Thermodynamics Notes
Sections 5.5-5.7

(mostly from Thermo_for_slides.tex)

5.5 Changes of phase and latent heats

In the atmosphere, liquid water and water vapor can coexist in thermodynamic equilibrium, as can ice and water vapor.

- Vapor, liquid, and solid are called *phases.*

- The following *phase changes* of water substance occur in the atmosphere: evaporation, condensation, sublimation, deposition, melting, and freezing.

  - *Evaporation* occurs when liquid water changes to water vapor, while *condensation* is the opposite.

  - *Sublimation* occurs when ice changes to water vapor, while *deposition* is the opposite.

  - *Melting* occurs when ice changes to liquid water, while *freezing* is the opposite.

- Both condensation and freezing require *nuclei* to initiate the phase change.

- If sufficient nuclei are not present, *supersaturation* of water vapor, or *supercooling* of liquid water, may occur.

- *Cloud condensation nuclei* are usually abundant, so supersaturation is negligible in clouds without ice.

- *Ice nuclei* are not abundant, so *supercooling* of liquid water is typical.

Heating or cooling of the environment occurs during phase changes, even though the phase change is isothermal.

- The energy transferred is called the *latent heat.*

- *Cooling* occurs during evaporation, sublimation, and melting.

- *Heating* occurs during condensation, deposition, and freezing.

At 0°C

- the *latent heat of evaporation* is $L_e = 2.5 \times 10^6$ J kg^{-1},

- the *latent heat of melting* is $L_m = 0.334 \times 10^6$ J kg^{-1}, and

- the *latent heat of sublimation* is $L_s = 2.834 \times 10^6$ J kg^{-1}.

5.6   Adiabatic processes of saturated air

When condensation occurs during ascent, the latent heat that is released significantly reduces the rate of temperature decrease due to adiabatic expansion. Consider two cases:

> All condensed water remains suspended. This is called a *moist adiabatic* or *saturation adiabatic* process, and is *reversible.*

> All condensed water falls out of the parcel immediately. This is called a *pseudo-adiabatic* process, and is *irreversible.*

The real situation lies between these two extremes.

Note that the rate of cooling in a pseudo-adiabatic process is essentially equal to that in a truly moist adiabatic one.

We will now consider a pseudo-adiabatic process in which there is saturation but not supersaturation.

The amount of water vapor condensed is then $-dw_s$ and the latent heating is $-Ldw_s$.

kg/kg

J/kg kg/kg = J/kg

(Here we use $L = L_e$ for simplicity.)

The first law for the mixture of dry air and water vapor is

energy conservation

L/cp = 2.5e6 J/kg /1e3 J/kg/K

2.5e3 K kgkg = 2.5 K / g/kg

$$-Ldw_s = c_p \, dT - RT \frac{dp}{p}. \tag{29}$$

latent heat   **enthalpy**

work done by expanson

Since w_s and e_s are known functions of T and p, this is a differential relationship between T and p during a pseudo-adiabatic process.
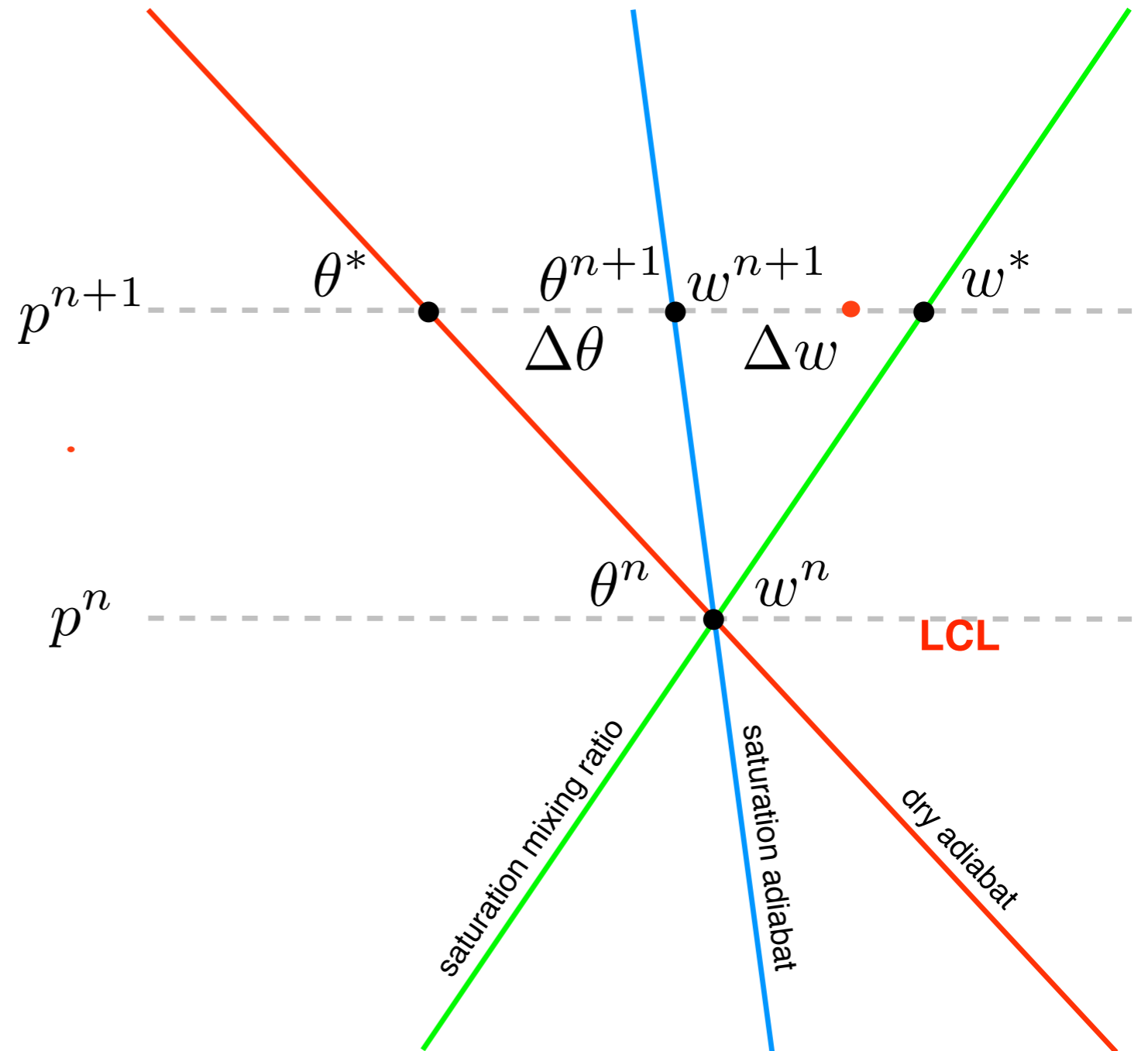
Saturated Adiabatic Ascent

