An Upper Limit to the Metastability of Supersaturated Vapors

Sidney W. Benson and Edward Gerjuoy

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SIDNEY W. BENSON AND EDWARD GERJUOY

Division of Physical Sciences, University of Southern California, Los Angeles, California

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A thermodynamic criterion for (mechanical) instability is applied to the condensation of supersaturated vapors. Values of the maximum thermodynamic compressibility of a vapor as a function of temperature are calculated from the Van der Waals' and Berthelot Equations of State and from a newly developed, modified equation. In all cases, the upper limits predicted lie above the reported experimental values. With the exception of the Van der Waals' equation the predicted values appear much too high. The bearing of these results on the utility of the same thermodynamic criterion for estimating maximum tensile strength of liquids is discussed.

IN a previous paper[1] a purely thermodynamic criterion has been used to determine the limits of metastability of liquids under tension. This criterion is $(\partial P/\partial V)_T = 0$. When applied to liquids, making use of the Van der Waals' and Berthelot Equations of State in reduced form, quite acceptable values are obtained for the maximum tensile strengths. It was also demonstrated that these equations give good qualitative representations of such properties of liquids and vapors as reduced volume, coefficient of thermal expansion, bulk compressibility and energy of vaporization. Consequently it was thought worthwhile to extend the method to systems of supersaturated vapors.

For each equation of state, the equations obtained by setting the partial derivative $(\partial \pi/\partial \phi)_\theta = 0$ was solved for ϕ (the reduced volume) and π (the reduced pressure) as a function of the reduced temperature, θ. The value of π so obtained is the value of the reduced pressure at the maximum in the reduced isotherm of the equation of state. For each equation of state, the vapor pressure curves as a function of θ were calculated from the equation (actually used in reduced form):

$$P_v(V_v - V_l) = -\int_{V_l}^{V_v} P\,dV$$

which is equivalent to equating the free energies of liquid and vapor.

From the curves for the maximum reduced pressures and the reduced vapor pressures it was then possible to calculate for any reduced temperature the values of $\pi_{max.}/\pi_{vap.} = R_s$, the ratio of the maximum supersaturation pressure to the vapor pressure.

In addition to the previously mentioned equations, a third equation developed recently by one of the authors (S. W. Benson) was tried. It is a modified Van der Waals' type equation which can be put into reduced form:

$$\pi = Z\left[\frac{\theta}{\phi - b\phi^{-\frac{1}{3}}} - \frac{a}{\theta^{\frac{1}{3}}\phi^{5/3}}\right].$$

It gives an excellent fit to most of the properties of liquids and vapors, far better than either the Van der Waals' or Berthelot equations and will be reported on soon in a forthcoming paper. The quantities Z, a, and b are universal constants in the above equation.

Values for the maximum supersaturation ratios R_s for different reduced temperatures are shown in Table I.

For purposes of comparison we quote the values obtained by Volmer and Flood[2] for polar vapors in the presence of air: methyl alcohol $(\theta = 0.526)R_s = 3.20$; ethyl alcohol $(\theta = 0.527)R_s = 2.34$; n-propyl alcohol $(\theta = 0.502)R_s = 3.05$; i-propyl alcohol $(\theta = 0.520)R_s = 2.80$; n-butyl alcohol $(\theta = 0.484)R_s = 4.60$; nitromethane $(\theta \cong 0.45)R_s = 6.05$; ethyl acetate $(\theta = 0.465)R_s = 9$ to 12; water $(\theta = 0.425)R_s = 4.2$.

Measurements of supersaturation ratios have also been reported by other investigators.[3–5] Scharrer's results[3] agree fairly well with those of Volmer and Flood for water and alcohols. He includes in addition ratios for non-polar substances, i.e., benzene $(\theta = 0.45)R_s = 5.4$; chlorobenzene $(\theta = 0.41)R_s = 9.5$. Scharrer reports much the same values as these when the condensation took place in the presence of ions with or without de-ionizing fields. (For chlorobenzene he finds, surprisingly, that R_s is increased in the presence of positive ions, going from 9.5 to 10.2.)

TABLE I. Maximum supersaturation ratios R_s.

Reduced temp. θ	Van der Waals' equation R_s	Berthelot equation R_s	Modified equation R_s
0.450	11	—	350
0.500	6.4	900	88
0.550	4.4	170	30
0.600	3.2	40	13
0.650	2.7	15	7.5
0.700	2.2	6.9	4.9
0.750	2.0	4.2	3.4

[1] S. W. Benson and E. Gerjuoy, "Tensile strength of liquids I," J. Chem. Phys. 17, 914 (1949).

[2] M. Volmer and H. Flood, Zeits. f. Physik. Chemie A170, 273 (1934).

[3] L. Scharrer, Ann. d. Physik 35, 619 (1939).

