Journal of Thermal Analysis and Calorimetry, Vol. 56 (1999) 739-747

THE DETERMINATION OF LATENT HEATS OF VAPORIZATION UNDER QUASI-ISOTHERMAL CONDITIONS

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Abstract

A method was devised to evaluate latent heats of vaporization from quasi-isothermal isobaric analysis data. The procedure requires the recording of at least two diagrams: one for the investigated liquid, and the other for a standard liquid with a known latent heat of vaporization. Use of the method to determine the heats of vaporization of some alcohols, with water as standard liquid, led to results close to those previously reported in the literature.

The main advantage of the procedure consists in the fact that it requires only small amounts of sample (5–10 mg).

Keywords: alcohols, isobaric analysis, latent heats, quasi-isothermal conditions, vaporization heat

Introduction

Thermal analysis under quasi-isothermal isobaric (QI) [1, 2] conditions and at constant rate [3], elaborated by Hungarian and French schools, has been successfully applied in analytical chemistry and in chemical kinetics [4, 5].

This paper presents the theoretical background for the application of QI analysis in order to evaluate heats of vaporization.

Experimental

Methanol, ethanol and isopropanol from Reactival, and pentanol from Merck were used.

The thermal analysis curves under QI conditions were recorded with a C-Derivatograph (MOM, Budapest, Paulik-Paulik type).

Liquid samples with a mass of $m \approx 10$ mg were placed in flat cylindrical platinum crucibles. The reference crucible was empty. Under such conditions, the thermocouple welding indicated the temperature of the external wall of the crucible.

The vaporization rate was programmed at 0.1 mg min^{-1}.

1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Theory

The thermal analysis curves (*T* – temperature, TG – thermogravimetric, DTG – derivative thermogravimetric and DTA – differential thermal analysis), recorded with time as the independent variable, exhibit three domains: AB, BC and CD (Figs 1 and 2).

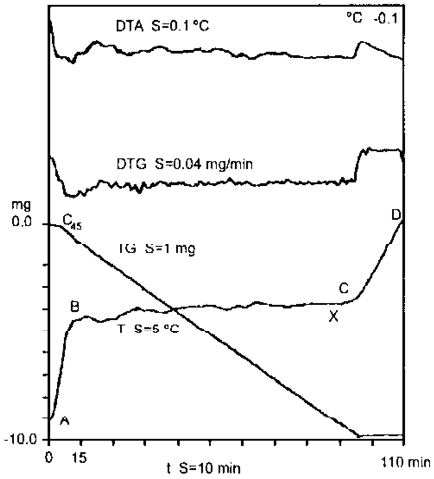

Fig. 1 Quasi-isothermal curves of water

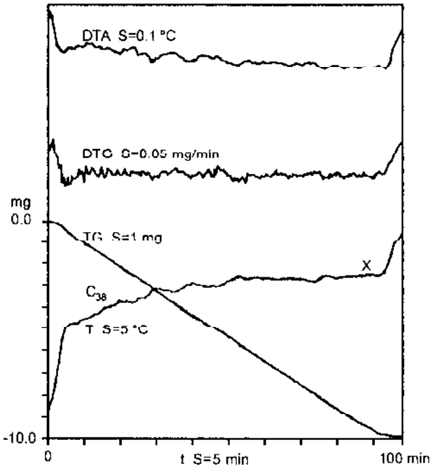

Fig. 2 Quasi-isothermal curves of butanol

The first domain (AB) corresponds to the heating of the sample until the vaporization rate reaches the programmed value *Y* (point B).

The equation of the thermal balance is obtained by taking into account the fact that the thermal flux φ which enters the system leads to the heating of the crucible (index c), of the thermocouple welding (index s), and of the liquid (index p), and to its partial vaporization. Through summation of these amounts of heat transferred in unit time, the following equation is obtained:

$$\varphi = (m_c c_c + m_s c_s + m_p c_p)\beta - \frac{\Delta H}{M}\frac{dm}{dt} \tag{1}$$

In Eq. (1), m represents the mass, c is the specific heat at constant pressure, ΔH is the latent heat of vaporization, M is the molecular mass and t is time.

