THE ENTHALPY OF VAPORIZATION AND THE LIQUID SURFACE CURVATURE

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The effect of liquid surface curvature on enthalpy of vaporization is investigated. The limits are found at which this effect begins to manifest itself both for the concave and convex surface.

Enthalpy of vaporization, ΔH_{∞}, which appears in the Clapeyron equation is related to the plane liquid surface. The aim of this work is the investigation of the effect of the liquid surface curvature on enthalpy of vaporization which is significant for the description of the disperse systems such as fog or liquid in pores.

This work resumes the study by Adamson and Manes[1]. It extends their considerations by investigating the liquid surfaces with convex meniscus and complements them with the data on curvature radii for which the effect on the enthalpy of vaporization or condensation begins to manifest itself. The effect of the surface curvature on the liquid surface tension is included into the calculation, too.

THEORETICAL

The theoretical basis of the problem is given by the Kelvin equation. For the case of ideal behaviour of the vapour phase over liquid drops of equal size, it can be written in the form

$$RT \ln \frac{P_r(T, r)}{P_{\infty}(T)} = \frac{2\gamma(T, r)\, V(T)}{r} . \qquad (1)$$

If the liquid surface is formed by a convex meniscus, then Eq. (*1*) takes the form

$$RT \ln \frac{P_m(T, r)}{P_{\infty}(T)} = - \frac{2\gamma(T, r)\, V(T)}{r} . \qquad (2)$$

Quantities P_r, P_m, and P_{∞} denote the saturated vapour pressure over the drop surface, convex meniscus, and plane surface, γ is the surface tension, V the liquid molar volume, T the temperature, R the gas constant, and r the curvature radius. Quantities P_∞ and V are functions of temperature only. P_r, P_m, and γ are functions of temperature and curvature radius.

The relation sought can be derived, e.g., in terms of Eq. (*1*) (or analogously in terms of Eq. (*2*)). By differentiating with respect to temperature, we get the relation

$$RT \ln P_r + RT\left(\frac{\partial \ln P_r}{\partial T}\right)_r - R \ln P_\infty - RT\frac{\mathrm{d} \ln P_\infty}{\mathrm{d}T} = \frac{2}{r}\left[V\left(\frac{\partial \gamma}{\partial T}\right)_r + \gamma\frac{\mathrm{d}V}{\mathrm{d}T}\right]. \qquad (3)$$

By inserting from the Clausius–Clapeyron equation into the left-hand side of Eq. (*3*) for the second and fourth term and on using Eq. (*1*), we can write

$$\Delta H_\infty - \Delta H_r = \Delta(\Delta H_v) = \frac{2\gamma V}{r} - \frac{2T}{r}\left[V\left(\frac{\partial \gamma}{\partial T}\right)_r + \gamma\frac{\mathrm{d}V}{\mathrm{d}T}\right], \qquad (4)$$

where $\Delta H_\infty(\Delta H_r)$ denotes the enthalpy of vaporization from the plane (curved) surface and $\Delta(\Delta H_v)$ their difference.

CALCULATION AND RESULTS

Equation (*4*) was used for calculating quantity $\Delta(\Delta H_v)$ for water at 298·15 K with curved surface. The calculation was carried out for three chosen values of curvature radii, viz. $r = 10^{-7}$, 10^{-8}, and 10^{-9} m. So the information on the effect of curvature radius size on the change of enthalpy of vaporization was obtained simultaneously. The data on surface tension and its temperature dependence as well as the data on molar volume and its temperature dependence were taken from the literature[2–4]. The data on the effect of surface curvature on surface tension were taken from work by Tolman[5].

The values of input quantities for calculating $\Delta(\Delta H_v)$ at 298·15 K are as follows: $\gamma = 71{\cdot}95 \,.\, 10^{-3}$ N/m, $\mathrm{d}\gamma/\mathrm{d}T = 1{\cdot}6 \,.\, 10^{-4}$ N/mK, $V = 18{\cdot}1682 \,.\, 10^{-6}$ m^3/mol, and $\mathrm{d}V/\mathrm{d}T = 5{\cdot}897 \,.\, 10^{-9}$ m^3/mol K. It was assumed in calculating that the dependence of $(\partial\gamma/\partial T)_r$ and $\mathrm{d}V/\mathrm{d}T$ does not change with the curvature radius size. Further for $r = 10^{-9}$ m, $\gamma = 59{\cdot}72 \,.\, 10^{-3}$ N/m, for $r = 10^{-8}$ m, $\gamma = 70{\cdot}51 \,.\, 10^{-3}$ N/m, and for $r = 10^{-7}$ m, the original value $\gamma = 71{\cdot}95 \,.\, 10^{-3}$ N/m was used.

