LECTURE OUTLINE

1. Description of air with saturated water vapor and liquid water

   - Enthalpy

   - Internal energy
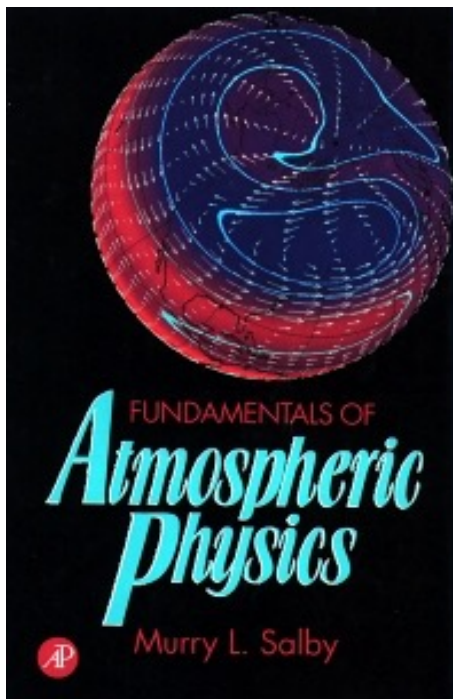
   - Entropy

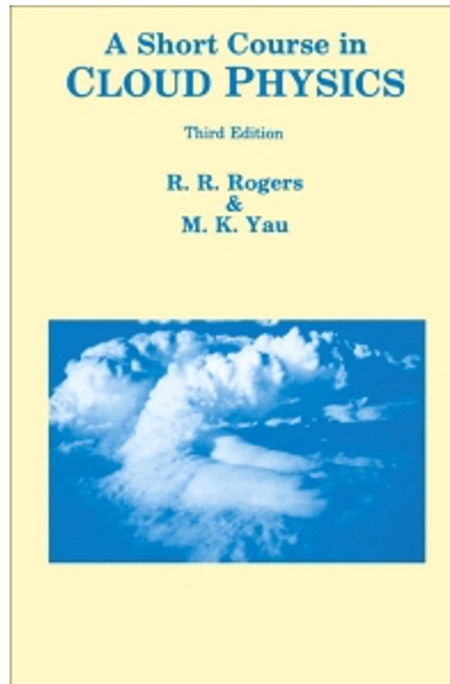2. Potential temperatures

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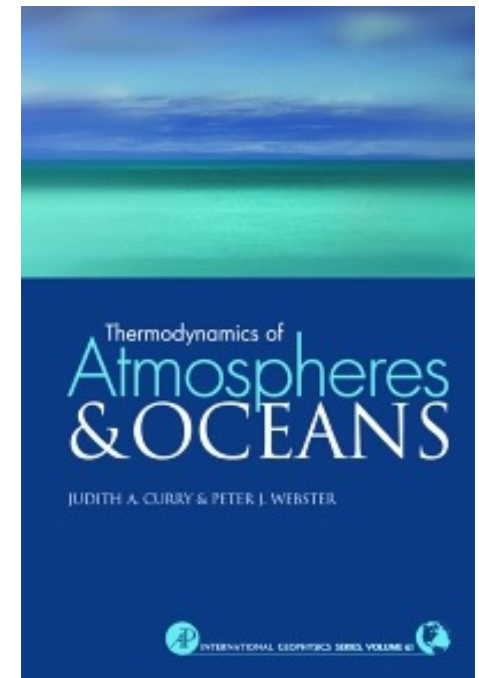OF WARSAW

Salby, Chapter 5

C&W, Chapter 4

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

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

Thermodynamics of Atmospheres
and Oceanes,
J.A. Curry and P.J. Webster; C&W
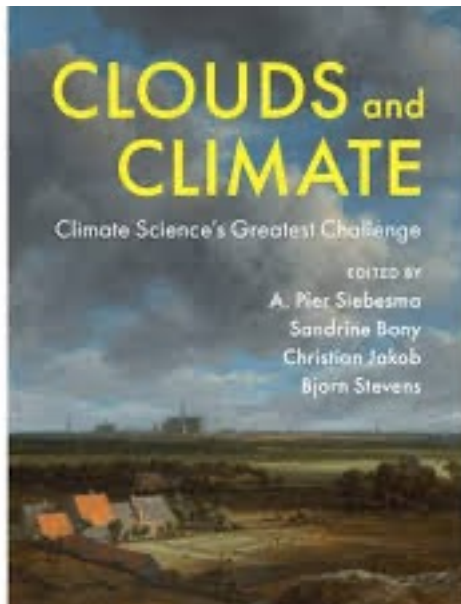
Chapter 2: Clouds as Fluids

Siebesma, A., Bony, S., Jakob, C., & Stevens, B. (Eds.). (2020). *Clouds and Climate: Climate Science's Greatest Challenge*. Cambridge: Cambridge University Press. doi:10.1017/9781107447738

Water vapor in the atmosphere

At temperatures and pressures representative of the atmosphere, the saturated vapor pressure seldom exceeds 60 hPa and the saturation mixing ratio seldom exceeds 30 g kg^{-1}, i.e. 0.03.

It is for this reason that water vapor exists only in trace abundance in the atmosphere.

According to the Clausius-Clapeyron equation, saturation vapor pressure depends exponentially on temperature. Air can support substantially more vapor at high temperature tnan in low temperature.

