

THE LOW-TEMPERATURE QUARTZ RESONATOR METHOD FOR DETERMINATION OF THE ENTHALPY OF SUBLIMATION

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ABSTRACT

A low-temperature quartz resonator method for determining the enthalpy of sublimation has been described. A quartz crystal cooled to the temperature of liquid nitrogen becomes a sensitive microbalance. The method permits the value of ΔH_{sub} to be obtained within 4–5 h and is especially useful in measuring ΔH_{sub} values of substances with low saturated vapour pressures. The following values of ΔH_{sub} were received for standard substances: benzoic acid, $\Delta H_{\text{sub}} = (90.8 \pm 0.6)$ kJ mol⁻¹ at 293–319 K; naphthalene, $\Delta H_{\text{sub}} = (72.3 \pm 0.8)$ kJ mol⁻¹ at 293–331 K.

INTRODUCTION

Many methods of experimental determination of the sublimation enthalpy presently exist: calorimetric, effusion, effusion–torsion, manometric, etc. All these methods may be characterized as time consuming, laborious and using up high amounts of the substance. Particular difficulties are associated with determinations of sublimation enthalpies of volatile substances. Therefore, it has been attempted to develop a method which would eliminate the above difficulties.

METHOD AND PROCEDURE

One of the methods applied for determination of the sublimation enthalpy is the quartz resonator method [1]. A quartz crystal is used to detect the rate of sublimation, in fact fulfilling the role of a highly sensitive microbalance.

The relationship between the resonance frequency of the quartz crystal,

Δf , and surface density, ρ , of the substance deposited on the crystalline surface is expressed as [2]

$$\Delta f = - \frac{f^2 k m}{N \rho A} \quad (1)$$

where f = average resonance frequency, m = mass of the investigated substance deposited on the surface, A , of the quartz crystal, N = crystal constant, k = a constant dependent on mass distribution on the crystal surface. The change in frequency, Δf , is directly proportional to the mass of the substance deposited on the crystal, assuming that the total frequency change is small, i.e., $f \gg \Delta f$, and the substance is deposited on the same region of the crystal. The error by assumption of these conditions is negligible. To obtain high sensitivity, i.e., large frequency changes per thickness of layer unit, d , crystals of high resonance frequency should be used, since $\Delta f/d \approx f^2$.

The experimentally measured rate, v , of resonance frequency change in time Δt for the quartz crystal,

$$v = \Delta f / \Delta t \quad (2)$$

is proportional to the sublimation rate, v' , of the investigated substance

$$v' = \Delta m / \Delta t \quad (3)$$

We now obtain

$$v = \frac{\Delta f}{\Delta t} = c \frac{\Delta m}{\Delta t} = c' \exp\left(-\frac{\Delta H_{\text{sub}}}{kT}\right) \quad (4)$$

$$\ln v = \ln c' - \frac{\Delta H_{\text{sub}}}{k, T} \quad (5)$$

where c and c' = constants independent of temperature (assessed experimentally), k = Boltzmann constant. We observe that ΔH_{sub} is determined as the tangent of the line inclination angle in coordinates (T^{-1} , $\ln v$).

This method, however, could not be applied to substances of high saturated vapour pressure which have relatively high sublimation rates at ambient temperature, the desorption rates from the crystal surface at ambient temperature being comparable with condensation rates of molecular stream at the surface. The measurement of ΔH_{sub} in such cases is impossible.

The low-temperature quartz resonator method has been developed for determination of ΔH_{sub} for both the volatile and non-volatile substances [3].

