

# LECTURE OUTLINE

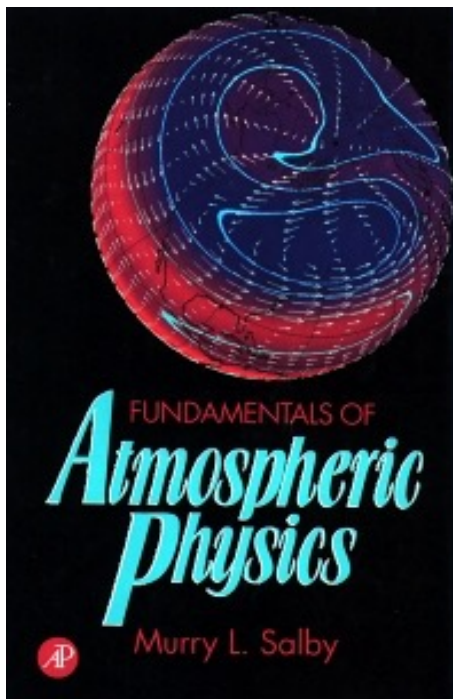
1. Water vapor in the atmosphere
2. Moist air



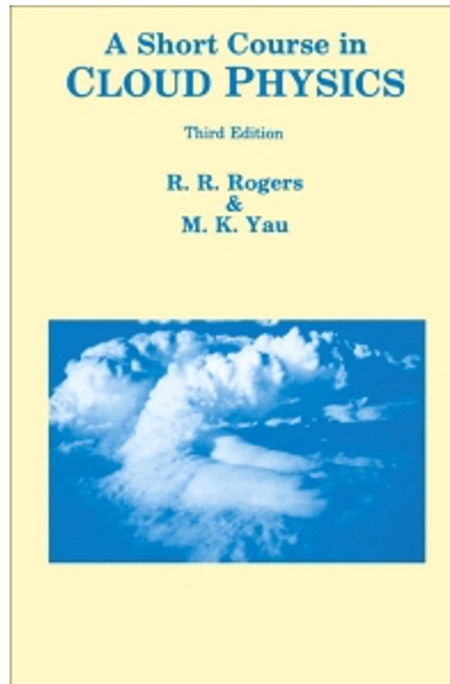
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R&Y, Chapter 2