1. **Adiabatic.** No phase changes involving cloud droplets (C=0):

$$\theta^n, \ w^n \rightarrow \theta^*, \ w^*$$

2. **Isobaric.** Only phase changes involving cloud droplets operate (|C| > 0):

$$\theta^*, \ w^* \rightarrow \theta^{n+1}, \ w^{n+1}$$

Saturated Adiabatic Ascent

2. **Isobaric.** Only phase changes involving cloud droplets operate ($|C| > 0$):

$$\theta^{n+1}, \, w^{n+1} = (\theta^* + \Delta\theta, \, w^* + \Delta w)$$
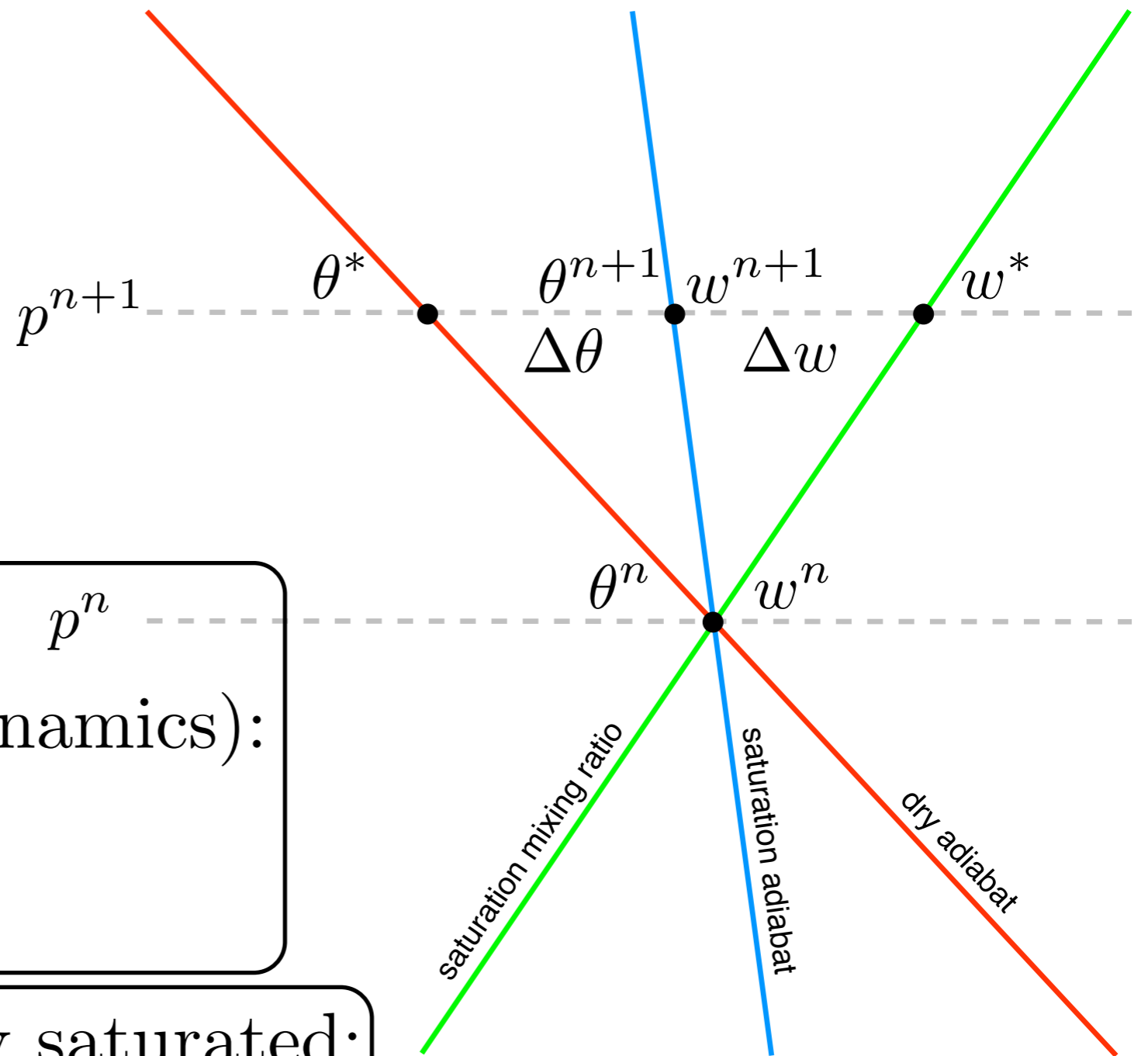
Conservation of energy (First Law of Thermodynamics):
$0 = c_p \pi \Delta\theta + L\Delta w$ or
$0 = c_p \Delta T + L\Delta w$

