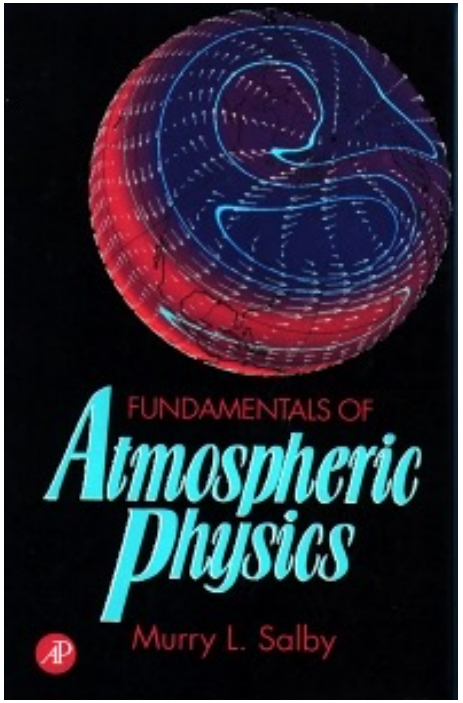
# LECTURE OUTLINE

1. The Clausius-Clapeyron equation

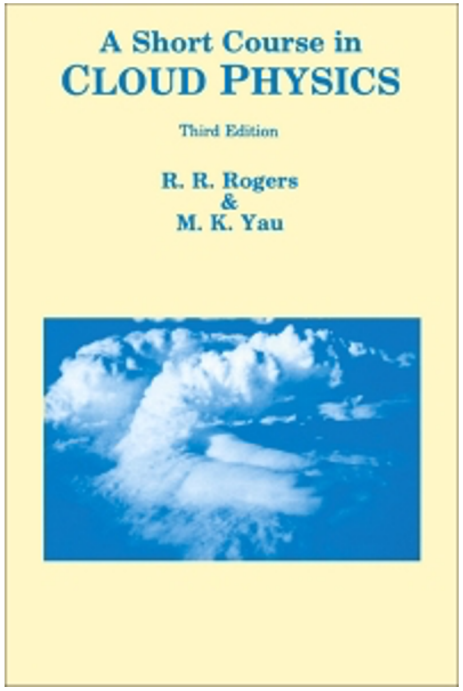
UNIVERSITY
OF WARSAW

R&Y, Chapter 2

Salby, Chapter 4

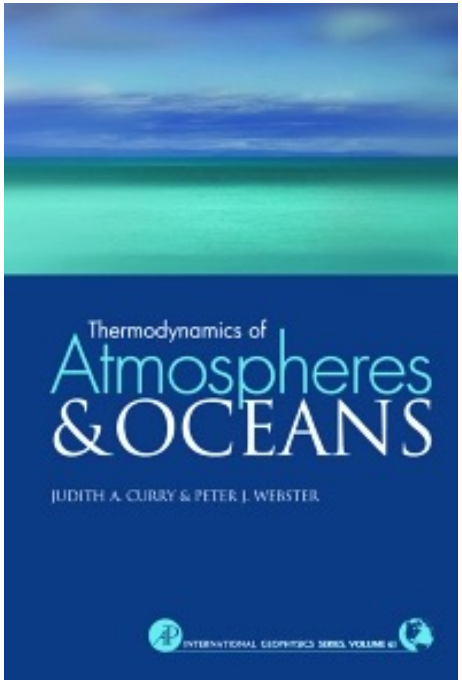



Fundamentals of Atmospheric Physics,
M.L. Salby; Salby

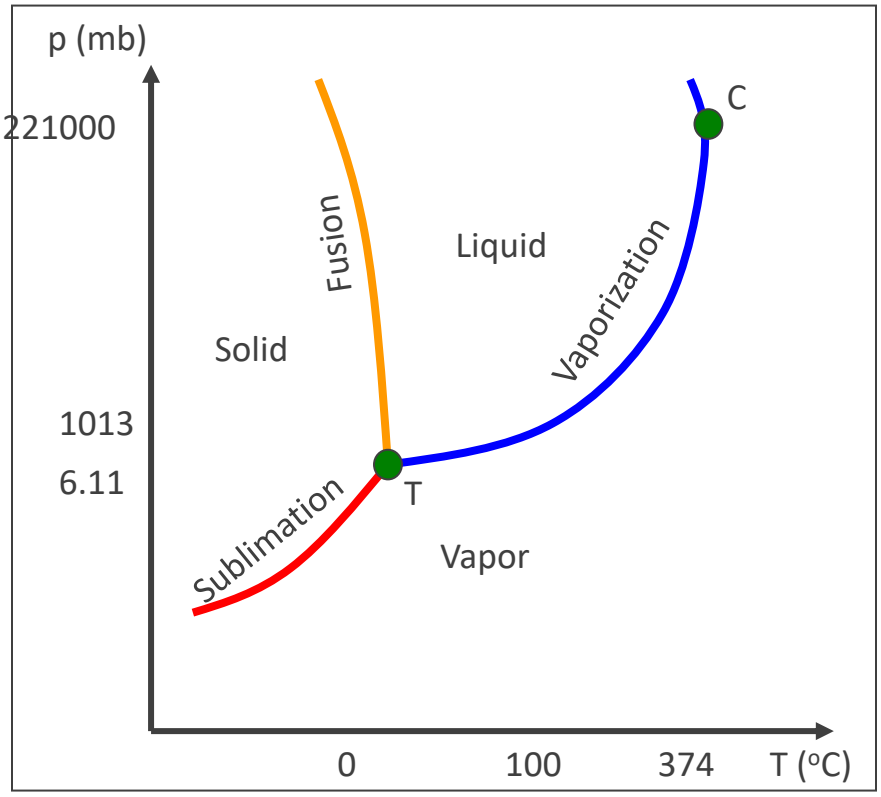



A Short Course in Cloud Physics,
R.R. Rogers and M.K. Yau; R&Y

C&W, Chapter 4




Thermodynamics of Atmospheres
and Oceanes,
J.A. Curry and P.J. Webster; C&W

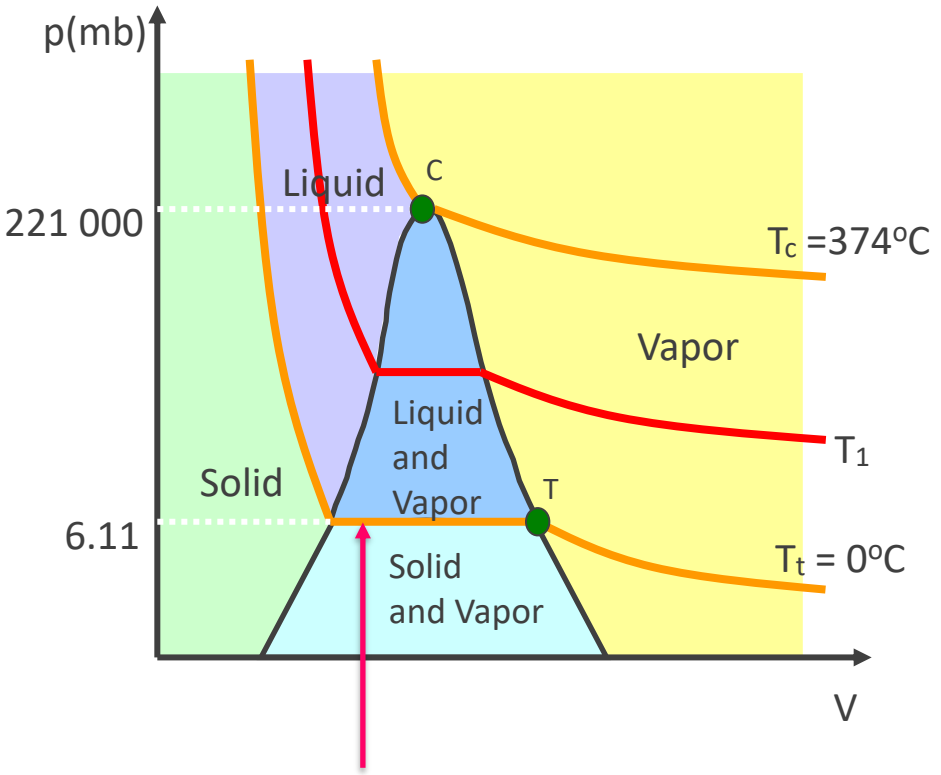


Water in the atmosphere is usually in equilibrium with water vapor (i.e. an air parcel is saturated with water vapor).

The Clausius-Clapeyron equation relates the equilbrium vapor pressure to the temperature of the heterogeneous system.

Phase transformation:

- equilibrium state (saturation)
- the substance does not behave like an ideal gas
- the change of volume is:
  - isothermal
  - isobaric.




One-component system involving two phases at equilibrium with one another possesses only one thermodynamic degree of freedom.

Such system must therefore possess an equation of state of the form $p = p(T)$.

Fixing the temperature of a single-component mixture of two phases also fixes its pressure and vice versa.

Consider two phases a i b and a transformation between them that occurs reversibly.

For the system to be in chemical equilibrium, the chemical potential, $\mu$, of phase a must equal that of phase b.

Since $\mu = g \cdot M$ ($g$- specific Gibbs function; $M$—molar mass, the same for phase a and b) the equaility of chemical potentials involves the equality of specific Gibbs functions of phases a and b.