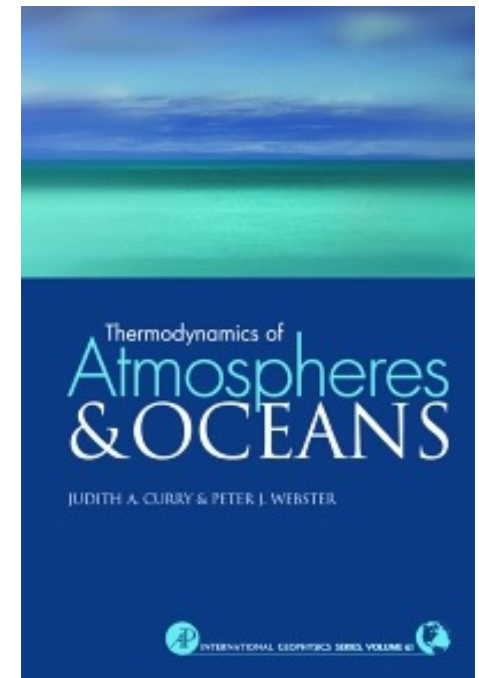
Salby, Chapter 4



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



C&W, Chapter 4



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

# LECTURE OUTLINE

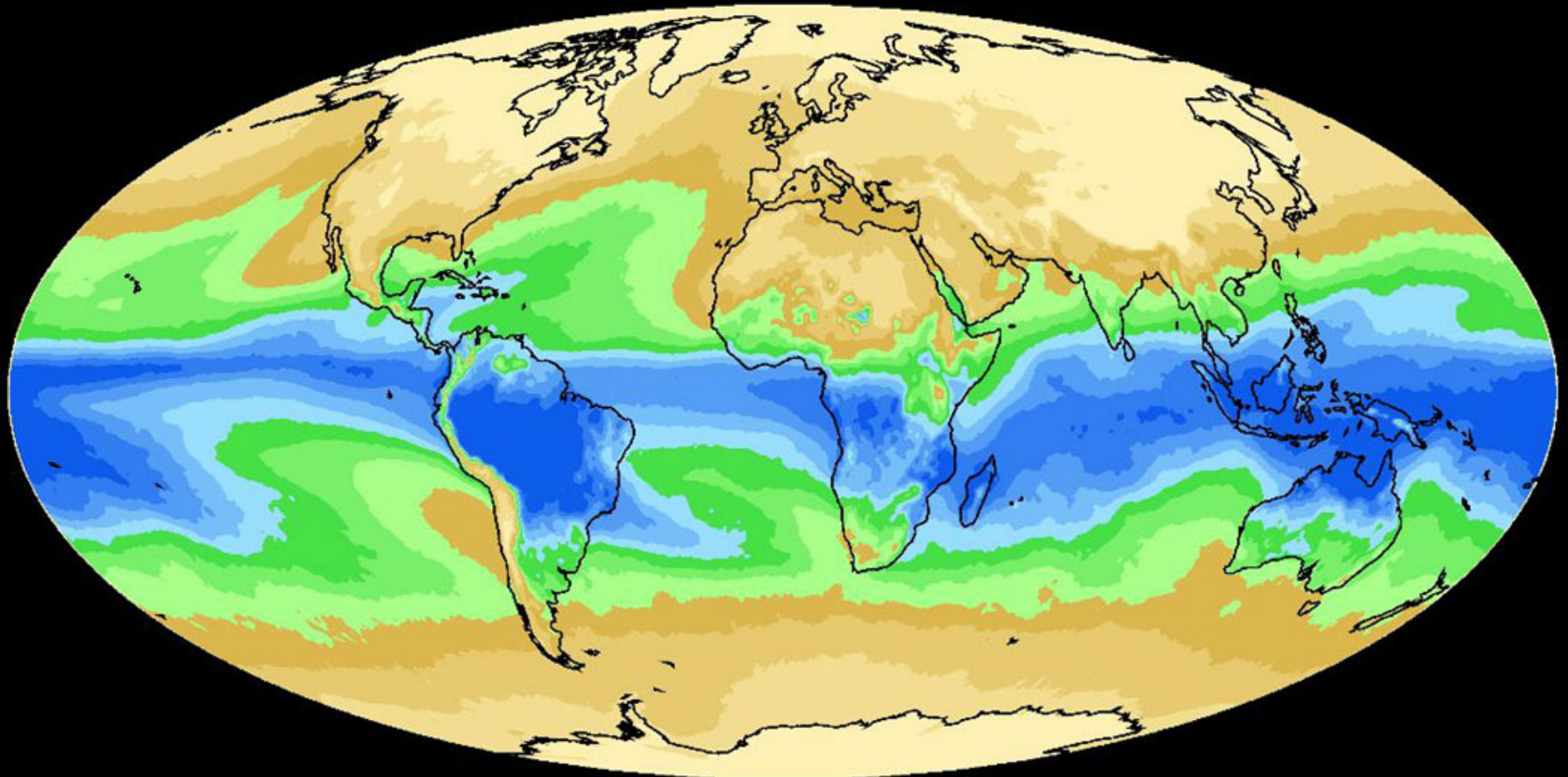
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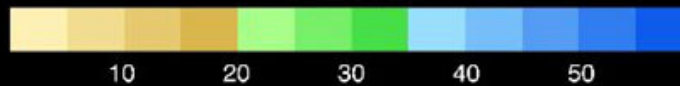
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# Mean Clear Air Precipitable Water

