Chemistry 201

Vapor pressure

NC State University

Concept: vapor pressure

• Vapor pressure is an equilibrium property that determines the relative pressure of a gas above a liquid or solid.

• Vapor pressure increases with temperature. It defines a curve on a pressure-temperature phase diagram.

• The vapor pressure of a solvent can be reduced by a solute according to the equation.

$$P_1 = x_1 P_1^*$$

Here x is the mole fraction of the solvent and P_1^* is the vapor pressure of the pure solvent.

What causes vapor trails above a cold lake?

What causes dew to form?

Salt water has higher conductivity than H_2O

Ideal solutions: Raoult's law

Raoult's law states

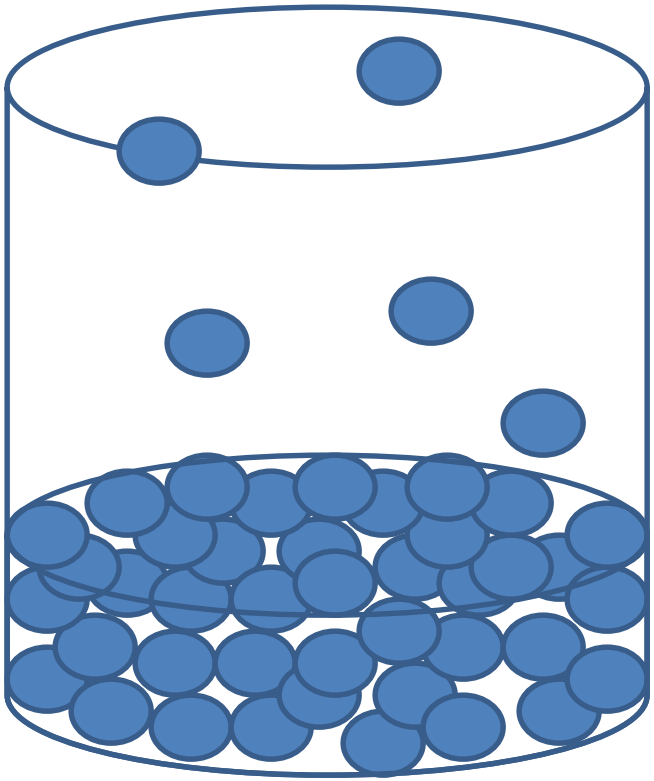
$$P_j = x_j P_j^*$$

where P_j^* is the vapor pressure of pure component j. The vapor pressure of component j in an ideal solution is given by the product of its mole fraction and P_j^*.

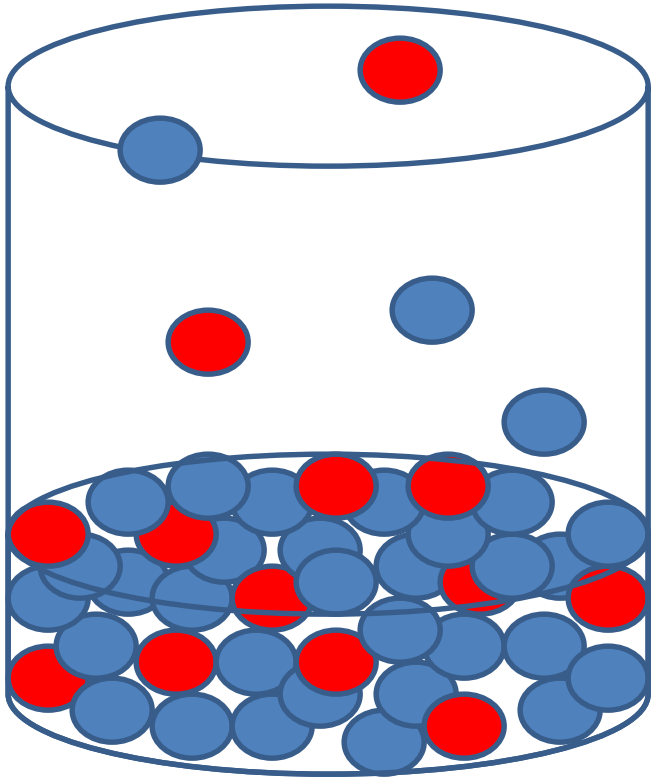
There are two cases we can consider.

1. Volatile solute – both solvent and solute are found in the vapor above the solution. A solution of ethanol in is an example.
2. Non-volatile solute – only the solvent has a vapor pressure. The solute does not contribute to the pressure so there is a "vapor pressure lowering".