Adjusted state is exactly saturated:
$w^{n+1} = w_s(\pi\theta^{n+1}, p^{n+1})$ or
$w^{n+1} = w_s(T^{n+1}, p^{n+1})$

We will use the definition of potential temperature given by

$$\frac{T}{\theta} = \left(\frac{p}{p_0}\right)^{\kappa}.$$

to write another form of the first law. Take the logarithm to get

log (x/y) = log x - log y

log x^a = a log x

$$\ln \frac{T}{\theta} = \frac{R}{c_p} \ln \frac{p}{p_0}.$$

Differentiate this to obtain

d (log y)/dy = 1/y

d (log y) = dy/y

$$d \ln T - d \ln \theta = \frac{R}{c_p}(d \ln p - d \ln p_0),$$

which becomes

$$\frac{dT}{T} - \frac{d\theta}{\theta} = \frac{R}{c_p}\frac{dp}{p}.$$

Rearrange this to get

$$c_p \frac{d\theta}{\theta} = c_p \frac{dT}{T} - R \frac{dp}{p}. \tag{30}$$

Recall First Law.

$$-\frac{L\,dw_s}{T} = c_p\frac{dT}{T} - \frac{RT}{T}\frac{dp}{p}. \qquad (29)$$

Our new form:

$$c_p\frac{d\theta}{\theta} = c_p\frac{dT}{T} - R\frac{dp}{p}. \qquad (30)$$

By comparing (29) divided by T and (30), we see that the *first law of thermodynamics for a pseudo-adiabatic process* is

$$-L\frac{dw_s}{T} = c_p\frac{d\theta}{\theta}.$$

It can be shown that (see Wallace and Hobbs, Second Edition, Problem 3.52)

$$d\left(\frac{w_s}{T}\right) \approx \frac{dw_s}{T}, \quad \text{\textit{-Ws dT/T\textasciicircum2}}$$

neglected term (much smaller)

so

$$-L\,d\left(\frac{w_s}{T}\right) \approx c_p\frac{d\theta}{\theta} = c_p\,d\ln\theta.$$

$$-L\,d\left(\frac{w_s}{T}\right) \approx c_p\frac{d\theta}{\theta} = c_p\,d\ln\theta.$$

Integrate this from the original, *saturated* state $(T, w_s(T,p), \theta(T,p))$
to a state where $w_s = 0$ and $\theta = \theta_e$: **at the LCL**

$$-\int_{w_s/T}^{0} L\,d\left(\frac{w_s}{T}\right) \approx \int_{\theta}^{\theta_e} c_p\,d\ln\theta$$

to get

$$\frac{Lw_s}{c_pT} = \ln(\theta_e/\theta),$$

$$-L\,d\left(\frac{w_s}{T}\right) \approx c_p\frac{d\theta}{\theta} = c_p\,d\ln\theta.$$

Integrate this from the original, *saturated* state $(T, w_s(T, p), \theta(T, p))$
to a state where $w_s = 0$ and $\theta = \theta_e$: **at or above the LCL**

$$-\int_{w_s/T}^{0} L\,d\left(\frac{w_s}{T}\right) \approx \int_{\theta}^{\theta_e} c_p\,d\ln\theta$$

to get

$$\frac{Lw_s}{c_pT} = \ln(\theta_e/\theta),$$

This describes a saturated adiabat, which is characterized by theta_e, which is a constant for each such adiabat.