AIRS data, January 2003



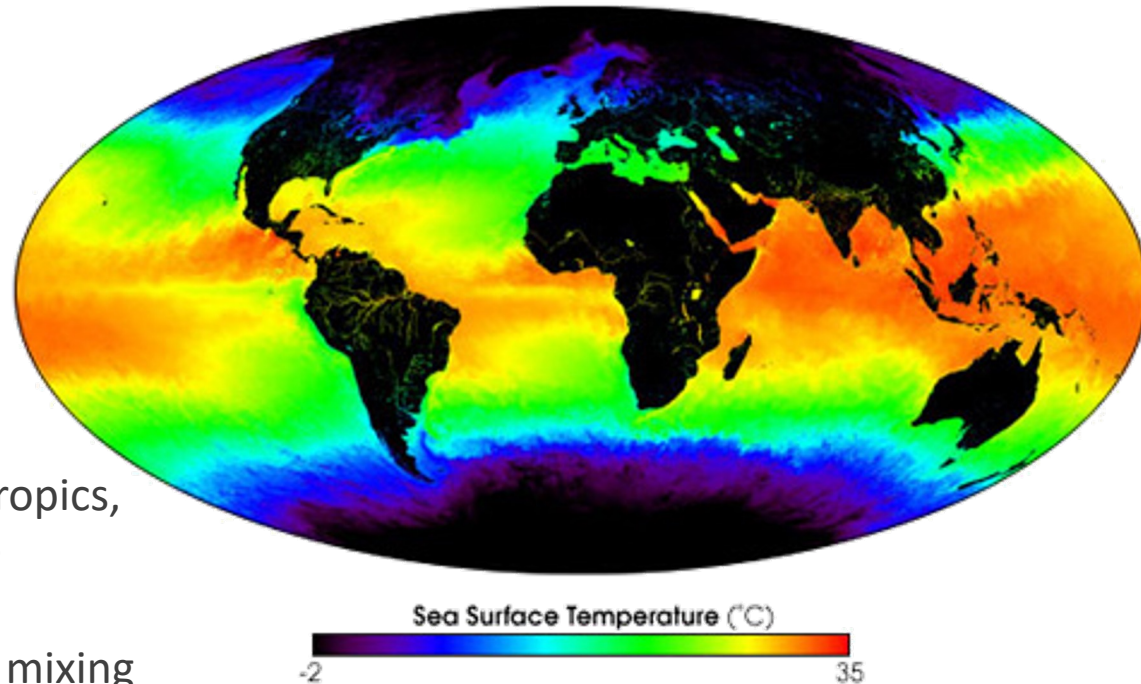
Millimeters



For atmospheric temperatures and pressures the water vapor pressure seldom exceeds 60 hPa, and the water vapor mixing ratio does not exceed  $30 \text{ g kg}^{-1}$  ( $0.03 \text{ kg kg}^{-1}$ ).

The water vapor in the atmosphere is in trace quantities.

According to the Clausius-Clapeyron relation the saturated water vapor pressure increases exponentially with temperature.



The water vapor is produced in the tropics, where high sea surface temperature corresponds to the highest value of saturated water vapor pressure (and mixing ratio).

This value decreases poleward.

- The atmosphere is a mixture of dry air and water in varying proportions.
- Usually the water content in the atmosphere does not exceed few percent.
- We shall consider a two-component system comprised of dry air and water, with water appearing in possibly one condensed phase (liquid water and/or ice).
- The Gibbs-Dalton law (accurate at pressures below the critical point) states that an individual component of a mixture of non-reacting gases behaves the same as if other components were absent.
- The abundance of vapor at equilibrium with a condensed phase in a mixture of water and dry air is the same as if water component were in isolation.
- Concepts established for a single-component system of pure water carry over to a two-component system of dry air and water.