The flux, heating rate β and vaporization rate Y are expressed by the definition relations

$$\varphi = \frac{dQ}{dt} \tag{2}$$

$$\beta = \frac{dT}{dt} \tag{3}$$

$$Y = \frac{dm}{dt} \tag{4}$$

For a low volatile liquid such as water, the vaporization rate near point A is negligible, as can be seen from the initial portion of the TG and DTG curves (Fig. 1). Under such conditions, the last term in Eq. (1) can be neglected.

The plateau BC represents the steady-state domain, in which the sample temperature, the vapour pressure at the liquid surface and the vaporization rate are constant. The heat flux which enters the sample compensates only the latent heat of vaporization, and the balance equation is simplified as follows:

$$\varphi = -\frac{\Delta H}{M}Y \tag{5}$$

The furnace temperature is adjusted to keep the vaporization rate at a value close to the programmed one.

The last domain (CD) is characterized by the fact that the total amount of the liquid is evaporated (Y=0). Under such conditions, the thermal flux entering the crucible leads to its heating and to the heating of the thermocouple welding at a constant rate. Correspondingly, the balance equation has the form

$$\varphi = (m_c c_c + m_s c_s)\beta \tag{6}$$

In order to evaluate the latent heat of vaporization, it is advantageous to use relation (5), checking the data corresponding to the region BC.

As a cylindrical platinum crucible was used, the thermal flux can be written in the form

$$\varphi = \varphi_l + \varphi_b \tag{7}$$

where φ_l and φ_b are the components which enter lateral area and the base of radius R, respectively.

When a plate crucible is used, which contains a small amount of liquid, it is obvious that

$$\varphi_l \ll \varphi_b \tag{8}$$

The liquid layer and the crucible base can be likened to a plane wall with two layers. For such a system, the thermal flux is expressed through the ratio between the temperature difference and the thermal resistance, and relationship (5) takes the form

$$\frac{T_1 - T_2}{\left(\frac{d_p}{k_p} + \frac{d_c}{k_c}\right)\frac{1}{\pi R^2}} = \frac{\Delta H}{M}Y \tag{9}$$

where k and d are the thermal conductivity and the thickness of the liquid layer (index p) and of the crucible base (index c), respectively. T_1 and T_2 are the temperatures at the free layer surface and at the outer crucible surface, respectively.

The mass m of liquid (with density ρ) from the crucible at a given moment is obtained from the ordinate of the TG curve; thus, the thickness of the liquid layer is given by the obvious relation

$$d = \frac{m}{\rho_p \pi R^2} \tag{10}$$

No reference material is used; this is the reason why the welding of the thermocouple indicates the temperature of the crucible base. It turns out that, in the final part of the quasi-isothermal domain BC, the difference $T_1 - T_2$ is directly proportional to the modulus the DTA curve ordinate.

When this observation is taken into account, Eq. (9) can be transcribed into the form

$$\Delta H_p = \frac{\pi R^2 M K(-\Delta T)}{Y\left(\frac{d_p}{k_p} + \frac{d_c}{k_c}\right)} \tag{11}$$

where K is the dimensionless proportionality constant.

In relation (11) and the following ones, the conventions used are

$$\Delta H > 0; \quad \Delta T < 0; \quad Y < 0 \tag{12}$$

as the liquid vaporization is an endothermic process which occurs with diminution of the sample mass.

The use of crucibles with thin walls and high thermal conductivity is suitable as

$$\frac{d_c}{k_c} \ll \frac{d_p}{k_p} \tag{13}$$

In this work, platinum crucibles with $d_c=10^{-4}$ m and $k_c=69.69$ J (s mK)$^{-1}$ were used. Corrrespondingly, $d_c/k_c=1.43\cdot 10^{-6}$ s K J^{-1}.

For a butanol sample with thickness $d_p=10^{-3}$ m (in the final portion of the QI domain), we obtain $d_p/k_p=6.53\cdot 10^{-3}$ s K J^{-1}, which is three orders of magnitude higher than the previous relation.

After elimination of the ratio d_c/k_c and the taking into account of expression (10), relation (11) assumes the form

$$\Delta H_p = \frac{\pi^2 R^4 M K(-\Delta T)k_p\rho_p}{Y_p m_p} \tag{14}$$

The constants can be eliminated from Eq. (14) by using a standard liquid with a known latent heat of vaporization and with a boiling temperature close to that of the sample.