Vapor pressure above solution



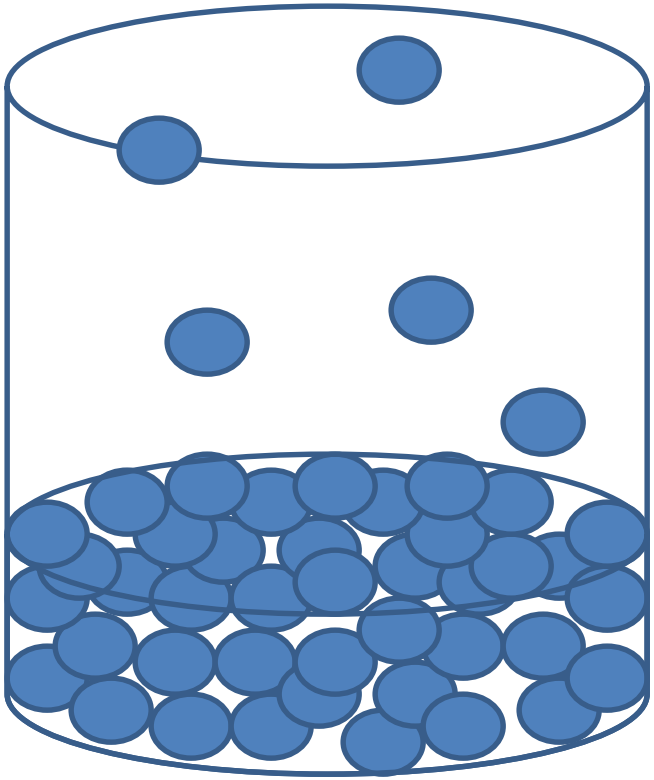
P_1^*



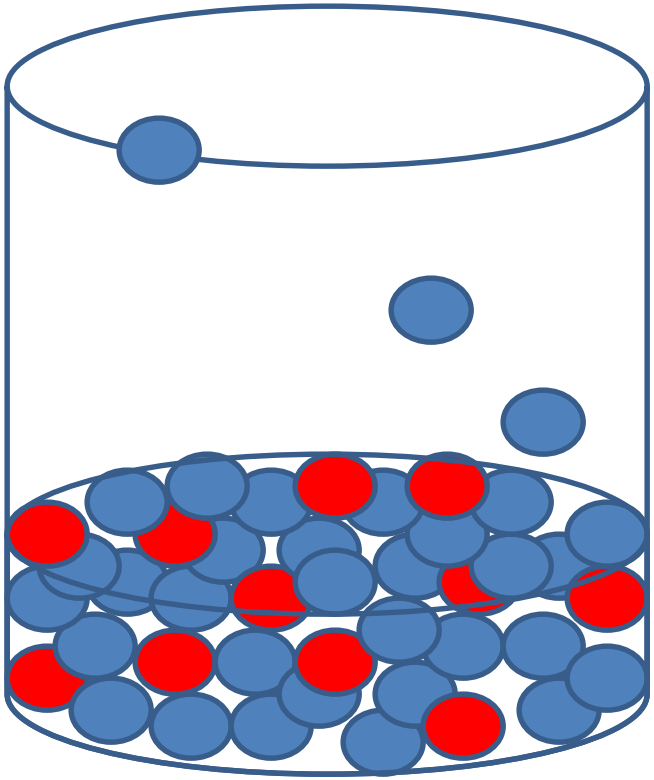
$P_1 = x_1 P_1^*$

$P_2 = x_2 P_2^*$

Vapor pressure above solution of non-volatile solute