$$\mu_a = \mu_b \quad \longrightarrow \quad g_a = g_b \quad \longrightarrow \quad dg_a = dg_b$$

$$-(s_b - s_a)dT + (v_b - v_a)dp = 0$$

$$\frac{dp}{dT} = \frac{\Delta s}{\Delta v}$$

Δ refers to the change between phases

$$dg = -sdT + vdp$$

$$\Delta s = \frac{\delta q}{T} \longrightarrow \Delta s = \frac{L}{T}$$

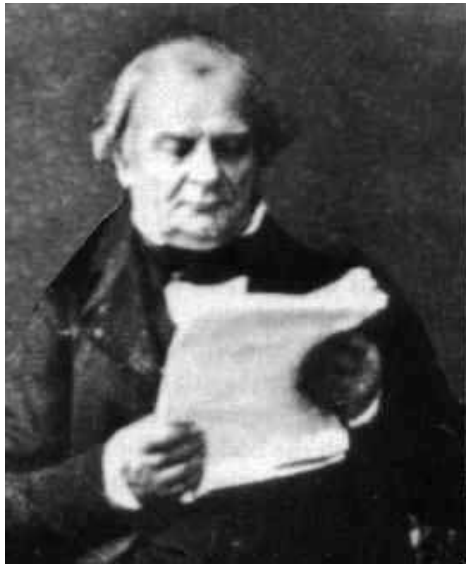
The heat transfer during a phase transformation equals the latent heat of transformation: $\delta q = L$

$$\frac{dp}{dT} = \frac{L}{T\Delta v}$$

The Clausius-Clapeyron equation

Rudolf Clausius
1822-1888
German
physicist and mathematician

He is considered one of the central founders of the science of thermodynamics.
In 1850 he first stated the basic ideas of the second law of thermodynamics. In 1865 he introduced the concept of entropy.



Benoit Paul Emile Clapeyron
1799-1864
French
engineer and physicist

One of the founders of thermodynamics.

$$\frac{dp}{dT} = \frac{L}{T\Delta v}$$

Clausius-Clapeyron equation relates the equilibrium vapor pressure to the temperature of the heterogeneous system.

It constitutes an equation of state for the heterogeneous system when two phases are present.

# Fusion/melting

Clausius-Clapeyron equation $\frac{dp}{dT} = \frac{L}{T\Delta v}$

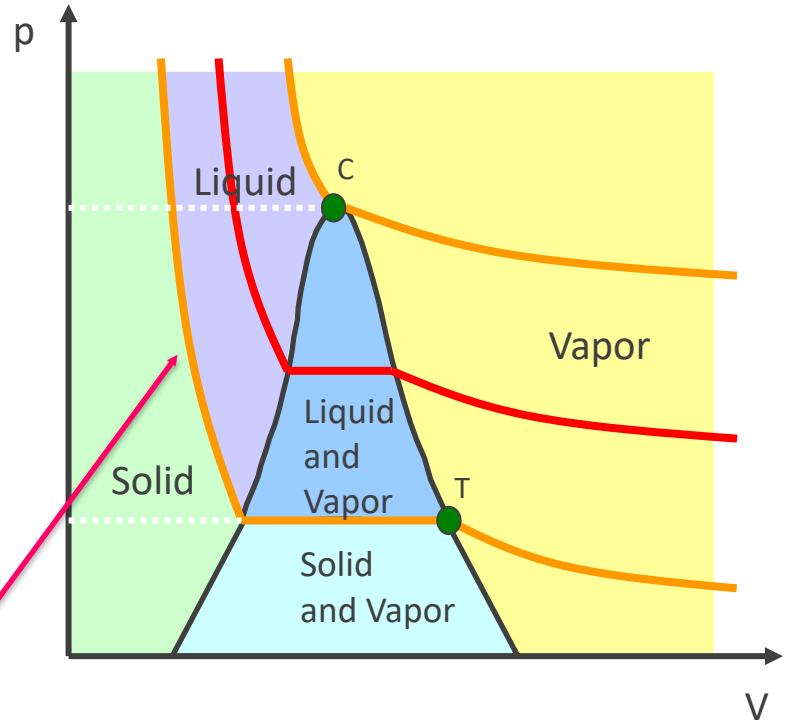
for fusion/melting transformations: ice – liquid the equation is expressed most conveniently inverted form:

$$\frac{dT}{dp} = \frac{T\Delta v}{L}$$

Because the change of volume during fusion is negligible, the equation of state in the region of water and ice reduces to:

$$\left(\frac{dT}{dp}\right)_{fusion} \cong 0$$

The surface of water and ice in the figure is vertical.



