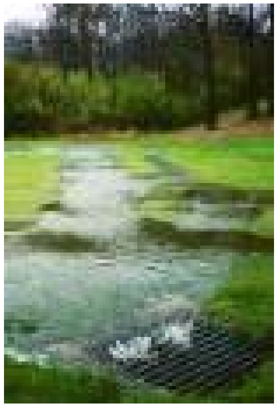
Lecture 16, Water, Humidity, Pressure and Trace Gases, Part 1

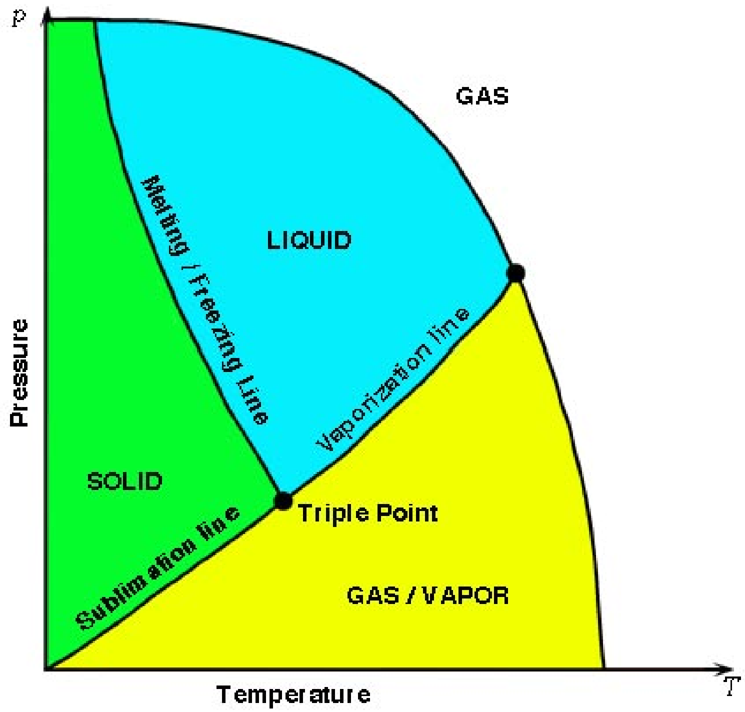
- Physical and chemical properties of water
- Chemical Potential of Water
- Gas Laws
  - absolute humidity
  - relative humidity
  - virtual temperature
  - Saturation Vapor Pressure
  - Clausius-Clapeyron Equation
- Rainfall/Drought

Water

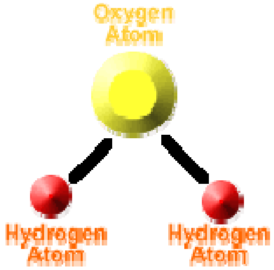
- Gas
- Liquid
- Solid



Triple Point for Water



How can we Exploit the Triple Point Curve to prevent water from condensing on our air sampling tube?



Properties of Water

Property	Value
molecular weight	18 g $mole^{-1}$
melting point	273.15 K
boiling point	373.15 K
latent heat of vaporization	2.442 MJ kg^{-1} or 44.00 kJ mol^{-1} at 20 C
latent heat of sublimation	2.826 MJ kg^{-1} or 51.00 kJ mol-1at 0 C
dialectric constant	80
thermal conductivity	0.599 W m^{-1} at 20 C
heat capacity of water	4182 J kg^{-1} at 20 C
molecular diffusivity, water in air	2.42 10^{-5} m^2 s^{-1} at 20 C
Density	1.000 kg m^{-3} at 4 C

Properties of Water, f(T)

temperature	density	latent heat of evaporation	kinematic viscosity
^oC	$Mg\ m^{-3}$	$kJ\ mol^{-1}$	$mm^2\ s^{-1}$
0	0.99987	45.0	1.79
4	1.0000	44.8	1.57
10	0.99973	44.6	1.31
20	0.99823	44.1	1.01
30	0.99568	43.7	0.80
40	0.99225	42.8	0.66

Chemical Potential of Water

Chemical potential quantifies
the driving force for movement of water between two locations

The chemical potential of water is related to the amount of change
in the Gibbs free energy of the system, subjected by pressure,
temperature and minor constituents
, e,g., salts, .
It is a function of its chemical concentration, pressure, electrical potential
and gravity

The chemical potential has units of energy (J mol^{-1}).