From the ratio of the variants of relation (14) written for the sample (p) and for the standard (e) with the condition

$$m_p - m_e \tag{15}$$

we obtain

$$\Delta H_p = \Delta H_e \frac{M_p\rho_p k_p(\Delta T)_p Y_e}{M_e\rho_e k_e(\Delta T)_e Y_p} \tag{16}$$

If either a mixture is investigated or the molecular mass of the liquid is unknown, relation (16) can be used in the form

$$\Delta h_p = \Delta h_e \frac{\rho_p k_p(\Delta T)_p Y_e}{\rho_e k_e(\Delta T)_e Y_p} \tag{17}$$

where the molar heat is substituted by the specific heat Δh (J kg^{-1}).

Relation (5) can also be used in order to establish the TG curve equation under QI conditions.

After the elimination of Y between Eqs (4) and (5), variable separation and integration, we obtain the following expression:

$$m = m_0 - \frac{\varphi M}{\Delta H}(t - t_0) \tag{18}$$

where m_0 is the mass of the liquid from the crucible at the moment t_0 when the condition

$$\frac{\mathrm{d}m}{\mathrm{d}t} = Y = \text{const.} \tag{19}$$

is fulfilled.

Relation (18) is actually the equation of a straight line with negative slope, as $\Delta H>0$. On the other hand, by integrating Eq. (19) over the ranges $0-t$ and m_0-m, we obtain

$$m = m_0 + Y(t - t_0);\quad (Y < 0) \tag{20}$$

A comparison of Eqs (18) and (19) leads to

$$Y = \frac{\Delta m}{\Delta t} = -\frac{\varphi M}{\Delta H}(t - t_0) \tag{21}$$

After determination of the thermal effect of the constant Y from the ordinate of the DTG curve and/or the slope of the straight line TG, the thermal flux which determines the vaporization of the liquid under QI conditions can be calculated.

The previous considerations could be applied with special caution to the investigation of sublimation.

Experimental

The diagrams of vaporization corresponding to the sample and the standard are recorded under QI conditions with the same value of the programmed vaporization rate.

The values Y and ΔT are determined for the point X with TG curve ordinate corresponding to the same mass of liquid (condition (15)).

Table 1 Numerical data for Eq. (16)

Substance	Formula	M/ kg mol^{-1}	$\rho\cdot 103$/ kg m^{-3}	k/ W m^{-1} K^{-1}	$-\Delta T$/ K	$-Y\cdot 10^{-9}$/ kg s^{-1}
Water	H_2O	18.02	0.9971	0.5979	0.57	2.00
Methanol	CH_3OH	32.04	0.7924	0.2019	0.55	1.17
Ethanol	C_2H_5OH	46.07	0.7910	0.1669	0.67	1.50
Isopropanol	C_3H_7OH	60.09	0.7850	0.1405	0.12	2.83
Butanol	C_4H_9OH	74.12	0.8091	0.1531	0.56	1.67
Pentanol	$C_5H_{11}OH$	88.15	0.8144	0.1619	0.22	1.00

Symbols: M is the molecular mass, ρ is the density, k is the coefficient of thermal conductivity, and ΔT and Y are the ordinates of the DTA and DTG curves under quasi-isothermal conditions

Point X should also be located in the final portion of the domain BC in order to fulfil inequality (8).

Although recorded with the same programmed value of the heating rate, the values Y_e and Y_p are not identical because of the experimental errors. In the calculations, averages are introduced.

Figures 1 and 2 reveal the similarity of the QI curves for water and butanol. Thus, water can be used as standard liquid in order to determine the heats of vaporization of the alcohols.

The data necessary for the calculation via Eq. (16) are listed in Table 1

In Table 2, the values of the vaporization heats (ΔH_q) determined under QI conditions are compared with those from the literature (ΔH) [3]. A quantitative evaluation of the relative errors, defined by the relation

$$\varepsilon/\% = \frac{\Delta H - \Delta H_q}{\Delta H}100 \tag{22}$$

is also given. The Table 2 additionally lists the boiling temperature T_b and the average temperature T_q of the quasi-isothermal portion.