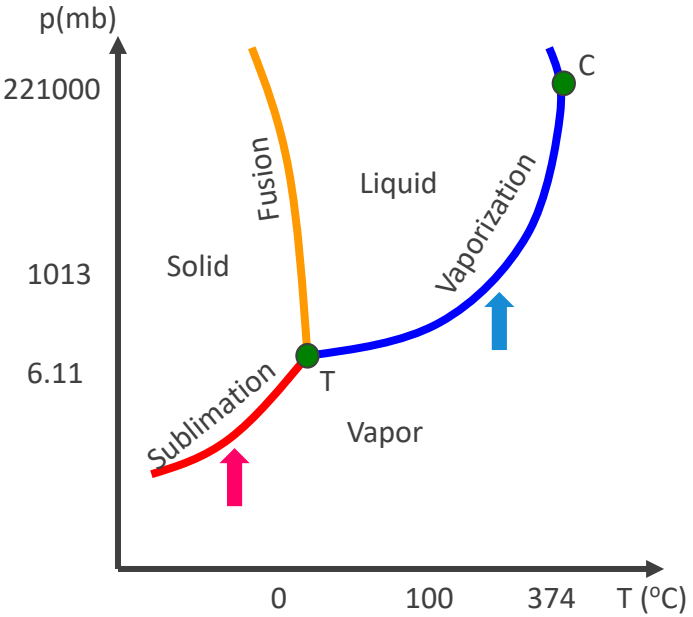
# Vaporization/sublimation

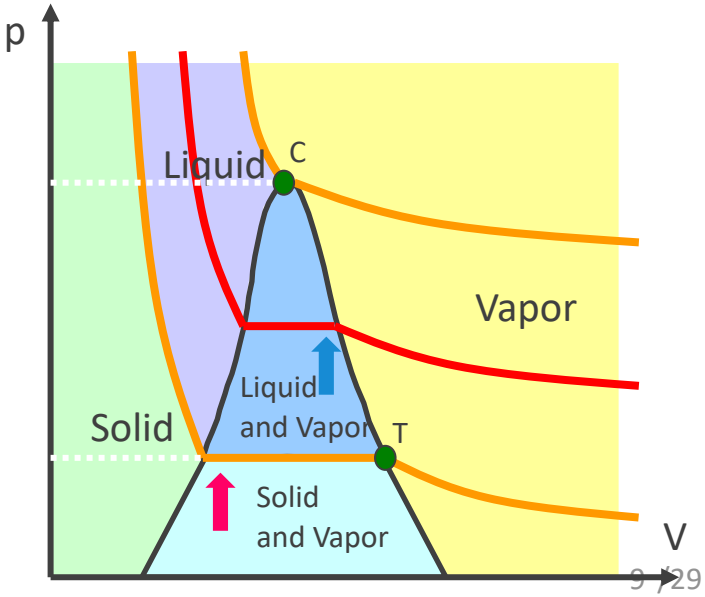
$$\frac{dp}{dT} = \frac{L}{T\Delta v}$$

The change of volume in vaporization or sublimation is approximately equal to that of the vapor produced: $\Delta v \cong v_v = \frac{R_v T}{p}$

$$\left(\frac{dp}{dT}\right)_{\substack{\text{vaporization}\\\text{sublimation}}} = \frac{Lp}{R_v T^2}$$

$$\left(\frac{d\ln p}{dT}\right)_{\substack{\text{vaporization}\\\text{sublimation}}} = \frac{L}{R_v T^2}$$




The equilibrium vapor pressure with respect to:

- water: $e_{sl}$ $\quad \frac{de_{sl}}{dT} = \frac{L_{lv} e_{sl}}{R_v T^2}$
- ice: $e_{si}$ $\quad \frac{de_{si}}{dT} = \frac{L_{iv} e_{si}}{R_v T^2}$

The Clausius-Clapeyron equation

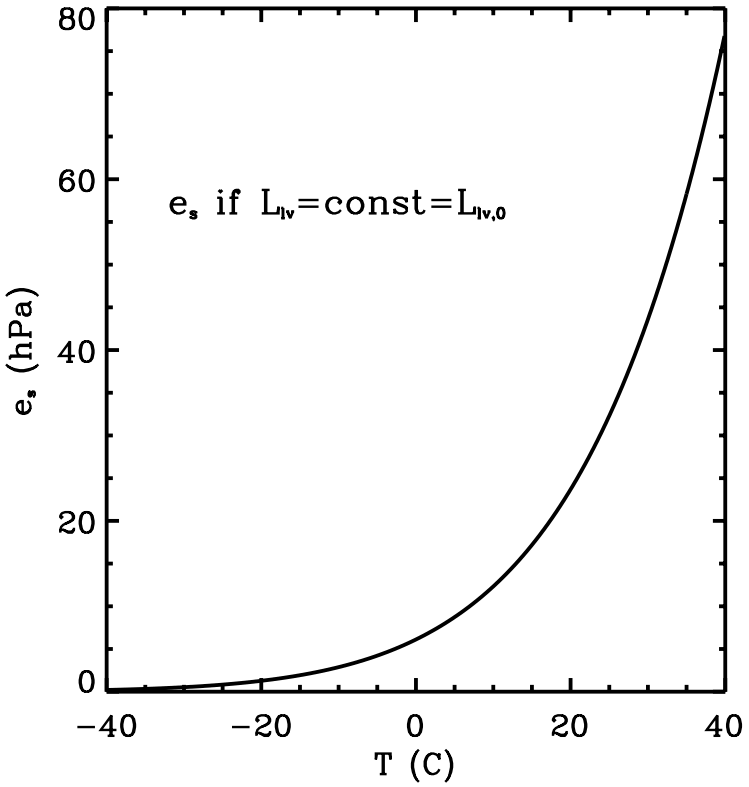
$$\frac{de_{sl}}{dT} = \frac{L_{lv} e_{sl}}{R_v T^2}$$

can be easily integrated:

- $L_{lv} = const = L_{lv0}$ – latent heat at $T_0$=273,15K

$$\ln\left(\frac{e_{sl}}{e_{sl0}}\right) = -\frac{L_{lv0}}{R_v}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

$$e_{sl} = e_{sl0}\exp\left[-\frac{L_{lv0}}{R_v}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$$




$T_0 = 0°\mathrm{C}$

$e_{sl0} = 611\ \mathrm{Pa}$

$L_{lv0} = 2.5 \cdot 10^6\ {}^{\mathrm{J}}/_{\mathrm{kg}}$

The Clausius-Clapeyron equation

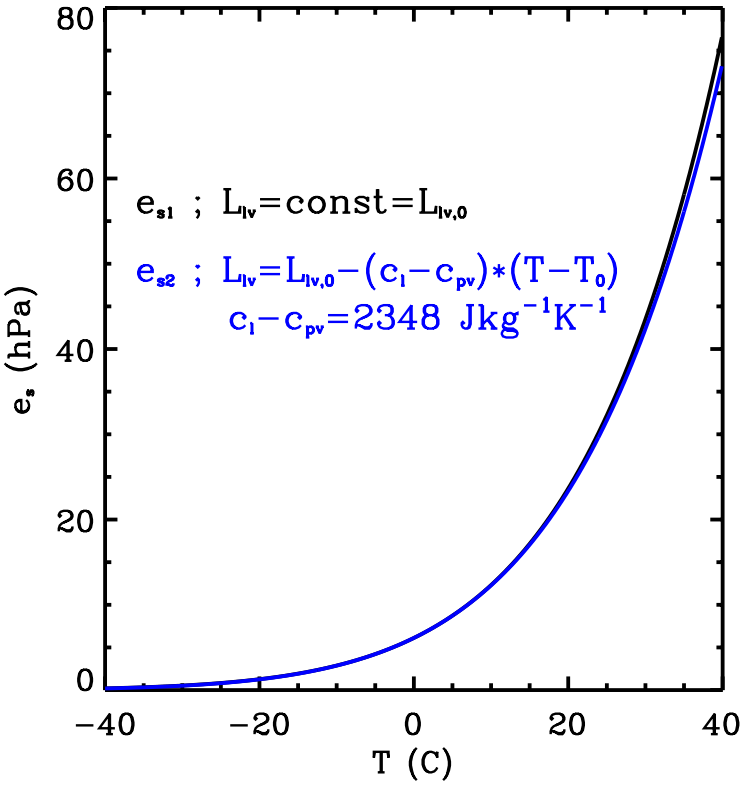
$$\frac{de_{sl}}{dT} = \frac{L_{lv} e_{sl}}{R_v T^2}$$

can be easily integrated:

- $L_{lv} = const = L_{lv0}$ – latent heat at $T_0$=273,15K

$$\ln\left(\frac{e_{sl}}{e_{sl0}}\right) = -\frac{L_{lv0}}{R_v}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

$$e_{sl} = e_{sl0}\exp\left[-\frac{L_{lv0}}{R_v}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$$




- $L_{lv} = L_{lv0} - \Delta c(T - T_0)$, where $\Delta c = c_l - c_{pv} = const = 2348 \frac{\mathrm{J}}{\mathrm{kgK}}$

$$\ln\left(\frac{e_{sl}}{e_{sl0}}\right) = -\frac{L_{lv0} + \Delta c T_0}{R_v}\left(\frac{1}{T} - \frac{1}{T_0}\right) - \frac{\Delta c}{R_v}\ln\frac{T}{T_0}$$

$$e_{sl} = e_{sl0}\left(\frac{T}{T_0}\right)^{-\Delta c/R_v} \exp\left[-\frac{L_{lv0} + \Delta c T_0}{R_v}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$$

$T_0 = 0°\mathrm{C}$

$e_{sl0} = 611\ \mathrm{Pa}$

$L_{lv0} = 2.5 \cdot 10^6\ {}^{\mathrm{J}}/_{\mathrm{kg}}$

The Clausius-Clapeyron equation

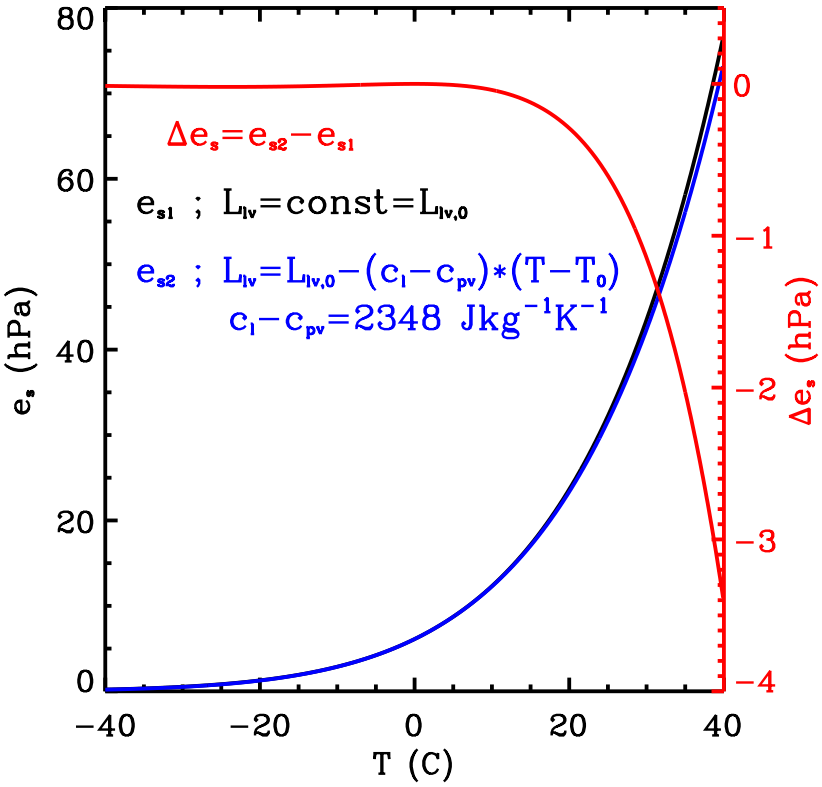
$$\frac{de_{sl}}{dT} = \frac{L_{lv} e_{sl}}{R_v T^2}$$

can be easily integrated:

- $L_{lv} = const = L_{lv0}$ – latent heat at $T_0$=273,15K

$$\ln\left(\frac{e_{sl}}{e_{sl0}}\right) = -\frac{L_{lv0}}{R_v}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

$$e_{sl} = e_{sl0}\exp\left[-\frac{L_{lv0}}{R_v}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$$




- $L_{lv} = L_{lv0} - \Delta c(T - T_0)$, where $\Delta c = c_l - c_{pv} = const = 2348 \frac{\mathrm{J}}{\mathrm{kgK}}$

$$\ln\left(\frac{e_{sl}}{e_{sl0}}\right) = -\frac{L_{lv0} + \Delta c T_0}{R_v}\left(\frac{1}{T} - \frac{1}{T_0}\right) - \frac{\Delta c}{R_v}\ln\frac{T}{T_0}$$

$$e_{sl} = e_{sl0}\left(\frac{T}{T_0}\right)^{-\Delta c/R_v} \exp\left[-\frac{L_{lv0} + \Delta c T_0}{R_v}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$$

$T_0 = 0°\mathrm{C}$

$e_{sl0} = 611\ \mathrm{Pa}$

$L_{lv0} = 2.5 \cdot 10^6\ \mathrm{J/kg}$

# An approximated solution of Clausius-Clapeyron equation

$$e_{sl}(T) = e_{sl0}\exp\left[\frac{17.67(T-273.15)}{(T-273.15)+243.5}\right]$$

*Bolton, D., (1980) The computation of equivalent potential temperature. Mon. Wea. Rev., 108, 1046-1053.*

# Validity of Clausius-Clapeyron equation

In deriving the Clausius-Clapeyron equation, the gaseous phase under consideration was taken to be pure water vapor.

In the atmosphere we have a mixture of dry air gases and water vapor.

Application of the Clausius-Clapeyron equation to determining the saturation vapor pressure in the atmosphere is not strictly valid because:

- the total pressure is not the sum of the partial pressures of two ideal gases (i.e. the Dalton's law of partial pressures is not strictly valid)
- the condensed phase is under the total pressure that is augmented by the presence of dry air: $e + p_d$ not only $e$
- the condensed phase is not purly liquid water, but contains dissolved air (the pressure of vapor over a mixture is lower than the pressure of vapor over pure substance).

# Validity of Clausius-Clapeyron equation

The departure from the ideal case can be shown to be less than 1 %.

Values of the saturation vapor pressure calculated from the Clausius-Clapeyron equation, especially in its simplest integrated form, are not exact.

Empirical values of the saturated vapor pressure are used when high accuracy is needed.

# A polynomial fit to observations (empirical values of the saturation vapor pressure)

$$e_s = a_1 + \sum_{n=2}^{7} a_n (T - T_0)^{n-1}$$

| Coefficient | Liquid water | Ice |
|---|---|---|
| $a_1$ | 6.11176750 | 6.10952665 |
| $a_2$ | 0.443986062 | 0.501948366 |
| $a_3$ | 0.143053301E-01 | 0.186288989E-01 |
| $a_4$ | 0.265027242E-03 | 0.403488906E-03 |
| $a_5$ | 0.302246994E-05 | 0.539797852E-05 |
| $a_6$ | 0.203886313E-07 | 0.420713632E-07 |
| $a_7$ | 0.638780966E-10 | 0.147271071E-09 |

The expression provides the high accuracy needed for numerical cloud models; it is valid for the temperature range -50°C to 50°C.

Empirical values are given in Appendix D in Curry&Webster

*Flatau, P.J., R.L. Walko and W.R. Cotton, 1992: Polynomial fits to saturation vapor pressure, J. Appl. Meteor., 31, 1507-1513*

# Saturated vapor pressure over ice

$$\frac{de_{si}}{dT} = \frac{L_{iv} e_{si}}{R_v T^2}$$

$L_{iv} = const = L_{iv0}$ – latent heat of sublimation at $T_0$=273,15K (exact to within ~0,1%)

$$\ln\left(\frac{e_{si}}{e_{si0}}\right) = -\frac{L_{iv0}}{R_v}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

$$e_{si} = e_{si0}\exp\left[-\frac{L_{iv0}}{R_v}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$$

$T_0 = 273{,}15\ \mathrm{K}$

$e_{si0} = 611\ \mathrm{Pa}$

$L_{iv0} = 2.834 \cdot 10^6\ {}^{\mathrm{J}}/_{\mathrm{kg}}$

# Saturated vapor pressure over ice

$$\frac{de_{si}}{dT} = \frac{L_{iv} e_{si}}{R_v T^2}$$

$L_{iv} = const = L_{iv0}$ – latent heat of sublimation at $T_0 = 273.15\ K$ (exact to within ~0,1%)

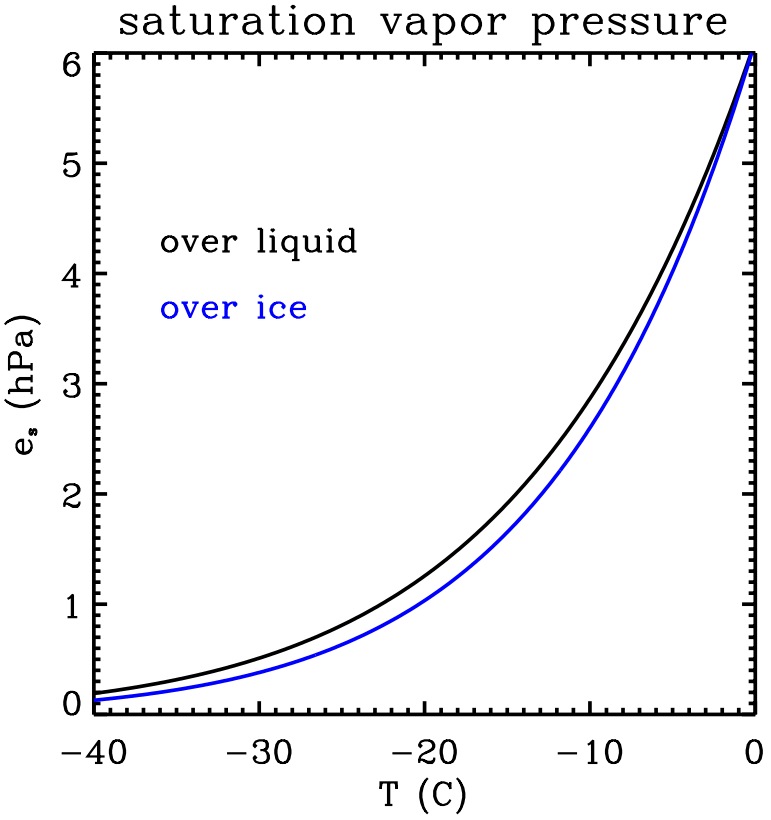
$$\ln\left(\frac{e_{si}}{e_{si0}}\right) = -\frac{L_{iv0}}{R_v}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

$$e_{si} = e_{si0} \exp\left[-\frac{L_{iv0}}{R_v}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$$