Water vapor is produced efficiently in the tropics, where warm sea surface temperature (SST) corresponds to high equilibrium vapor pressure (and the mixing ratio). Those values decrease poleward.

Sea Surface Temperature (°C)

-2   35
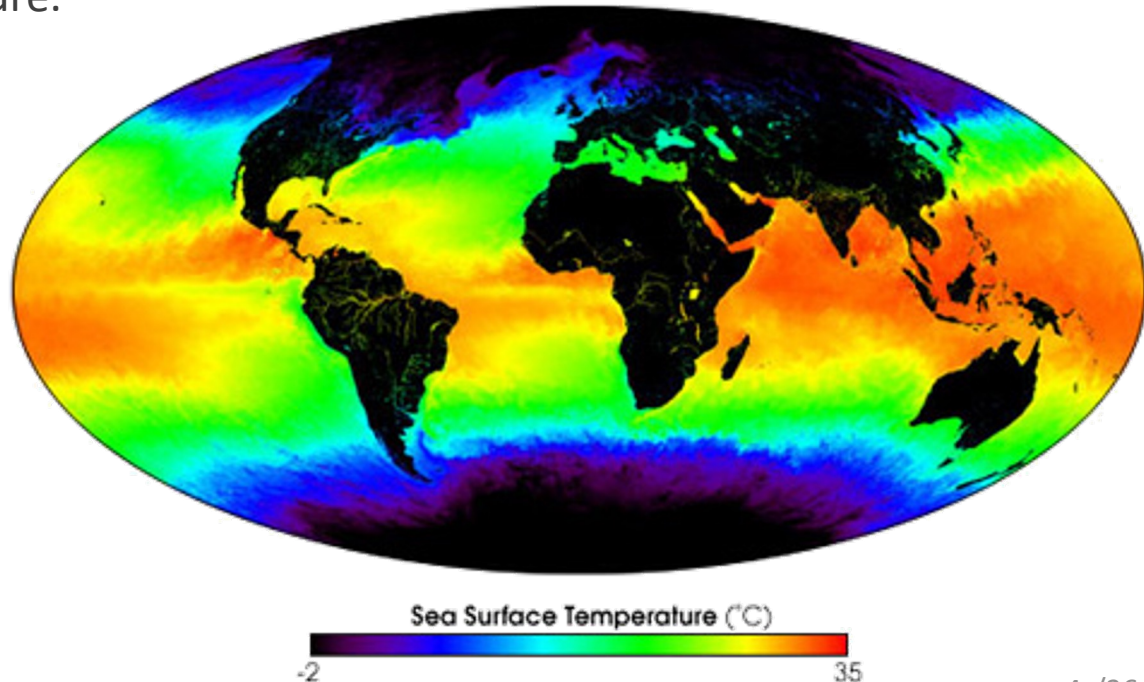
The amount of water vapor decreases with height because of condensation and consequent removal by precipitation – the adiabatic cooling due to the vertical expansion (upward motion) reduces the saturation vapor pressure.

Condensation at higher latitudes is due also to the radiative cooling.

Production of water vapor at an sea surface can occur only if the water component absorbs latent heat to support the transformation of phase.

The heat is absorbed from the ocean OR directly from the shortwave radiation.

When the water vapor condenses the latent heat is released to the environment an dremains in the atmosphere after the condensate has precipitated back to the surface.
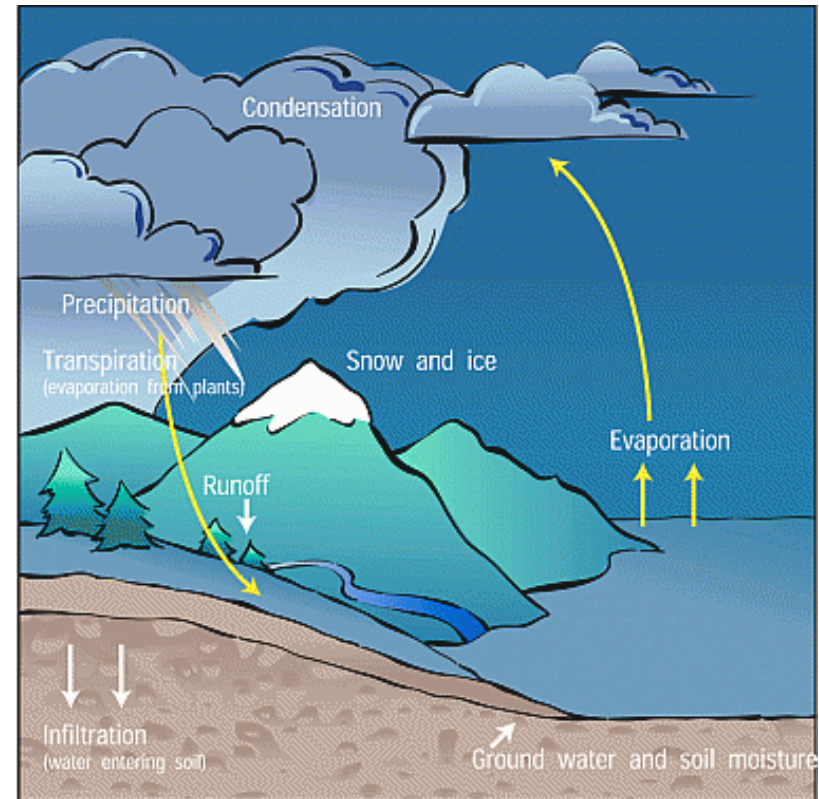
The water cycle in the atmosphere results in no permanent exchange of mass but a net transfer of heat from the ocean to the atmosphere.