The results of calculation are as follows: $\Delta(\Delta H_v)$ ($r = 10^{-7}$ m) = 40·9 J/mol. It is the value which is ΔH_r lower than ΔH_∞ under the chosen conditions. As to its size, it corresponds to 0·1% of the value of enthalpy of vaporization ΔH_∞(298·15 K) = = 40·63 kJ/mol. Further, $\Delta(\Delta H_v)$ ($r = 10^{-8}$ m) = 405 J/mol, i.e., 1% of ΔH_∞ and $\Delta(\Delta H_v)$ ($r = 10^{-9}$ m) = 3·69 kJ/mol, i.e. 9·1% of the value of ΔH_∞.

It is evident that in the same way we can achieve, in terms of Eq. (2), analogous conclusions for a liquid whose surface forms convex meniscus. In this case, the values of enthalpy of vaporization would be 0·1, 1, and 9·1% higher than those determined from plane surface.

Further interesting consequences follow from the following consideration: Let us assume the case when $\ln (P_r/P_\infty) = 0$ and consequently $P_r = P_\infty$. This condition is satisfied for two states. In the first case, P_r approaches P_∞ as far as reaches the state when the surface curvature radius is so large that the Kelvin equation ceases to be valid. In the second case it is necessary to admit that decreasing the curvature radius leads to increasing the difference of $P_r - P_\infty$ but at the same time, this difference decreases with increasing temperature for a chosen constant curature. In accordance with this assumption, a temperature must exist for which $P_r - P_\infty = 0$. Let us find this temperature.

Let us rearrange Eq. (2) so as to fulfil the assumption of $\ln (P_r/P_\infty) = 0$ at a sought temperature T_x. Then

$$\Delta(\Delta H_v) = -\frac{2T_x}{r}\left[V\left(\frac{\partial \gamma}{\partial T}\right)_r + \gamma\frac{dV}{dT}\right]. \quad (5)$$

On comparing Eqs (4) and (5), it is apparent that $T_x = T$ just for $2\gamma V/r = 0$. This condition is met when $\gamma = 0$. This is possible only at critical temperature T_c, and from that follows $T_x = T_c$.

The general view of the problems studied can be seen in Fig. 1. For the sake of simplicity let us assume the validity of the Clausius–Clapeyron equation which, plotted in coordinates $\ln P$ vs $1/T$, represents a linear dependence. Then line segment AK illustrates the dependence of saturated vapour pressure on temperature for a liquid with plane surface, line segments BK, CK, and DK the dependence of satu-

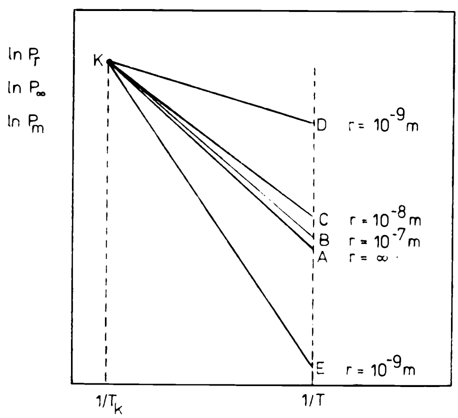

FIG. 1

The dependence of ln P on $1/T$ for the curved liquid surfaces rated vapour pressure on temperature for the chosen gradually increasing drop curvatures. Line segment EK illustrates symbolically the analogous situation for the surface formed by convex menniscus of curvature radius $r = 10^{-9}$ m. The decrease in enthalpies of vaporization for liquids with curved surface and the increase in enthalpies of vaporization for the surfaces formed by meniscus is evident from the figure as well. It follows from the changes of derivatives of $\ln P$ with respect to $1/T$ for single liquid surfaces.

From the results presented follows that the effect of liquid surface curvature on enthalpy of vaporization begins to manifets itself markedly only from curvature radii $r < 10^{-7}$ m. The decrease in droplet radius (meniscus) by one order of magnitude leads to the decrease (increase) in difference $\Delta(\Delta H_v)$ by one order, too. The results of calculating $\Delta(\Delta H_v)$ showed as well that the effect of curvature on quantity γ manifests itself only at extreme $r = 10^{-9}$ m.

Thc conclusions following from this study should be accepted, however, with a certain degree of caution. The main reason consists not in the application of simplifying assumptions in deriving the Kelvin equation or expressing the dependence of surface tension on the curvature radius. It is hiden in the doubt whether the methods of thermodynamics are still usable for such low values of curvature radii within the range of $10^{-7} - 10^{-9}$ m. However, we can say with certainty that in systems met in experimental practice, the effect of liquid surface curvature on enthalpy of vaporization does not manifest itself.

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