Water Potential

The **potential energy** of water is related to the difference between its chemical potential (μ_w) and a reference state (μ_{wo}):

$$\psi = \frac{\mu_w - \mu_w^o}{V_w}$$

By convention, Water potential is normalized by V_w, the partial molal volume of water (18.05 10^{-6} m^3 mol^{-1}), giving it units of **Pressure**.

The **total water potential** of a system consists of the sum of water potentials associated with

Turgor (pressure), **osmotic**, **matrix** and **gravitational** forces

$$\psi = \psi_p + \psi_\pi + \psi_m + \psi_g$$

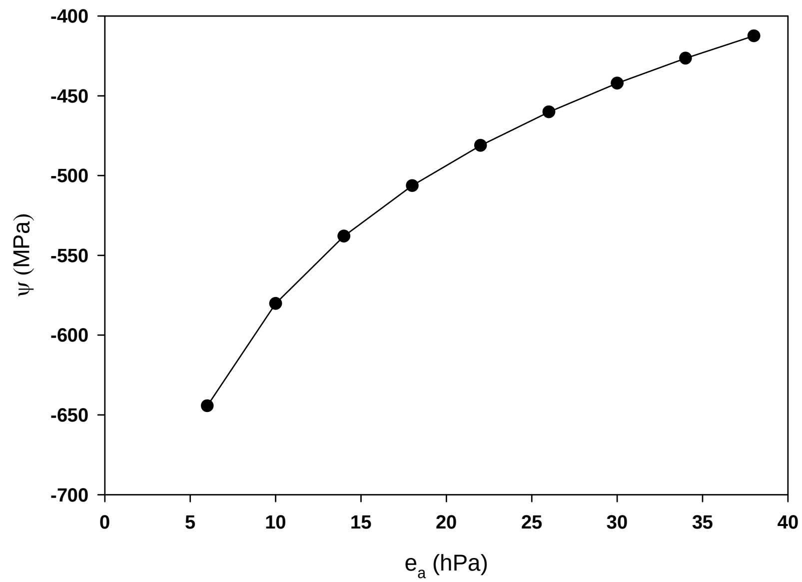
Units, Pressure: Pa

- **Turgor (pressure) potential**
  - is related to the hydrostatic pressure, as when someone is blow on or sucking on straw that is inserted in a reservoir of water. Its sign can be positive or negative.
- **osmotic potential**
  - The presence of solutes reduces the activity of water.
- **matric potential**
  - interactions between water and solid surfaces act to reduce the activity of water.
- **gravity Potential**
  - gravitational force is a function of the density of water, the acceleration due to gravity and the height of the water reservoir above or below a reference height:

$$\psi_g = \rho_w g h$$

Water Potential of atmospheric humidity is function of its mole fraction

$$\psi_p = \frac{R \cdot T}{V_w} \ln\left(\frac{e_a}{P}\right)$$



R: Universal gas constant
T: absolute temperature
e_a: vapor pressure
P: pressure
V_w: molal volume of water, 18.05 10^{-6} m^3 $mole^{-1}$

Atmospheric Gas Composition

constituent	**percent by volume**	**percent by mass**	**molecular weight (g mole^{-1})**
N_2	78.091	75.5	28.02
O_2	20.95	23.1	32.00
Ar	0.930	1.3	39.94
CO_2	0.036	0.05	44.01

Charles Law and Boyle's Law

pressure, volume and temperature are inter-related.

$$PV = nRT$$

R is the universal gas constant, 8.3144 J mol^{-1} K^{-1},
T is absolute temperature (K),
P is pressure (Pa, N m^{-2}),
V is volume
n is the number of moles

the molar volume of air
(volume occupied by one mole of air, n=1)
for standard pressure (0.1013 MPa, 101.3 kPa, 1013 mb)
and temperature (273.15 K),

$$V = \frac{nRT}{P}$$

22.41 liters $mole^{-1}$ or 0.02241 m^3 mol^{-1}.

Gas Law used by Meteorologists

$$P\alpha = \frac{RT}{m} = \frac{\rho RT}{m}$$

m is the molecular weight of a gas (g mol-1)
ρ is the mass density (g m-3)
α is 1/ρ.