The low-temperature vacuum cryostat used for cooling the quartz crystal is pictured schematically in Fig. 1a. The vacuum must be better than 5×10^{-7} Torr. A quartz crystal cut along the BT surface and having a resonance frequency at $f = 6.23$ MHz has been used. The temperature dependence of the relative frequency change is given in Fig. 2. We may observe that three temperature ranges exist at which the frequency of quartz

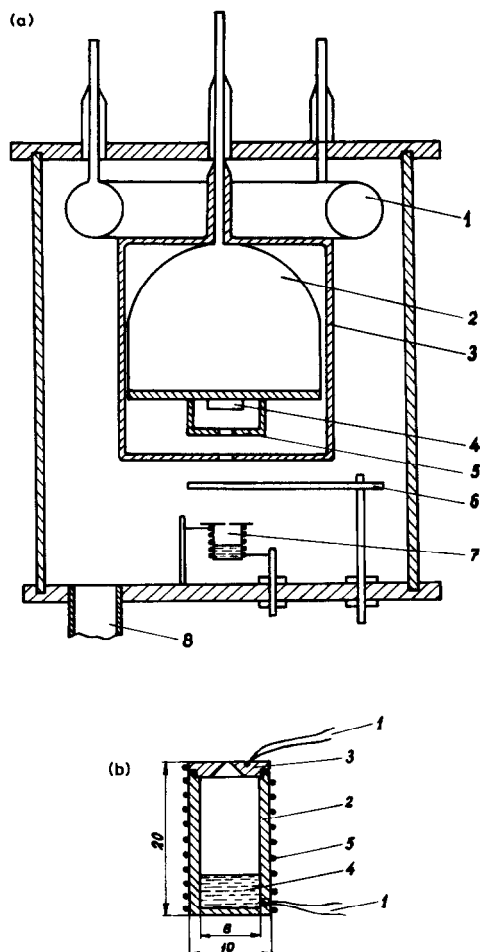


Fig. 1. (a) Scheme of the vacuum cryostat: (1) nitrogen trap; (2) cryostat; (3), (5) nitrogen screens; (4) the quartz crystal; (6) screen; (7) Knudsen cell; (8) vacuum conduit. (b) The Knudsen cell: (1) Cu-constantan thermocouples; (2) Knudsen cells; (3) cover; (4) investigated substance; (5) NiCr heater.

remains constant: 4.2–23, 73–100 and 283–300 K, i.e., the frequency of quartz is constant not only at ambient temperature, but also in the temperature ranges corresponding to liquid helium, hydrogen and nitrogen. This is very important, since it enables the experiment to be greatly simplified, while in ref. 4, where the AT plane cross-section was used, the frequency of quartz remained constant only in the range of temperatures corresponding to liquid helium. The frequency stability in our method is $3\text{--}5 \text{ Hz h}^{-1}$, introducing an error of the order of 0.001%.

The frequency of quartz vibrations has been measured with a differential system, based on a comparison of quartz vibration frequencies with the frequency of a reference system. The change in the resonance frequency of

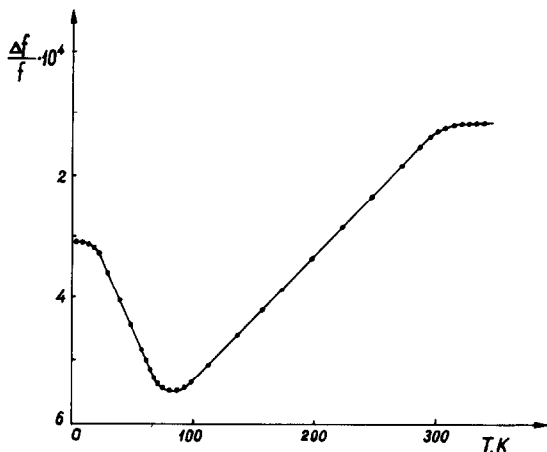


Fig. 2. The dependence of relative quartz crystal frequency change on temperature.

quartz is determined by mixing the output of a quartz generator with the reference frequency, and measuring the difference thus produced with a highly stable quartz frequency meter (type 3-34A).

Crystals of the investigated substance were evaporated in a Cu Knudsen effusion cell (Fig. 1b) heated with an NiCr heater. The ratio of the effusion-orifice surface area to the cross-sectional area of the cell was 1 : 200 (diameter of the effusion orifice, $\phi = 1$ mm) for benzoic acid and 1 : 1300 ($\phi = 0.15$ mm) for naphthalene. The Cu-constantan thermocouple was directly in contact with the investigated substance. The absence of a temperature gradient along the effusion Knudsen cell was controlled with a differential Cu-constantan thermocouple situated at the upper surface of the cell. Experimentally, it had been shown that the temperature gradient disappears within 3–6 min after achieving the set temperature at the bottom of the cell. Stabilization and measurement of the thermoelectric force were automatic. The error in temperature measurement does not exceed ± 0.1 K.

