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THE VAPOUR PRESSURE AND THE ENTHALPY OF SUBLIMATION
Determination by inert gas flow method

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Abstract

A new device, based on the inert gas flow method, for measuring the vapour pressure and the determination of the enthalpy of sublimation in a wide range of temperatures (up to 573 K) is described in this paper. The limits of the flow rate as important experimental parameter were determined for the given instrument. The results of calibration showed a good precision and reproducibility of the measurements of the enthalpy of sublimation. The results of the determination of some derivatives of pyrimidine were presented.

Keywords: 2,4-diamino-6-hydroxypyrimidine, enthalpy of sublimation, inert gas flow method, 1-methyl-4N-methoxycytosine, 2,4,6-trihydroxypyrimidine, vapour pressure

Introduction

We were interested in the determination of thermodynamic properties of derivatives and analogues of nucleic acid bases and some pharmaceutics. The compounds studied are mostly characterised by low vapour pressure and are individually synthesised in small amounts (complex to synthesise, not commercially available). The necessary condition to perform a cycle of thermodynamic determination is the substance recovery after the measurements. In the Knudsen effusion method used by up-to-day [1–4] the substance recovery was difficult, whereas the amount of substance required for single measurement is quite large, making in some cases the accomplishment of the series of investigations impossible. A stability control of a studied compound in the course of the sublimation process is also difficult or impossible.

In the present paper we give a description of a new device for measurements of vapour pressure and sublimation enthalpy of the low volatile compounds by flow inert gas method. Although the principle of the method is well known [5–8], the proposed new construction seems to be interesting due to its practical usefulness and obtained precision of measurements of the enthalpy of sublimation. The constructed device was applied for the determination of the vapour pressure and the enthalpy of sublimation of some methyl-, methoxy- and hydroxy-derivatives of cytosine.

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Experimental

Method

The inert gas flow method consists in the passing a stream of an inert gas over the sample at a known rate and at a constant temperature, slowly enough to achieve practically saturation of the carrier gas with a vapour of the substance studied. Marti *et al.* [7] made careful studies on the ideal interval of the inert gas flow, which is revealing at high rates a decrease of the vapour pressure measured. At rather low values of the gas flow a marked increase of the vapour pressure is observed by the diffusion of the substances transported in addition to the flow. The vapour is then condensed at some point downstream; in order to determine the mass of the sublimated compound and its purity. The vapour pressure for the given inert gas temperature in the saturation area is next calculated from this amount and with the given volume of the inert gas.

Apparatus

The constructed device is presented on Fig. 1. The inert gas (nitrogen) from tank flows through a column packed with silica to adsorb a humidity from the gas. In a water thermostat where a temperature is controlled to ±0.01 K, the stabilisation of the gas temperature occurs. The stability of the gas flow with precision better than 0.01% is realised by use of mass flow controller MKS type 1259CC-00050SU. The inert gas of constant temperature and velocity passes then to the glass tube (L=1000 mm long, with a diameter d=30 mm, L/d=33.3), which is placed in the air thermostat. Three zones of the glass tube can be distinguished to perform: zone (A) for stabilising of the inert gas; zone (B) in which sublimation process occurs; ensuring slow sublimation of the investigated substance; zone (C) in which the inert gas together with the sublimated substance is overheated by 4–5 K, controlled by platinum resistance thermometer. The determined temperature of the air thermostat is kept constant with a precision of 0.01 K by means of the temperature controller PID