NASA Water Vapor Project (NVAP)
Total Column Water Vapor
1992
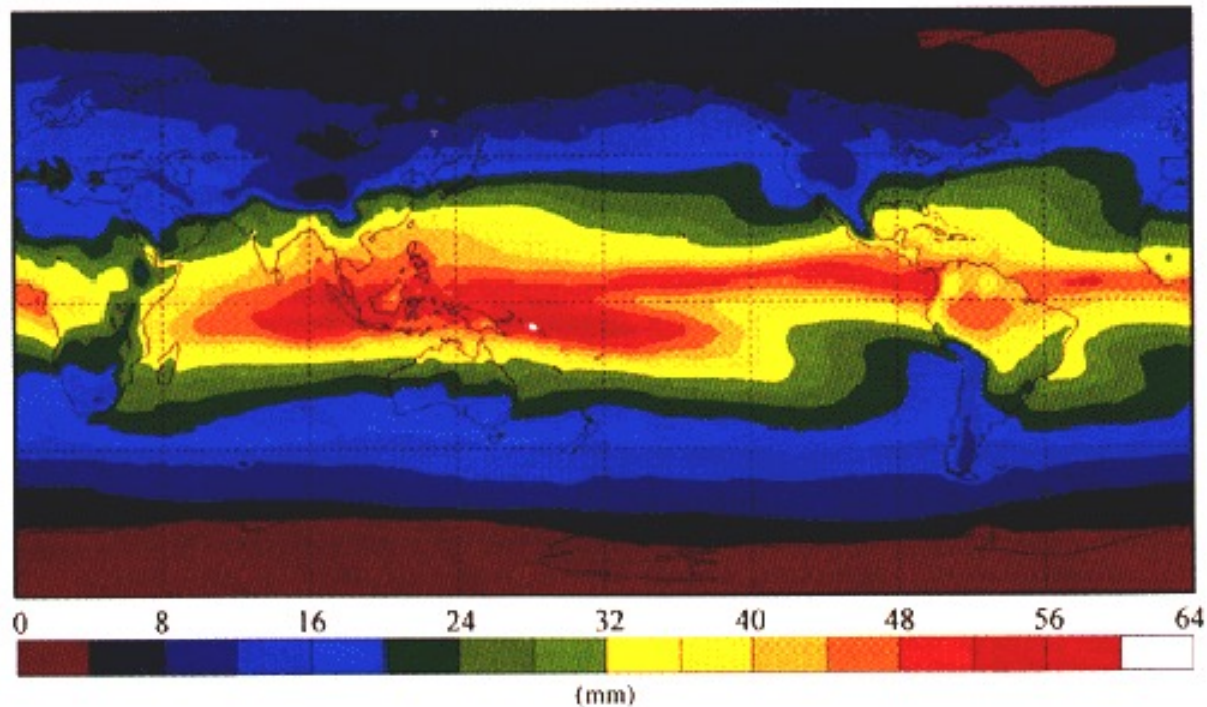
The mean distribution of precipitable water, or total atmospheric water vapor above the Earth's surface, for 1992. This depiction includes data from both satellite and radiosonde observations. (Image courtesy of Thomas Vonder Haar and David Randel, Colorado State University, Fort Collins.)

LECTURE OUTLINE

1. Description of air with saturated water vapor and liquid water

   - Enthalpy

   - Internal energy

   - Entropy

2. Potential temperatures

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The exact differential of the enthalpy $H = H(T, p, m_d, m_v, m_l)$ can be expanded as follows:

$$dH = \left(\frac{\partial H}{\partial T}\right)_{pm} dT + \left(\frac{\partial H}{\partial p}\right)_{Tm} dp + \left(\frac{\partial H}{\partial m_d}\right)_{pTm_{v,l}} dm_d + \left(\frac{\partial H}{\partial m_v}\right)_{pTm_{d,l}} dm_v + \left(\frac{\partial H}{\partial m_l}\right)_{pTm_{d,v}} dm_l$$

For a closed system

$$dm_d = 0 \text{ and } dm_l = -dm_v$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_{pm} dT + \left(\frac{\partial H}{\partial p}\right)_{Tm} dp + (h_v - h_l)dm_v$$

$$h_v = \left(\frac{\partial H}{\partial m_v}\right)_{pTm_{d,l}} \quad h_l = \left(\frac{\partial H}{\partial m_l}\right)_{pTm_{d,v}}$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_{pm} dT + \left(\frac{\partial H}{\partial p}\right)_{Tm} dp + L_{lv}dm_v$$

$$h_v - h_l = L_{lv}$$

We will evaluate: $\left(\frac{\partial H}{\partial T}\right)_{pm}$ and $\left(\frac{\partial H}{\partial p}\right)_{Tm}$

$$\left(\frac{\partial H}{\partial T}\right)_{pm}$$

Consider the total enthalpy as the sum of the individual contributions of dry air (d), water vapor (v), and liquid water (l):

$$H = m_d h_d + m_v h_v + m_l h_l$$

$$\left(\frac{\partial H}{\partial T}\right)_{pm} = m_d \frac{\partial h_d}{\partial T} + m_v \frac{\partial h_v}{\partial T} + m_l \frac{\partial h_l}{\partial T}$$

$$\left(\frac{\partial H}{\partial T}\right)_{pm} = m_d c_{pd} + m_v c_{pv} + m_l c_l$$

$$\frac{\partial h_d}{\partial T} = c_{pd}$$

$$\frac{\partial h_v}{\partial T} = c_{pv}$$

$$\frac{\partial h_l}{\partial T} = c_l$$

There is little difference between the specific heats of liquid water at constant pressure and volume; therefore we do not distinguish between them and denote it by c_l.

