If I mix 5 gallons of gasoline with 20 gallons of water in a 55 gallons drum, what is the makeup of the vapor? I know gasoline floats on water, but does that block all water vapor?

Water is almost insoluble in gasoline, but it dissolves in a very small amount – 0.015 % w. (data from chemical handbook). So, if these two liquids will stay for long enough in contact, gasoline will saturate with water, and water will evaporate with gasoline from that mixture.

We will assume that the total pressure in the drum is 760 mm Hg, and temperature is 20°C.

To calculate the makeup of vapor, we use the Raoult's Law:

$$x_{H2O}^{vap} = \frac{p_{H2O} \cdot x_{H2O}^{liq}}{P_\Sigma}, \quad x_{gas}^{vap} = \frac{p_{gas} \cdot x_{gas}^{liq}}{P_\Sigma}, \quad \text{where } P_\Sigma - \text{total pressure in the drum (760 mm Hg);}$$

$x_{H2O}^{vap}, x_{gas}^{vap}$ – molar fractions (or volume fractions) of water and gasoline in vapor;

p_{H2O}, p_{gas} - saturated vapor pressure of pure water and pure gasoline at 20°C, they are 17.5 mm Hg and 80 mm Hg, respectively (data from chemical handbook);

$x_{H2O}^{liq}, x_{gas}^{liq}$ - molar fractions of water and gasoline in liquid phase;

First we need to find the $x_{H2O}^{liq}, x_{gas}^{liq}$, which we can calculate from the solubility of water in gasoline: in 1 kg of water-gasoline solution will be 0.00015 kg of water, and 0.99985 kg of gasoline.

Average molecular weight of gasoline is 114 g/mol, molecular weight of water is 18 g/mol.

$$x_{H2O}^{liq} = \frac{m_{H2O}/M_{H2O}}{\dfrac{m_{H2O}}{M_{H2O}} + \dfrac{m_{gas}}{M_{gas}}} = \frac{0.00015/18}{\dfrac{0.00015}{18} + \dfrac{0.99985}{114}} = 9.5 \cdot 10^{-4} \, mol. \, frac.$$

$$x_{gas}^{liq} = 1 - x_{H2O}^{liq} = 1 - 9.5 \cdot 10^{-4} = 0.99905 \, mol. \, frac.$$

Volume content of water in vapor will be:

$$x_{H2O}^{vap} = \frac{17.5 \cdot 9.5 \cdot 10^{-4}}{760} = 2.19 \cdot 10^{-5} \, vol. \, frac. = 2.19 \cdot 10^{-3} \, \% vol.$$

Volume content of gasoline in vapor will be:

$$x_{gas}^{vap} = \frac{80 \cdot 0.99905}{760} = 0.1052 \, vol. \, frac. = 10.52 \, \% vol.$$