$T_0 = 273{,}15\ \mathrm{K}$

$e_{si0} = 611\ \mathrm{Pa}$

$L_{iv0} = 2.834 \cdot 10^6\ {}^{\mathrm{J}}/_{\mathrm{kg}}$



# Saturated vapor pressure over ice

$$\frac{de_{si}}{dT} = \frac{L_{iv} e_{si}}{R_v T^2}$$

$L_{iv} = const = L_{iv0}$ – latent heat of sublimation at $T_0 = 273.15\ K$ (exact to within ~0,1%)

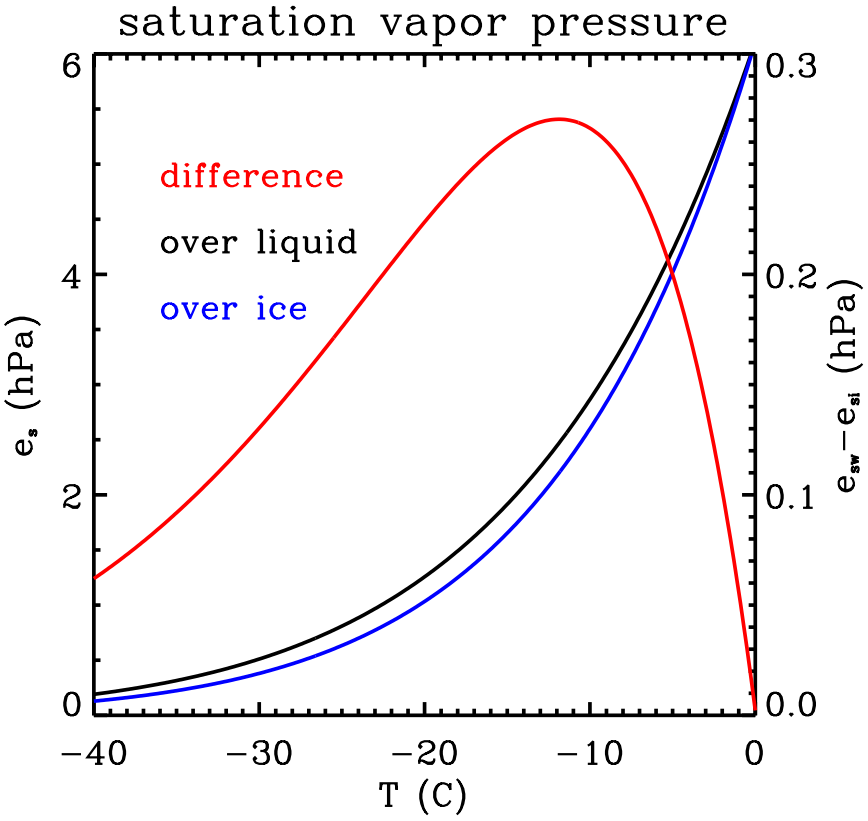
$$\ln\left(\frac{e_{si}}{e_{si0}}\right) = -\frac{L_{iv0}}{R_v}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

$$e_{si} = e_{si0} \exp\left[-\frac{L_{iv0}}{R_v}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$$

$T_0 = 0°\mathrm{C}$

$e_{si0} = 611\ \mathrm{Pa}$

$L_{iv0} = 2.834 \cdot 10^6\ {}^{\mathrm{J}}/_{\mathrm{kg}}$



# Relative humidity over water and ice

The relative humidity is defined as: $f = e/e_s$. At temperatures below 0°C, it is necessary to specify whether the relative humidity is being evaluated relative to the saturation vapor pressure over liquid or over ice.

Using the simplest integrated forms of the Clausius-Clapeyron equation:

$$\frac{f_i}{f} = \frac{e_s(T)}{e_{si}(T)} = \exp\left[\frac{L_{lv} - L_{iv}}{R_v}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]$$

$$= \exp\left[-\frac{L_{il}}{R_v}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]$$

$$= \exp\left[\frac{L_{il}}{R_v T_0}\left(\frac{T_0}{T} - 1\right)\right]$$

$$e_s = e_{s0}\exp\left[\frac{L_{lv}}{R_v}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]$$

$$e_{si} = e_{si0}\exp\left[\frac{L_{iv}}{R_v}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]$$

$$L_{iv} = L_{il} + L_{lv}$$

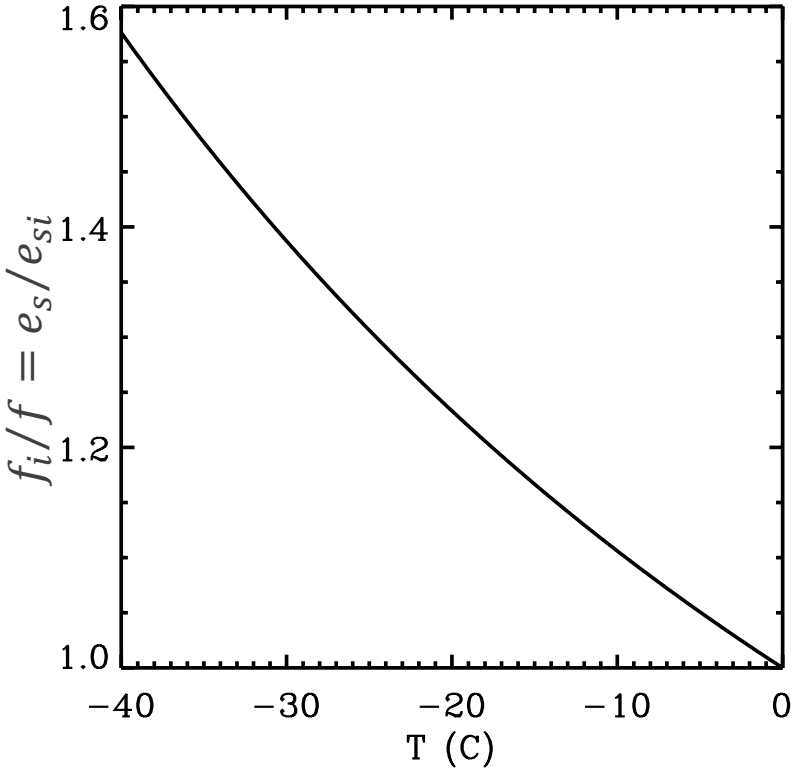
For $T < T_0$ $e_s(T)/e_{si}(T) > 1$ for all subfreezing temparatures and the ratio increases as the temperature decreases.