$$\left(\frac{\partial H}{\partial p}\right)_{Tm}$$

$$\left(\frac{\partial H}{\partial p}\right)_{Tm} = m_d \frac{\partial h_d}{\partial p} + m_v \frac{\partial h_v}{\partial p} + m_l \frac{\partial h_l}{\partial p}$$

For an ideal gas the enthalpy depends only on temperature ($h_d = c_{pd}T$, $h_v = c_{pv}T$)

$$\frac{\partial h_d}{\partial p} = \frac{\partial h_v}{\partial p} = 0$$

For liquid water: $dh_l = Tds + vdp$

Maxwell relation

$$\left(\frac{\partial h_l}{\partial p}\right)_T = T\left(\frac{\partial s}{\partial p}\right)_T + v$$

$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$$

isobaric expansion coefficient

$$\left(\frac{\partial h_l}{\partial p}\right)_T = v_l(1 - T\alpha_p) \cong v_l$$

$$\alpha_p = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p$$

α_p is very small for liquid

The contribution from the pressure term is negligible compared to the corresponding contribution from temperature, therefore:

$$\left(\frac{\partial H}{\partial p}\right)_{Tm} \cong 0$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_{pm} dT + \left(\frac{\partial H}{\partial p}\right)_{Tm} dp + L_{lv}dm_v$$

$$\left(\frac{\partial H}{\partial T}\right)_{pm} = m_d c_{pd} + m_v c_{pv} + m_l c_l \qquad \left(\frac{\partial H}{\partial p}\right)_{Tm} = 0$$

$$dH = \left(m_d c_{pd} + m_v c_{pv} + m_l c_l\right)dT + L_{lv}dm_v$$

Specific heat for a multi-component system:

$$c_p = \frac{m_d c_{pd} + m_v c_{pv} + m_l c_l}{m} = q_d c_{pd} + q_v c_{pv} + q_l c_l$$

$$dH = mc_p dT + L_{lv}dm_v \quad /m \qquad\qquad h = \frac{H}{m}$$

specific enthalpy

$$dh = c_p dT + L_{lv}dq_v$$

In some textbooks the enthalpy is referred to the mass of dry air.

In that case the c_p and h are defined as follows:

$$c_p = \frac{m_d c_{pd} + m_v c_{pv} + m_l c_l}{m_d} = c_{pd} + r_v c_{pv} + r_l c_l$$

$$dH = m_d c_p dT + L_{lv} dm_v \quad /m_d$$

$$dh = c_p dT + L_{lv} dr_v$$

$$h = \frac{H}{m_d}$$

enthalpy per unit mass of dry air

INTERPRETATION OF ENTHALPY

Depending on how the thermodynamic system is defined, the term $L_{lv}dq_v$ in the enthalpy equation $dh = c_p dT + L_{lv}dq_v$ may be included as a part of enthalpy, or it may constitute an external heat source.

For a closed system, we can write:

$$\delta q = c_p dT + L_{lv}dq_v - vdp$$

For an adiabatic process:

$$0 = c_p dT + L_{lv}dq_v - vdp \qquad (1)$$

$$dh = \delta q + vdp$$
$$dh = c_p dT + L_{lv}dq_v$$

Now consider a system that consists of moist air, with an external heat source associated with evaporation from a water source (moist air over a lake) $\delta q = L_{lv}dq_l = -L_{lv}dq_v$.

The enthalpy can be written as: $dh = c_p dT$ and the first law of thermodynamic $\delta q = dh - vdp$

$$-L_{lv}dq_v = c_p dT - vdp \qquad (2)$$

Equations (1) and (2) are matematically equivalent, however in the first equation the term $L_{lv}dq_v$ is a part of the enthalpy, while in the second equation the term $L_{lv}dq_v$ is a heat source.

This example illustrates the care that must be taken to interpret correctly the thermodynamic equation in the context in which the system is defined.

Enthalpies

In the literature one often encounters closed forms expressions for the enthalpy.

It is often not clear that these expressions depend on an assumes reference state.

We will derive expressions in a manner that makes the assumed reference state explicit.

We will assume that there is only one condensed phase.

For a closed system $\delta q_t = \delta q_d = 0$. These constraints reduce the degrees of freedom in:

$$h = q_d h_d + q_v h_v + q_l h_l$$

We will rewrite this expression in terms of q_t and eliminate either q_v, or q_l in favour of q_t.

