R & D NOTES

A Reasonable Gibbsian Definition of the Dew Point and its Experimental Verification

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The dew point of a mixture is conventionally defined as "that pressure and temperature at which the first infinitesimal amount of liquid condenses from a relatively large amount of gas."

Experimentally, the dew point is usually determined by visual or optical means. The potential errors in such subjective measurements are large, as it is difficult to perceive an infinitesimal quantity of liquid.

Accurate values of the dew point are not merely of academic interest. Many important industrial operations are affected by dew point phenomena, for example, gas transmission in pipelines tries to avoid precipitation of liquids at compressor suction conditions, and petroleum reservoir production must anticipate retrograde behavior in order to optimally recover gas and/or oil.

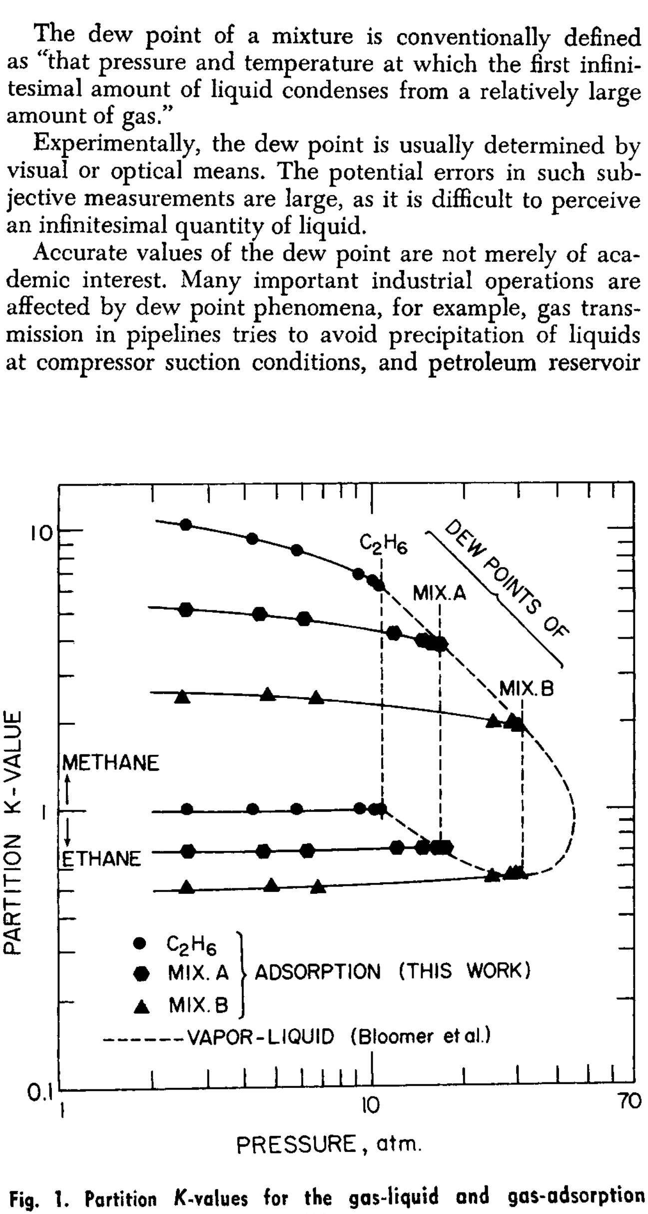

Fig. 1. Partition *K*-values for the gas-liquid and gas-adsorption equilibria.

Perhaps there is an alternative definition of the dew point for mixtures which allows experimental determination with far better accuracy. Masukawa and Kobayashi (1968) studied multilayer adsorption of methane-ethane mixtures on glass beads. Partition *K*-values were measured for the gas-liquid and gas-adsorption equilibria (Figure 1). The pressure and temperature condition at which the partition *K*-value for the gas-liquid interaction equals the partition *K*-value for gas-adsorption satisfies the criterion

$$\mu_i^{(\mathrm{gas})} = \mu_i^{(\mathrm{liquid})} = \mu_i^{(\mathrm{adsorbed\ phase})} \tag{1}$$

where

$\mu_i^{(\mathrm{gas})}$ = chemical potential of component i in the gas phase

$\mu_i^{(\mathrm{liquid})}$ = chemical potential of component i in the liquid phase

$\mu_i^{(\mathrm{ads.\ phase})}$ = chemical potential of component i in the adsorbed phase

Equation (1) is equivalent to and simply an extension of the common dew point criterion, that is,

$$\mu_i^{(\mathrm{gas})} = \mu_i^{(\mathrm{liquid})} \tag{2}$$

Experimentally, the dew point can be determined by the adsorption technique to within 50 angstrom units (which amounts to about 8 to 10 molecular layers adsorbed onto the substrate). The resulting data have much less uncertainty than visual measurements. The ease of measurement will depend somewhat upon the nature of the gas components and upon the adsorption material.

For systems containing molecules which are apt to assume specific orientation with respect to the fluid-fluid interface, however, *K*-value (gas-adsorption) = *K*-value (fluid-fluid) might never be strictly valid. For example, gases containing a long chain alcohol in addition to the hydrocarbon would not present surface conditions representative of the bulk concentration.

