

RELATION OF THE TEMPERATURE DERIVATIVE OF INTERNAL AND COHESIVE ENERGIES OF VAPORIZATION TO THE DIFFERENCE OF HEAT CAPACITIES OF LIQUIDS AND GASES

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Methods of calculating the difference of heat capacities of liquids and gases at constant volume are discussed. The known methods of calculation are confronted with the method proposed in this work. It starts from the relations describing the mutual dependence of the temperature derivative of internal and cohesive energies of vaporization to the difference of heat capacities of liquids and gases at constant volume.

Advance in the experimental calorimetric technique in recent years has caused that the regions have been extended substantially which had hitherto been accessible experimentally only exceptionally. This fact is reflected also in new possibilities of vaporization calorimetry which was usually confined to the measurements of heats of vaporization only at one temperature. Today the determination of the temperature dependence of heats of vaporization becomes a routine even if, for the present, only at a few leading laboratories. The development of this branch of knowledge is conditioned not only by the given level and possibilities of the experimental technique but also by the possibility to exploit the data obtained for calculating or estimating other thermodynamic quantities and properties. Seeking these new application possibilities is one of the main tasks of the present time.

The quantity characterizing the difference of molar heat capacities of the liquid and gaseous phases at a constant volume belongs as well to the complete description of the phase equilibrium of the vapour-liquid type. It is called the heat capacity difference at constant volume.

The aim of this work is to judge critically the possibilities to calculate the heat capacity difference at constant volume by means of the known methods and confront them with the proposed one. It is well-known that the values of internal energy (ΔU_V) and cohesive energy (ΔU_c) of vaporization are today determined mostly by calculating from heat of vaporization (ΔH_V). We know as well that an experimental method for determining ΔU_c (ref.¹) is being developed and that methods

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were proposed for estimating ΔU_V and ΔU_c (ref.²⁻⁴) which enable one to estimate the quantities discussed with an accuracy which approaches that of determination of heats of vaporization (0.1–0.2%). Therefore it is to be assumed that we will be able to obtain the needed data on the temperature dependence of ΔU_V and ΔU_c not only from laborious calorimetric measurements of the temperature dependence of heats of vaporization but also by means of estimation methods or generalizations of the temperature dependences of ΔU_V and ΔU_c as it is known with heats of vaporization. Even though these results are so far incomplete and partly also speculative we consider useful to concern in these problems above all for the reason that the way of calculating Δc_V and Δc_V^0 proposed in this work has not hitherto been described in the literature.

At the present time we determine the difference of heat capacities of liquids and gases at constant volume $\Delta c_V = c_V^l - c_V^g$ and the difference of the same heat capacities when gas is in the state of ideal gas $\Delta c_V^0 = c_V^l - c_V^{g0}$ in two ways: The first one starts from the known experimental values of heat capacities of liquids at constant volume c_V^l , heat capacities of gases at constant volume c_V^g and calculated values of heat capacities of gases in the state of ideal gas c_V^{g0} . The values c_V^{g0} cannot be determined experimentally. This way of calculation can be used just in particular cases. The information on heat capacities at constant volume of both phases are very infrequent⁵. Their experimental determination is very difficult; the accuracy of measured values of c_V^l and c_V^g is reported to be 2–3%, exceptionally for c_V^l up to 0.5% (ref.^{5,6}). The estimation methods yield the data on c_V^l and c_V^g with an accuracy of approximately 4–5% (ref.⁵).

More passable is the second way which uses the relation between c_V and c_P (heat capacity at constant pressure) in the form

$$c_V = c_P - T(\partial P/\partial T)_V (\partial V/\partial T)_P, \quad (1)$$

where T , P , V denote temperature, pressure and volume, respectively.