Table 2 Comparison between the vaporization heat values (ΔH_q) and the corresponding values [6] taken from the literature (ΔH). ε% is the relative percentage error, T_b is the boiling point, and T_q is the mean temperature of the quasi-isothermal domain

Substance	ΔH_q/kJ mol^{-1}	ΔH/kJ mol^{-1}	ε%	T_b/K	T_q/K
Water	–*	43.97	–	373.16	306.62
Methanol	34.3	35.24	+2.7	337.7	291.43
Ethanol	38.9	38.54	+1.7	351.5	296.42
Isopropanol	40.4	39.94	–1.2	355.3	299.96
Butanol	44.1	43.76	–0.8	390	310.03
Pentanol	43.5	44.21	+1.6	404	311.11

*Water is used as standard liquid

Although less precise with respect to the calorimetric method, our procedure has the advantages of being simple and requiring low amounts of liquid. This procedure equally permits series measurements after appropriate calibration.

After determination of the calibration constant defined through the relation

$$C = \frac{(\Delta H)_e Y_e}{M_e \rho_e k_e (\Delta T)_e} \tag{23}$$

the following form of the calculation formula is used:

$$\Delta H_p = \frac{C M_p \rho_p k_p (\Delta T)_p}{Y_p} \tag{24}$$

It can be seen that, for the investigated alcohols, the relative deviation does not exceed 3%.

Figure 3 shows a trend towards increasing error with increase in the absolute value of the difference δ between the boiling points of the investigated alcohols and that of the standard. By definition:

$$\mathrm{Abs}(\delta) = |T_\mathrm{b} - 373| \tag{25}$$

This trend can be explained by taking into account the fact that the value of the magnitude in relation (25) depends on the temperature.

For the same vaporization rate, a correlation was evidenced between the average temperature of the QI domain and the boiling temperature (Fig. 4) of the alcohol.

Such a correlation is to be expected: for a given vaporization rate, a liquid should be heated to a higher temperature, the lower its volatility.

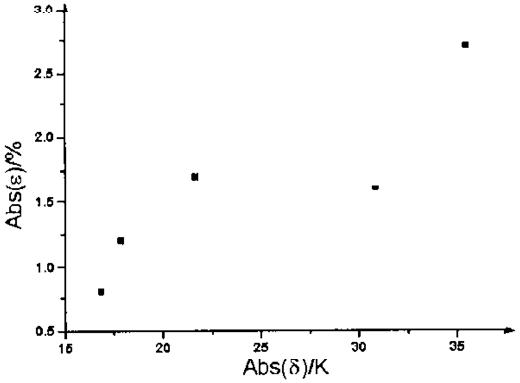

Fig. 3 Correlation between the absolute error ε and difference δ

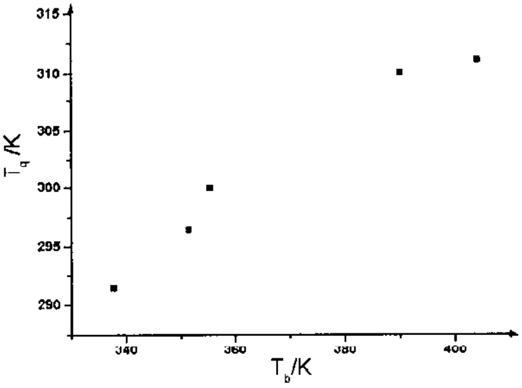

Fig. 4 Correlation between QI temperatures and boiling points

Conclusions

The theoretical background permitting the use of quasi-isothermal isobaric analysis for determination of latent heats of liquid vaporization was elaborated.

The equation of the TG straight line under QI conditions was derived.

The suggested procedure was checked through evaluation of the vaporization heats of five alcohols.

The relative error found did not exceed 3%.

The precision of the method is improved by using a standard with boiling point close to that of the sample.

The average temperature of the QI domain for the same vaporization rate is higher for liquids with higher boiling points.

The main advantage of the method with respect to the classical one consists in the fact that it requires only small amounts of liquids (5–10 mg).

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