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Comment on ''Generalized Kelvin equation and the water content of a cloud''

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Kuz [Phys. Rev. E. **51**, 5136 (1995)] presents the novel Kelvin equation, which would reduce to ordinary forms if some assumptions were made regarding the ratio of the number of molecules in the gas to that in the liquid phase. We feel that the definition used for the Gibbs free energy as a starting point of calculations is not a proper one and, in addition, it is not correctly treated. We present practical situations contradicting the conclusion concerning the liquid-water content in clouds. Some minor inaccuracies are also highlighted. [S1063-651X(96)03911-6]

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In Ref. [1] the author reconsiders thermodynamics of a system of droplets immersed in a saturated vapor. As a result of his analysis the novel form of the Kelvin equation is formulated containing ratios of the molar numbers (number of molecules) of the gas phase and the interface to that of the liquid. By comparing the Kelvin equation to earlier experiments the author states that the number of gas and liquid particles is equal for droplets down to 0.1 μm, but this relation is 3 for small droplets in the embryonic states of formation. Finally, the author proposes to use the former statement when predicting the liquid-water content of a cloud. Our remarks are as follows.

(i) In the paper a thermodynamic description is done by using the Gibbs free energy G of the binary system in the form of [2]

$$dG=-SdT+V^g dp^g+V^l dp^l-Ad\sigma + \sum_{i=1,2} [\mu_i^g dn_i^g+\mu_i^l dn_i^l+\mu_i^\sigma dn_i^\sigma], \qquad (1)$$

where S is the entropy, T is the temperature, V is the volume, p is the pressure, A is the interfacial area, σ is the interfacial tension, n_i is the molar number of component i, and μ_i is the chemical potential. Superscripts g, l, and σ refer to the gas, liquid, and interface, respectively. However, this expression stems from the following function [3]:

$$G=U-TS+p^g V^g+p^l V^l-\sigma A, \qquad (2)$$

where U is the internal energy of the system. This function can be applied to the systems where the interface is not closed upon itself and contact the environment (that is, the surroundings enclosing the entire system concerned), and the environment may perform surface work upon the system [3]. This is not the case now, since the system of the drops and the gas phase may perform only volume work on its surrounds, i.e., drops are making contact with the environment only through the gas. Furthermore, the summational term in Eq. (1) can be assumed to be zero since the chemical potentials are equal at physicochemical equilibrium and the total molar number is constant. The paper has ignored this fact. In conclusion, the correct formulation of the Gibbs free energy for droplets in the gas is [3]

$$G=U-TS+p^g(V^g+V^l) \qquad (3)$$

and using that the ordinary Kelvin equation can be derived. Note also that the two pressures (p^g and p^l) appearing in the preceding equations should both be the pressure of the surrounding vapor p^g that couples to the environment. The proof of this is presented in [3].

(ii) The paper concludes that if a cloud contains droplets of such a size that the Kelvin equation is valid, it is clear that the number of gas and liquid particles (molecules or moles) is the same. This result is absurd in itself. It is true that in tropospheric water clouds such a condition can be achieved: for example, 1000 droplets per cm^3 with the radius of 10 μm gives the liquid-water content of 0.23 mole per m^3 and assuming the relative humidity of 100% with the gas temperature of 273 K the molar concentration in the gas is found to be 0.27 mole per m^3. However, conditions in clouds result from dynamic micrometeorological processes and no general rule to predict the liquid-water content can be offered. Had the radius been 5 μm instead of 10 μm and the temperature 278 K instead of 273 K (which are still realistic) the liquid-water content would decrease to 0.029 mole per m^3 and the molar concentration would increase to 0.38 mole per m^3. The proposed law of the equal molar numbers is not valid. Finally, the relation depends strongly on substances considered. As an example, consider again the cloud of 1000 droplets per cm^3 with the radius of 10 μm but assuming that each droplet is composed of well-mixed ammonia and water (mole fractions are 0.5). This is now a binary system considered in the paper, and such a cloud can be found during the dispersion of the accidental release from a pressure-liquefied ammonia container. Let the temperature be 266 K. The density of the liquid mixture is 840 kg per m^3 [4] giving 0.20 mole per m^3 for the liquid content. According to [5] and [6] the equilibrium vapor pressures are 91300 Pa (ammonia) and 82 Pa (water) giving 41 mole per m^3, which is much larger than the liquid content.

(iii) The paper contains some minor inaccuracies and inconsistencies. It seems that Eq. (4) is derived from Eq. (3) by assuming that V^g, V^l, and A are constant during integration. The assumption is not obviously true. The definition of N^g/N^l should be $\Sigma_{i=1,2}n_i^g/\Sigma_{i=1,2}n_i^l$ and similarly for N^σ/N^l. The paper deals with droplets immersed in the gas, thus the relevance to capillary condensation studied by Fisher and Israelachvili [7] is not clear. The largest droplet considered in Table I consists of 6248 particles and the gas-liquid particle relation is calculated to be 1.0. However, the size corresponds to a water droplet of 3.5 nm (radius), far beyond the law of the equal molar numbers.

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