Water vapor obeys the equation of state of ideal gas.

$$e = R_v T \rho_v, \quad \rho_v = \frac{1}{v_v}$$

e- water vapor partial pressure,  $\rho_v$  – water vapor density ,  $R_v$  – specific gas constant

$$R_v = \frac{R^*}{M_v} = \frac{M_d \cdot R_d}{M_v} = \frac{R_d}{\varepsilon}$$

$R^*$  universal gas constant

$M_v$  molar mass of water vapor

$$M_d = 28.96 \text{ g} \cdot \text{mol}^{-1}, \quad M_v = 18 \text{ g} \cdot \text{mol}^{-1} \quad \varepsilon = \frac{M_v}{M_d} = \frac{R_d}{R_v} \approx 0.622$$

$$R^* = 8.314 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1}, \quad R_d = 287 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1}, \quad R_v = 461.5 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1}$$

$$e = \frac{R_d}{\varepsilon} T \rho_v$$



# DESCRIPTION OF GAS PHASE

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Vapor pressure,  $e$  – partial pressure of water vapor [ $mb$ ,  $hPa$ ]

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Absolute humidity,  $\rho_v = 1/v_v$  – concentration of water vapor [ $kg/m^3$ ]

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Specific humidity,  $q_v = m_v/m$  – the ratio of the masses of vapor and mixture, [ $kg/kg$ ,  $g/kg$ ]

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Mixing ratio,  $r_v = m_v/m_d$  – the ratio of the masses of vapor and dry air, [ $kg/kg$ ,  $g/kg$ ]

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Relative humidity  $f$ , - the ratio of the actual partial pressure of water vapor in the air ( $e$ ) to the saturation vapor pressure ( $e_s$ )

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# DESCRIPTION OF GAS PHASE

Specific humidity,  $q_v$  – the ratio of the masses of vapor and mixture, [kg/kg, g/kg]

$$q_v = \frac{m_v}{m}$$

$$q_v = \frac{m_v}{m} = \frac{\rho_v}{\rho} = \frac{\rho_v}{\rho_d + \rho_v}$$

$$\begin{aligned} \rho_v &= \frac{e}{R_v T} = \varepsilon \frac{e}{R_d T} \\ \rho_d &= \frac{p_d}{R_d T} = \frac{p - e}{R_d T} \end{aligned}$$

$$q_v = \varepsilon \frac{e}{p - (1 - \varepsilon)e} \approx \varepsilon \frac{e}{p}$$

One can analogically define specific dry air mass:  $q_d = \frac{m_d}{m}$

# DESCRIPTION OF GAS PHASE

Mixing ratio,  $r_v$  – the ratio of the masses of vapor and dry air, [kg/kg, g/kg]

$$r_v = \frac{m_v}{m_d}$$

$$r_v = \frac{m_v}{m_d} = \frac{\rho_v}{\rho_d} = \frac{\rho_v}{\rho_d}$$

$$\rho_v = \frac{e}{R_v T} = \varepsilon \frac{e}{R_d T}$$
$$\rho_d = \frac{p_d}{R_d T} = \frac{p - e}{R_d T}$$

$$r_v = \varepsilon \frac{e}{p - e} \approx \varepsilon \frac{e}{p}$$

---

Mixing ratio is approximately equal to the specific humidity

$$r_v = \frac{m_v}{m_d} = \frac{m_v}{m - m_v} = \frac{q_v}{1 - q_v} \cong q_v$$

Specific humidity ( $q_v$ ) and mixing ratio ( $r_v$ ) can be used interchangeably.

Both are conserved for an individual parcel outside regions of condensation.

By contrast measures of absolute concentration like  $e$  and  $\rho_v$  change for an individual air parcel through changes of its pressure, even if the mass of vapor remains fixed.

- **Relative humidity  $f$** , - the ratio of the actual partial pressure of water vapor in the air ( $e$ ) to the saturation vapor pressure ( $e_s$ )

approximately – the ratio of the actual mixing ratio of the water vapor to the saturation water vapor mixing ratio.

$$f = \frac{e}{e_s} \cong \frac{r_v}{r_s(p, T)} \cong \frac{q_v}{q_s(p, T)}$$

$$f = \frac{e}{e_s} = \frac{r_v}{r_s} \cdot \frac{\varepsilon + r_s}{\varepsilon + r_v} \cong \frac{r_v}{r_s(p, T)} \cong \frac{q_v}{q_s(p, T)}$$

$$r_v = \frac{\varepsilon \cdot e}{p - e} \Rightarrow e = \frac{p \cdot r_v}{\varepsilon + r_v}$$

# STATE EQUATION FOR MOIST AIR

An moist air parcel occupies a volume  $V$  at pressure  $p$ .