By applying Eq. (1) to the investigated quantity Δc_V , we get the relation

$$c_V^l - c_V^g = c_P^l - c_P^g - [T(\partial P/\partial T)_V (\partial V/\partial T)_P]^l + [T(\partial P/\partial T)_V (\partial V/\partial T)_P]^g \quad (2)$$

and, for the quantity Δc_V^0 , the relation

$$c_V^l - c_V^{g0} = c_P^l - c_P^{g0} - [T(\partial P/\partial T)_V (\partial V/\partial T)_P]^l + R. \quad (3)$$

The superscripts g (go), l denote the gaseous (the gaseous in the state of ideal gas) and the liquid phases, R the gas constant. This way of calculation makes use of the fact that the experimental determination of heat capacities of liquids and gases at constant pressure is as much as an order more accurate than that of c_V and the values c_P^{g0}

can be easily and accurately evaluated from the experimental data on c_p^g (ref.⁷⁻⁹). Moreover, the experimental data on c_p are known much more than those on c_v . In the literature cited, the accuracy of the experimental c_p^l is reported to be between 0.1–1% according to the type of substance measured and its physical properties (above all saturated vapour pressure), c_p^g is usually given with an accuracy of 0.2 to 0.4% and consequently also c_p^{go} with the accuracy of 0.2–0.3%. The estimation methods enable to calculate these quantities with a substantially worse accuracy: c_p^l with an error of about 3–5%, c_p^g approximately 3% and c_p^{go} with an error of 2–4% (ref.^{10,12}).

The estimation methods for calculating c_v and c_p do not yield sufficiently accurate values of heat capacities and therefore they are not considered in our further discussion.

THEORETICAL

As it has been shown by Planck¹³, the temperature derivatives of heat of vaporization lead to a relation which is among others a function of heat capacity difference of liquids and gases at constant pressure. It is to be assumed that the temperature derivatives of ΔU_v and ΔU_c will be among others also a function of the difference Δc_v and Δc_v^0 which is investigated in this work. Further we will outline the derivation of relations sought.

Temperature Derivative of Internal Energy of Vaporization

Let us consider a closed one-component two-phase system whose state is determined by the pair of state variable, *viz.* temperature and volume. Then the change in the internal energy accompanying whatever phase change is given by the difference of state quantities (ΔU) and is a unique function of these variables. We can write

$$\Delta U = \Delta U(T, V).$$

The change of internal energy of the phase change due to an infinitesimal change in temperature and volume is given by the relation

$$d\Delta U = (\partial \Delta U / \partial T)_v dT + (\partial \Delta U / \partial V)_T dV. \quad (4)$$

Let us apply Eq. (4) to a phase change of the vapour–liquid type. Then for the temperature change of the internal energy of vaporization along the equilibrium (saturated) vapour pressure curve we obtain a relation in the form

$$(\partial \Delta U_v / \partial T)_\sigma = (\partial \Delta U_v / \partial T)_v + (\partial U / \partial V)_T^g (\partial V / \partial T)_\sigma^g - (\partial U / \partial V)_T^l (\partial V / \partial T)_\sigma^l. \quad (5)$$

The symbol $\Delta U_v = U(g, T, P^0) - U(l, T, P^0)$ denotes the internal energy of vaporization, the superscripts g and l the gaseous and liquid phases, T temperature and P^0 the saturated vapour pressure.

In the next step we replace the expressions on the right-hand side of Eq. (5) by accessible or easily measurable quantities. The first term on the right-hand side of Eq. (5) equals the difference of molar heat capacities of the gaseous and liquid phases at constant volume

$$(\partial \Delta U_v / \partial T)_v = c_v^g - c_v^l. \quad (6)$$

The dependence of internal energy on volume is given by the thermodynamic equation of state

$$(\partial U / \partial V)_T = T(\partial P / \partial T)_v - P. \quad (7)$$

After inserting Eqs (6) and (7) into Eq. (5) we get the final form for the temperature dependence of internal energy of vaporization