Eliminating q_l:

$$h = q_d h_d + q_v h_v + q_l h_l$$
$$= (1 - q_t)h_d + q_v h_v + (q_t - q_v)h_l$$
$$= (1 - q_t)h_d + q_t h_l + q_v L_{lv}$$

$$q_d + q_v + q_l = 1$$
$$q_t = q_v + q_l$$
$$q_d = 1 - q_t$$
$$L_{lv} = h_v - h_l$$

For some (not-necessarily infinitesimal) perturbation about a reference state, the enthalpy change can be written as:

$$\Delta h = (1 - q_t)\Delta h_d + q_t \Delta h_l + \Delta(q_v L_{lv})$$

Assuming a reference state temperature, $T_{0,e}$ such that all the condensate is in the form of liquid, yields the following expression for the enthalpy at a reference state:

$$h_{0,e} = (1 - q_t)\left. h_d \right|_{0,e} + q_t \left. h_l \right|_{0,e}$$

By fixing the (arbitrary) values of the constituent specific enthalpies at the reference temperature to be:

$$h_d(T_{0,e}) = c_{pd}T_{0,e}, \quad h_l(T_{0,e}) = c_l T_{0,e}$$

the enthalpy, $h_e = \Delta h + h_{0,e}$ can be written:

$$h_e = c_{pe}T + q_v L_{lv} \qquad \text{where} \qquad c_{pe} = c_{pd} + q_t(c_l - c_{pd})$$

The subscript e has been added to the enthalpy as a reminder of the reference state with respect to which it has been defined.

Eliminating q_v:

$$\begin{aligned} h &= q_d h_d + q_v h_v + q_l h_l \\ &= (1 - q_t) h_d + (q_t - q_l) h_v + q_l h_l \\ &= (1 - q_t) h_d + q_t h_v - q_l L_{lv} \end{aligned}$$

$$\begin{aligned} q_d + q_v + q_l &= 1 \\ q_t &= q_v + q_l \\ q_d &= 1 - q_t \\ L_{lv} &= h_v - h_l \end{aligned}$$

Assuming a reference state temperature, $T_{0,\ell}$ wherein all the water is in the vapour phase yields the following expression for the enthalpy at a reference state:

$$h_{0,\ell} = (1 - q_t) \left. h_d \right|_{0,\ell} + q_t \left. h_v \right|_{0,\ell}$$

By fixing the (arbitrary) values of the constituent specific enthalpies at the reference temperature to be:

$$h_d(T_{0,\ell}) = c_{pd} T_{0,\ell}, \quad h_v(T_{0,\ell}) = c_v T_{0,\ell}$$

the enthalpy, $h_\ell = \Delta h + h_{0,\ell}$ can be written:

$$h_\ell = c_{p\ell} T - q_l L_{lv} \qquad \text{where} \qquad c_{p\ell} = c_{pd} + q_t (c_{pv} - c_{pd})$$

The subscript ℓ serves as a reminder of the reference state with respect to which it has been defined.

The two enthalpies h_e and h_ℓ differ from one another by a constant, reflecting their different reference states.

However $dh_e = dh_\ell$

$$dh_e = c_{pe}dT + d(q_v L_{lv})$$

$$= \left(c_{pd} + q_t(c_l - c_{pd})\right)dT + q_v dL_{lv} + L_{lv}dq_v$$

$$= (q_d c_{pd} + q_v c_{pv} + q_l c_l)dT + L_{lv}dq_v$$

$$dh_e = c_p dT + L_{lv}dq_v$$

$$dh_\ell = c_{pl}dT - d(q_l L_{lv})$$

$$= \left(c_{pd} + q_t(c_{pv} - c_{pd})\right)dT - q_l dL_{lv} - L_{lv}dq_l$$

$$= (q_d c_{pd} + q_v c_{pv} + q_l c_l)dT + L_{lv}dq_v$$

$$dh_\ell = c_p dT + L_{lv}dq_v$$

$$c_{pe} = c_{pd} + q_t(c_l - c_{pd})$$

$$dL_{lv} = (c_{pv} - c_l)dT$$

$$c_p = q_d c_{pd} + q_v c_{pv} + q_l c_l$$

$$c_{p\ell} = c_{pd} + q_t(c_{pv} - c_{pd})$$

$$dq_l = -dq_v$$

LECTURE OUTLINE

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The exact differential of the internal energy $U = U(T, v, m_d, m_v, m_l)$ can be expanded as for the case of enthalpy:

$$dU = \left(\frac{\partial U}{\partial T}\right)_{vm} dT + \left(\frac{\partial U}{\partial v}\right)_{Tm} dv + \left(\frac{\partial U}{\partial m_d}\right)_{vTm_{v,l}} dm_d + \left(\frac{\partial U}{\partial m_v}\right)_{vTm_{d,l}} dm_v + \left(\frac{\partial U}{\partial m_l}\right)_{vTm_{d,v}} dm_l$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_{vm} dT + \left(\frac{\partial U}{\partial v}\right)_{Tm} dv + (u_v - u_l)dm_v$$

For a closed system

$$dm_d = 0 \text{ and } dm_l = -dm_v$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_{vm} dT + \left(\frac{\partial U}{\partial v}\right)_{Tm} dv + L_{lv}dm_v - R_vT + pv_l$$

$$u_v = \left(\frac{\partial U}{\partial m_v}\right)_{vTm_{d,l}} \qquad u_l = \left(\frac{\partial U}{\partial m_l}\right)_{vTm_{d,v}}$$

We will omit pv_l and R_vT in the above equation because:

$pv_l \sim 10^5/10^3 = 10^2 \text{J/kg}$ is very small compared to $L_{lv} \sim 2.5 \cdot 10^6 \text{J/kg}$

$R_vT \sim 1.3 \cdot 10^5 \text{J/kg}$ is about 5% of L_{lv}.