According to the Gibbs law for ideal gas, the pressure  $p$  is a sum of partial pressures of mixture's components, i.e. dry air ( $p_d$ ) and vapor ( $e$ ) :  $p = p_d + e$

$$p_d = R_d T \rho_d = m_d \frac{R_d T}{V}$$

$$e = R_v T \rho_v = m_v \frac{R_v T}{V}$$

$$p = p_d + e$$

$$\begin{aligned} &= m_d \frac{R_d T}{V} + m_v \frac{R_v T}{V} = \\ &= \frac{m_d}{m_d + m_v} \rho R_d T + \frac{m_v}{m_d + m_v} \rho R_v T \end{aligned}$$

$$p = (q_d R_d + q_v R_v) T \rho$$

$m_d$  – mass of dry air occupying a volume  $V$

$m_v$  – mass of water vapor occupying a volume  $V$

$$\rho = \frac{m_d + m_v}{V} \quad \text{moist air density}$$

$$q_d = \frac{m_d}{m_d + m_v} \quad \text{specific dry air mass}$$

$$q_v = \frac{m_v}{m_d + m_v} \quad \text{specific humidity}$$

# GAS CONSTANT FOR MOIST AIR

$$p = (q_d R_d + q_v R_v) T \rho$$

$R_m = q_d R_d + q_v R_v$  is the gas constant for moist air

$$R_m = R_d \left( q_d + q_v \frac{R_v}{R_d} \right) \quad \text{from definition } q_d + q_v = 1$$

$$R_m = R_d \left[ 1 + q_v \left( \frac{1}{\varepsilon} - 1 \right) \right] = R_d (1 + 0.608 q_v)$$

The composition of air varies with the abundance of water vapor, so too do composition-dependent properties like specific gas constant ( $R_m$ ) .

The moist air ideal gas law takes form:

$$p = R_d \left[ 1 + q_v \left( \frac{1}{\varepsilon} - 1 \right) \right] T \rho$$

# VIRTUAL TEMPERATURE

$$p = R_d \left[ 1 + q_v \left( \frac{1}{\varepsilon} - 1 \right) \right] T \rho$$

$$T_v = T \left[ 1 + q_v \left( \frac{1}{\varepsilon} - 1 \right) \right]$$

$$T_v = T(1 + 0.608q_v) \cong T(1 + 0.608r_v)$$

The **virtual temperature** may be interpreted as the temperature of dry air having the same values of pressure,  $p$ , and density,  $\rho$ , as the moist air under consideration.

The equation of state for dry air may be used for describing the moist air if temperature  $T$  is replaced by virtual temperature  $T_v$ .

$$p = R_d T_v \rho$$



$$T_v = T(1 + 0.608q_v) \cong T(1 + 0.608r_v)$$

Since  $q_v$  or  $r_v$  seldom exceeds 0.02, the virtual temperature correction rarely exceeds more than 2 or 3°C, so  $T$  can be used in place of the  $T_v$  to a good approximation.

$$T_v - T = T \cdot 0.608q_v$$

$$q_v \sim 10^{-2}$$

$$T_v - T = 10^{-2}T$$

However the small virtual temperature correction has an important effect on buoyancy and hence vertical motion in the atmosphere.

# SUBSCRIPTS NOTATION

d	dry air
v	water vapor
l	liquid water
i	solid water (ice)
c	condensate
t	total water (irrespective of phase)
s	saturated state, or process
e	equivalent (all condensate) reference state
$\ell$	liquid-free (all vapor) reference state