$$\begin{aligned} (\partial \Delta U_v / \partial T)_\sigma &= c_v^g - c_v^l + \\ &+ [T(\partial P / \partial T)_v - P]^g (\partial V / \partial T)_\sigma^g - [T(\partial P / \partial T)_v - P]^l (\partial V / \partial T)_\sigma^l, \end{aligned} \quad (8)$$

where $P^g(P^l)$ is saturated vapour pressure of the gaseous (liquid) phase. For equilibrium it holds

$$P^g = P^l = P^0.$$

Temperature Derivative of Cohesive Energy

The second way which leads to the relation for calculating $c_v^l - c_v^{g0}$, is the derivation of relation for the temperature derivative of cohesive energy. The cohesive energy is defined as a change in internal energy according to the scheme

$$\Delta U_c = U(g, P^0 \rightarrow 0, T) - U(l, P^0, T).$$

Therefore also the course of derivation of the relation for the change of cohesive energy with temperature will formally be the same as that for internal energy of vaporization (Eq. (5)). The rearranged form of this equation for the cohesive energy has the form

$$\begin{aligned} (\partial \Delta U_c / \partial T)_\sigma &= [\partial(U^{g0} - U^l) / \partial T]_v + \\ &+ [(\partial U^{g0} / \partial V)_T (\partial V^{g0} / \partial T)_\sigma - (\partial U^l / \partial V)_T (\partial V^l / \partial T)_\sigma]. \end{aligned} \quad (9)$$

The first expression on the right-hand side of Eq. (9) represents the difference of molar heat capacities at constant volume $c_v^{g0} - c_v^l$. In the second term of the same equation,

the expression $(\partial U^{\text{so}}/\partial V)_T$ equals zero because the internal energy of an ideal gas is independent of volume. Then Eq. (9) can be rewritten to then form

$$(\partial \Delta U_c/\partial T)_\sigma = c_v^{\text{so}} - c_v^l - (\partial U^l/\partial V)_T (\partial V^l/\partial T)_\sigma, \quad (10)$$

which after rearranging in the sense of Eq. (7) leads to the final form of the equation for the temperature derivative of cohesive energy along the equilibrium vapour pressure curve:

$$(\partial \Delta U_c/\partial T)_\sigma = c_v^{\text{so}} - c_v^l - [T(\partial P/\partial T)_v - P]^l (\partial V/\partial T)_\sigma^l. \quad (11)$$

DISCUSSION

As it is evident from the preceding, the determination of Δc_v and Δc_v^0 from direct experimental values is connected with an error whose upper limit for Δc_v is about 20% assuming the average value for $\Delta c_v = 20 \text{ J/mol K}$; $c_v^l = 100 \text{ J/mol K}$ and $c_v^g = 80 \text{ J/mol K}$. The value of Δc_v^0 is determined with an accuracy of about 16% providing the same assumption holds for c_v^l as in the preceding case and the value of c_v^{so} is obtained by calculating from c_p^{so} .

In the next part we will investigate the difference in difficulties of calculating Δc_v and Δc_v^0 on the one hand from the data on c_p^l , c_p^g , c_p^{so} and on the other hand from the temperature derivative of ΔU_v and ΔU_c . For this purpose let us rewrite Eqs (8) and (11) into the form

$$c_v^l - c_v^g = -(\partial \Delta U_v/\partial T)_\sigma - [T(\partial P/\partial T)_v - P]^l (\partial V/\partial T)_\sigma^l + [T(\partial P/\partial T)_v - P]^g (\partial V/\partial T)_\sigma^g \quad (12)$$

and

$$c_v^l - c_v^{\text{so}} = -(\partial \Delta U_c/\partial T)_\sigma - [T(\partial P/\partial T)_v - P]^l (\partial V/\partial T)_\sigma^l. \quad (13)$$