Partial Pressure Law

$$P = p_{N_2} + p_{O_2} + p_{Ar} + p_{CO_2} + p_{H_2O} \cdots$$

$$p = \frac{R}{m} \rho T$$

$$\frac{\rho_a}{m_a} + \frac{\rho_v}{m_v} + \frac{\rho_c}{m_c} + \ldots = \frac{p}{RT}$$

Air Density

$$\frac{\rho_a}{m_a} + \frac{\rho_v}{m_v} = \frac{p}{RT}$$

T	dry	Saturated
^oC	Kg m^{-3}	kg m^{-3}
0	1.292	1.289
5	1.269	1.265
10	1.246	1.240
15	1.225	1.217
20	1.204	1.194
25	1.183	1.169
30	1.164	1.145
40	1.128	1.096

Does a baseball fly less far on a humid day?

mass gas density (grams of a gas molecule per unit volume)

$$\rho_c = \frac{n_c m_c}{V} = \frac{p_c m_c}{RT}$$

n_c is the number of moles
V is volume
R is universal gas constant

m_c is the molecular mass (g $mole^{-1}$) of the compound.

molar gas density (moles of a gas molecule per unit volume)

$$c = \frac{n_c}{V} = \frac{p_c}{RT} = \frac{\rho_c}{m_c}$$

n_c is the number of moles
V is volume

m_c is the molecular mass (g mole^{-1}) of the compound.

Mass fraction (mass per unit mass of air)

$$M_c = \frac{\rho_c}{\rho_a} = \frac{\chi_c m_c}{m_a}$$

m_a is the molecular weight of dry air (g mol^{-1})
m_c is molecular weight of trace gas
ρ_a is the mass density of dry air (g m^{-3})
ρ_c is the mass density of trace gas air (g m^{-3})

Mole fraction,
the number of moles of a trace gas divided by
the total number of moles present in the mixture

Moist air

$$C_c = \frac{n_c}{n} = \frac{m_a}{m_c}\frac{\rho_c}{\rho} = \frac{p_c}{p}$$

Dry air

$$C_c = \frac{n_c}{n_d} = \frac{p_c}{p_d} = \frac{p_c}{p_a - p_{H_2O}}$$

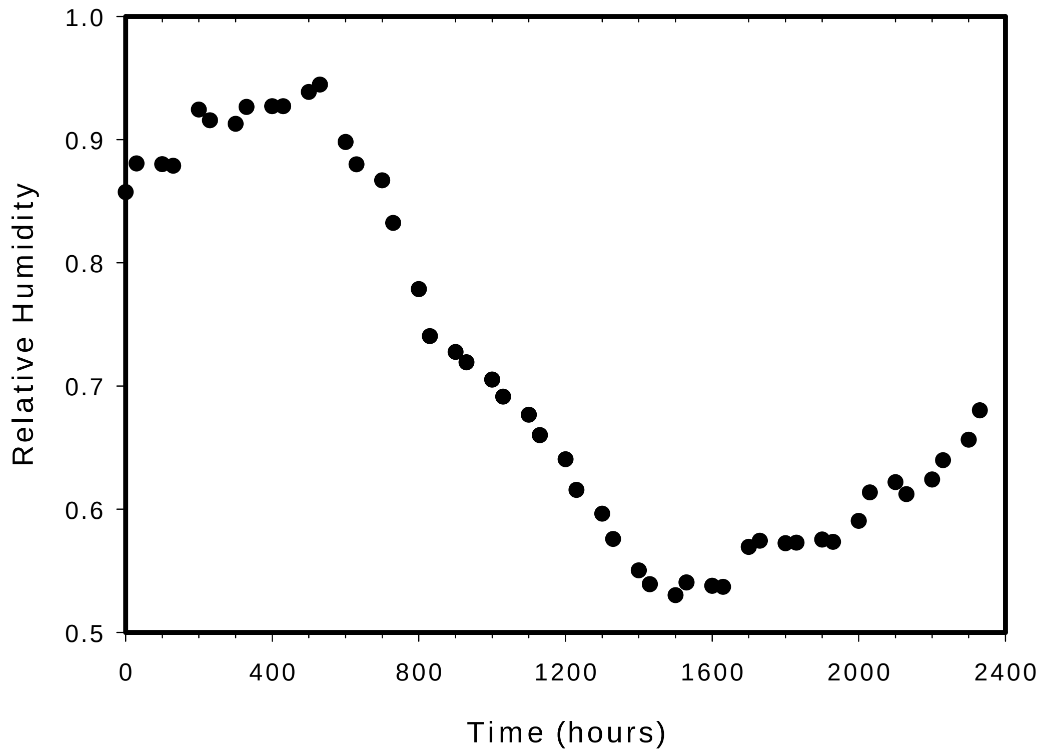
Relative Humidity, h_r,

the ratio between the actual (e_a) and saturation vapor pressures ($e_s(T)$).