A great number of important gas mixtures do not fall into this category and can be studied with the adsorption technique. For such systems, the mixture dew point can be defined as "that condition of temperature and pressure at which the partition K-value for gas-liquid equilibrium is equal to the partition K-value for gas-adsorbed phase equilibrium" as shown in Figure 1. The data indicated in Figure 1 are described in the prior article by Masukawa and Kobayashi (1968).

LITERATURE CITED

Masukawa, S., and R. Kobayashi, "Thermodynamics of Multilayer adsorption studied by Elution Gas Chromatography," *J. Gas Chromatography*, 6, 461 (1968).

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Diffusivity Ratios In Fully Developed Turbulent Pipe Flow

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In a recent R & D Note Hughmark (1974) has calculated some temperature profiles for the turbulent flow of liquids in pipes from a velocity profile equation of Brinkworth and Smith (1969) and the assumption that the eddy diffusivity for heat ϵ_H is equal to the eddy viscosity ϵ. Then using the data of several studies, mostly on liquid metals, he has plotted $\phi \equiv (T - T_c)$ calc/$(T - T_c)$ exp vs. y/R. The points scatter within 20% of unity, and the author states that this fact indicates equal diffusivities. We believe it does not for the reasons indicated.

The data of Sleicher, Awad and Notter (1973) were taken in a system where condensing steam was used to approximate a uniform wall temperature boundary condition, and the data were analyzed with this assumption. Hughmark's Equation (2) is valid for the boundary condition of uniform wall heat flux; it is invalid for uniform wall temperature. Because of a finite heat transfer resistance in the tube wall, the experiments of Sleicher, Awad, and Notter are actually somewhere between the extremes of uniform wall temperature and uniform wall heat flux, although the former is a better approximation as the Reynolds number decreases. In any case, we merely note here that Hughmark's temperature profiles were calculated on a uniform flux basis rather than a uniform wall temperature basis. However, this point is really peripheral and does not directly affect the conclusions reached below.

A more direct objection to the conclusion of equal diffusivities is that the calculated values of ϕ [see Figure 1 (Hughmark, 1974)] scatter about unity in a systematic way. In particular, the data of Buhr, Carr, and Balzhiser (1968) on NaK and Hg show $\phi > 1$ for all points whereas the data of Sleicher, Awad, and Notter on NaK show $\phi < 1$ for all points. In the latter paper we suggest that the difference between our results and those of Buhr, Carr, and Balzhiser (1968) is caused by swirl flow in their test section. Hughmark states that the Reynolds numbers he considers (of order 10^5) are low enough so that this effect is unimportant. Although the effect of the swirl on ϵ_H was greatest at high Reynolds number, swirl was present at all Reynolds numbers and, we believe, is the most reasonable explanation of the fact that ϕ is greater than unity for the data of Buhr, Carr, and Balzhiser. It is also significant that three different models of turbulence with widely differing assumptions and approximations (Jenkins, 1951; Deissler, 1952; Azer and Chao, 1960) all yield $\epsilon_H/\epsilon < 1$ for liquid metals.

Two other points are relevant with regard to Hughmark's calculations. First, Hughmark used the velocity profile expression of Brinkworth and Smith to calculate ϵ in the pipe core. This wholly empirical expression is an excellent analytical approximation to data, but it is not better than the data. In the core region we used data in tabular form given in the paper. That the profiles calculated by the two methods are very similar is a tribute to the expression of Brinkworth and Smith. Second, for fluids of even moderately high Prandtl number, like water, and for Reynolds number above about 50,000 the temperature profiles are so flat in the inner 90% of the pipe radius that calculations of ϵ_H are imprecise. For these conditions relatively large variations in ϵ_H (or ϵ_H/ϵ) near the pipe centerline will always yield values of ϕ that are close to unity, as found by Hughmark for water. Hence, Hughmark's calculations of ϕ from water data in the core of turbulent pipe flow are an insensitive test of ϵ_H/ϵ.

Finally, we should like to emphasize that although our data show ϵ_H/ϵ to be less than 1 for liquid metals, this is not true for other fluids in fully developed turbulent pipe flow. The diffusivity ratio is a function of position as well as of the Reynolds and Prandtl numbers. Experiments with various fluids of moderate Prandtl number under a variety of turbulent conditions have found values of ϵ_H/ϵ in the range 1.1 to 1.4, and a short review of this question is included in a recent paper by us (Notter and Sleicher, 1971).

In conclusion, we believe the contention of Hughmark (1974) that for fully developed pipe turbulence the ratio ϵ_H/ϵ is equal to one at all Prandtl numbers and at all radial positions is unwarranted. Not only is it in conflict with all theoretical analysis of ϵ_H/ϵ and with temperature profile measurements in liquid metals, but it also leads to errors in calculated heat transfer rates. For example, Notter and Sleicher (1972) show that eddy diffusivity profiles with ϵ_H/ϵ less than one at all radial positions yield Nusselt numbers that agree well with experimental data on carefully purified liquid metals in fully developed turbulent flow in smooth pipes for the boundary conditions of either uniform wall temperature or uniform wall heat flux. If ϵ_H/ϵ is assumed to be equal to one, similar calculations yield Nusselt numbers that exceed the data.