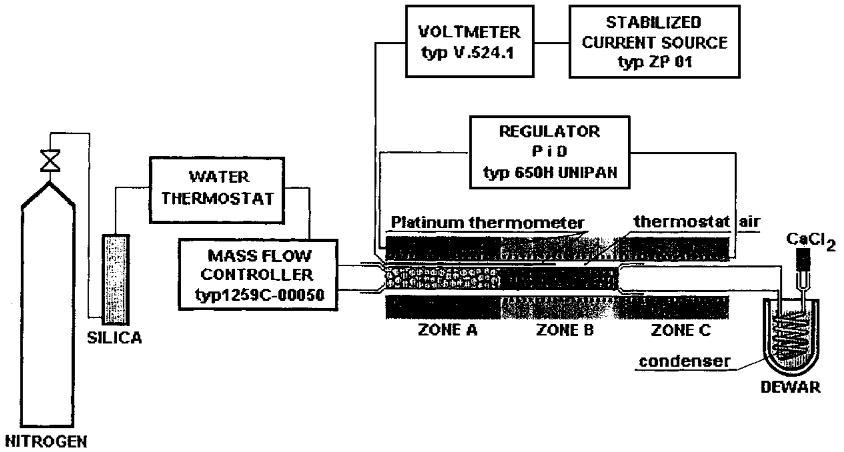

Fig. 1 The scheme of device based on the flow inert gas method

type 650 H UNIPAN equipped with a resistance thermometer. The zone (C) is coupled with the condenser built from glass helix, placed (outside the thermostat) located in a Dewar vessel filled with a liquid nitrogen. To avoid a penetration of humidity from the air, a condenser is connected to a vessel filled with $CaCl_2$.

Calculation

The amount of sublimated substance is determined by following procedure. The condensed substance is dissolved in a defined volume of solvent V_{sol}. The determination of the mass of the substance is based on the measuring of absorbance A of its solution by means of CARY 1E UV-Visible Spectrophotometer, Varian. Knowing a value of the extinction coefficient ε ($dm^3\ mol^{-1}\ cm^{-1}$) of the studied compound dissolved in the solvent one can express the concentration of the solution c($mol\ dm^{-3}$) according to the Lambert-Beer law, by the following relation (1):

$$A = \varepsilon cl \tag{1}$$

whereas the mass of sublimated substance is calculated from:

$$m = cV_{sol}M \tag{2}$$

where l is an absorbing path length; M is a molar mass of studied substance. Considering that the vapour pressure of the substance is very low, the ideal gas rule can be applied:

$$pV_x = nRT \tag{3}$$

where V_x is a total inert gas volume at temperature T, of the measurement corrected with the thermal expansivity coefficient; R is a gas constant; $n=m/M$ – number of moles of sublimated substance. The V_x value is calculated from Eq. (4):

$$\frac{V_x}{V_{gas}} = \frac{T}{T_r} \tag{4}$$

where T_r is a temperature of the water thermostat, V_{gas}(dm^3) is a gas volume at temperature T_r, calculated by Eq. (5):

$$V_{gas} = \nu t \tag{5}$$

where ν(dm^3/h) is a gas flow velocity; t(h) is a sublimation period. Taking into account (2)–(5) we then obtain:

$$P = c\frac{V_{sol}}{V_{gas}}RT_r \tag{6}$$

The experimentally determined vapour pressure data are usually presented with the use of co-ordinates ($\ln P$; $1/T$):

$$\ln P = A + \frac{B}{T} \tag{7}$$

The value of the enthalpy of sublimation is calculated by use Clausius-Clapeyron equation:

$$\Delta_{\mathrm{sub}}^{\mathrm{g}}H_{\mathrm{m}} = -R\frac{\partial(\ln P)}{\partial(1/T)} \tag{8}$$

Whereas the entropy of sublimation at given temperature T was calculated from relation:

$$\Delta_{\mathrm{sub}}^{\mathrm{g}}S_{\mathrm{m}} = \frac{\Delta_{\mathrm{sub}}H_{\mathrm{m}}^{\mathrm{g}} - \Delta_{\mathrm{sub}}^{\mathrm{g}}G}{T} \tag{9}$$

where

$$\Delta_{\mathrm{sub}}^{\mathrm{g}}G = -RT\ln\frac{P}{P_{\mathrm{o}}}$$

where $P_{\mathrm{o}}=1.013\cdot10^{5}$ Pa.

However, the correction related to the changes of value $\Delta_{\mathrm{sub}}^{\mathrm{g}}H_{\mathrm{m}}$ with temperature was omitted.

Results and discussion

The flow inert gas method is a dynamic method. Therefore, from ‘principle’ there is no thermodynamic equilibrium between solid and vapour of the substance studied.

