MASTER

OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
NUCLEAR DIVISION
for the
U.S. ATOMIC ENERGY COMMISSION

ORNL - TM - 2695

COPY NO. -

DATE - Sept. 2, 1969

RECEIVED BY OSTI SEP 08 1969

A COMMENT ON TEMPERATURE-PRESSURE EQUILIBRIUM BETWEEN DISPERSED AND CONTINUOUS PHASES OF A MATERIAL

R. N. Lyon

ABSTRACT

This memo calls attention to the fact that the relationship between equilibrium temperature and the pressures in two phases of a material is

$$\Delta s dT = \Delta(v dP) \quad ,$$

and not, as now routinely assumed by bubble investigators, the Clausius-Clapeyron equation

$$\Delta s dT = \Delta v dP \quad .$$

If one phase is discontinuous (subscript "d") and consists of spheres of radius r in a continuous phase (subscript "c") whose pressure is held constant, then the equilibrium temperature will be above the saturation temperature of the continuous phase by an amount

$$(\Delta T_{sup})_c = 2 \int_0^{(\sigma/r)_e} \frac{v_d}{\Delta s} \, d\left(\frac{\sigma}{r}\right)$$

and above the saturation temperature of the discontinuous phase by an amount

$$(\Delta T_{sup})_d = 2 \int^{(\sigma/r)_e} \frac{v_c}{\Delta s} \, d\left(\frac{\sigma}{r}\right) \quad .$$

NOTICE This document contains information of a preliminary nature and was prepared primarily for internal use at the Oak Ridge National Laboratory. It is subject to revision or correction and therefore does

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

A COMMENT ON TEMPERATURE-PRESSURE EQUILIBRIUM BETWEEN DISPERSED AND CONTINUOUS PHASES OF A MATERIAL

R. N. Lyon

Routinely, investigators of bubbles erroneously assume that the Clausius-Clapeyron equation applies to the equilibrium between dispersed and continuous phases of a given material even though surface tension causes the discontinuous phase to be at a higher pressure. This leads them to the further error of assuming that the equilibrium temperature of the system is the saturation temperature associated with the pressure of the dispersed phase.

As long as the density of the continuous phase is very large compared with that of the dispersed phase, the errors are slight. Thus, large errors would occur only in the case of droplets in vapor or where pressures approach the critical pressure. For bubbles, however, the more rigorous relationship substitutes the specific volume of the vapor for the volume change in the Clapeyron equation, and thus unaware bubble investigators who make that substitution in order to simplify their calculations are actually improving their analyses.

The following is simple classical thermodynamics *a la* Gibbs. I present it here merely to call attention to the above points and not with any claim of originality.

For simplicity, we will consider only the potentials of pressure (P) and temperature (T) with their corresponding specific extensive factors, specific volume (v) and specific entropy (s). The increase in specific internal energy, E, of a quantity of a material as it moves from a continuous

DISTRIBUTION OF THIS DOCUMENT IS LIMITED
To AEC Offices and AEC Contractors

phase (subscript "c") to a discontinuous phase (subscript "d") will be

$$E_d - E_c = (Ts)_d - (Ts)_c - (Pv)_d + (Pv)_c \quad . \tag{1}$$

The relationship between small changes in the various conditions is found by differentiating Eq. (1) to give

$$dE_d - dE_c = T_d ds_d - T_c ds_c - P_d dv_d + P_c dv_c + [s_d dT_d - s_c dT_c - v_d dP_d + v_c dP_c] \quad . \tag{2}$$

But the first law states that for each phase under our restrictions

$$dE = q - w = Tds - Pdv \tag{3}$$

so that the bracketed part of Eq. (2) must equal zero, and at equilibrium where $T_d = T_c = T$,

$$(s_d - s_c)dT = v_d dP_d - v_c dP_c \quad , \tag{4}$$

or $\Delta sdT = \Delta(vdP)$.

Equation (4) reduces to the Clausius-Clapeyron equation

$$\Delta sdT = \Delta vdP \quad , \tag{5}$$

when $P_d = P_c = P$. It reduces to an equation developed by Poynting,

$$v_d dP_d = v_c dP_c \quad , \tag{6}$$

when the equilibrium temperature is held constant.

In our case, however, we are concerned with the effect of the pressure of the dispersed phase, P_d, on the equilibrium temperature, T. Holding P_c constant, we get (first derived by G. N. Lewis)

$$\Delta sdT = v_d dP_d \quad . \tag{7}$$

Let us consider a vapor-liquid mixture of a material in which the dispersed phase consists of one or more spheres of radius, r, with

surface tension, σ. Then

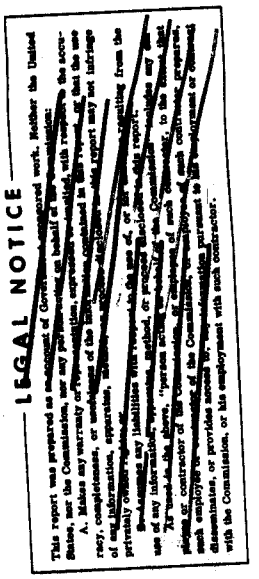
$$P_d = P_c + \frac{2\sigma}{r} \tag{8}$$

