

UNCLASSIFIED

AD NUMBER
AD841624
NEW LIMITATION CHANGE
TO Approved for public release, distribution unlimited
FROM Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; JUL 1968. Other requests shall be referred to Commanding Officer, Fort Detrick, Attn: SMUFD-AE-T, Frederick, MD 21701.
AUTHORITY
BDRL ltr, 13 Sep 1971

THIS PAGE IS UNCLASSIFIED

AD 841624

①

TRANSLATION NO. 7

DATE: July 1968

DDC AVAILABILITY NOTICE

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of Commanding Officer, Fort Detrick, ATTN: SMUFD-AE-T, Frederick, Md. 21701.

OCT 2 1968  
[Handwritten initials]

DEPARTMENT OF THE ARMY  
Fort Detrick  
Frederick, Maryland

THERMODYNAMICS - Condensation Theory, Vapor Equilibrium in the Presence of Drops.  
Note by M. Yves Rocard, presented by M. Jean Cabannes

The modern attempts of condensation theories, either because of ignorance of the liquid stage (J. E. Mayer), or by including it (Lee and Yang), all maintain that at any given temperature  $T$  less than the critical temperature  $T_c$  they can predict an angular point of the Andrews  $[P = f(\rho)]$  isotherm followed by a liquefaction level. These theories therefore offer no means of predicting super saturation, which after all is normal. In fact if  $H$  is the surface tension, the pressure  $P_1$  will exist in the center of a drop of radius  $R_0$ , which differs from the pressure  $P_2$  of the vapor (density  $\rho_2$ ) in  $P_1 - P_2 = 2H/R_0$ . Furthermore, thermodynamics in its first approximation shows that in the presence of this drop the equilibrium pressure of vapor  $P_2$  differs from the normal pressure  $P$  of saturated vapor by  $P_2 - P = (2H/R_0)(\rho_2/\rho_1)$ , if  $\rho_1$  is the liquid's density. The "discontinuity" pressure  $P_2$  is therefore a function of  $T$  and of  $R$ , which is not foreseen by the quoted modern theories.

On the contrary, a perfectly continuous theory and one completely in conformance with the kinetic theory of gases, allows all these elements to be calculated,  $\rho_2$  and  $\rho_1$ , as well as  $(P_2 - P)$  and  $(P_1 - P_2)$ , and to obtain accurate expressions, more powerful than those of thermodynamics, which assumes  $\rho_2 \ll \rho_1$ , the vapor being a perfect gas and the liquid being compressible and nondilatable. This theory which is based on the principles given above to explain surface tension, will be developed in another article. It allows for the following results:

Take  $\rho_v$  as the normal density of saturating vapor at  $T$ . Let us assume  $\rho_2$  to be slightly higher than  $\rho_v$ , the density  $\rho_1$  of the liquid in the center of a drop which would be in equilibrium with the vapor  $\rho_2$ , with a radius  $R_0$  to be

established, is given by the strict relation

$$P(T, \rho_1) - P(T, \rho_2) = \rho_1 \int_{\rho_2}^{\rho_1} \frac{P(T, \rho) - P(T, \rho_2)}{\rho^2} d\rho.$$

Assuming  $\rho_2 = \rho_v$ ,  $\rho_1$  is equal to the usual "liquid" density,  $P(T, \rho_1) = P(T, \rho_2)$  and the integral of the second member is (0), a purely mechanical demonstration of the known theorem

$$\oint P dv = 0.$$

The following differential equation may be established, completely fixing the density variation starting from the center of the drop

$$\frac{\alpha \sigma^2 \lambda}{5M^2} \left[ \frac{d^2 \rho}{dR^2} + \frac{1}{R} \frac{d\rho}{dR} \right] = \int_{\rho_2}^{\rho} \frac{P(T, \rho) - P(T, \rho_2)}{\rho^2} d\rho + \frac{P(T, \rho) - P(T, \rho_2)}{\rho}$$

$\alpha$  = constant Van der Waals internal pressure,  $\sigma$ , molecular diameter,  $M$  molecular mass,  $\lambda$  numerical constant depending only on the law of molecular attraction and equal to approximately 3 for London's law. This equation which is rigorous once  $\lambda$  has been correctly defined, integrated with  $\rho = \rho_2$  for  $R \rightarrow \infty$  and  $d\rho/dR = 0$  for  $R = 0$  defines absolutely all, especially  $\rho_1$  for  $R = 0$ , as the drop center.

However if one agrees to speak of a radius  $R_0$  of the drop, defined by  $P_1 - P_2 = P(\rho_1) - P(\rho_2) = 2H/R_0$ , with  $H$  calculated as in the referenced work, one may establish a useful relation between  $\rho_2$  and  $R_0$  which defines the size of the drop in equilibrium with the vapor of  $\rho_2 > \rho_v$  density.

1° Lord Kelvin's law may be found as a first approximation for  $\rho_1 \gg \rho_2$  and a vapor which acts as a perfect gas

$$P_2 - P = \frac{2H}{R_0} \cdot \frac{P_2}{\rho_1}$$

2° A second approximation may be found if one accepts Van der Waal's equation  $P = \frac{RT}{v-b} - \frac{a}{v^2}$

$$P_2 - P = \frac{\frac{2H}{R} \cdot \frac{M}{P_1}}{\frac{RT}{P} - \frac{2a}{RT} + b}$$

3° One reaches explicit calculations near the critical point. At temperature  $T$  close to  $T_c$ , a drop with radius  $R_0$  causes a vapor pressure  $P_2$  and an excess pressure  $P_1$  in the liquid resulting in

$$\frac{P_2 - P}{P_c} = \sqrt{\frac{32}{15}} \left(1 - \frac{T}{T_c}\right) \frac{\sigma}{R_0}, \quad \frac{P_1 - P}{P_c} = 2 \sqrt{\frac{32}{15}} \left(1 - \frac{T}{T_c}\right)^{\frac{3}{2}} \frac{\sigma}{R_0}$$

One observes that  $P_1 - P_2$  is much less than  $P_2 - P$  in this case. Moreover these values are extremely low because the surface tension is eliminated at the critical point, as  $(T_c - T)^{3/2}$ . These results are quite out of the reach of classical thermodynamics. The numerical coefficient  $\sqrt{32/15}$  would undergo slight changes with the use of basic equations other than Van der Waals'.

It should be noted in connection with the size order, that the large ions  $R_0 = 0.6 \times 10^{-5}$  cm in the case of water vapor lead far from the critical point, to  $P_2 - P = 0.02 P$  while the saturation which may reach 8P in well dusted Wilson chambers, corresponds to a  $R_0$  slightly superior to a molecular diameter.

*Trans. by Stancioff  
fr. the French*