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S. F. Harrison and Joseph E. Mayer

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Statistical Mechanics of Condensing Systems. IV

S. F. HARRISON AND JOSEPH E. MAYER
Chemical Laboratory, Johns Hopkins University, Baltimore, Maryland
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It is shown that the theoretical equations of the preceding paper lead to the prediction that, in a finite density and temperature range above the temperature of disappearance of the meniscus, a range of microscopic densities are equally stable, and in a sealed bomb different densities may be observed at a given temperature and average density. The densities observed in various parts of the bomb will depend in a predictable way on its previous history. This is in agreement with the published results of O. Maass on systems in the neighborhood of the critical point.

IN the previous paper the authors have deduced certain equations for the thermodynamic properties of a system of chemically saturated molecules. Their deductions were based on general equations and did not involve any special assumptions as to the behavior of the system.

In the neighborhood of the critical point the equations lead to a $P-V$ diagram for the system qualitatively similar to that of Fig. 1. In this figure pressure is plotted as a function of volume, at various temperatures: the heavy solid lines. The curves at two characteristic temperatures T_m and T_c are especially marked. The shaded area enveloped by the dashed line is the region in which the lines are horizontal, that is where $(\partial P/\partial V)_T=0$. The right-hand boundary of this region is called v_s, the volume of the saturated vapor, the left-hand boundary v_f is the volume of the condensed phase. The dotted lines inside the shaded area represent the extrapolated pressure of the supersaturated vapor. The dot-dash line on the left-hand side of the shaded area at T_m represents a discontinuous transition in the properties of the condensed phase.*

Below T_m the isothermals show discontinuous changes in slope at v_s and v_f. At T_m the surface tension of the condensed phase disappears, and above T_m there will be no visible sharp meniscus between condensed and dispersed phase. The discontinuous transition in the condensed phase shows no heat of transition, at least at the vapor pressure P_m. In general the transition temperature will be expected to vary with volume, and it is shown here increasing with decreasing volume (the dot-dashed line lies above the T_m isothermal), but of this there is no certainty. The isothermals go continuously with continuous change of slope through the shaded region between T_m and T_c. At T_c the isothermal has a horizontal tangent at only the one point v_c, P_c. Above T_c the isothermal is never horizontal.

The part of the diagram to the right of V_c, and all of it above T_c, is deduced strictly from the equations of the previous article. The portion to the left of V_c and below T_c represents a logical guess from the nature of the kinetic picture deduced from these equations. The authors, however, are less certain of the details of this portion of the diagram.

Below T_m and above T_c the diagram corresponds to the usual conception of the diagram

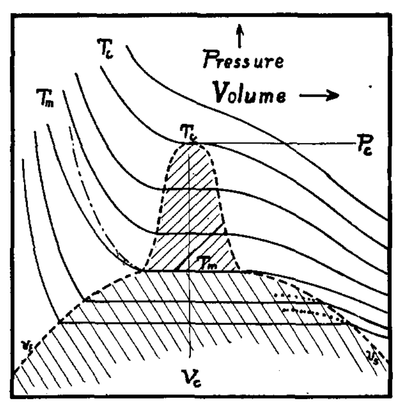

FIG. 1.

below and above the critical point respectively. Between T_m and T_c a system in the shaded area will be expected to have certain unusual properties.

Below T_m compression of the system through the volume region between v_s and v_f will be

* This transition is probably present. It is not a necessary consequence of the equations of the previous article.

accompanied by the separation of two distinct phases of density $1/v_f$ and $1/v_s$. The microscopic density corresponding to a volume between v_s and v_f is unstable. This is indicated on the diagram by the dotted lines showing the higher pressure of the supersaturated vapor. As is well known this phenomenon is associated with the fact that the surface tension increases the vapor pressure of very small droplets of liquid.

Between T_m and T_c, however, the denser phase has no surface tension, and corresponding to this, the isothermals pass smoothly through the condensing region, allowing no extrapolation to a higher pressure for the supersaturated vapor. Indeed all microscopic densities in the shaded region between T_m and T_c will correspond to the same pressure (at the same temperature), and to the same Gibb's free energy. Compression of the system at constant temperature T with $T_m < T < T_c$ will be accompanied by a uniform increase in density throughout the whole system, the pressure remaining unchanged between v_s and v_f.

It is true that after infinite time, owing to the gravitational gradient in a real system, and the consequent higher pressure at the bottom than at the top, the system should attain an equilibrium state with the density higher at the bottom than at the top of the tube. However, the gravitational pressure gradient amounts to about one part in 10^5 per cm of height, and it would therefore not be surprising if uniform density could be maintained for weeks or months.