then exponentiate and rearrange to obtain

$$\theta = \theta_e \exp(-Lw_s/c_pT).$$

a function of T and ws(T,p) so it can be plotted on a skew-T diagram

This describes a *pseudo-adiabat* which is characterized by θ_e, the
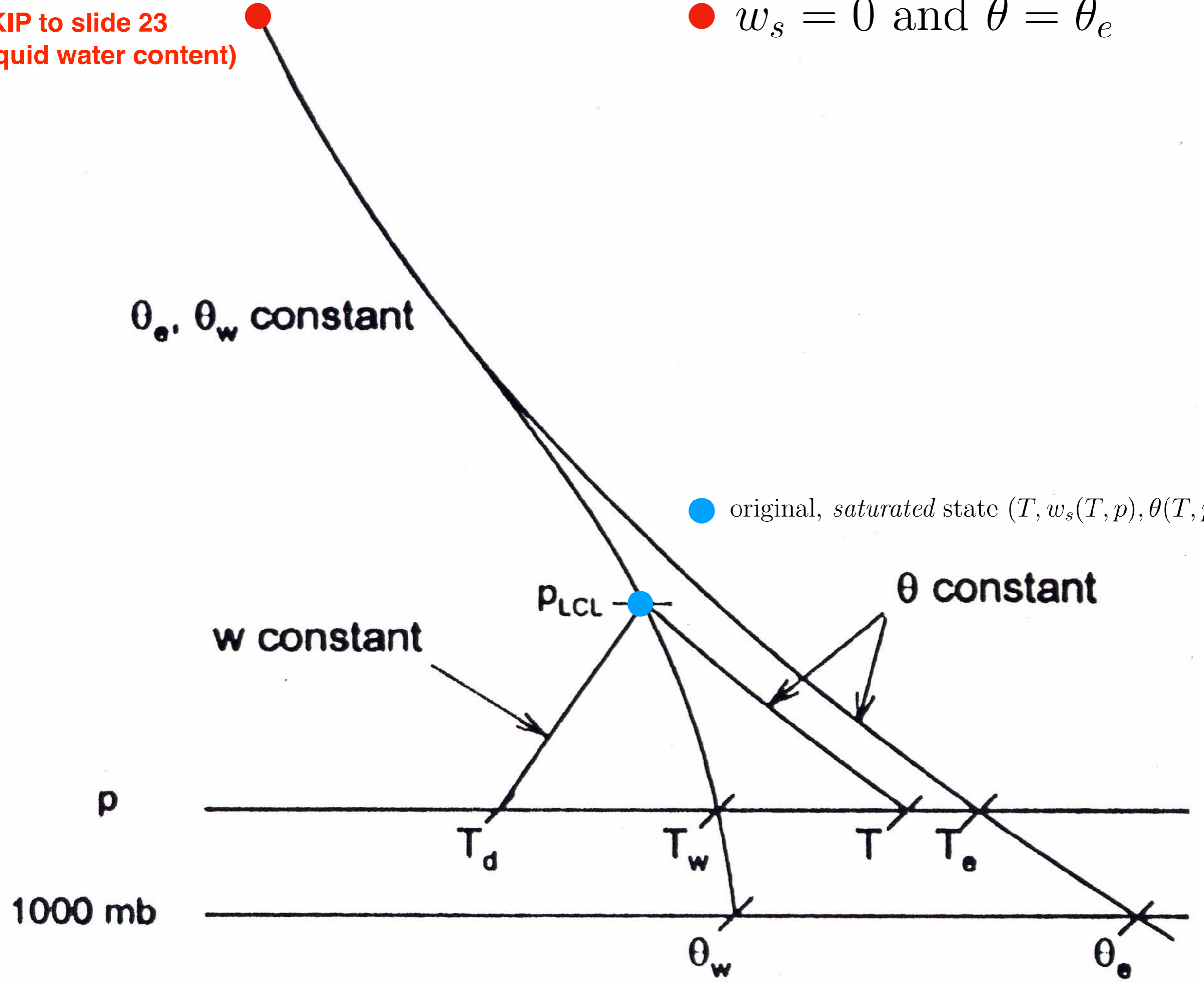*equivalent potential temperature:*

$$\theta_e = \theta \exp(Lw_s/c_pT). \tag{31}$$

SKIP to slide 23
(liquid water content)