The velocity of a carrier gas flow through the sublimation chamber should be chosen very carefully, in order to establish and maintain the conditions of thermodynamic equilibrium for the substance present in solid and vapour phases. It was already shown in a paper [12], when the gas flow velocity is too low $\nu=0.024(\mathrm{dm}^3/\mathrm{h})$, the error of the determination of the P value increases, when the gas flow velocity is too high, the conditions of solid vapour equilibrium cannot be achieved and the measured vapour pressure values express some temporary states of a system. Efforts were made to maintain the conditions close to the thermodynamic equilibrium between gas and solid phase through securing the adequate velocity of inert gas flowing over the expansive surface of the medium on which the sublimating substance was put. The laminar gas flow was secured. The Reynolds number Re corresponds to 200 with the packing coefficient assumed to 0.45, the mass of sublimated substance per hour was 0.5–2 mg which corresponds to $6\cdot10^{-3}$–$2\cdot10^{-2}$ milligrams in hour per unit of surface (cm^2) from which sublimation occurs. The dimension of the surface is about 600 cm^2.

The device was tested before starting the exact measurements by determining the relation between P and ν and choosing the gas flow velocity value adequate to the appearance of a plateau on $P=f(\nu)$ curve.

The benzoic acid, as a standard substance obtained from Polish Committee of Quality and Standards was used for the calibration. Its enthalpy of combustion $\Delta_{\mathrm{c}}H=-3228.1$ kJ mol^{-1} and heat of melting corresponds to $\Delta_{\mathrm{fus}}H=18.0$ kJ mol^{-1}, which are in good agreement with literature data [19]: Δ_cH=–3226.9 kJ mol^{-1}, $\Delta_{fus}H$=18.06 kJ mol^{-1}.

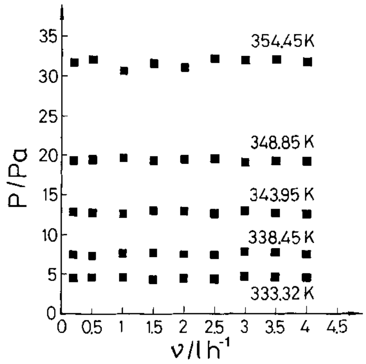

Fig. 2 The relation of the partial pressure of benzoic acid as a function of temperature and inert gas flow rate

The vapour pressure measurements were performed in the range of temperature 307–355 K. For each temperature value the experiments were repeated at 9 different gas flow rates: v=0.2; 0.5; 1; 1.5; 2; 2.5; 3; 3.5 and 4 dm^3/h. At the conditions where the gas flow rate and temperature were kept constant, every experiment was repeated at least three times. The results of the determinations are presented numerically (Table 1) and graphically (Fig. 2). It is quite obvious, that there is no significant difference between the saturated vapour pressure data determined in constant temperature at different gas flow rates. The existing differences are within the experimental error limits. It proves, that is described above experiments, the thermodynamic phase-equilibrium is very good approximated between vapour and solid forms of substance.

In Table 2 the obtained dependence of $P=f(T)$:

$$\ln P = (34.18\pm0.14) - \frac{10888\pm45}{T};$$

$$\sigma = 1.98\cdot10^{-2};\ R = 0.9998;\ n = 10;$$

and value of sublimation enthalpy $\Delta^{g}_{sub}H_m$=90.5±0.3 kJ mol^{-1} are reported and compared with a data taken from literature [5–17]. There is a good agreement between our determined value of the enthalpy of sublimation and this recommended by IUPAC $\Delta^{g}_{sub}H_m$=89.7±0.5 kJ mol^{-1} [16].

However, obtained $\ln P=f(T)$ values implicates the existence of two sets of data. The $P=f(T)$ data determined in this work is consistent with the results of Davies [5] and Colomina [15] within the limits of experimental error, but differ somewhat from the results obtained by Klosky [9], Malaspina [10] and Wiedemann [11].

To verify the usefulness of constructed device in the investigations on the derivatives of nucleic acids bases, the measurements of $\Delta^{g}_{sub}H_m$ for 1-methyl-4N-methoxycytosine were performed.