P_1^*



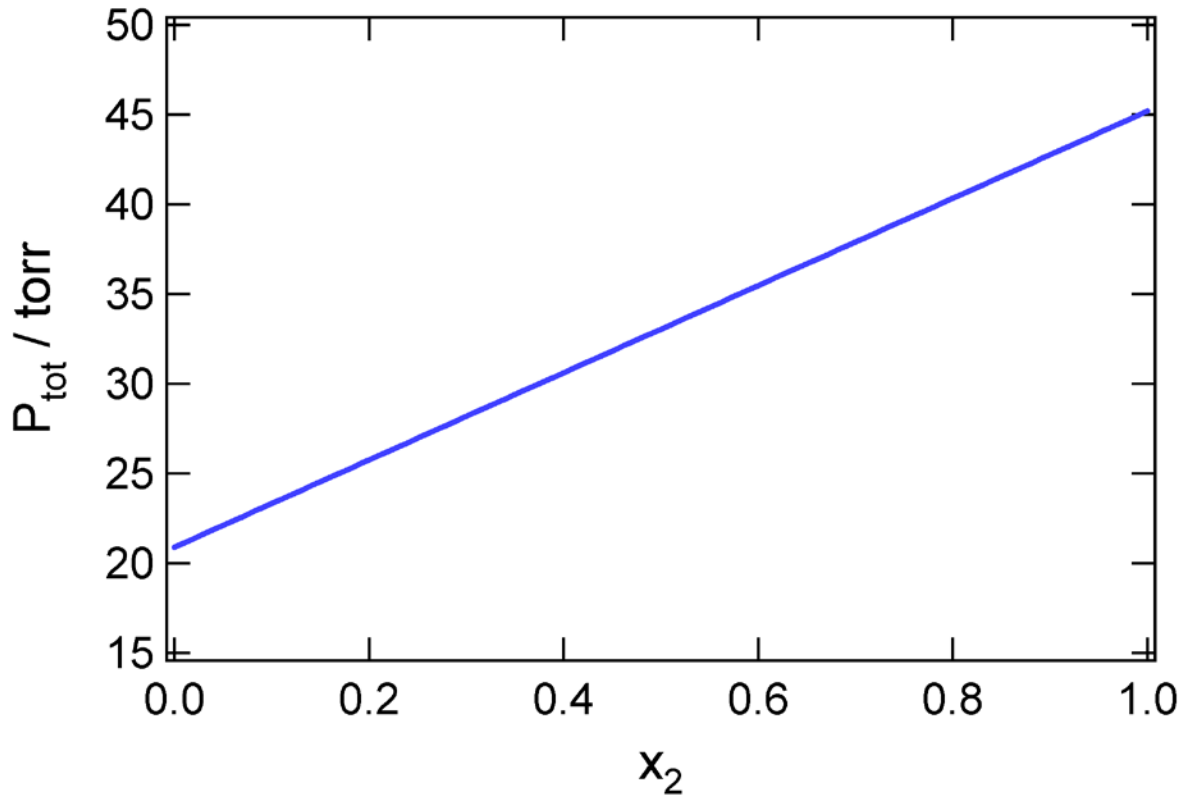
$P_1 = x_1 P_1^*$

Two component phase diagrams

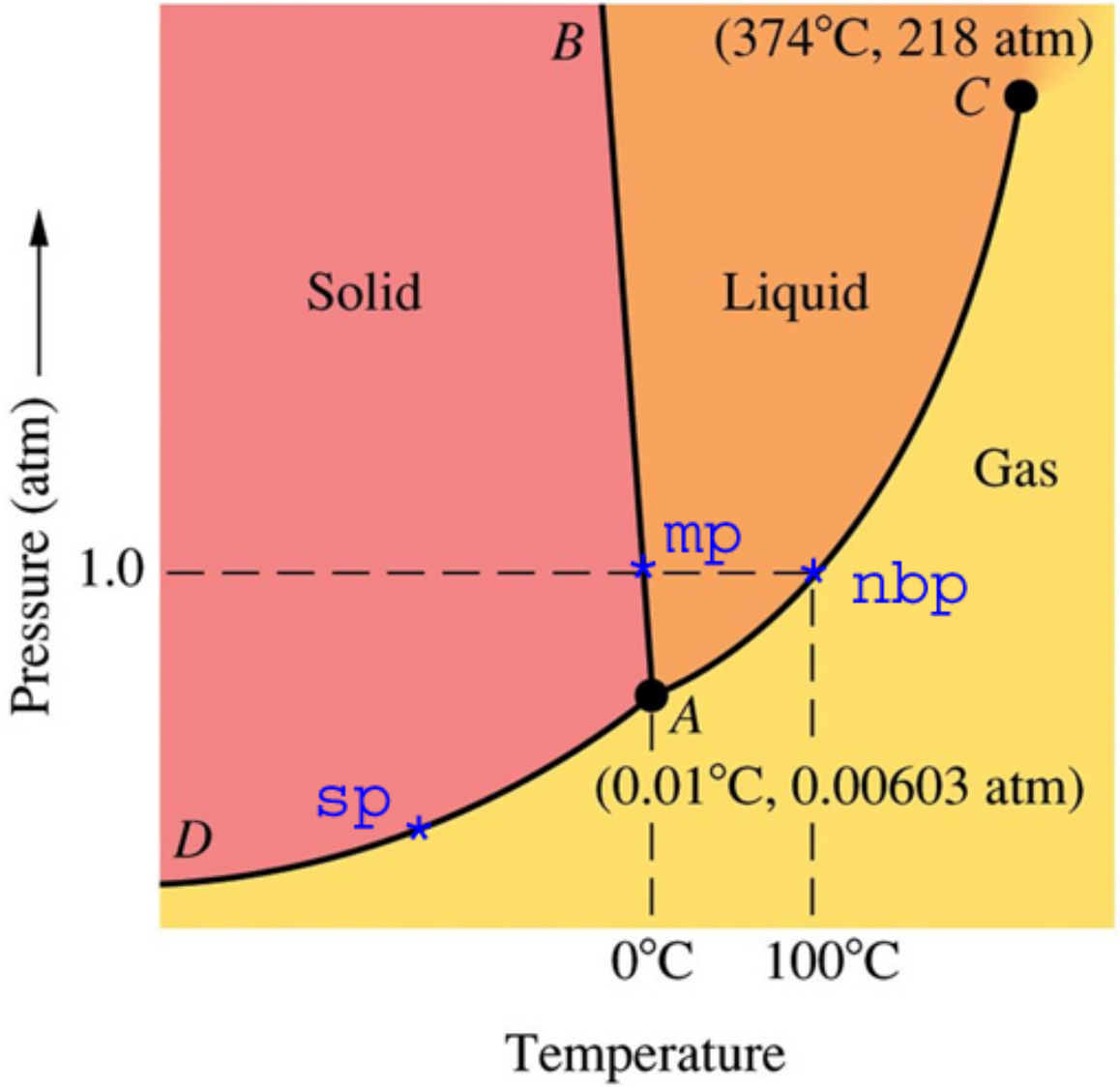
The total vapor pressure over an ideal solution is given by