It ranges between zero and 1.0, with one indicating saturation.

$$h_r = \frac{e_a}{e_s(T)}$$

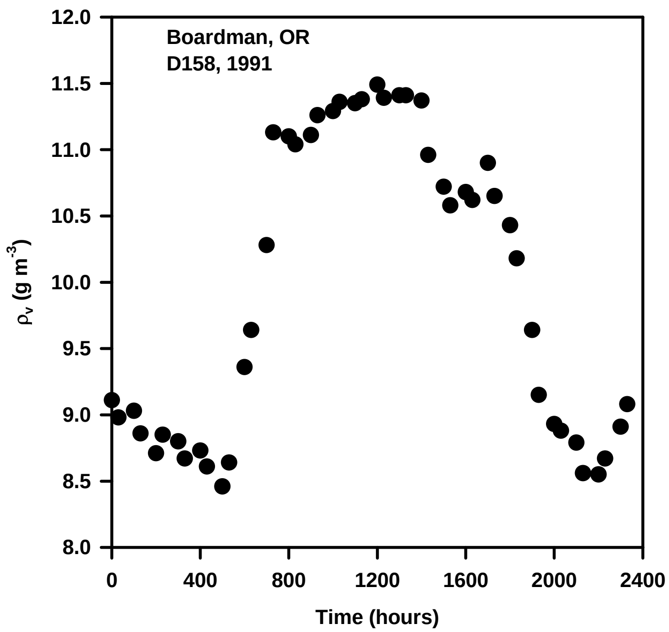
$e_a = p_{H2O}$



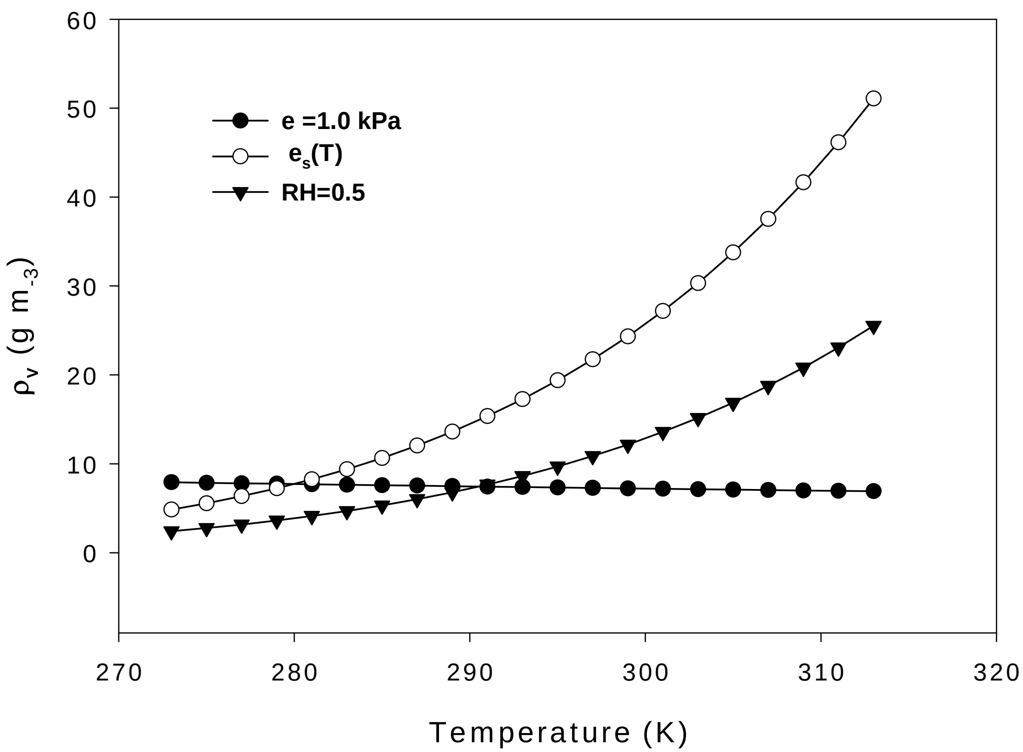
Absolute humidity or vapor density (g m^{-3}):

$$\rho_v = \frac{e_a m_v}{R T_k} \qquad \rho_v(g \cdot m^{-3}) = \frac{2.165 \cdot e_a(kPa)}{T_k}$$