Table 1 The relation $P=f(T)$ for different velocity of gas flow for benzoic acid

T/K	307.35	312.55	317.85	323.10	328.35	333.32	338.45	343.95	348.85	354.45
ν/dm^3 h^{-1}					Pressure, P/Pa					
0.2	0.286	0.505	0.903	1.623	2.783	4.447	7.453	12.763	19.290	31.640
0.5	0.278	0.516	0.913	1.846	2.762	4.517	7.283	12.687	19.420	32.050
1.0	0.275	0.508	0.893	1.667	2.830	4.504	7.564	12.542	19.574	30.590
1.5	0.280	0.524	0.949	1.624	2.740	4.194	7.692	12.953	19.250	31.540
2.0	0.291	0.518	0.910	1.795	2.676	4.334	7.430	12.872	19.371	31.000
2.5	0.285	0.509	0.943	1.680	2.758	4.261	7.389	12.542	19.460	32.103
3.0	0.293	0.516	0.945	1.506	2.881	4.509	7.742	12.810	18.967	31.897
3.5	0.277	0.519	0.954	1.700	2.980	4.539	7.654	12.623	19.180	31.987
4.0	0.290	0.506	0.953	1.640	2.910	4.338	7.390	12.444	19.048	31.592
$\overline{P}$	0.284	0.514	0.929	1.676	2.813	4.410	7.511	12.693	19.284	31.600
$\Delta P/\overline{P}$[a]	2.17	1.22	2.44	5.60	3.20	2.65	2.11	1.34	1.02	1.61
P [5]	0.286	0.519	0.933	1.637	2.820	4.647	7.662	12.881	20.183	33.211
P [9]	0.544	0.943	1.620	2.723	4.500	7.135	11.321	18.290	27.686	43.847
P [10]	0.452	0.793	1.378	2.340	3.908	6.257	10.025	16.358	24.977	39.938
P [11]	0.478	0.841	1.467	2.501	4.191	6.730	10.815	17.704	27.105	43.472

[a] Variation coefficient %

Table 2 Vapour pressure and enthalpy of sublimation of benzoic acid determined in the present and previous works

Method	T_{range}/ K	$\Delta^{g}_{sub}H_m$/ kJ mol^{-1}	T/ K	Vapour pressure equation P/Pa	Authors	Ref.
Flow	323–394	90.5±0.3	323–394	$\ln P=(34.18\pm0.14)-(10888\pm45)/T$	This work	
Flow method	343–387	91.4±0.4	365.5	$\ln P=34.53\text{-}10996.8/T$	Davies et al.	[5]
Isoteniscope	323–394	87.1	298.15	$\ln P=32.428\text{-}10153.9/T$	Klosky et al.	[9]
Isoteniscope	377–389	90.2	298.15		Hirsbrunner	[17]
Effusion	293–308	90.0±0.3	293–308		Colomina et al.	[14]
Effusion	293–313	90.6±0.2	293–313	$\ln P=(34.24\pm0.05)-(10869.2\pm16.4)/T$	Colomina et al.	[15]
Effusion	293–313	90.35±0.13	303.4		Colomina et al.	[15]
Effusion	290–315	86.6±1.7	303	$\ln P=33.21\text{-}(10432.6.\pm186.5)/T$	Wiedemann et al.	[11]
Effusion	338–383	89.0±0.4	338–383	$\ln P=(32.93\pm0.13)-(10365.8\pm39.2)/T$	Malaspina et al.	[10]
Calorimetry	338–383	89.3±0.4	338–383		Malaspina et al.	[10]
Calorimetry	298.15	89.5±0.2	298.15		Moravetz	[6]
Calorimetry	298.15	89.7±0.6	298.15		Chastel et al.	[13]

Table 3 The relation $P=f(T)$ for 1-methyl-4N-methoxycytosine determined by Knudsen-effusion and inert gas flow method