$$P_{total} = P_1 + P_2 = x_1P_1^* + x_2P_2^* = (1 - x_2)P_1^* + x_2P_2^*$$
$$= P_1^* + x_2(P_2^* - P_1^*)$$

A plot of the total pressure has the form of a straight line.



Concept: phase diagram



Effect of solutes: vapor pressure reduction

20.0 g of $CaCl_2$ are dissolved in 100.0 g of H_2O. Density = 1.147 g/mL. Given that the vapor pressure of pure water is 0.034 atm at 25 ^oC, what is the vapor pressure of the solution?

Effect of solutes: vapor pressure reduction

20.0 g of $C_{12}H_{22}O_{11}$ are dissolved in 100.0 g of H_2O. Density = 1.067 g/mL. Given that the vapor pressure of pure water is 0.034 atm at 25 ^oC, what is the vapor pressure of the solution?

Solution: calculate the mole fraction of the solute.

$$n_{sucrose} = \frac{m}{M_m} = \frac{20\ g}{342\ g/mol} = 0.058\ moles$$

$$n_{water} = \frac{m}{M_m} = \frac{100\ g}{18\ g/mol} = 5.55\ moles$$

Effect of solutes: vapor pressure reduction

20.0 g of $C_{12}H_{22}O_{11}$ are dissolved in 100.0 g of H_2O. Density = 1.067 g/mL. Given that the vapor pressure of pure water is 0.034 atm at 25 ^oC, what is the vapor pressure of the solution?

Solution: calculate the mole fraction of the solute.

$$x_{sucrose} = \frac{n_{sucrose}}{n_{sucrose} + n_{water}}$$

$$x_{sucrose} = \frac{0.058}{5.55 + 0.058} = 0.01$$

Effect of solutes: vapor pressure reduction

20.0 g of $C_{12}H_{22}O_{11}$ are dissolved in 100.0 g of H_2O. Density = 1.067 g/mL. Given that the vapor pressure of pure water is 0.034 atm at 25 ^oC, what is the vapor pressure of the solution?

Solution: Use Raoult's law to calculate the vapor pressure.

$$P_{water} = x_{water} P^*_{water}$$

$$P_{water} = (0.99)(0.0340) = 0.0337$$

Water-ethanol solutions: The breath-a-lyzer

Assuming that water and ethanol for an ideal mixture, what is the vapor pressure of ethanol above a solution of 0.08% ethanol by mass in water (the legal limit for blood alcohol level)? Data: $P^*_{EtOH} = 0.171$ atm

Solution: The mole fraction

$$x_E = \frac{n_E}{n_E + n_W} = \frac{m_E/M_{m,E}}{m_E/M_{m,E} + m_W/M_{m,W}}$$

is related to mass fraction

$$f_E = \frac{m_E}{m_E + m_W}$$

by

Water-ethanol solutions: The breath-a-lyzer

0.08% ethanol by mass in water . $P^*_{EtOH} = 0.171$ atm

Solution: The mole fraction is related to mass fraction by

$$f_E(m_E + m_W) = m_E$$

$$m_W = \frac{(1 - f_E)}{f_E} m_E$$

$$x_E = \frac{m_E/M_{m,E}}{m_E/M_{m,E} + \frac{(1 - f_E)}{f_E} m_E/M_{m,W}}$$

$$x_E = \frac{1}{1 + \frac{(1 - f_E)M_{m,E}}{f_E M_{m,W}}}$$

Water-ethanol solutions: The breath-a-lyzer

0.08% ethanol by mass in water . $P^*_{EtOH} = 0.171$ atm

Solution: The mole fraction is related to mass fraction by

$$x_E = \frac{1}{1 + \frac{(1 - 0.0008)46}{(0.0008)18}} = 0.0003$$

$$P_E = x_E P_E^*$$

$$P_E = (0.0003)(0.171\ atm) = 5\ x\ 10^{-4}\ atm$$