(R=8.3143 J mol^{-1} K^{-1} m_v=18 g mol^{-1})



Humidity vs Temperature



Virtual Temperature.
is the temperature **dry air would have**
if it had the same density as moist air at the same pressure

it is related to the **speed of sound**

and

buoyancy of the air.

$$v_{sound} = \sqrt{\frac{C_p}{C_v}\frac{P}{\rho}} = \sqrt{\frac{C_p}{C_v}\frac{RT_v}{m_{air}}}$$

$$a = g\frac{(\rho - \rho_{parcel})}{\rho_{parcel}}$$

$$\frac{\rho'}{\overline{\overline{\rho}}} = \frac{T_v'}{\overline{\overline{T_v}}}$$

Acceleration, a

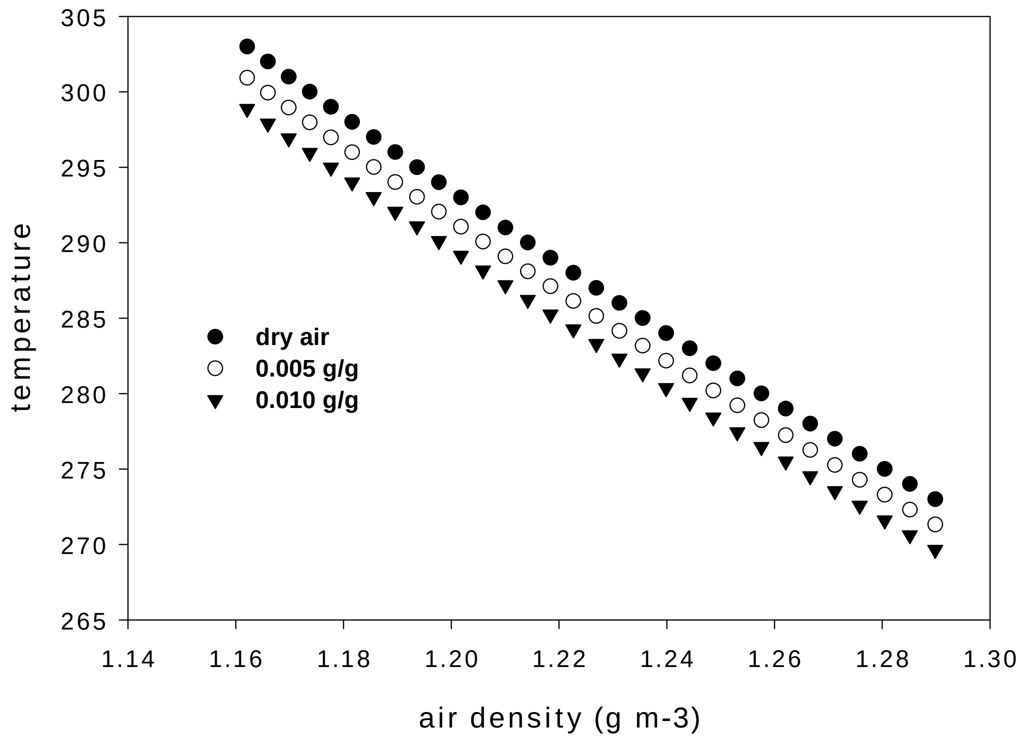
Derivation: Virtual Temperature

$$P = (P - e)|_{dry} + e|_{moist} = \frac{\rho RT}{m} = RT\left(\frac{\rho_a}{m_a} + \frac{\rho_v}{m_v}\right) = \frac{\rho R T_v}{m_a}$$

$$T_v = T\left(\frac{1 + \frac{m_a \rho_v}{m_v \rho_a}}{1 + \frac{\rho_v}{\rho_a}}\right)$$