Effusion method		Flow method	
T/K	P/Pa	T/K	P/Pa
315.68	0.0636	320.31	0.273
317.27	0.0779	325.73	0.527
319.36	0.1014	330.25	0.913
321.68	0.1361	335.46	1.72
323.42	0.1686	340.72	3.06
325.15	0.2097	345.18	4.95
		350.14	8.41
		357.40	17.37

The saturated vapour pressures were measured at different temperatures (Table 3) using two methods: Knudsen-effusion method, described in previous investigations [1–4] and the method of an inert gas flow with the use of the new constructed apparatus. The calculated dependencies $\ln P=f(T)$ and $\Delta^{g}_{sub}H_m$ are as follows:

Effusion method:

$$\Delta^{g}_{sub}H_m = 107.6\pm0.3 \text{ kJ mol}^{-1},\ \Delta^{g}_{sub}S_m = 222.15 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\ln P = (38.24\pm0.11) - \frac{12943\pm35}{T}$$

$$\sigma = 2.76\cdot10^{-3};\ R = 0.999;\ n = 6$$

Flow method:

$$\Delta^{g}_{sub}H_m = 106.9\pm0.4 \text{ kJ mol}^{-1};\ \Delta^{g}_{sub}S_m = 227.12 \text{ J mol}^{-1}\text{K}^{-1}$$

$$\ln P = (38.84\pm0.14) - \frac{12857\pm48}{T}$$

$$\sigma = 1.39\cdot10^{-2};\ R = 0.999;\ n = 8$$

It can be noticed a good agreement between $\Delta^{g}_{sub}H_m$ data obtained by two mentioned methods. The $P=f(T)$ data determined by means of the inert gas flow method are slightly higher than those determined by use of the effusion method.

Probably it results from the different preparation procedures applied to the samples of substance, used in each experiment. In the inert gas flow method, the substance was preliminary dissolved in water and then evenly deposited by a slow evaporation of water on the surfaces of the glass spheres. In the next step, the substance was carefully dried in the stream of an inert gas. It is possible, that in the course of this procedure the certain modification change of 1-methyl-4N-methoxycytosine or also a certain content of the amorphous form might be produced in the flow method. Such differences in the crystal form could be an explanation for the observed differences. It could affect the value of free energy of sublimation, but would not have any influence on the value of standard enthalpy of sublimation. It should be pointed out, that in the effusion-studies the coefficients of absorption of the substance, were determined before and after each measurement, as well as for the substance remaining on the base. The comparison of those two quantities revealed, that in the sublimation process no decomposition of substance investigated occurred.

The presented device was used for the determination of the enthalpy of sublimation of some methyl-, methoxy- and hydrocytosines published previously [18] as well as for 2,4-diamino-6-hydroxypyrimidine and 2,4,6-trihydroxypyrimidine for which the experimental results were presented in Table 4.

Table 4 The vapour pressure and the molar enthalpy of sublimation data for 2,4-diamino-6-hydroxypyrimidine and 2,4,6-trihydroxypyrimidine

2,4-diamino-6-hydroxypyrimidine		2,4,6-trihydroxypyrimidine	
T/K	P/Pa	T/K	P/Pa
422.61	0.0249	393.70	0.2438
437.32	0.0385	398.57	0.4531
447.32	0.0968	403.39	0.5873
456.43	0.2126	413.05	1.3391
461.34	0.3032	418.06	1.9913
466.36	0.5157	428.08	3.8301
470.97	0.6861	437.64	8.2268
$\ln P=(37.33\pm0.49)-(17749\pm22)/T$		$\ln P=(32.69\pm0.79)-(13392\pm33)/T$	
$\Delta_{sub}^{g}H_m = 147.6\pm0.2$ kJ mol^{-1}		$\Delta_{sub}^{g}H_m = 111.3\pm0.3$ kJ mol^{-1}	
$\sigma=1.25\cdot10^{-2}$; R=0.9996; n=7		$\sigma=2.37\cdot10^{-2}$; R=0.9985; n=7	

The results of calibration as well as of the determination of the vapour pressure and the enthalpy of sublimation of cytosine derivatives shown on the good reproducibility and accuracy obtained in the described device.

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