,\mathrm{cm^3\,g^{-1}}$, so care must be taken to avoid breakage of the glass cell due to expansion of the acid on melting. Among the factors affecting the freezing temperature of the acid are the gas pressure above the molten acid, the impurity content, and the water vapour content. Schwab and Wichers in their study on the freezing temperature of benzoic acid and have evaluated the effect of impurities on the freezing temperature. Based on these results it was possible to evaluate the cryoscopic constant A for benzoic acid as equal to $1.33\,\mathrm{mol\,\%\,K^{-1}}$ [1]. The purity of the acid can be evaluated once its freezing temperature has been determined, from Raoult's law

$$X_2 = A(T_0 - T_s) \qquad (1)$$

where X_2 is the mol % of impurity, A is the cryoscopic constant T_0 is the freezing point of pure benzioc acid and T_s is the initial freezing point of the sample. The freezing temperature of the pure acid T_0 has been given the value 122.378° C in terms of the International Practical Temperature Scale of 1968 [3].

Table II gives the results of the determinations of the liquidus temperature of benzoic acid purified by the entrainer sublimation technique. The table also lists the thermometer resistance R_t at the liquidus temperature. These values have been corrected for self heating due to the thermometer current.

Table III gives the results of the liquidus temperature determinations for benzoic acid before purification, using the same thermometer and the same freezing technique.

The impurity concentration in the unpurified benzoid acid sample can be estimated from Raoult's law by using the average value of the freezing temperature T_s given in Table II. It is found to be 0.145 mol % i.e. the sample is 99.85% pure. The freezing temperature for the benzoic acid sample after purification is 122.358° C, from Raoult's formula, the estimated impurity content is 0.027 mol % which means that the sample purity has increased to 99.973%, after one purification cycle by the entrainer sublimation technique. If purity better than 99.99% is required a second purification cycle will be necessary.

TABLE II Intercomparison of the plateau temperature (after purification)

$R_t(\Omega)$	R_t/R_0	T_{68}(° C)
37.803 55	1.478 758	122.3609
37.803 40	1.478 752	122.3593
37.803 20	1.478 744	122.3573
37.803 00	1.478 736	122.3553
37.803 50	1.478 756	122.3604
37.803 30	1.478 748	122.3583
37.803 10	1.478 740	122.3563

The average value 122.3583 ± 0.0027° C.

Fig. 3 shows two freezing curves obtained by the slow mush freezing technique on both samples. It is clear that the plateau in the case of the purified sample (of estimated purify 99.973%) is more stable and higher than that obtained for the sample before purification. We can also notice that near the end of the freezing curves the slope increases, and the declination is more rapid for the impure sample than it is for the purified one. The declination from the maximum temperature is due to the fact that near the end of the freeze most of the impurities which have been swept to the central region of the cell, start to depress the temperature more rapidly. Hence the rate of change of the slope of the freezing curve near the end of the freeze is a measure of the impurity concentration in the original sample.

The consistency of the data given in Table I is evidence that benzoic acid, when heated to a temperature near its freezing value, does noes not undergo a measurable irreversible decompositon. However, the acid may undergo a reversible decomposition to benzoic anhydride and water, but this reaction is reversible and if the cell is cooled slowly the benzoic anhydride and water recombine to give benzoic acid, and the fixed point is restored to its initial value [1].

4. Conclusions

The above mentioned discussion may lead to the following conclusions

(1) Benzoic acid is adequately stable for use as a reference point for calibration of thermometers,

TABLE III Intercomparison of the plateau temperatures (before purification)

$R_t(\Omega)$	R_t/R_0	T_{68}(° C)
37.794	1.478 384	122.264
37.795	1.478 423	122.274

The average value 122.269 ± 0.005° C.

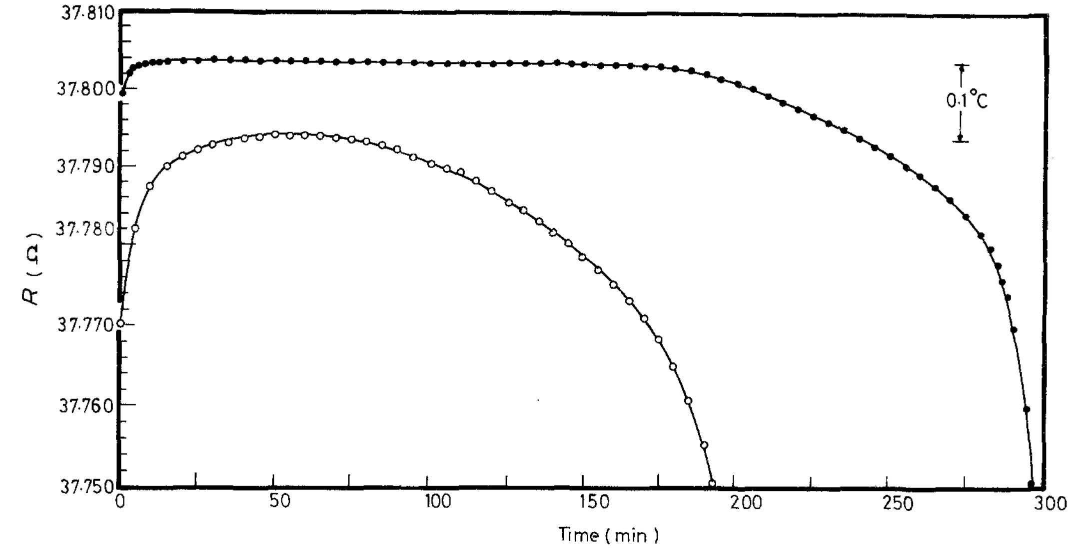

Figure 3 Freezing curves for benzoic acid (○ before purification, ● after purification).

provided it is not heated for a long period at temperatures much above 150° C.

(2) High purity benzoic acid can be obtained by the entrainer sublimation technique described in the present paper. This technique is superior to the fractional freezing technique used by Schwab and Wichers.

(3) The present work indicates a value of 122.358 ± 0.005° C for the freezing point of benzoic acid of purity 99.97%, where the uncertainty represents the overall uncertainty at the 95% confidence level. In the secondary reference points of IPTS-68. The triple point of benzoic acid is assigned a value of 122.37° C, Vaughan and Butler [3] gave a value of 122.365 ± 0.005° C for the triple point of benzoic acid.

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