$$u_v = h_v - ev_v = h_v - R_vT$$

$$u_l = h_l - pv_l$$

$$h_v - h_l = L_{lv}$$

$$u_v - u_l = L_{lv} - R_vT + pv_l$$

$$\left(\frac{\partial U}{\partial T}\right)_{vm} = m_d c_{vd} + m_v c_{vv} + m_l c_l = mc_v$$

$$c_v = \frac{m_d c_{vd} + m_v c_{vv} + m_l c_l}{m} = q_d c_{vd} + q_v c_{vv} + q_l c_l$$

$$\left(\frac{\partial U}{\partial v}\right)_{Tm}$$

$$\left(\frac{\partial U}{\partial v}\right)_{Tm} = m_d \frac{\partial u_d}{\partial v} + m_v \frac{\partial u_v}{\partial v} + m_l \frac{\partial u_l}{\partial v}$$

For an ideal gas the internal energy depends only on temperature ($u_d = c_{vd}T$, $u_v = c_{vv}T$)

$$\frac{\partial u_d}{\partial v} = \frac{\partial u_v}{\partial v} = 0$$

For liquid water: $du_l = Tds - pdv$

$$\left(\frac{\partial u_l}{\partial v}\right)_T = T\left(\frac{\partial s}{\partial v}\right)_T - p$$

$$\left(\frac{\partial u_l}{\partial v}\right)_T = p(T\alpha_v - 1) \cong -p$$

$$\left(\frac{\partial U}{\partial v}\right)_{Tm} \cong -m_l p$$

Maxwell relation

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$$

isochoric expansion coefficient

$$\alpha_v = \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_v$$

α_v is very small for liquid

$$dU = \left(\frac{\partial U}{\partial T}\right)_{vm} dT + \left(\frac{\partial U}{\partial v}\right)_{Tm} dv + L_{lv} dm_v$$

$$\left(\frac{\partial U}{\partial T}\right)_{vm} = m_d c_{vd} + m_v c_{vv} + m_l c_l = m c_v \qquad \left(\frac{\partial U}{\partial v}\right)_{Tm} \cong -m_l p$$

$$dU = m c_v dT + L_{lv} dm_v - m_l p dv \qquad /m$$

$$du = c_v dT + L_{lv} dq_v - q_l p dv$$

The term $q_l p dv$ $(= q_l R dT)$ is much smaller than the other terms, eg. $c_v dT$:

$$q_l R \sim 10^{-4} \cdot 300 = 0.03 \frac{J}{kgK} \qquad c_v \cong 717 \frac{J}{kgK}$$

$$du = c_v dT + L_{lv} dq_v$$

$$u = \frac{U}{m}$$

specific internal energy

$$c_v = q_d c_{vd} + q_v c_{vv} + q_l c_l$$

As in a case of enthalpy in some textbooks the internal energy is referred to the mass of dry air.

In that case the c_v and u are defined as follows:

$$c_v = \frac{m_d c_{vd} + m_v c_{vv} + m_l c_l}{m_d} = c_{vd} + r_v c_{vv} + r_l c_l$$

$$dU = m_d c_v dT + L_{lv} dm_v \quad /m_d$$

$$du = c_v dT + L_{lv} dr_v$$

$$u = \frac{U}{m_d}$$

Internal energy per unit mass of dry air

LECTURE OUTLINE

1. Description of air with saturated water vapor and liquid water
   - Enthalpy
   - Internal energy
   - Entropy
2. Potential temperatures

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ENTROPY

The Second Law postulates the existence of an entropy state function S, defined by the property that in equilibrium the state of the system is that which minimizes the entropy function.

For reversible transformations the First Law can be written in the form:

$$dH = TdS + Vdp$$

thereby identifying the entropy and the pressure as the independent variables in the enthalpy formulation.

As an extensive state function, the entropy can be decomposed into its constituents parts:

$$s = q_d s_d + q_v s_v + q_l s_l$$

Unlike the enthalpy, the absolute entropy is not arbitrary to within a constant value.
The Third Law specifies that the entropy must go to zero as T goes to zero.
Hence the reference entropies cannot be arbitrarily specified. This has consequences for the description of irreversible processes.

For an ideal gas, such as dry air, the specific form of the First Law:

$$dh = Tds + vdp$$

can be integrated to yield an expression of entropy written in terms of a reference entropy:

$$s_d = s_{d,0} + c_{pd} \ln(T/T_0) - R_d \ln(p_d/p_0)$$

where $s_{d,0}$ is the reference entropy of dry air at the temperature T_0 and pressure p_0.

An analogous expression can be derived for s_v.

$$s_v = s_{v,0} + c_{pv} \ln(T/T_0) - R_v \ln(e/e_0)$$

For the condensed phase, the condensate is assumed to be ideal so that changes in pressure do not contribute to the entropy.

$$s_l = s_{l,0} + c_l \ln(T/T_0)$$

Reference values for the entropy of dry air and water vapour at standard pressure and temperature ($p_0 = 1000$ hPa, $T_0 = 273.15$ K) are:

$s_{d,0} = 6.783$ kJ kg^{-1}K^{-1}, $s_{v,0} = 10.321$ kJ kg^{-1}K^{-1}, $s_{l,0} = 1.1652$ kJ kg^{-1}K^{-1}.

A general expression for the composite entropy can be derived with respect to the chosen reference state.