[4] Loeb, Kip, and Einarrson, J. Chem. Phys. 6, 264 (1938).

[5] Richard Head, "Investigations of spontaneous condensation phenomena," Ph.D. thesis, California Institute of Technology (1949).

Loeb's results[4] seem to indicate higher values for R_s* than the previously quoted authors but he also adopted a more severe requirement for condensation, namely cloud formation rather than the 1–4 droplets/cc used by the others.** He also finds that small amounts of impurities have a considerable effect on the values observed. Thus in the case of benzene amounts of moisture in the neighborhood of 0.02 percent decrease the values of R_s by more than 30 percent.

Head[5] using a variety of experimental techniques involving pressure changes produced in fast moving, moist air streams has observed values of R_s as high as 80 for water vapor ($\theta \sim 0.36$).

It would seem on comparing these data with the values in Table I that the Van der Waals' equation gives rather good agreement whereas the other two equations predict much too high values. However, this conclusion is tempered by the observation that this is due to the fact that the Van der Waals' equation gives a very poor representation of vapor pressures, the computed values being much too high. Similarly, the Berthelot equation predicts the highest supersaturation ratios because it gives vapor pressures which are far too low. The modified equation gives a fairly good fit to vapor pressures and so its predicted supersaturation ratios should probably be given the most credence. In all cases it is encouraging to note that the temperature dependence reported is in agreement with the equations with respect to sign.

DISCUSSION

These results lend some support to the author's previous work on the tensile strength of liquids.[1] The basic assumption involved in using $(\partial P/\partial V)_T = 0$ as a criterion for the maximum tensile strength of a liquid is that the liquid has an equation of state even at negative pressures, and that this equation gives *all* metastable states of the liquid. If the Van der Waals or Berthelot equations approximate the true equations of state at negative pressures, then the criterion $(\partial P/\partial V)_T = 0$, yields the maximum tension which the liquid can possibly support at any temperature. Whether or not this tension can be attained, depends of course on the experimental conditions and on the available mechanisms for taking the metastable one-phase system over into the stable, two-phase, liquid-vapor system.

Similar considerations apply to the maximum supersaturation pressure attainable by a vapor. Thus it is significant that the values in Table I do lie above the observed values. (The one or two exceptions are with the Van der Waals' equation, where, as has already been pointed out, the values of R_s are probably too low.) If observed supersaturation ratios exceed the predicted maximum ratios it would be necessary either to abandon the criterion $(\partial P/\partial V)_T = 0$ as an estimate of the limits of metastability, or else to infer that the Van der Waals' and Berthelot equations do not yield even approximately accurate representations of the metastable regions of the vapor isotherms. In either event the authors' previous calculations on tensile strength would not be credible.

That the observed values of R_s are so much lower than the predicted ratios for what is believed to be the best of the three equations of state, the modified equation, is no cause for alarm. For liquids, tensile strengths varying all the way from zero to hundreds of atmospheres have been reported. Presumably, the higher values result because of greater experimental care and because the experimental conditions are less favorable to the formation of critical sized bubbles. Although fewer experimental data are available for vapor condensation than for liquid tensile strength measurements† the experimental results quoted above indicate the existence of a greater variability in supersaturation ratios than has previously been supposed.

It must be mentioned finally that for condensation processes, there is the theory of Becker and Doring[6] which predicts values, fairly close to most of the experimental results of Volmer and Flood. This theory uses a model which involved only the statistical production of molecular clusters at the saturation limits. It is thus quite possible that such cluster formation provides a molecular mechanism for taking the metastable, supersaturated vapor system over into the stable two-phase system so that the thermodynamic ratios of Table I can never be attained. However, a considerable amount of experimental work would be required to justify such a conclusion at present. The experiments done so far leave room for considerable criticism. In particular it has been reported that condensation is often accompanied by considerable turbulence,[3] indicating that the process may not occur homogeneously and may be initiated at selected sites in the apparatus. The Becker-Doring model makes no provision for such possible heterogeneity. It may be of some value in this regard to study the effects of both dust particles and container surface on condensation phenomena. Loeb's findings on the effects of exceedingly small amounts of impurities seem also very significant with respect to the possible heterogeneous nature of the phenomenon.

ACKNOWLEDGMENT

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* From Loeb's data for "pure" benzene one can calculate a value of $R_s \sim 75$ at $\theta \sim 0.41$, considerably higher than any of the other values reported.
** There seems to be considerable dispute as to the actual criteria to be employed for the condensation onset.

† In particular it is to be noted that there is a lack of diversity in the experimental techniques employed in measuring condensation in vapors. A similar paucity in the case of liquids would have led to much narrower limits of variability in the observed tensile strengths.
[6] R. Becker and W. Doring, Ann. d. Physik 24, 719 (1935).