RESULTS AND DISCUSSION

The enthalpy of sublimation, ΔH_{sub} , was determined from the temperature dependence of the rate of sublimation, v . Figure 3 shows the typical dependencies of $\ln v$ on $1/T$ for one of the measurements made for benzoic acid and naphthalene. Three to six Δf measurements for $\Delta t = 100$ s each were performed for each point. Data from Fig. 3 are presented in Table 1. The enthalpy of sublimation has been determined as an average of five measurements for benzoic acid and of four measurements for naphthalene. Values are summarized in Table 2.

$\Delta H_{\text{sub}} = (90.8 \pm 0.6)$ kJ mol⁻¹ at 293–319 K for benzoic acid and ΔH_{sub}

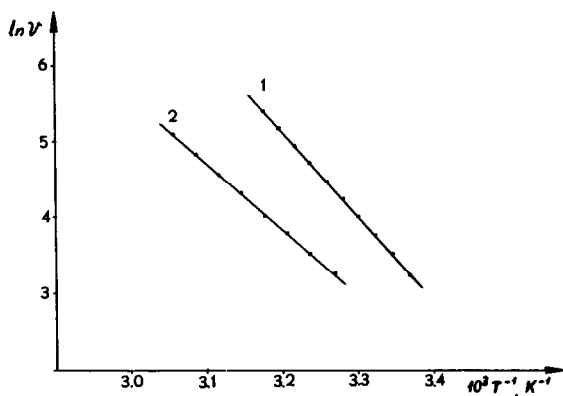


Fig. 3. The dependence of $\ln \nu$ on T^{-1} for: (1) benzoic acid; (2) naphthalene.

$= (72.3 \pm 0.8) \text{ kJ mol}^{-1}$ at 293–331 K for naphthalene agree well with literature data [5–16].

Thus, the presented method of determining the enthalpy of sublimation with a quartz resonator at low temperatures is not inferior to other methods in accuracy, may be characterized with comparatively short duration of

TABLE 1

Experimental results for determining the enthalpy of sublimation of benzoic acid and naphthalene

No.	Temperature, T (K)	Average sublimation rate, ν (Hz)	Standard deviation, σ_n (Hz)
<i>Benzoic acid</i>			
1	297	25.4	0.5
2	299	34.0	0
3	301	43.0	0
4	303	55.6	0.5
5	305	69.8	0.7
6	307	87.6	0.5
7	309	111.0	0.9
8	311	139.6	0.5
9	313	175.5	1.0
10	315	222.6	1.4
<i>Naphthalene</i>			
1	305	26.0	0
2	309	33.7	0.5
3	312	44.0	0.8
4	315	54.0	0.4
5	318	76.3	0.9
6	321	95.3	0.5
7	324	126.0	6.0
8	327	163.3	6.5

TABLE 2

Sublimation enthalpies, $\Delta H_{i \text{ sub}}$ calculated for individual measurements and average sublimation enthalpies, ΔH_{sub} , for benzoic acid and naphthalene

No.	Benzoic acid		Naphthalene	
	Temperature (K)	$\Delta H_{i \text{ sub}}$ (kJ mol ⁻¹)	Temperature (K)	$\Delta H_{i \text{ sub}}$ (kJ mol ⁻¹)
1	293–313	91.5	293–331	72.4
2	293–313	91.1	303–327	71.8
3	295–319	89.9	307–328	71.5
4	295–317	90.2	305–327	73.5
5	297–315	91.3		
H_{sub}	293–319	90.8 ± 0.6	293–331	72.3 ± 0.8

experiments and may be used to investigate substances having a wide range of ΔH_{sub} values. The method may be employed over a wide range of temperatures with substances of varying volatility. The sample weight for experiments is low (20–30 mg) and the measurement itself is simple to perform.

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