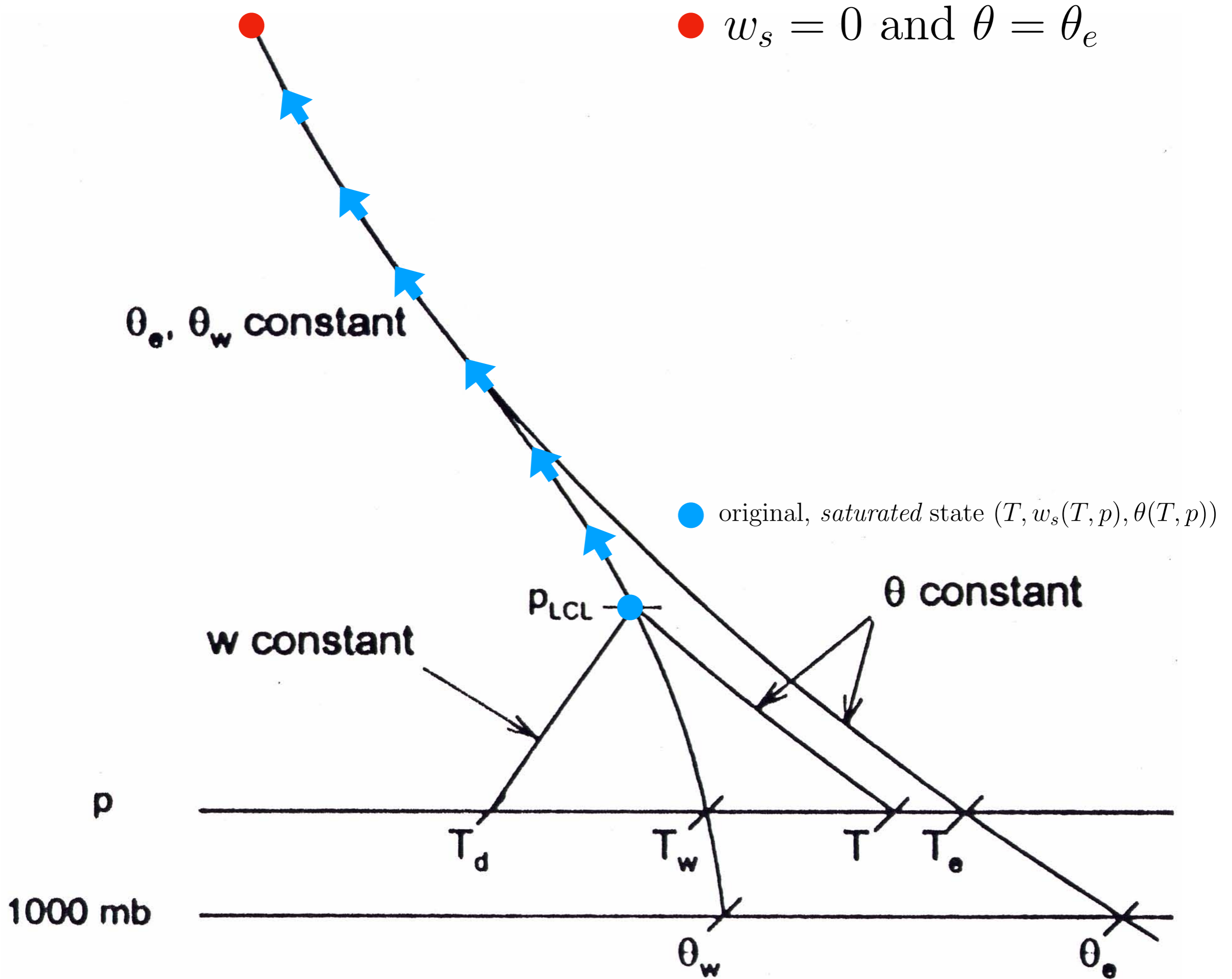● $w_s = 0$ and $\theta = \theta_e$

θ_e, θ_w constant

● original, *saturated* state $(T, w_s(T, p), \theta(T, p))$

p_{LCL}

w constant

θ constant

p

T_d T_w T T_e

1000 mb

θ_w θ_e

$w_s = 0$ and $\theta = \theta_e$

θ_e, θ_w constant

original, *saturated* state $(T, w_s(T,p), \theta(T,p))$

θ constant

p_{LCL}

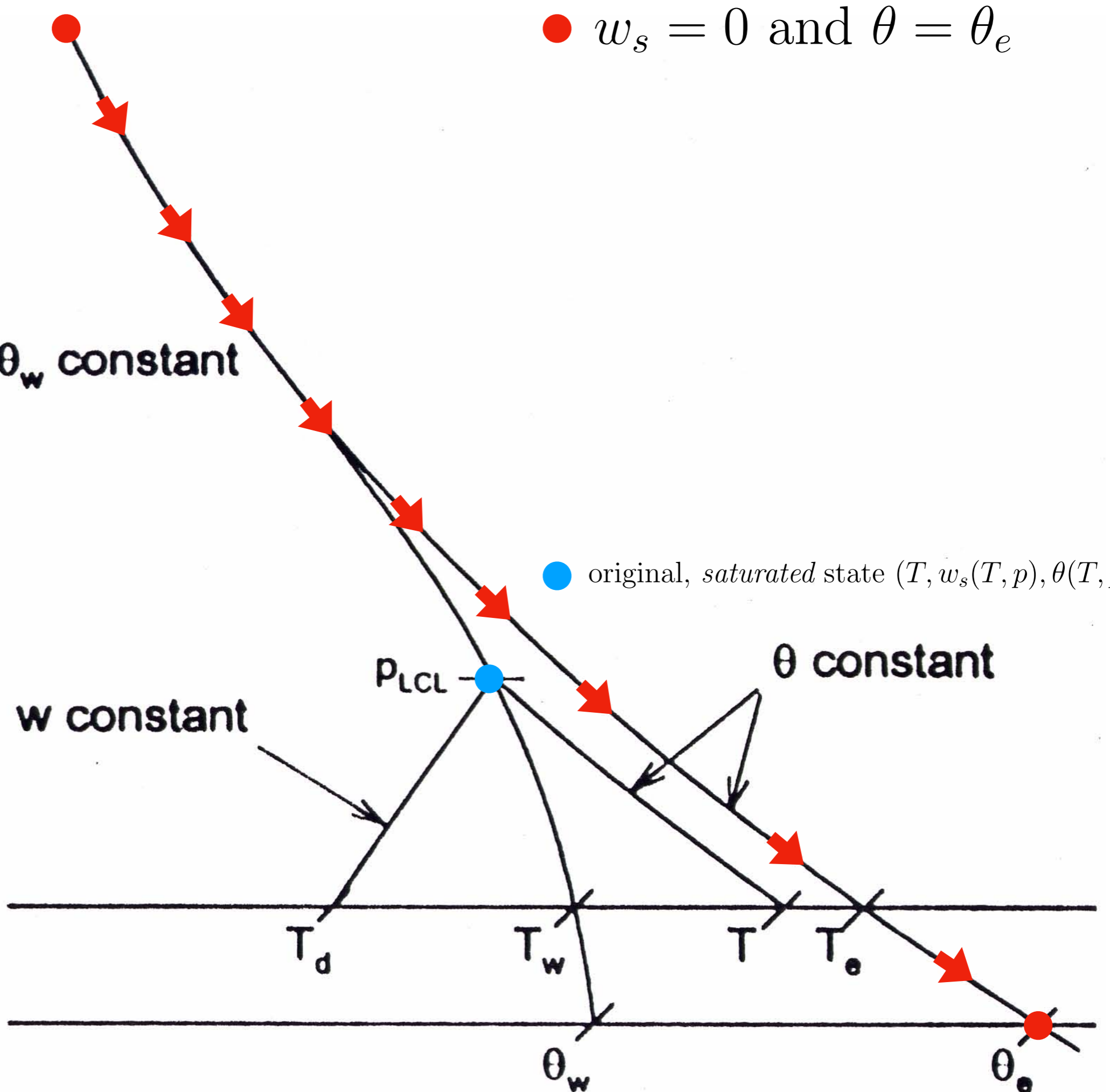w constant

p

T_d T_w T T_e

1000 mb

θ_w θ_e

5.7　More moisture variables

