COMMUNICATIONS

DE LA FACULTÉ DES SCIENCES
DE L'UNIVERSITÉ D'ANKARA

Série B: Chimie

TOME 24 ANNÉE 1978

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by

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Faculté des Sciences de l'Université d'Ankara
Ankara, Turquie

Communications de la Faculté des Sciences de l'Université d'Ankara

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Triple Point Depression of Capillary Condensed Water

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ABSTRACT

The triple point temperature of water condensed in silica gel, that is chosen as a porous solid, is abserved as 24°C below the normal triple point temperature, by thermal analysis method. The mean radius of capillaries in silica gel, which is observed after the triple point depression, is 19 A°. Using this value, the triple point pressure is obtained as 2.27 mm Hg less than the normal triple point pressure.

INTRODUCTION

The properties of gases adsorbed on the solid surfaces are different from those of normal gases. It is experimentally observed that the density[1], heat capacity[2,3,4], entropy[5,6], coefficient of expansion[7], light absorption[8], and all the spectroscopic properties[9,10,11,12,13] of the adsorbed gas have changed.

Assuming that monomolecularly adsorbed gas molecules can move in two dimensions, thermal state equations are theoretically derived[14] for adsorbed gases and the integrity of these equations are experimentally investigated[15].

The properties of liquids, condensed in capillaries, are different from those of bulk liquids because of their surface curvature. The vapour pressure depression of a liquid in a capillary is calculated by means of the relation derived by Kelvin[16]

$$\ln \frac{p}{p_0} = - \frac{2\,\sigma^{l,g}}{r} \cdot \frac{V^l}{RT} .$$

Where r is the radius of the capillary; T is the temperature; p_0 and p respectively represent the vapour pressure of the bulk and capillary liquids, of which the surface tension is $\sigma^{l,g}$ and molar volume is V^l. Melting point, bailing point and critical temperature of the substance are changing with the vapour pressure depression of a liquid in a capillary.

The depression of melting or triple point temperature of a substance in a capillary can be determined by measurements of density[17], dielectric properties[18], electrolytic conduction[19,20], vapour pressure[21], and also dilotometric[22,23] and calarimetrric[24,25,26] methods. It is experimentally observed that the triple point temperature depression is exponentially related to the capillary radius[27].

Batchelor and Foster[23] amprically derived the relation

$$T - T_0 = \frac{2T}{r}\left[\frac{V^l\sigma^{l,g} - V^s\sigma^{s,g}}{\Delta H_f}\right]_{T_0}$$

to show the triple point temperature depression by means of the vapour pressure measurment. Where T_0 and T represent the triple point temperatures of the bulk and capillary liquids respectively, and r is the mean radius of the capillaries. In this equation ΔH_f is the molar melting enthalpy; $V^l\sigma^{l,g}$ and $V^s\sigma^{s,g}$ are the molar volume surface tension product of the liquid and solid respectively at the normal triple point temperature. On the other hand, the relation between the T_0 and T temperatures is derived theoretically as shown in the equation[28] below, from the mechanic and thermodynamic equilibria of a capillary liquid.

$$\ln\frac{T}{T_0} = -\frac{V^s}{\Delta H_f}\cdot\frac{2\,\sigma^{s,l}}{r}$$

Where $\sigma^{s,l}$ represents the surface tension between solid and liquids, V^s is the molar volume of solid, ΔH_f is the molar melting enthalpy at the T normal triple point temperature, and r is the capillary radius.

EXSPERIMENTAL

Thermal analysis insturument, to measure the triple point temperature of water in silica gel (supplied by BDH) capillaries, is shown in Fig. 1. At the external part there is an iron cylinder