Relative to a system in an 'equivalent' reference state, wherein all the water mass is in the condensed phase ($q_l = q_t - q_v$):

$$s_e = s_{e,0} + c_{pe} \ln(T/T_0) - R_e \ln(p_d/p_0) + q_v(s_v - s_l)$$

$$s_{e,0} = s_{d,0} + q_t\big(s_{l,0} - s_{d,0}\big)$$

$$c_{pe} = c_{pd} + q_t\big(c_l - c_{pd}\big)$$

$$R_e = (1 - q_t)R_d$$

One can use this equation to ask what would the reference state temperature need to be, for the system in the reference state configuration (as specified through the pressure, amount and distribution of water mass) to have the same entropy as in the given state.

For the choice of the 'equivalent' reference state the equation leads to the interpretation of T_0 as the temperature the system would attain if all of its water was reversibly condensed , and then separated mechanically from the gas but maintained in thermal equilibrium with the dry air as the system was brought reversibly to the reference state pressure – a proces that is easier to imagine than to realise.

For the liquid-free reference state, wherein all the liquid water is evaporated ($q_v = q_t - q_l$):

$$s_\ell = s_{\ell,0} + c_{p\ell}\ln(T/T_0) - q_d R_d \ln(p_d/p_{d,0}) - q_t R_v \ln(e/e_{t,0}) - q_l(s_v - s_l)$$

$$s_{\ell,0} = s_{d,0} + q_t(s_{v,0} - s_{d,0})$$

$$c_{p\ell} = c_{pd} + q_t(c_{pv} - c_{pd})$$

The pressures, $p_{d,0}$ and $e_{t,0}$, assume a reference state that is subsaturated but with the same mass of total water and dry air as in the actual state, so that $p_0 = p_{d,0} + e_{t,0}$.

Physically, the reference state temperature is that which the system would attain if reversibly brought to the reference (liquid-free) state pressure, which requires that the vapour pressure be less than the saturation vapor pressure at this temperature, so that any condensate that may initially be in the system transforms to vapour.

Exact differential of entropy

If water vapor is in equilibrium with liquid water, then: $e = e_s$
The total pressure, p, is usually very close to the dry air pressure, p_d; therefore we can neglect the difference between p and p_d.

It makes expressions for specific entropy appear in simpler versions. One can show that $ds_e = ds_\ell = ds$ (derivation is easy in case of ds_e, a little more complicated in case of ds_ℓ)

$$s = S/m: \quad ds = \left(q_d c_{pd} + q_t c_l\right)\frac{dT}{T} - q_d R_d \, d\ln p + d\left(\frac{L_{lv}q_v}{T}\right)$$

For the specific entropy relative to the mass of the dry air the expression takes the form:

$$s = S/m_d: \quad ds = \left(c_{pd} + r_t c_l\right)\frac{dT}{T} - R_d \, d\ln p + d\left(\frac{L_{lv}r_v}{T}\right)$$

$$s_\ell = s_{\ell,0} + c_{p\ell}\ln(T/T_0) - q_d R_d \ln(p_d/p_{d,0}) - q_t R_v \ln(e/e_{t,0}) - q_l(s_v - s_l)$$

$$ds_\ell = c_{p\ell}d\ln T - q_d R_d - q_t R_v d\ln e - q_t(ds_v - ds_l) + d\big(q_v(s_v - s_l)\big)$$

$$= c_{p\ell}d\ln T - q_d R_d d\ln p - \cancel{q_t R_v d\ln e} - q_t\Big(c_{pv}d\ln T - \cancel{R_v d\ln e} - c_l d\ln T\Big) + d\left(\frac{q_v L_{lv}}{T}\right)$$

$$= \Big(c_{pd} + q_t(\cancel{c_{pv}} - c_{pd}) - \cancel{q_t c_{pv}} + q_t c_l\Big)d\ln T - q_d R_d d\ln p + d\left(\frac{q_v L_{lv}}{T}\right)$$

$$ds_\ell = ds = \big(q_d c_{pd} + q_t c_l\big)d\ln T - q_d R_d d\ln p + d\left(\frac{q_v L_{lv}}{T}\right)$$

POTENTIAL TEMPERATURES

In the atmospheric sciences, there is a tradition of using temperature variables to measure the system's entropy.

They are called potential temperatures as they measure the temperature the system would have to have in some specified reference state for the entropy of this state to be identical to that of the given state.

These temperatures are invariant (for a closed system) under an isentropic proces, but their properties and absolute values depend on the specification of the reference state.

LECTURE OUTLINE

1. Description of air with saturated water vapor and liquid water
   - Enthalpy
   - Internal energy
   - Entropy

2. Potential temperatures

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Equivalent potential temperature

Consider a reference state where all of the vapor is condensed into liquid and $p_0 = 10^5$ Pa.

This particular reference state is called an equivalent state.

The temperature attained by the air parcel when reversibly transformed to this state is denoted by e; and called the equivalent potential temperature θ_e.