The thermodynamic processes that define the following four variables are easily visualized on a a skew T-log p diagram, as shown in Fig. 7.

Equivalent potential temperature, θ_e　The potential temperature of a parcel that has ascended pseudo-adiabatically until all water vapor has been condensed. Eq. (31):

$$\theta_e = \theta \exp(Lw_s/c_pT) \approx \theta + Lw_s/c_p.$$

5.7   More moisture variables

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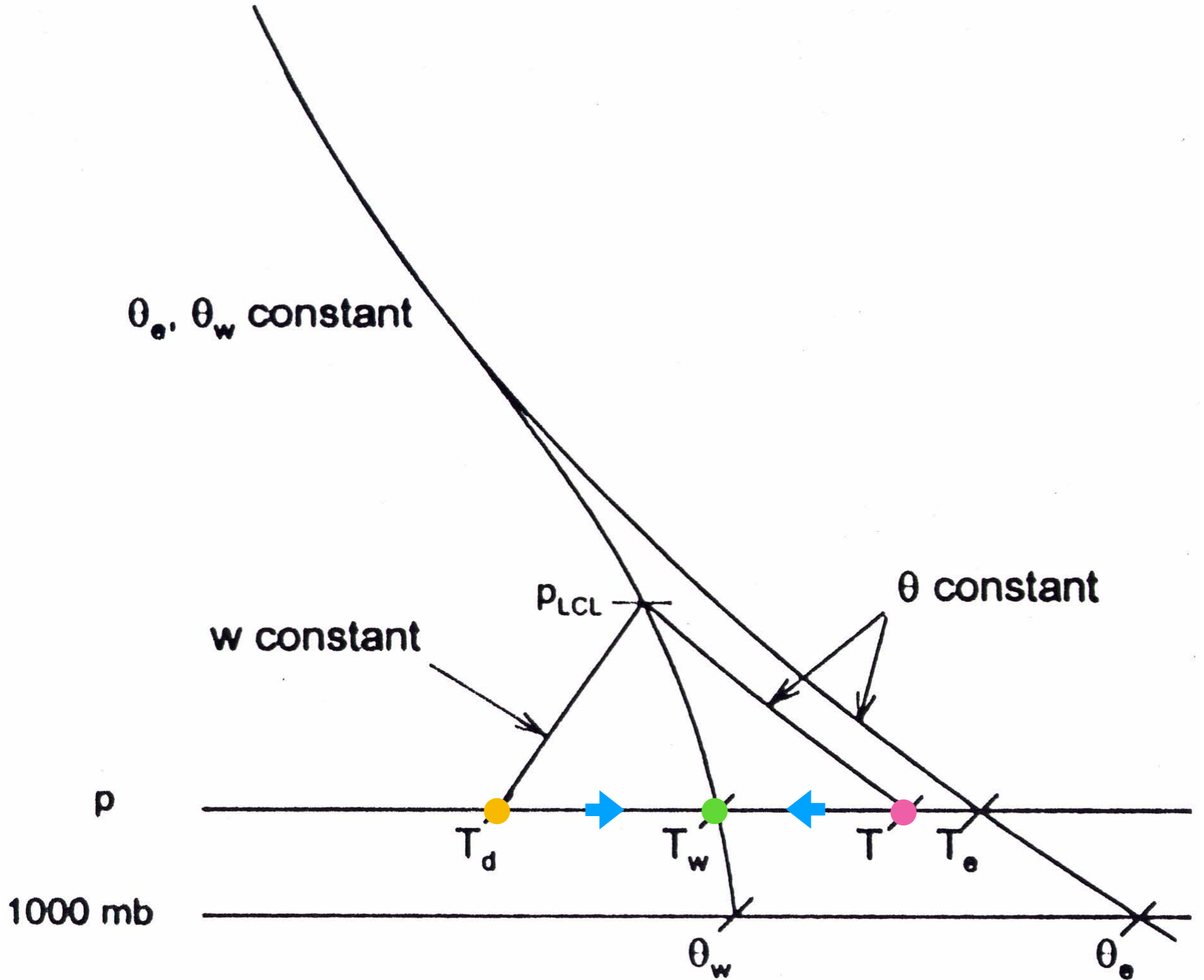are easily visualized on a a skew T-log p diagram, as shown in Fig. 7.