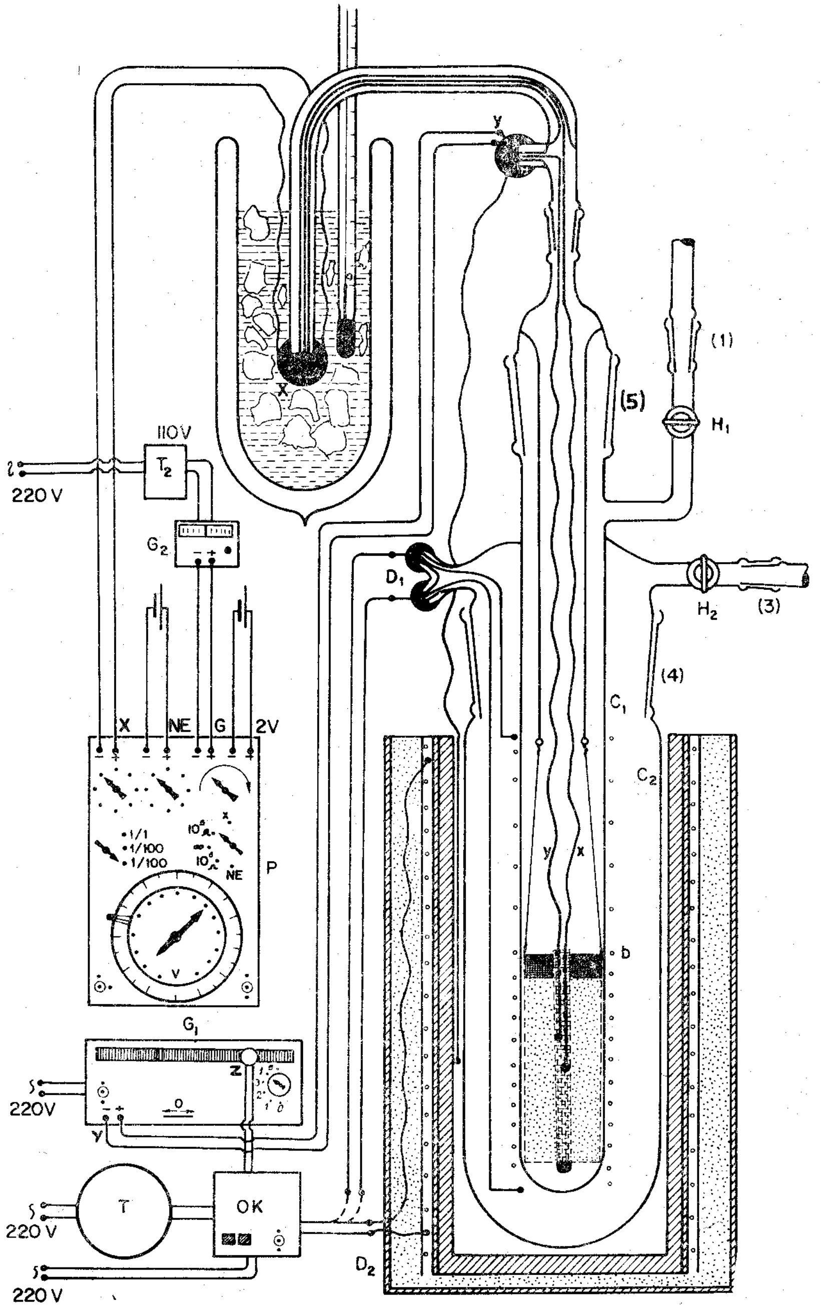

Fig. 1. Thermal analysis instrument

0,5 cm thick. C_2 tube is placed in this cylinder as shown in the figure. In order to decrease the rate heat transfer the volume B, which is between C_1 and C_2 tubes, is evacuated up to 10 mm Hg pressure, using the H_2 stopcock. There is also a vessel, which is made from silver sieve, in the C_1 tube. X and Y copper-constantan thermocouples junctions are welded in the middle of silver vessel. The other junctions of X thermocouple are immersed in the water-ice bath (0 °C). This thermocouple is connected to the P potentiometer to measure absolute temperature. The other out put of the thermocouple Y is placed between C_2 and the iron oven as shown in Fig. 1. This thermocouple is connected to the G_1 galvanometer to measure temperature differences.

The silica gel, which is activated by heating up to 350 °C under vacuum, is filled into the vessel and saturated by with water. The excess of air and water is pumped off via H_1 stopcock, and at the some time D_1 resistance is heated.

Silica gel – water system is cooled down to – 170 °C by placing liquid nitrogen between the iron cylinder and the C_2 tube. The P potantiometer is calibrated by using G_2 galvonameter occording to the NE standart cell.

After all the preperations have been completed, the oven shaped iron cylinder is slowly heated by D_2 resistance. The temperature difference between the two seperate junctions places is kept constant by OK electronic temperature outocontrol system and G_1 galvanometer. So, the same amount of heat, at the same time intervals is transfered from the outher space into the system. This is done by using the Z photocell and the temperature calibrated G_1 galvanometer. When the light of the galvanometer is appeared exactly in front of the photocell, the circuit of the oven is automatically turned off by the OK. During this time heating at the system stops, cooling begins and as the light returnes to the front of the photocell, the circuit of the oven is automatically turned on. Therofore, desired temperature is obtained.

The temperature rising, which occurs by heating the system slowly, is read from the P potantiometer as μV by the help of G_1 galvanometer. On the other hand, Δt time intervals, required for rising the temperature for each 100 μV, is read at the chronometer. This time interval increases during the melting and after a maximum it decreases back. This way the triple point temperature, which is equal to the maximum point of obtained peak, is read at the $\Delta t = f (\mu V)$ graph.