# Relative humidity over water and ice

$$\frac{f_i}{f} = \frac{e_s(T)}{e_{si}(T)} = \exp\left[\frac{L_{lv} - L_{iv}}{R_v}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]$$

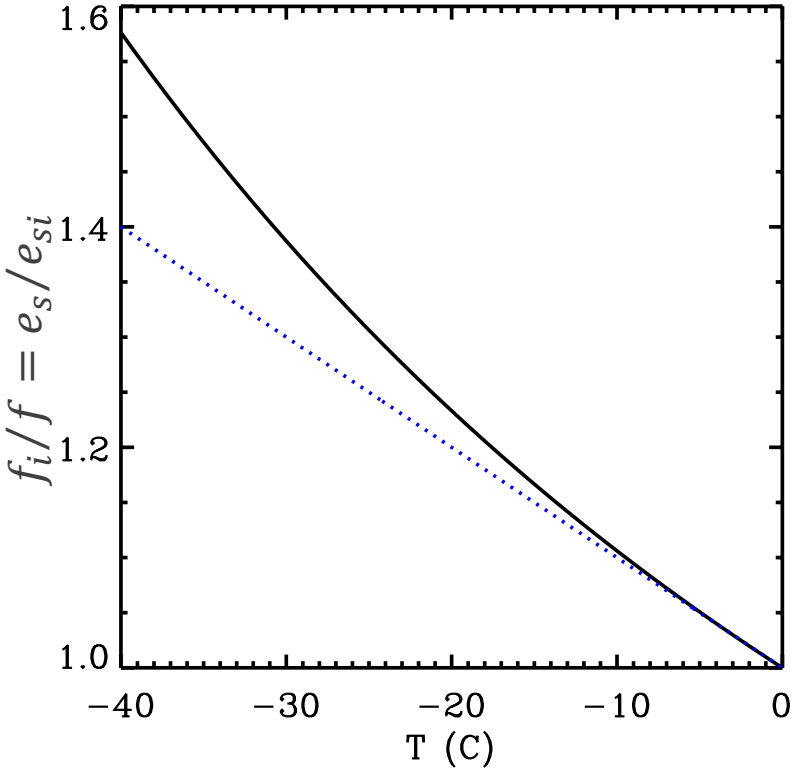
For $T < T_0 \quad e_s(T)/e_{si}(T) > 1$

for all subfreezing temparatures



# Relative humidity over water and ice

$$\frac{f_i}{f} = \frac{e_s(T)}{e_{si}(T)} = \exp\left[\frac{L_{lv} - L_{iv}}{R_v}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]$$




For $T < T_0 \quad e_s(T)/e_{si}(T) > 1$

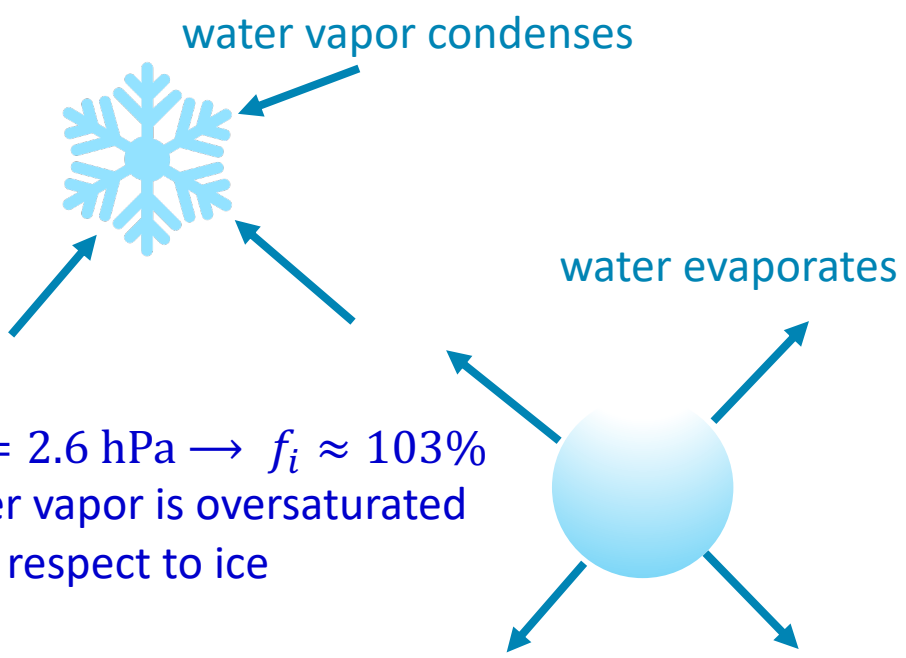
for all subfreezing temparatures

The rate of change $d\left(\frac{f_i}{f}\right)/dT$ increases as the temperature decreases

dotted line shows: $$\frac{f_i}{f} = \left.\frac{f_i}{f}\right|_{T_0} + \left.\frac{d\left(\frac{f_i}{f}\right)}{dT}\right|_{T_0} \cdot (T - T_o)$$