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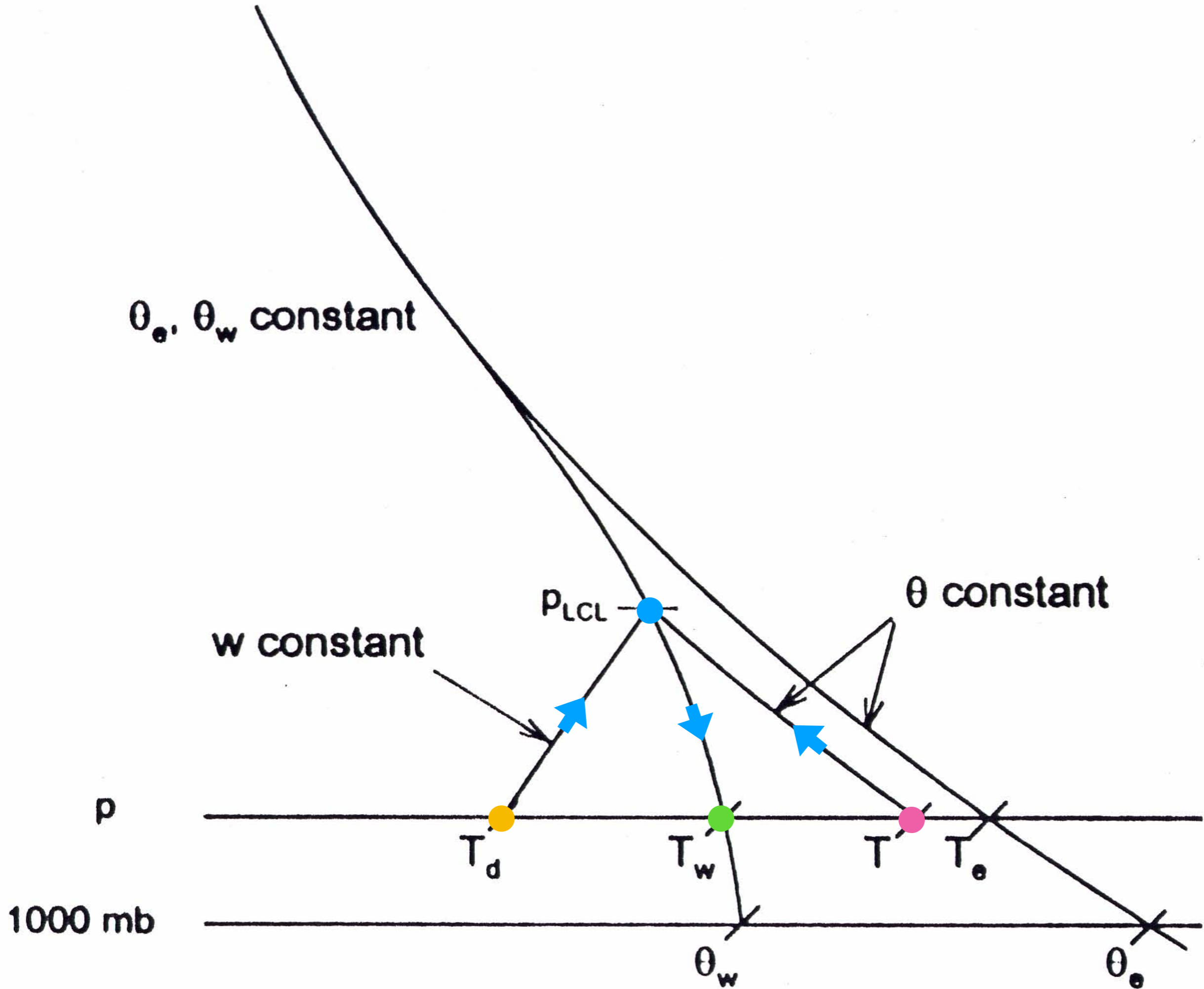
$$\theta_e = \theta \exp(Lw_s/c_pT) \approx \theta + Lw_s/c_p.$$

Equivalent temperature, T_e The temperature of a parcel that has
first ascended pseudo-adiabatically until all water vapor has
been condensed, then descended (dry adiabatically) to its
original pressure:

$$T_e = \theta_e \left(\frac{p}{p_0}\right)^{R/c_p} = T \exp(Lw_s/c_pT) \approx T + Lw_s/c_p.$$

Wet-bulb temperature, T_w (i) The temperature of a parcel that has been isobarically cooled by evaporation until saturated. (ii) The temperature of a parcel that has first ascended dry adiabatically to its LCL, then descended moist (saturated) adiabatically to its original pressure.