and

$$dP_d = 2d\left(\frac{\sigma}{r}\right) \tag{9}$$

or

$$\Delta s dT = 2v_d d\left(\frac{\sigma}{r}\right) . \tag{10}$$



If we define "continuous superheat," $(\Delta t_{sup})_c$, as the equilibrium temperature (T) minus $(T_{sat})_c$, the saturation temperature corresponding to P_c, then

$$(\Delta T_{sup})_c = 2\int_0^{(\sigma/r)_e} \frac{v_d}{\Delta s} d\left(\frac{\sigma}{r}\right) , \tag{11}$$

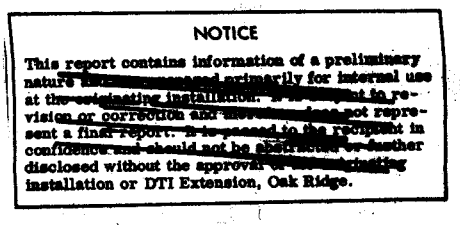
where the subscript "e" indicates the final equilibrium value of (σ/r). Notice that v_d rather than Δv occurs in the integral. The latter would be used with the Clapeyron equation where $P_c = P_d$, and can be used to compute the saturation temperature at P_d.

We can also define "discontinuous superheat" as T minus the saturation temperature corresponding to P_d. Combining Eq. (7) with the Clapeyron equation [Eq. (5)], we get

$$(\Delta T_{sup})_d = 2\int_0^{(\sigma/r)_e} \frac{v_d - \Delta v}{\Delta s} d\left(\frac{\sigma}{r}\right) = 2\int_0^{(\sigma/r)_e} \frac{v_c}{\Delta s} d\left(\frac{\sigma}{r}\right) . \tag{12}$$

For bubbles, except near the critical pressure,

$$v_c \ll v_d \quad \text{and} \quad (\Delta T_{sup})_d \ll (\Delta T_{sup})_c .$$



For drops, however, both $(\Delta T_{sup})_d$ and $(\Delta T_{sup})_c$ will be negative, since Δs is negative. That is, the equilibrium temperature will be less than saturation temperature corresponding to either the pressure in the drop or that of the surrounding vapor. Since the pressure in the drop is greater than in the vapor, the drop is more subcooled than the vapor, as predicted by Eqs. (11) and (12).

It is worth noting that since Δv is negative, an attempt to apply the Clapeyron equation in place of Eq. (7) in a droplet system would erroneously predict T to be above the saturation temperature corresponding to P_c.

In summary, equilibrium between two phases of a single material in a system involving only heat and pressure energy is described by the equation

$$\Delta s dT = v_d dP_d \quad , \tag{7}$$

where the pressure of the continuous phase is not changed.

When the dispersed phase consists of one or more spheres of radius, r,

$$(\Delta T_{sup})_c = 2 \int_0^{(\sigma/r)_e} \frac{v_d}{\Delta s} d\left(\frac{\sigma}{r}\right) \tag{11}$$

and

$$(\Delta T_{sup})_d = 2 \int^{(\sigma/r)_e} \frac{v_c}{\Delta s} d\left(\frac{\sigma}{r}\right) \quad . \tag{12}$$

An attempt to use the Clausis-Clapeyron equation – that is, to substitute Δv for v_d in Eq. (7) – will usually not cause serious errors in analyzing a bubble system, but can cause drastic errors in analyzing a droplet system.

INTERNAL DISTRIBUTION

1. L. G. Alexander
2. S. E. Beall
3. R. H. Chapman
4. J. W. Cooke
5. W. B. Cottrell
6. B. Cox
7. F. L. Culler
8. J. A. Dahlheimer
9. J. A. Edwards
10. A. P. Fraas
11. W. R. Gambill
12. P. N. Haubenreich
13. H. W. Hoffman
14. J. K. Jones
15. P. R. Kasten
16. J. J. Keyes, Jr.
17. O. H. Klepper
18. T. S. Kress
19. C. G. Lawson
20. M. I. Lundin
21. R. N. Lyon
22. R. E. MacPherson
23. H. C. McCurdy
24. A. J. Miller
25. A. M. Perry
26. M. W. Rosenthal
27. W. K. Sartory
28. A. W. Savolainen
29. J. D. Sheppard
30. M. J. Skinner
31. I. Spiewak
32. D. A. Sundberg
33. D. G. Thomas
34. D. B. Trauger
35. G. D. Whitman
36. R. P. Wichner
37-38. Central Research Library (CRL)
39-40. Y-12 Document Reference Section (DRS)
41-43. Laboratory Records Department (LRD)
44. Laboratory Records Department — Record Copy (LRD-RC)

EXTERNAL DISTRIBUTION

45-59. Division of Technical Information Extension (DTIE)
60. Laboratory and University Division (ORO)