$$T_v = T\left(1 + 0.38\frac{e}{P}\right)$$

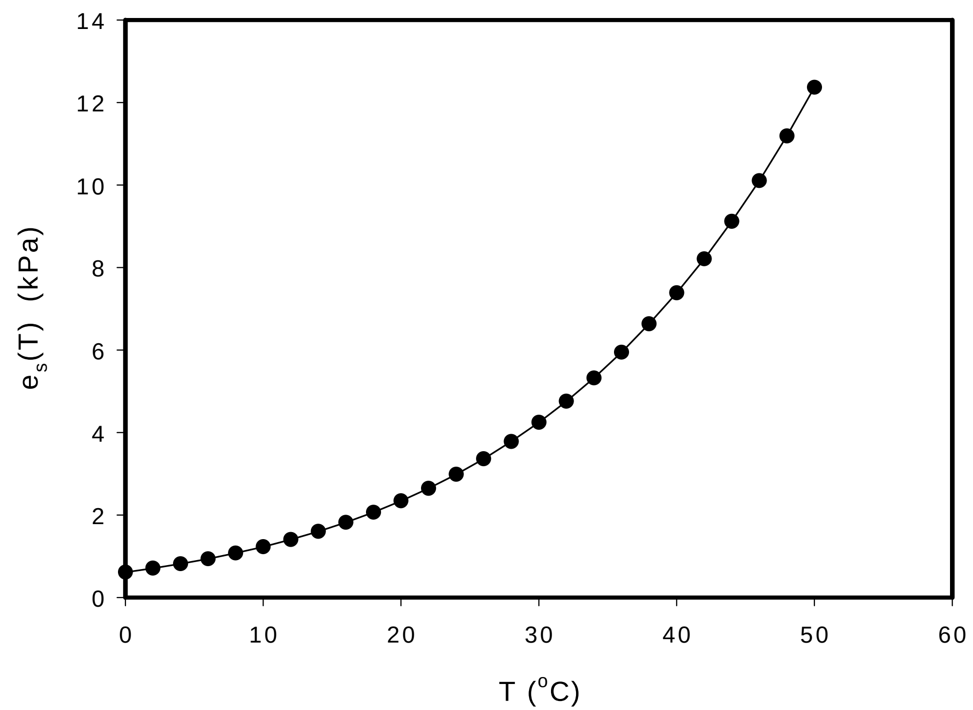
Air Temperature and Virtual Temperature

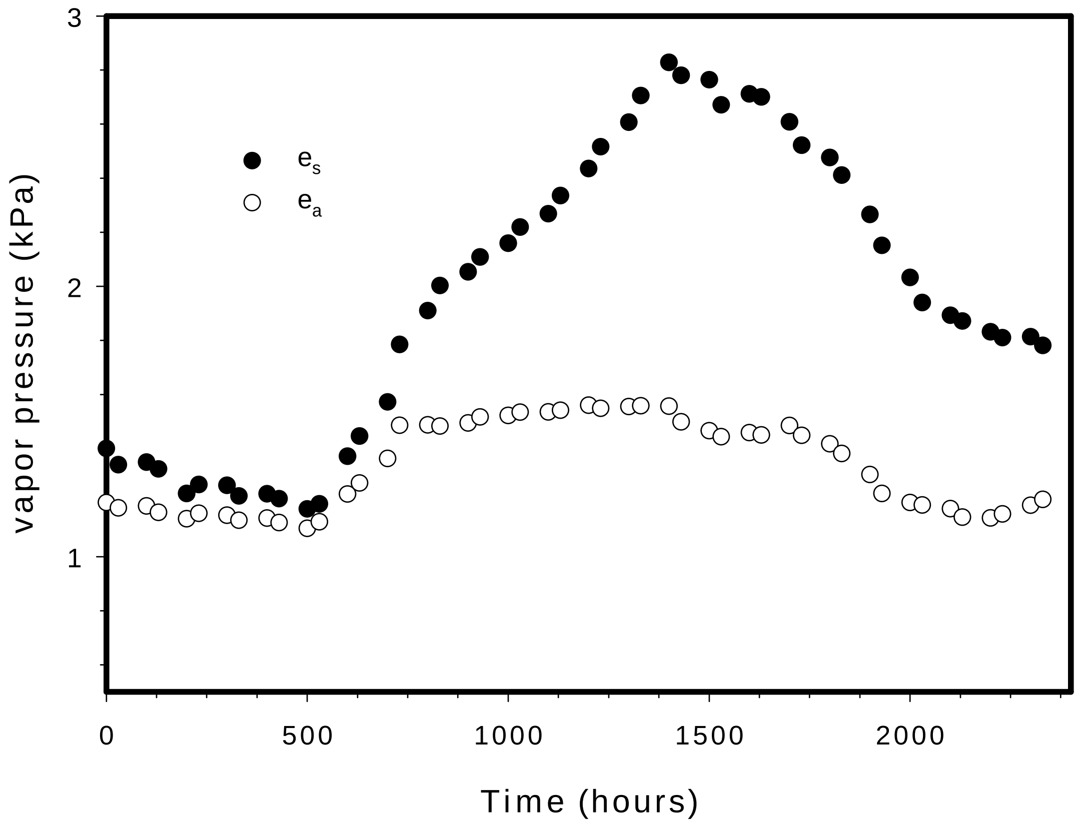


Saturation Vapor Pressure

- When a pool of water is at constant temperature in a closed container, some water molecules are leaving the liquid and others are condensing and returning to the liquid. Molecules in the head space exert a partial pressure on the system.
- The equilibrium vapor pressure that occurs is called the saturation vapor pressure.
- It is a function of temperature and is independent of pressure.

$$e_s(T_C) = 0.611\exp\left(\frac{17.502 \cdot T_C}{T_C + 240.97}\right)$$





3
2
1
vapor pressure (kPa)
e_s
e_a
0
500
1000
1500
2000
Time (hours)

Probability of Time between Storms

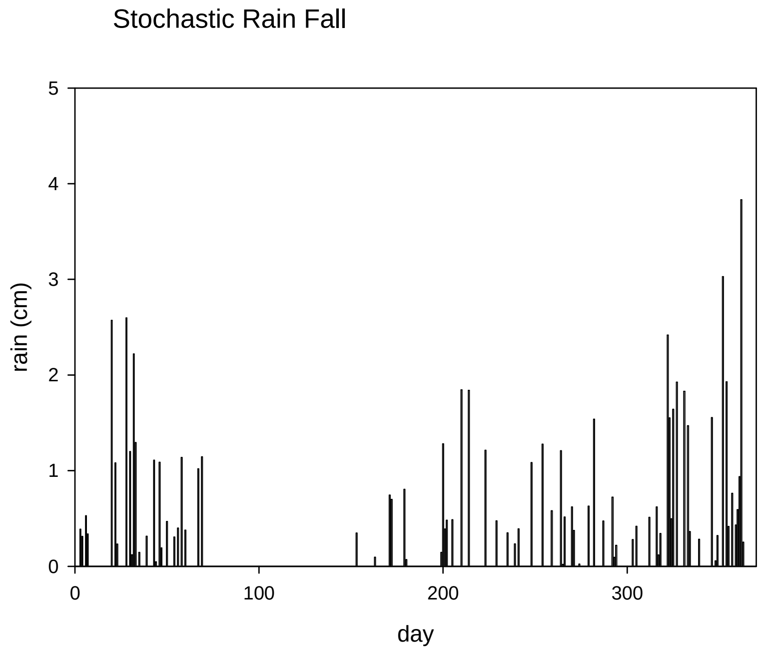
$$f(\tau) = \lambda \exp(-\lambda \tau)$$

λ is the rate of rain (units of rain events per day). It is computed by summing the number of rain days per year and dividing by 365

Probability of amount of rain per storm

$$f(h) = \frac{1}{\alpha} \exp(-\frac{h}{\alpha})$$

$1/\alpha$ is the depth of the rain. α is computed by summing the amount of rain per year and dividing by the number of rainy days.



Drought

- Meteorological
  – Periods when precipitation is significantly below the long-term average
- Hydrological
  – When water level in lakes and rivers fall significantly below normal conditions
- Agricultural
  – Occurrence of low levels of plant available water
- Sociological
  – When drought disrupts societies and/or societies disrupt supplies of water, eg via civil war, famine, political decisions

Drought Metrics

- Palmer Drought Index
- Budyko Aridity Index
- Thornthwaite Index
  - Ratio of between potential and actual evaporation
  - Ratio between precipitation and available energy

Summary

- The concept of chemical potential energy quantifies the driving force for movement
- of water between two locations, such as in the soil, in a plant and between the soil, plant and atmosphere.
- Matrix, pressure, osmotic, gravitational potential sum to determine the chemical potential of water.
- Saturation vapor pressure is an exponential function of temperature
- The probability of rainfall events and its amount can be computed with a Poisson probability distribution