Moreover, should a density difference once be obtained by any means, with higher density at the bottom of the system than at the top, while the temperature was between T_m and T_c, and both densities were well within the shaded area between v_f and v_s, then uniform compression of the system should result in a uniform logarithmic change in the densities of both portions without a change in their relative abundance. Similarly a change in temperature should result in no change of the two densities, but be accompanied by an increase in the pressure of the system.

If, however, by means of a volume or temperature change, the density in one portion of the tube reached a value corresponding to v_s or v_f on the envelope of the shaded region, then that portion should resist, by increase in relative abundance, any effort to change its density to one outside the shaded region of the diagram. Cooling of such a system should be expected to result in the formation of the meniscus at some temperature lower than T_m, a typical supercooling effect. The extent of the supercooling would be expected to be greater the further the densities in various parts of the system were from the values corresponding to the volume v_{fm} and v_{sm} at T_m. A system with uniform density $1/v_c$, approximately midway between $1/v_{fm}$ and $1/v_{sm}$, would be expected to show the greatest supercooling.

Experimental evidence for the correctness of these concepts is good. Various experimenters have observed discontinuities in different properties of the condensed phase in the neighborhood of T_m, the temperature of disappearance of the meniscus, which is that listed in all existing tables as the critical temperature. These results are summarized in an article by O. Maass.[1] Solubility, dielectric constant and adsorption values have all been found to change discontinuously or rapidly at this temperature. Perhaps the most convincing change is that in the reactivity of HCl with propylene, which shows the usual increase in reaction rate with temperature as long as the HCl is liquid, but the rate drops suddenly to zero as the critical temperature (T_m) of HCl is exceeded even though the density of the gaseous HCl is made comparable to that obtaining previously in the liquid. This has been investigated extensively by Maass.[2]

The evidence that the densities of the "liquid" and "gas" are not identical at temperatures considerably above the temperature of the disappearance of the meniscus is extensive and convincing. Again the paper of Maass previously referred to[1] contains a good historical summary. Apparently all investigators who have made measurements just above the critical temperature have found differences of density in the material remaining above the meniscus level and that below. Any contrary evidence would, in addition, have to be regarded extremely critically in view of the experimental results of Maass and

[1] Tapp, Steacie and Maass, Can. J. Research **9**, 217–239 (1933).

[2] Sutherland and Maass, Can. J. Research **5**, 48–63 (1931); Holder and Maass, ibid., **15B**, 345–351 (1937).

the conclusions of the authors that a uniform density, if once attained, would persist almost indefinitely.

Maass[1] has drawn a simple conclusion from a common observation. It is found that the disappearance of the meniscus in a closed tube can be observed with varying total quantities of material in the tube. This can only be true if the density above and below the meniscus is not equal at the time of its disappearance.

Callendar[3] has stated that the dividing line between the material in bottom and top of a quartz tube containing pure water can be seen above 374°C, the temperature at which the meniscus disappears. He reports a difference in density in the ratio 5 to 3 at this temperature for water, and indicates that the true critical point is somewhat over 6°C higher.

The best and most complete experimental evidence is contained in the excellent work of Maass[1, 4, 5] and several co-workers. Densities were measured to about 0.2 percent by means of float suspended on a quartz spiral which could be moved to different parts of the system. Temperature control and the purification of materials were attended to with the greatest care. The density difference observed above the temperature T_m was as much as 100 times the experimental error. The work was done on methyl ether, propylene, and ethylene.

The experimental results which appear to us to be most significant, perhaps under the influence of the fact that they are in perfect agreement with our theory, were as follows. Upon heating a closed bomb containing definite quantities of material through T_m, the temperature at which the meniscus was seen to disappear, the densities in top and bottom of the tube followed curves corresponding roughly to the envelope v_s and v_f of the shaded area in our figure. After reaching a temperature between T_m and T_c, and subsequent cooling, the density in top and bottom remained constant until a temperature somewhat below T_m was reached. At this temperature the meniscus reappeared and the density difference increased rapidly with falling temperature. Density differences persisted for as long as 6 hours without any tendency to decrease. The density difference was unaffected by mechanical stirring. This appears to be reasonable, since ordinary stirring, although effective in raising macroscopic portions of the high density material into the top of the tube, would not be expected to break up the material into the submicroscopic size droplets which would be prevented from settling by Brownian motion. If the density was once equalized by raising the temperature above T_c, or by cooling the top of the tube 1/10°C, a uniform density persisted unchanged. With uniform densities the supercooling phenomenon was most marked. The pressure exerted by the system at any temperature above T_m was the same whether the system was cooling or the temperature was rising. The behavior of any one bomb, with a given filling, was reproducible day after day.