For the equivalent reference state $s = s_{e,0}$ and T_0 will be denoted by θ_e.

$$s_e = s_{e,0} + c_{pe} \ln(T/T_0) - R_e \ln(p_d/p_0) + q_v(s_v - s_l)$$

$$c_{pe} \ln \theta_e = c_{pe} \ln T - R_e \ln(p_d/p_0) + q_v(s_v - s_l)$$

$$c_{pe} \ln \theta_e = c_{pe} \ln T - R_e \ln(p_d/p_0) + q_v(s_v - s_l)$$

The pressure of the dry air will be expressed in terms of the total pressure and the specific humidity:

$$p_d = R_d T \rho_d$$

$$p = RT\rho \,, \quad R = q_d R_d + q_v R_v$$

$$\frac{p_d}{p} = \frac{R_d}{R} \frac{\rho_d}{\rho} \quad \longrightarrow \quad p_d = p \frac{q_d R_d}{R} = p \frac{R_e}{R}$$

The vapor-liquid entropy difference will be expressed relative to the vapor entropy in saturation:

$$s_v - s_l = s_v - s_s + s_s - s_l$$

$$= s_v - s_s + (L_v/T)$$

The condition of phase equilibrium is the equality of the specific Gibbs function of the phases, so $s_s - s_l = (h_s - h_l)/T = L_v/T$.

The difference between the vapour and saturation vapour entropy is measured by the difference in the partial pressures:

$$s_v - s_s = -R_v \ln\left(\frac{e}{e_s}\right)$$

$$c_{pe} \ln \theta_e = c_{pe} \ln(T) - R_e \ln(p_d/p_0) + q_v(s_v - s_l)$$

$$c_{pe} \ln \theta_e = c_{pe} \ln(T) - R_e \ln \left(\frac{p}{p_0} \frac{R_e}{R} \right) - q_v R_v \ln \left(\frac{e}{e_s} \right) + \frac{q_v L_v}{T}$$

$$\theta_e = T \left(\frac{p_0}{p} \right)^{\frac{R_e}{c_{pe}}} \Omega_e \exp \left(\frac{q_v L_v}{c_{pe} T} \right) \qquad \Omega_e = \left(\frac{R}{R_e} \right)^{\frac{R_e}{c_{pe}}} \left(\frac{e}{e_s} \right)^{-\frac{q_v R_v}{c_{pe}}}$$

$$c_{pe} = c_{pd} + q_t(c_l - c_{pd})$$

$$R_e = (1 - q_t)R_d$$

e/e_s defines the relative humidity. The term Ω_e depends only very weakly on the thermodynamic state and is close to 1.

The expression for θ_e in the full form is complicated, but it is rarely used in this form for practical applications.

For many purposes far simpler expressions capture much of the essential physics.

$$\theta_e = \theta \exp \left(\frac{q_v L_v}{c_{pe} T} \right)$$

LIQUID-WATER POTENTIAL TEMPERATURE

Choosing T_0 so that the liquid-free reference state has the same entropy as the given state introduces the liquid-water potential temperature θ_ℓ.
For the liquid-free reference state $s = s_{\ell,0}$.

$$s_\ell = s_{\ell,0} + c_{p\ell} \ln(T/T_0) - q_d R_d \ln(p_d/p_{d,0}) - q_t R_v \ln(e/e_{t,0}) - q_l(s_v - s_l)$$

$$c_{p\ell} \ln \theta_\ell = c_{p\ell} \ln T - q_d R_d \ln(p_d/p_{d,0}) - q_t R_v \ln(e/e_{t,0}) - q_l(s_v - s_l)$$

as in the previous case:

$$s_v - s_l = -R_v \ln\left(\frac{e}{e_s}\right) + (L_v/T)$$

The pressure of the dry air will be expressed in terms of the total pressure.

$$p_d = p\frac{q_d R_d}{R}$$

$$p_{d,0} = p_0 \frac{q_d R_d}{R_\ell}, \qquad \text{where} \quad R_\ell = q_d R_d + q_t R_v$$

At the reference state all water is in the state of vapour; therefore R is replaced by R_ℓ.

e and $p_{t,o}$ will be expressed in terms of the total pressure and specific humidity.

$$e = p\,\frac{q_v R_v}{R}$$

$$e_{t,0} = p_0\,\frac{q_t R_v}{R_\ell}\,, \qquad \text{where} \quad R_\ell = q_d R_d + q_t R_v$$

$$\ln\left(\frac{e}{e_{t,0}}\right) = \ln\left(\frac{q_v}{q_t}\cdot\frac{R_\ell}{R}\cdot\frac{p}{p_0}\right)$$

$$c_{p\ell}\ln\theta_\ell = c_{p\ell}\ln T - q_d R_d \ln\left(\frac{p}{p_0}\cdot\frac{R_\ell}{R}\right) - q_t R_v \ln\left(\frac{q_v}{q_t}\cdot\frac{R_\ell}{R}\cdot\frac{p}{p_0}\right) + q_l R_v \ln\left(\frac{e}{e_s}\right) - q_l\frac{L_v}{T}$$

$$\theta_\ell = T\left(\frac{p_0}{p}\right)^{\frac{R_\ell}{c_{p\ell}}}\Omega_\ell \exp\left(-\frac{q_l L_v}{c_{p\ell}T}\right) \qquad \Omega_\ell = \left(\frac{q_t}{q_v}\right)^{\frac{q_t R_v}{c_{p\ell}}}\left(\frac{R}{R_\ell}\right)^{\frac{R_\ell}{c_{p\ell}}}\left(\frac{e}{e_s}\right)^{-\frac{q_l R_v}{c_{p\ell}}} \cong 1$$

$$c_{p\ell} = c_{pd} + q_t\left(c_{pv} - c_{pd}\right)$$

$$R_\ell = q_d R_d + q_t R_v$$

$$\theta_\ell = \theta \exp\left(-\frac{q_l L_v}{c_{p\ell}T}\right)$$

Simplified form of the liquid-water potential temperature.