Comment on "Probing the Nuclear Liquid-Gas Phase Transition"

In a recent paper Pochodzalla *et al.* [1] report a tantalizing dependence of nuclear temperature upon excitation energy. This dependence is characterized by an initial rise, followed by a wide plateau, and a subsequent rise. The authors tentatively ascribe the initial rise to "ordinary" evaporation, the middle plateau to a liquid-vapor phase transition, and the final rise to a nearly ideal gas dependence for the overheated vapor.

Because of its potential significance, it is desirable that this dependence be verified with alternative methods of determining the temperature. Our Comment, however, deals with problems that arise from the tentative reading of the "caloric curve" given by the authors.

Apparently, the "paradigm" the authors have in mind is a standard picture of the diagram temperature T vs enthalpy H for a one component system at *constant pressure P*. In this diagram, the temperature of the liquid (no vapor is present) rises until the vapor pressure p matches the external pressure P. From this point on, the vapor appears, and the temperature remains constant until the liquid has completely evaporated. After the liquid has disappeared, the temperature of the (now overheated) vapor can rise again.

The question arises whether the entire experimental curve can be interpreted in terms of equilibrium thermodynamics. If this is the case, several problems arise. For instance, the claimed distinction between the initial rise (interpreted as the fusion-evaporation regime) and the plateau (hinted at as liquid-vapor phase transition) is not tenable, since evaporation *is* the liquid-vapor phase transition, and no thermodynamic difference exists between evaporation and boiling.

Furthermore, the caloric curve requires for its interpretation an additional relationship between the variables T, P, and V. More to the point, the plateau is a very specific feature of the constant pressure condition rather than being a general indicator of a phase transition. For instance, a constant-volume liquid-vapor phase transition is *not* characterized by a plateau but by a monotonic rise in temperature. This can be easily proven by means of the Clapeyron equation, which gives dP/dT along the univariance line (liquid-vapor transition) together with the ideal-gas equation for the vapor.

For the nearly ideal-vapor phase ($P = nT$), we write $dP = T dn + n dT$, where n is the vapor molar density. In order to stay on the univariance line, we need the Clapeyron equation: $dP/dT = \Delta H/T\Delta V$, where ΔH is the molar enthalpy of vaporization and ΔV is the molar change in volume from liquid to gas.

From this we obtain $n(\Delta H - T)dT = T^2 dn$. At constant pressure $dn = 0$, so $dT = 0$. For $dn > 0$, we see immediately that $dT > 0$. Using $dE \approx dn\Delta E$, where ΔE is the molar heat of vaporization at constant volume, we fi-

nally obtain

$$\partial T/\partial E|_V \approx T^2/n\Delta E^2 = 1/n\Delta S^2. \tag{1}$$

The positive value of this derivative shows that the phase transition at constant volume is characterized by a monotonic increase in temperature.

As an example, Fig. 1 shows a standard temperature T vs entropy S diagram for water vapor. The region under the bell is the phase coexistence region. For the constant pressure curves ($\Delta S = \Delta H/T$), the initial rise along the "liquid" curve is associated with pure liquid, the plateau with the liquid-vapor phases, and the final rise with overheated vapor. The constant volume curves ($\Delta S = \Delta E/T$) cut across the coexistence region at an angle, without evidence for a plateau.

Thus one concludes that the alleged reminiscence of the observed caloric curve with "the paradigm of a phase transition" may be more pictorial than substantive, and that indicators other than the plateau may be needed to substantiate a possible transition from one to two phases. More specifically, *an additional relationship* between the three variables P, T, V (such as $P = $ const, $V = $ const, etc.) *is needed to interpret a T-E diagram unequivocally.*
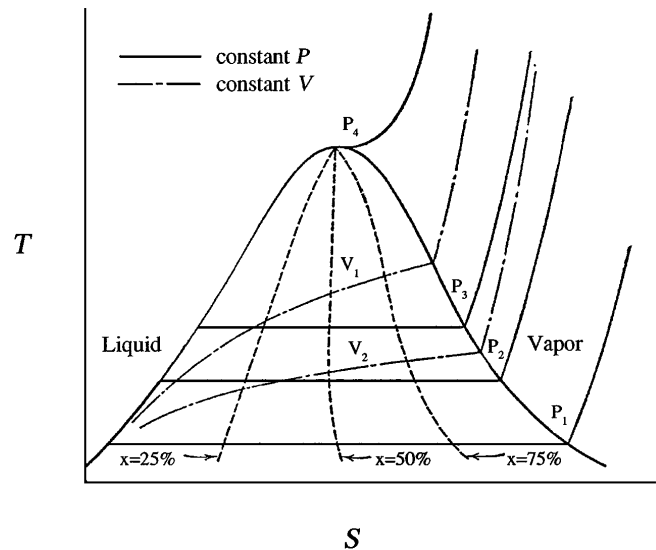

FIG. 1. Temperature-entropy diagram for steam. Curves are shown for constant pressure ($P_4 > P_3 > P_2 > P_1$), constant volume ($V_1 < V_2$), and constant percentage in the gas phase (dashed lines).

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[1] J. Pochodzalla *et al.,* Phys. Rev. Lett. **75**, 1040 (1995).