
Pablo G. Debenedetti* and Murat M. Atakan
Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08544-5263

Robin J. Speedy
Chemistry Department, Victoria University of Wellington, P.O. Box 600, Wellington, New Zealand

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Kauzmann pointed out that the difference between the entropy of the crystalline and supercooled liquid phases of a substance can vanish at a temperature $T_K$ below the melting point $T_m$. This condition, in which a disordered phase would attain a lower entropy at absolute zero than a perfect crystal, is known as Kauzmann’s paradox. Fehér extended Kauzmann’s ideas to superheated crystals. Recently, Kishore and Shobha proposed that the ultimate temperature to which a liquid can be superheated is the temperature at which its entropy equals that of the vapor. They argued, furthermore, that this temperature corresponds to the critical point, where both phases are identical. We then explain the errors involved in Kishore and Shobha’s argument.

Kauzmann’s paradox follows from comparing the entropies of the supercooled liquid and crystal of a substance at the same temperature and pressure. Accordingly, we fix a pressure $P_a$ (Fig. 1) and compare the entropies of the liquid and vapor phases at successively higher temperatures (e.g., 2 vs 2′, 3 vs 3′). We also compare the entropies of pairs of supercooled vapors and liquids at the same temperature and pressure (1′ vs 1). The hypothetical entropy crossing must occur before the metastable phase becomes unstable at the spinodal curve bed. Therefore, if there is a Kauzmann condition for the superheated liquid, it must occur at $T<T_a$ (liq); likewise for the supercooled vapor, it must occur at $T>T_a$ (vap.). Figure 2 shows the entropy of the Carnahan–Starling–van der Waals fluid, at a reduced pressure $P/P_c$ of 0.9, where $P_c$ is the critical pressure. The vertical line is the coexistence temperature. States to the right of the coexistence temperature on the liquid curve are superheated, and those to the left of the coexistence temperature on the vapor curve are supercooled. States to the left (right) of the coexistence temperature along the liquid (vapor) branch are unsaturated. The superheated liquid branch ends at the spinodal temperature $T_a$ (liq.) in Fig. 1; likewise, the supercooled vapor branch ends at the spinodal temperature $T_a$ (vap.) in Fig. 1. Thus, the superheated liquid becomes unstable before its entropy equals that of the unsaturated vapor, and the supercooled vapor becomes unstable before its entropy equals that of the unsaturated liquid. This conclusion is valid for any pressure $0<P_a<1$. At the critical point the vapor and liquid phases are identical, and the equality of entropies is trivial. At negative pressures, there is no vapor phase to which the superheated liquid’s entropy can be compared. Analogous conclusions are obtained from other equations of state, such as the van der Waals equation. Identical results for the entropy difference shown in Fig. 2 are obtained by integrating the heat capacity, and using the equation of state to calculate the excess heat capacity.

$$s_a(T_c, P) - s_a(T_0, P) = \int_{T_0}^{T_c} \frac{c_p^a(T', P)}{T'} dT',$$

$$c_p^a(T, P) - c_v^a(T) \frac{\partial^2 P}{\partial T^2} \int_{T_a}^{T_c} \frac{\partial P}{\partial T} dT$$

$$= T \left[ \frac{(\partial P/\partial T)^2}{(\partial^2 P/\partial T^2) \theta} - k, \right.$$

FIG. 1. Schematic pressure–volume projection of the phase diagram of a fluid. ebc and bcd are the binodal (coexistence) and spinodal (limit of stability) loci, respectively. $T_a$ (vap.) is the temperature on the vapor branch of the spinodal curve at a pressure $P_a$. $T_a$ (liq.) is the temperature on the liquid branch of the spinodal at a pressure $P_a$. $T_a$ (liq.); $T_a$ (vap.); $T_a$ (liq.); $T_a$ (vap.)
The entropy and pressure of the Carnahan–Starling–van der Waals fluid (Refs. 6, 7) are given by
\[ \Delta S/\Delta V = \Delta S_{\text{vap}}/\Delta V - \Delta S_{\text{liq}}/\Delta V = \frac{5/2 + \ln v}{\Delta V}, \]
where \( \Delta S_{\text{vap}} \) is the entropy of vaporization, \( \Delta S_{\text{liq}} \) is the entropy of liquid, \( \Delta V \) is the change in volume, and \( 
\Delta h = \Delta u + P \Delta V \geq 0 \quad (T = T_c; 0 \leq P \leq P_c), \]
where \( h, u, \) and \( v \) are the specific enthalpy, energy, and volume. The equality in Eq. (3) holds only at the critical point. A superheated liquid is less stable than the unsaturated vapor at the same temperature and pressure. Hence
\[ \Delta h = \Delta h - T \Delta s = 0 \quad [T \geq T_c(P); 0 \leq P \leq P_c], \]
where \( \Delta s = 0 \). This means
\[ \Delta h = \Delta h < 0 \quad [T = T_c(P); 0 \leq P \leq P_c], \]
which is clearly inconsistent with Eq. (3). Equation (5) requires that the enthalpy difference \( \Delta h \), which is positive at \( T_b \) and negative at \( T_k \), must vanish before \( \Delta s \) vanishes, but Eq. (3) only allows \( \Delta h = 0 \) at the critical point. Hence the entropy of a superheated liquid must be lower than that of the unsaturated vapor at the same temperature and pressure. The argument based on Eqs. (3)–(5) does not hold for the supercooled vapor because the sign of the inequality (4) is then reversed.

In extending the concept of a Kauzmann paradox to the vapor–liquid transition, Kishore and Shobha\(^a\) made two mistakes. First, they did not use pressure as a variable in their analysis. If there is a Kauzmann temperature for a superheated liquid, it should depend on pressure. Second, they did not take into account the stability of the superheated liquid. Their starting point is the correct equation
\[ \Delta s^s = \int_{T_c}^{T} \frac{T_b}{T} \Delta s \]
for the calculation of \( T_k \), where \( \Delta s^s \) is the entropy of vaporization at the given pressure, \( T_b \) is the boiling temperature at the given pressure, \( T_k \) is the Kauzmann temperature, and \( \Delta s \) is the difference between the heat capacities of the liquid and vapor phases at the given pressure. Using a polynomial of the form \( c_p = a + bT + bT^{-2} \), one obtains Kishore and Shobha’s Eq. (4) for the calculation of \( T_k \):
\[ \Delta s^s = \Delta s \ln \frac{T_k}{T_b} + \Delta \beta(T_k - T_b) - \Delta \gamma/2(T_k^2 - T_b^2), \]
where \( \Delta s_a^s = a^s - a^v \), and likewise for \( \beta \) and \( \gamma \). We note, however, that the isobaric heat capacity diverges at the spinodal. A polynomial of the form \( a^s + b^s T + b^s T^{-2} \) cannot be used to extrapolate \( c_p \) data deep into the metastable region, because it has an incorrect temperature dependence. One should instead use Eq. (2). Clearly, the second term in the right-hand side of Eq. (2) diverges at the spinodal. The calculation done by Kishore and Shobha is therefore incorrect. No such problem exists for the liquid–solid transition because there is no spinodal associated with this transition, at least for supercooled liquids with a positive thermal expansion coefficient.\(^{10}\)

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\(^{a}\)Author to whom correspondence should be addressed.

\(^{1}\)W. Kauzmann, Chem. Rev. 43, 219 (1948).