The following observations appear to be at variance with the authors' theory:

The behavior of the different bombs was not in complete numerical agreement. This may possibly be due to a conceivable failure of the float spiral balance to record absolute densities due to an unpredictable reversible variation in constants with pressure and temperature. (The instruments were apparently checked after the operations.) More likely, this lack of agreement between different bombs may be due to the effect of varying amounts of some impurity present in small amounts. For various reasons the influence of a trace of impurity might be expected to be considerable. However, since the total amount of impurity can scarcely exceed 0.1 percent, we believe that the effect is not caused by impurities alone.

The most extreme case of varying behavior of different bombs was that of bomb No. 13[1]. The over-all volume of this bomb corresponded to one exactly midway between v_{fm} and v_{sm} so that the meniscus remained stationary before disappearance. In this case no density differences were observed, but the supercooling was marked. The authors failed to reproduce this later with a different set-up.[4] This is certainly unaccountable, although one may assume that the stationary

[3] Proc. Roy. Soc. **A120**, 460–472 (1928); see also Engineering **126**, 594–5, 625–7, 671–3 (1928).

[4] Winkler and Maass, Can. J. Research **9**, 613–629 (1933).

[5] Maass and Geddes, Phil. Trans. Roy. Soc., London **A236**, 303–332 (1937).

meniscus was peculiarly favorable to superheating.

The curves of density at the top and bottom of the vessel plotted against temperature, on heating, do not show the sharp break in slope predicted by us at T_m. Since we cannot, as yet, estimate the magnitude of this change it may not exceed the experimental error. The effect may also be masked in some way by the influence of impurity traces or by other minor effects not considered here. The experimental curves do show a marked curvature at T_m.

Certain observations on the effect of varying the total volume of the system[4] are not in numerical agreement with the v_s, v_f, T, curves deduced from the behavior of other bombs. This may, however, be linked with the fact that individual bombs are not in exact numerical agreement with each other.

The $P-V$ isothermals of Maass do not show the horizontal portion demanded by us. The experimental points are scarcely sufficiently close together to decide this, and here, certainly, the effect of impurities can be predicted to be considerable, since total and not partial pressures are measured. It is inconceivable that pressure differences can persist in different parts of the same bomb, and this, coupled with the observation that varying density differences (obtained on heating and cooling) lead to the same pressure, appears to us to require the assumption of a horizontal region in the $P-V$ diagram.

In short, the authors believe that the observations of Maass and co-workers lead directly to conclusions essentially the same as those deduced from the equations of the preceding paper. The observations, however, show slight deviations from the predictions. Whether these can be accounted for by the influence of impurity traces, or by some unexpected failure of the experimental technique, or whether they indicate additional complications in the theory cannot be easily decided at the present time.

The paper of Verschaffelt[6] who shows that variations in the density in top and bottom of the tube may be due to impurities, and who is quoted as stating that differences as large as 40 percent may be caused by 0.1 mole percent of impurity, must be considered. Verschaffelt shows that, from the known influence of O_2 on the critical constants of CO_2, we can conclude that if 0.1 percent O_2 is in one "phase" and *none* in the other, then just above the critical point the density difference of the two regions would be 36 percent. However, if we assume 0.1 mole percent O_2 as impurity in the total CO_2, and 10 percent difference in concentration above and below the meniscus, we arrive (using Verschaffelt's figures) at about 6 percent density difference just above the critical point, and only about 1 percent density difference at 1°C above the critical point. Maass' material, especially in the case of dimethyl ether, can scarcely have contained as much as 0.1 percent impurity, and since the impurity must have about the same vapor pressure as the substrate it seems reasonable to assume a concentration difference in liquid and gas of approximately 10 percent. We must compare Verschaffelt's 1 percent predicted density difference with a difference of 15 percent observed by Maass 1° above T_m, and of 10 percent some 6°C above T_m, where Verschaffelt's predicted difference would be negligible. Although it seems that Verschaffelt showed adequately that work before 1904 could be explained by the influence of impurities, the work of Callendar and especially the careful experiments of Maass indicate that a more fundamental phenomenon is at hand than can be due to impurities alone. Nevertheless, the large effect of impurity traces is regarded by us as lending weight to our supposition that some of the numerical discrepancies of Maass' different bombs are to be explained in this way.

[6] J. E. Verschaffelt, Comm. Phys. Lab., Leiden, Supp. Nr. 10 (1904).