At first let us seek the difference in difficulty of calculating the P - V - T terms of Eqs (2), (12) and (3), (13). These terms are formally identical for both phases, the value of the state term for the liquid phase exceeding several times that of the gaseous phase. Therefore the comparison just for the liquid phase is sufficient. In the expression for the volume dependence of internal energy (so-called cohesive pressure) in Eq. (12), it is possible to neglect the value of pressure against the value of the expression $T(\partial P/\partial T)_v$ (ref.¹⁴). The difference between the coefficients $(\partial V/\partial T)_p$ and $(\partial V/\partial T)_\sigma$ is, for the temperatures below normal boiling point, negligible and becomes significant only for higher saturated vapour pressures¹⁵. From this follows that the terms in Eqs (2) and (12) expressing state behaviour of the liquid phase are comparable and it is possible to write

$$[T(\partial P/\partial T)_V (\partial V/\partial T)_P]^1 \approx [[T(\partial P/\partial T)_V - P] (\partial V/\partial T)_\sigma]^1 \approx 40 \text{ J/mol K} \quad (14)$$

for a vicinity of normal boiling point. For the gaseous phase this comparison is no more so accurate. With regard to the fact that the state behaviour of the gaseous phase manifests itself to a substantially small extent in the calculations, we can say that both methods discussed are equivalent. They require the same kind of P - V - T data and consequently the calculation itself is influenced by the same error which they introduce into the calculation. The difference between both methods reduces then to the difference between the error of the expression $c_p^1 - c_p^0$ or $c_p^1 - c_p^{00}$ and that of calculation of $(\partial \Delta U_V/\partial T)_\sigma$ or $(\partial \Delta U_c/\partial T)_\sigma$. On the assumption that c_p^1 has an average value of 180 J/mol K and, for calculating, it is known with an accuracy of 0.5% up to the normal boiling point, $c_p^0 = 125$ J/mol K with an accuracy of 0.3%, then Δc_p is determined with the upper limit of error equal 1.3 K/mol K (ref.^{8,11,15}). Analogously for the difference Δc_p^0 it is possible to find from the above-mentioned assumptions that the accuracy amounts to about 1.3 J/mol K. The error connected with the calculation of the term $(\partial \Delta U_V/\partial T)_\sigma$ was determined in this way: The values of the temperature dependence of ΔU_V (determined by calculation from ΔH_V) are determined with an accuracy of 0.2% (ref.¹⁶) (providing the accuracy of ΔH_V is 0.1%). The values of calculated temperature derivative have an error of approximately 0.5%. Then the term $(\partial \Delta U_V/\partial T)_\sigma$, which has the average value of -60 J/mol K, is subject to an error of 0.3 J/mol K. The values of ΔU_c (obtained from ΔH_V) can be calculated with an error of about 0.35% (ref.¹⁶) and their derivative is determined with an error of approximately 0.8%. Consequently the error in the determination of the term $(\partial \Delta U_c/\partial T)_\sigma \approx 0.5$ J/mol K. The estimation of the error in the derivative terms is connected with an inaccuracy. To estimate the error we started in this work from the information published previously¹⁷.

The preceding discussion indicates that the calculation of Δc_V and Δc_V^0 from the data on heat capacities at constant pressure and from those on temperature derivative of ΔU_V and ΔU_c is equivalent. Both methods require the knowledge of P - V - T behaviour of the liquid and gaseous phases and in substance they require calculation of the same dependences of the state functions. It is to be therefore expected that the accuracy of both methods will be the same, too. The upper limit of the expected error of calculation will correspond to the upper limit of error of data obtained from the direct experimental data, *i.e.* about 20%.

The use of the former or the latter will be motivated by the fact which input calorimetric data are available and for what group of substances the calculation is carried out. It is to be expected that in the vicinity of the temperature of 25°C, the data on c_p^1 but not those on c_p^0 or c_p^{00} are available. The determination of values of the temperature dependence of ΔU_V and ΔU_c is qualitatively the same in the entire temperature range considered, *i.e.* from 25°C to the temperatures in the vicinity of normal boiling point.

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