# EQUATION OF STATE FOR A SYSTEM: AIR + WATER VAPOR + LIQUID WATER

$$p = p_d + e$$

$$p = \rho_d R_d T + \rho_v R_v T$$

$$p = q_d \rho R_d T + q_v \rho R_v T$$

$$p = \rho R_d T \left[ 1 + q_v \left( \frac{R_v}{R_d} - 1 \right) - q_l \right]$$

$$\rho = \frac{m}{V} = \frac{m_d + m_v + m_l}{V}$$

$$q_d = \frac{m_d}{m} = \frac{\rho_d}{\rho} \quad q_v = \frac{m_v}{m} = \frac{\rho_v}{\rho}$$

$$q_l = \frac{m_l}{m}$$

$$q_d + q_v + q_l = 1$$

$$q_d = 1 - q_v - q_l$$

$$T_\rho = \left[ 1 + q_v \left( \frac{R_v}{R_d} - 1 \right) - q_l \right] \cong T(1 + 0,608q_v - q_l) \quad \text{density temperature}$$

$$p = R_d T_\rho \rho$$

# SPECIFIC HEAT



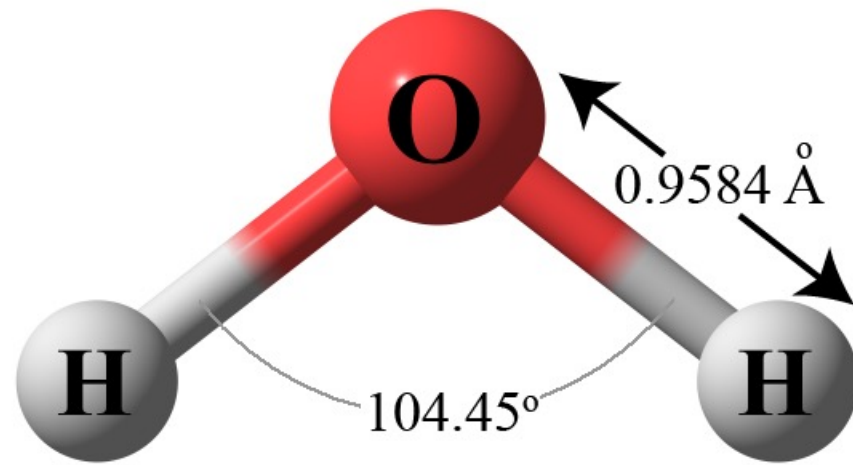
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The water molecule is built from one oxygen atom and two hydrogen atoms. The molecule has 3 degrees of translational and 3 degrees of rotational freedom.

The equipartition of energy allows to define heat capacities at constant volume and at constant pressure.

$$c_{vv} = \frac{6}{2} R_v = 3 \cdot 461.5 = 1385 \text{ Jkg}^{-1}\text{K}^{-1}$$

$$c_{pv} = c_{vv} + R_v = 4 \cdot 461.5 = 1846 \text{ Jkg}^{-1}\text{K}^{-1}$$



The water vapor radiation spectrum shows a contribution to the energy from a vibrational degree of freedom at wavelength 6.27μm.

Experimentally measured heat capacities differ slightly from above values. They show only weak temperature dependence. However we can assume constant values:

$$c_{vv} = 1410 \text{ Jkg}^{-1}\text{K}^{-1}$$

$$c_{pv} = 1870 \text{ Jkg}^{-1}\text{K}^{-1}$$

# SPECIFIC HEAT OF MOIST AIR AT CONSTANT VOLUME

Specific heat of moist air:  $c_{vm} = \left(\frac{dq}{dT}\right)_v$

Consider the addition of heat to a sample consisting of  $m_d$  of dry air and  $m_v$  of water vapor

$$mdq = m_d c_{vd} dT + m_v c_{vv} dT$$

We divide the above equation by:

$m$

$$dq = q_d c_{vd} dT + q_v c_{vv} dT$$

$$dq = (1 - q_v) c_{vd} dT + q_v c_{vv} dT$$

$$c_{vm} = (1 - q_v) c_{vd} + q_v c_{vv}$$

$$c_{vm} = c_{vd} [1 + q_v (k - 1)]$$

$$k = \frac{c_{vv}}{c_{vd}} = 1.96$$

$$c_{vm} = c_{vd} (1 + 0.96 \cdot q_v) \cong c_{vd} (1 + q_v)$$

# SPECIFIC HEAT OF MOIST AIR AT CONSTANT VOLUME

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$$dq = (1 - q_v) c_{vd} dT + q_v c_{vv} dT$$

