DISCONTINUITY IN THE THERMODYNAMIC SPEED OF SOUND AND DETERMINATION OF THE PARAMETERS OF SATURATED VAPORS

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There is a stepwise change in the specific heat or thermodynamic speed of sound c on crossing the saturation curve. The discontinuity in c is dependent on the substance; the largest values have been found for water, mercury and potassium, while small values are found for benzene, CCl_4, and diethyl ether [1].

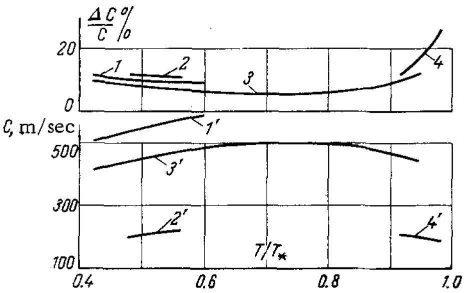

Fig. 1

An analytic expression may be derived for this discontinuity Δc. The following formula gives c for the region on the single-phase side of the saturation curve:

$$c^{(1)} = \left(-gv''^2 \left(\frac{\partial p}{\partial v}\right)_s\right)^{1/2}, \quad \text{or} \quad c^{(1)} = \left(-gv''^2 \frac{c_p}{c_v}\left(\frac{\partial p}{\partial v}\right)_T\right)^{1/2}. \tag{1}$$

Use has been made of

$$\left(\frac{\partial p}{\partial v}\right)_s = \frac{c_p}{c_v}\left(\frac{\partial p}{\partial v}\right)_T. \tag{2}$$

The c for the wet-vapor region is given by [2]

$$c^{(2)} = v'' \frac{dp''}{dT}\left(\frac{gT}{c_v^{(2)}}\right)^{1/2}. \tag{3}$$

Here double primes denote the saturated vapor, while the superscripts denote the single- and two-phase regions.

Then we have

$$\Delta c = c^{(1)} - c^{(2)} = \left(-gv''^2 \frac{c_p}{c_v}\left(\frac{\partial p}{\partial v}\right)_T\right)^{1/2} - v'' \frac{dp''}{dT}\left(\frac{gT}{c_v^{(2)}}\right)^{1/2}.$$

Let

$$c_v^{(2)} = c_v^{(1)} + \Delta c_v''.$$

Usually $c_V^{(2)} \gg c_V^{(1)}$ far from the critical point, and then $c_V^{(2)} \approx \approx \Delta c_V''$, so

$$\Delta c = \left(-gv''^2 \frac{c_p}{c_v}\left(\frac{\partial p}{\partial v}\right)_T\right)^{1/2} - v'' \frac{dp''}{dT}\left(\frac{gT}{\Delta c_v''}\right)^{1/2}. \tag{4}$$

The discontinuity in the specific heat is [3]

$$\Delta c_v'' = T\left(\frac{\partial p}{\partial v}\right)_T'' \left(\frac{dv''}{dT}\right)^2$$

and (4) can be put as

$$\Delta c = c^{(1)} - \frac{gv''^2}{c^{(1)}} \frac{dp''}{dv}\left(\frac{c_p}{c_v}\right)^{1/2},$$

$$\text{or} \quad \frac{\Delta c}{c^{(1)}} = 1 - \frac{gv''^2}{c^{(1)2}} \frac{dp''}{dv}\left(\frac{c_p}{c_v}\right)^{1/2}. \tag{5}$$

The equation for $c^{(2)}$ may be put as

$$c^{(2)} = r\left(\frac{g}{c_v^{(2)}T}\right)^{1/2}. \tag{6}$$

Then

$$\Delta c = c^{(1)} - \frac{grv''}{c^{(1)}T} \frac{dT''}{dv}\left(\frac{c_p}{c_v}\right)^{1/2}. \tag{7}$$

Figure 1 gives observed c for saturated vapors of water [4] (curves 3 and 3'), CO_2 [5] (curves 4 and 4'), and mercury [6] (curves 2 and 2'), while curves 1 and 1' show calculated results [7] for potassium; results calculated from (5) are also shown for mercury and water. The figure also shows Δc for water [2], potassium [7], and CO_2 [5]. We see that Δc at first has a negative temperature coefficient above the melting point, which is followed by a rise, whereas dc/dT is initially positive but then becomes negative. Decrease in c corresponds to increase in Δc and vice versa; it would appear that the maximum in c corresponds to the minimum in Δc, though this needs further examination.

It has been shown [1] that, if Δc is small, the experimental data on c far from the critical point (when $v'' \gg v'$) are described closely by [8]

$$c = \left(\frac{gpv}{1 - (pv/r)(2 - c_p''T/r)}\right)^{1/2}. \tag{8}$$

Derivation of c from (8) requires much less experimental data than does derivation from (1) and (2). For instance, use of (8) requires a knowledge of the p-v-t relation only along the saturation curve, together with the latent heat of evaporation and c_p'', the specific heat of the saturated vapor. The term $(pv/r)(2 - c_p''T/r)$ of (8) is usually small relative to 1, so there is little loss in accuracy if estimates are used for r and c_p''. For instance, 10% reduction in c_p'' reduces the c for saturated steam at 60° C by 0.1%.

Formulas (5) and (7) thus provide a criterion for the applicability of (8) to the calculation of c for saturated vapors.

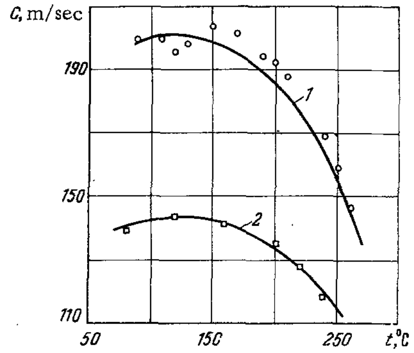

Fig. 2

From (5) we get a formula containing c and c_p/c_V (ratio of the specific heats); if $\Delta c \ll c$, we can put (5) as

$$c^2 = -gv''^2 \frac{dp''}{dv}\left(\frac{c_p}{c_v}\right)^{1/2}. \tag{9}$$

Here and subsequently, all quantities refer to the saturated vapor approached from the single-phase side, so the superscripts (1) and (2) have been omitted.

Comparison of (9) with (2) gives

$$\frac{c_p}{c_v}=\left[\frac{dp''/dv}{(\partial p/\partial v)_T{}''}\right]^2. \tag{10}$$

Only quantities at the saturation line are needed in order to derive c from (9), whereas use of (1) and (2) requires p-v-t data for the dry vapor near that line. Hence (9) is preferable to (2) when it is applicable.

Figure 2 shows c calculated from (9) for the saturated vapors of benzene (curve 1) and CCl_4 (curve 2) between the normal boiling point and a temperature such that $T/T_* = 0.93$. Here p, v, and t have been taken from [9], and c_p/c_v from [10], though the last is given only for normal pressure. However, the change in c_p/c_v is small within the temperature range involved, so the same c_p/c_v has been used for other pressures. The maximal deviation from observed values is 1.5-2%, which appears to arise from inaccuracy in the initial experimental data.

Formulas (9) and (10) may be used to find c_p/c_v for the saturated vapor. If c is known, c_p/c_v can be calculated from (9) simply from the p-v relation along the saturation line, whereas use of (2) requires the p-v-t relation for the superheated vapor. The c_p/c_v from (10) may be more accurate than that from the usual formulas

$$\left(\frac{\partial c_v}{\partial v}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v, \qquad \left(\frac{\partial c_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_p,$$

because these contain the second derivatives of p and v, whereas (10) contains only first derivatives of p.

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