RESULTS

The thermal analysis curve for low temperatures of silica gel – water system is shown in Fig. 2. The maximum point temperature of the peak at the curve is read as – 24 °C. So, the triple point temperature of the water, which is condensed in capillaries of silica gel, is measured as T = 249 K, which is 24 °C below the triple point temperature of bulk water (T_0 = 273 K).

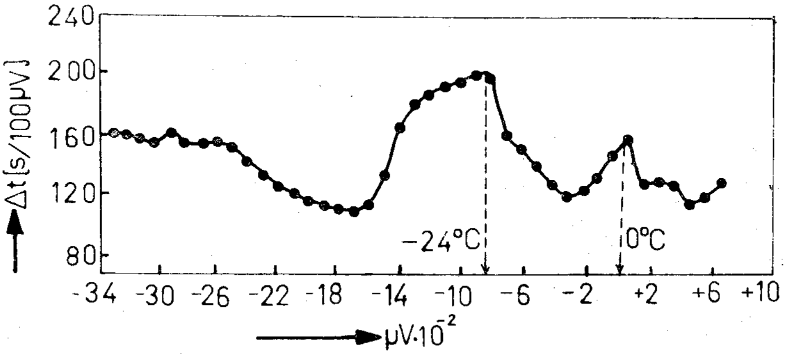

Fig. 2. Thermal analysis curve

At the 273 K, the molar volumes, the surface tensions and molar melting enthalpy for bulk water is given as:

$V^l = 18.05$ cm^3 mol^{-1} ; $V^s = 19.62$ cm^3 mol^{-1}

$\sigma^{l,g} = 75.7$ dyne mol^{-1} ; $\sigma^{s,g} = 100$ dyne cm^{-1}

$\Delta H_f = 6012.10^7$ erg mol^{-1}

For the surface tension at the solid – liquid interphase, the value

$\sigma^{s,l} = \sigma^{s,g} - \sigma^{l,g} = 24.3$ dyne cm^{-1}

may be used. If these values are used in the equations 2 and 3, the average radius of silica gel capillaries are calculated as 21 A° and

17 A° respectively, As seen above, the both r values, that are calculated from the amprically derived and theoretically derived equations respectively, are close to each other. From here, for the mean radius of silica gel capillaries 19 A°, which is the arithmetical average of both of the values, can be observed. If the vopour pressure at the triple point of bulk water is $p_0 = 4.58$ mm Hg, the triple point pressure of the water which is in the capillaries with a radius $r = 19$ A° can approximatally be calculated as $p = 2.31$ mm Hg by using Kelvin equation.

DISCUSSION

The mean radius of porous substance capillaries can be calculated by using the method written above, by measuring the depression of triple point temperature of water in capillaries. By the help of Kelvin equation we can observe how less the vapour pressure of water, that is in porous adsorbents and that contains the capillaries of which the radius are known, is from the vapour pressure of bulk water. It is definite that the water in the systems that contain porous substances, doesn't freeze below the normal freezing point and doesn't evaporate above the normal boiling point. Especially soil which contains pore subtances doesn't freeze easily at cold weather and doesn't dry easily at hot weather.

As seen in the thermal analysis curve, the peak which is equal to melting is too wide. According to this, melting musn't occur at a definite temperature, but must occur between two known temperature interval. We can say that there are three reasans why the peak is wide:

i) Because the heat transfer in the system is not homogen, in other words because the temperature is not the same at every point of the system at the same time, the peak is caused to be wide. In order to search this effect an experiment, at which the geometry of silica gel – water system is changed, is done and it is observed that the peak is a little narrowed.

ii) If the radii of the capillaries in the solid are not the same, but have a distribution, in accord with thermal analysis curve shows a wide peak. Thus, the melting which begins at lower temperatures in the narrow capillaries becomes maximum when the capillaries are the most at any width, more broder capillaries melt at higher temperatures.

iii) On the other hand, water molecules in the norrow capillaries may be dimerized, trimerized and also polimerized. This, it is not seen as weel as the melting of a crystal at a constant temperature, a wide maximimuzed thermal analysis peak showing the decreeasing of viscosity of a glassy substance by softening.

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ÖZET

Poröz katı olarak seçilen silica gel (BDH) içinde kondense olmuş suyun üçlü nokta sıcaklığı termik analiz yöntemiyle, normal üçlü nokta sıcaklığının 24 °C altında bulunmuştur. Üçlü nokta düşmesinden, silca gel kapilerlerinin ortalama yarıçapı 19 A°, bu değer yardımıyla da üçlü nokta basıncı, normal üçlü nokta basıncının 2,27 mm Hg altında bulunmuştur.

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Ankara Üniversitesi Basımevi. Ankara–1978