$$c_{vm} = (1 - q_v) c_{vd} + q_v c_{vv}$$

$$c_{vm} = c_{vd} [1 + q_v (k - 1)]$$

$m_d$

$$\frac{m_d + m_v}{m_d} dq = c_{vd} dT + r_v c_{vv} dT$$

$$(1 + r_v) dq = c_{vd} dT + r_v c_{vv} dT$$

$$c_{vm} = \frac{c_{vd} + r_v c_{vv}}{1 + r_v} = c_{vd} \left( \frac{1 + k r_v}{1 + r_v} \right)$$

$$c_{vm} \cong c_{vd} (1 + k r_v) (1 - r_v) \cong c_{vd} (1 + r_v (k - 1))$$

$$k = \frac{c_{vv}}{c_{vd}} = 1.96$$

$$c_{vm} = c_{vd} (1 + 0.96 \cdot q_v) \cong c_{vd} (1 + q_v) \quad c_{vm} \cong c_{vd} (1 + 0.96 \cdot r_v) \cong c_{vd} (1 + r_v)$$



# SPECIFIC HEAT AT CONSTANT PRESSURE ADIABATIC EXPONENT, $\kappa$

$$c_{pm} = c_{pd}(1 + 0.87q_v) \cong c_{pd}(1 + 0.87r_v)$$

$$\kappa_m = \frac{R_m}{c_{pm}} = \kappa(1 - 0.26q_v) \cong c_{pd}(1 - 0.26r_v)$$

# POTENTIAL TEMPERATURE OF MOIST AIR

## TEMPERATURE GRADIENT



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# MOIST AIR POTENTIAL TEMPERATURE

For undersaturated moist air thermodynamic processes are describe by the same equations as for the dry air, although different constant values should be used.

The amount of water vapor remains constant (  $r_v=\text{const}$ ,  $q_v=\text{const}$ ).

$$c_{pm}dT - vdp = 0 \quad /T$$

$$dh = c_{pm}dT = \cancel{\delta q} + vdp$$

$$c_{pm}d\ln T - R_m d\ln p = 0$$

$$Tp^{\frac{R_m}{c_{pm}}} = \text{const}$$

$$\theta_m = T \left( \frac{p_0}{p} \right)^{\kappa_m}$$

$$\kappa_m = \frac{R_m}{c_{pm}} = \kappa(1 - 0.26q_v)$$

The difference between dry air potential temperature and moist air potential temperature does not exceed 0,1K.

# VIRTUAL POTENTIAL TEMPERATURE

Alternatively one can replace temperature by the virtual temperature, and keep the same constants as for the dry air.

$$\theta_v = T_v \left( \frac{p_0}{p} \right)^\kappa$$

$$\kappa = \frac{R}{c_{pd}} = 0.286$$

$$\theta_v = \theta \cdot (1 + 0.608q_v)$$

**Virtual potential temperature** is the theoretical potential temperature of dry air that would have the same density as moist air.

Because water vapor is less dense than dry air, humid air has a warmer  $\theta_v$  than dry air.

# ADIABATIC GRADIENT FOR MOIST (UNDERSATURATED) AIR

The rate of decrease of temperature with height in an adiabatic ascent can be determined by considering the first law in enthalpy form for an adiabatic process:

$$c_{pm}dT - vdp = 0$$

$$dh = c_{pm}dT = \cancel{\delta q} + vdp$$

+ the hydrostatic relation:  $dp = -\rho g dz$

$$dp = -\frac{g}{v}dz \implies vdp = -g dz$$

$$c_{pm}dT + g dz = 0$$

The adiabatic lapse rate for moist air

$$\Gamma_m \equiv -\frac{dT}{dz} = \frac{g}{c_{pm}}$$

$$\Gamma_m = \frac{g}{c_{pd}(1 + 0.87q_v)} = \frac{\Gamma_d}{(1 + 0.87q_v)}$$

$$\Gamma_d = \frac{g}{c_{pd}} = 0.981 \frac{\text{K}}{\text{km}}$$