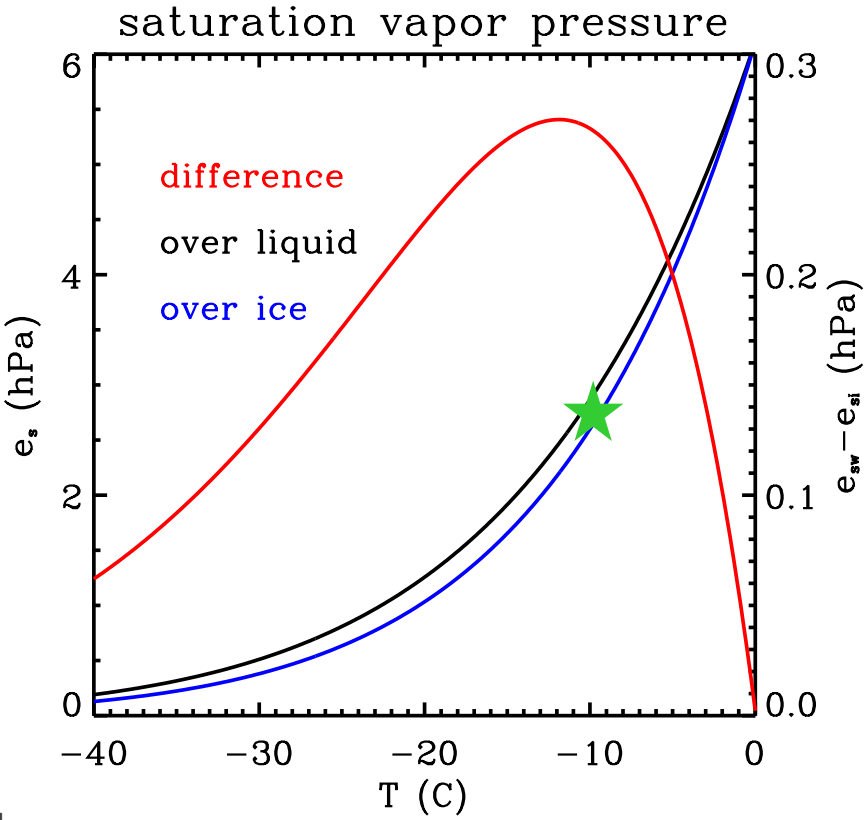
# Wegener-Findeisen-Bergeron process

A process of ice crystal growth that occurs in mixed phase clouds (containing a mixture of supercooled water and ice and ice) in regions where the ambient vapor pressure falls between the saturation vapor pressure over water and the lower saturation vapor pressure over ice.




$e_{si} = 2.6$ hPa $\longrightarrow$ $f_i \approx 103\%$
water vapor is oversaturated with respect to ice

$e_s = 2.86$ hPa $\longrightarrow$ $f \approx 94\%$
water vapor is undersaturated with respect to water




$T = -10°C$
$e = 2.7$ hPa

# COLLIGATIVE PROPERTIES OF WATER SOLUTIONS

In chemistry, *colligative properties* are properties of solutions that depend on the ratio of the number of solute particles to the number of solvent molecules in a solution, and not on the nature of the chemical species present.

UNIVERSITY OF WARSAW

A solution is a homogeneous system, or a single-phase system, that contains more than one component.

The composition of solutions is described by the mole fraction. A two-component solution containing $n_A$ moles of component A and $n_B$ moles of component B has a mole fraction of component A, $X_A$:

$$X_A = \frac{n_A}{n_A + n_B}$$

The component with the largest mole fraction is commonly referred to as the solvent, and the other component as the solute. If water is the solvent, the solution is said to be aqueous.

Colligative properties of a solution depend only on the mole fraction of the solute and not on the particular identity of the solute.

The effect of the mole fraction of the solute on the vapor pressure of the solvent is given by Raoult's law.

The vapor pressure ($p_A$) of solvent A above the solution is given by:

$$p_A = X_A p_A^0$$

$p_A^0$ is the vapor pressure of the pure phase (water).

If the solute is volatile (i.e. it has a vapor pressure), we can also write:

$$p_B = X_B p_B^0$$

A solution that follows Raoult's law is known as an ideal solution.

For an ideal solution: $p = p_A + p_B$ .

An ideal solution is characterized by complete uniformity of intermolecular forces; that is, a molecule in the solution cannot differentiate between an A and a B molecule.

An ideal solution is a hypothetical solution whose properties are approached but seldom encountered in real solutions.

The ideal solution concept is useful because it enables us to wstablish a reference state for consideration of more complex solutions.

We would like to find the ratio of the vapor pressure over an aqueous solution to the vapor pressure of pure water.

$$\frac{p_{soln}}{e_s} = \frac{X_{H_2O} e_s + X_{solt} p^0_{solt}}{e_s}$$

soln denotes solution

solt to denotes solute.

A dilute aqueous solution is defined as $X_{solt} << X_{H2O}$ .

$$\frac{p_{soln}}{e_s} \approx X_{H_2O} = \frac{n_{H_2O}}{n_{H_2O} + n_{solt}} \approx 1 - \frac{n_{solt}}{n_{H_2O}}$$

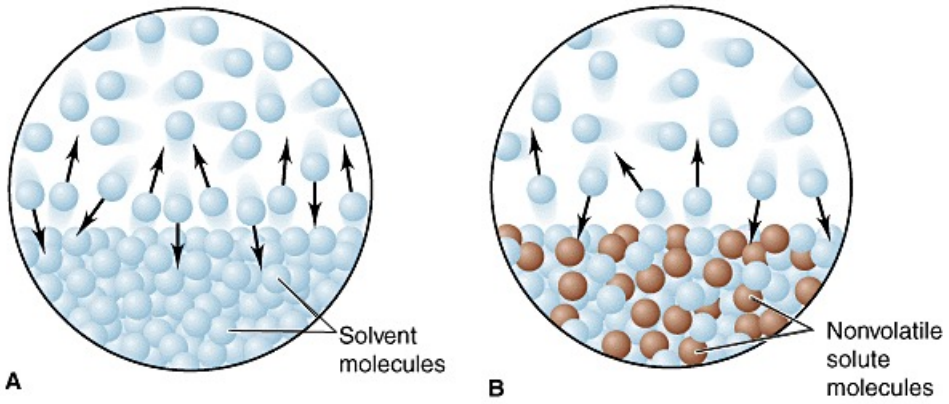
$p_{soln} < e_s$ in a dilute aqueous solution and $p_{soln}$ decreases as $n_{rs}$ increases.

To understand the lowering of the solution vapor pressure relative to that of pure water, it is useful to imagine a substance having essentially zero vapor pressure to be dissolved in water.

The molecules of the solute are distributed uniformly through the water, and some of the solute molecules will therefore occupy positions in the surface layer.

With the addition of the solute, the proportion of the surface area occupied by water molecules is:

$$\frac{n_{H_2O}}{n_{H_2O} + n_{solt}} < 1$$




The number of water molecules escaping from the surface, and therefore the equilibrium vapor pressure of the solution, should be reduced relative to that of pure water.

Solids can dissolve in water in two different ways:

- The molecules of the solid can remain intact (e.g. sugar in water)
- The molecules can break up into positively and negatively charged ions (salt in water). Aqueous solutions containing charged ions are electrically conducting and are called electrolytic solutions.

Raoult's law for dilute solutions was modifiedf or diluted electrolytic solutions by van't Hoff, who found that an electrolytic solution effectively contains an increase in the number of moles of solute:

$$n_{solt}^{ef} = i \cdot n_{solt}$$

i – the van't Hoff dissociation factor.

For strong electrolytic solutions , i is equal to the number of ions formed in solution; for the weak electrolytic solutions it is less than this number but still greater than one.

$$\frac{p_{soln}}{e_s} \approx 1 - \frac{i \cdot n_{solt}}{n_{H_2O}}$$