θ_e, θ_w constant

θ constant

p_{LCL}

w constant

p

1000 mb

T_d

T_w

T

T_e

θ_w

θ_e

θ_e, θ_w constant

θ constant

p_{LCL}

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T_d

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θ_w

θ_e

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Wet-bulb potential temperature, θ_w (i) The temperature of a parcel that has first been isobarically cooled by evaporation until saturated, then descended moist (saturated) adiabatically to 1000 hPa. (ii) The temperature of a parcel that has first ascended dry adiabatically to its LCL, then descended moist (saturated) adiabatically to 1000 hPa.

θ_e, θ_w constant

θ constant

p_{LCL}

w constant

p

T_d

T_w

T

T_e

1000 mb

θ_w

θ_e
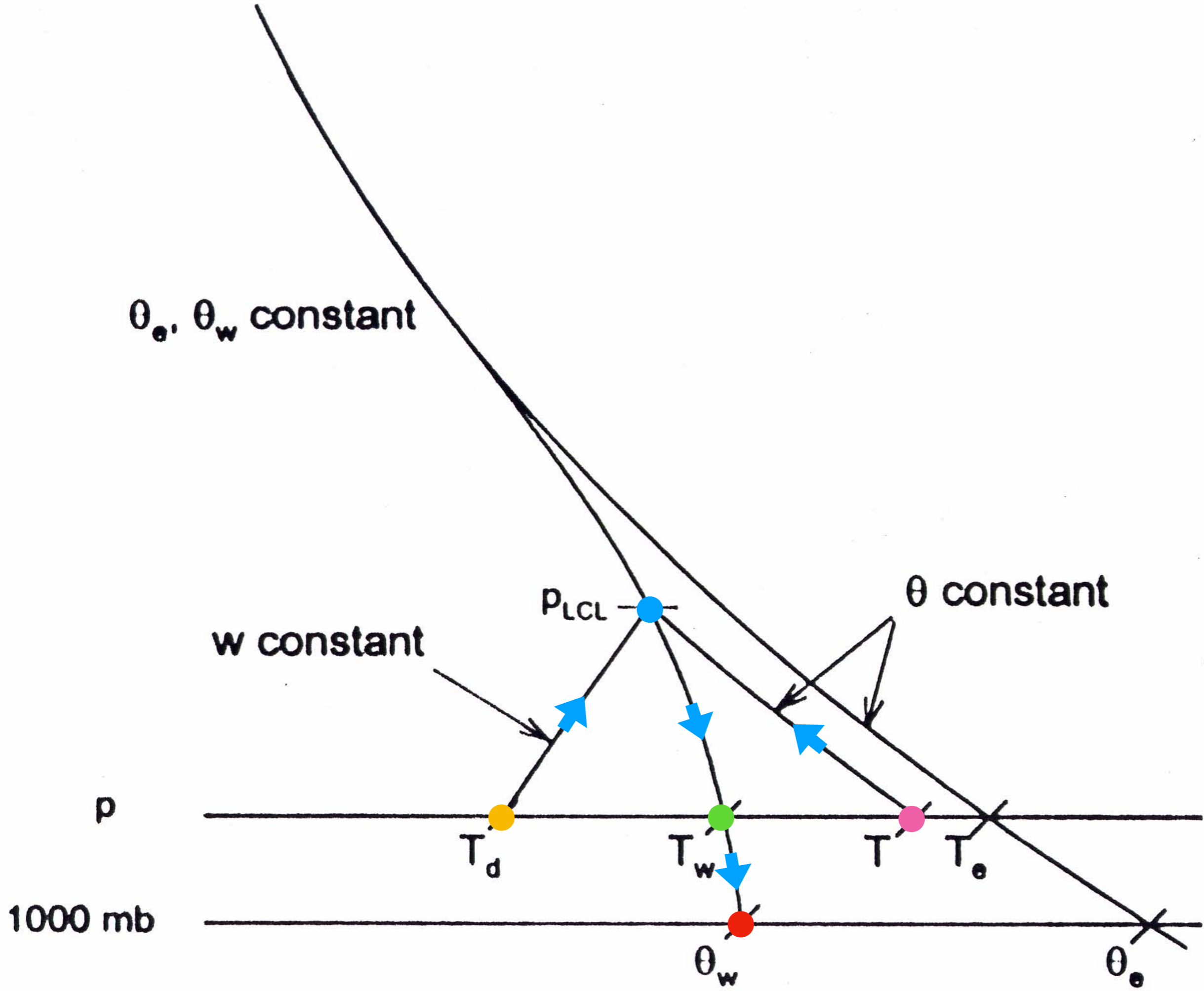
Liquid water mixing ratio, w_l The mass of liquid water (droplets) per unit mass of dry air.

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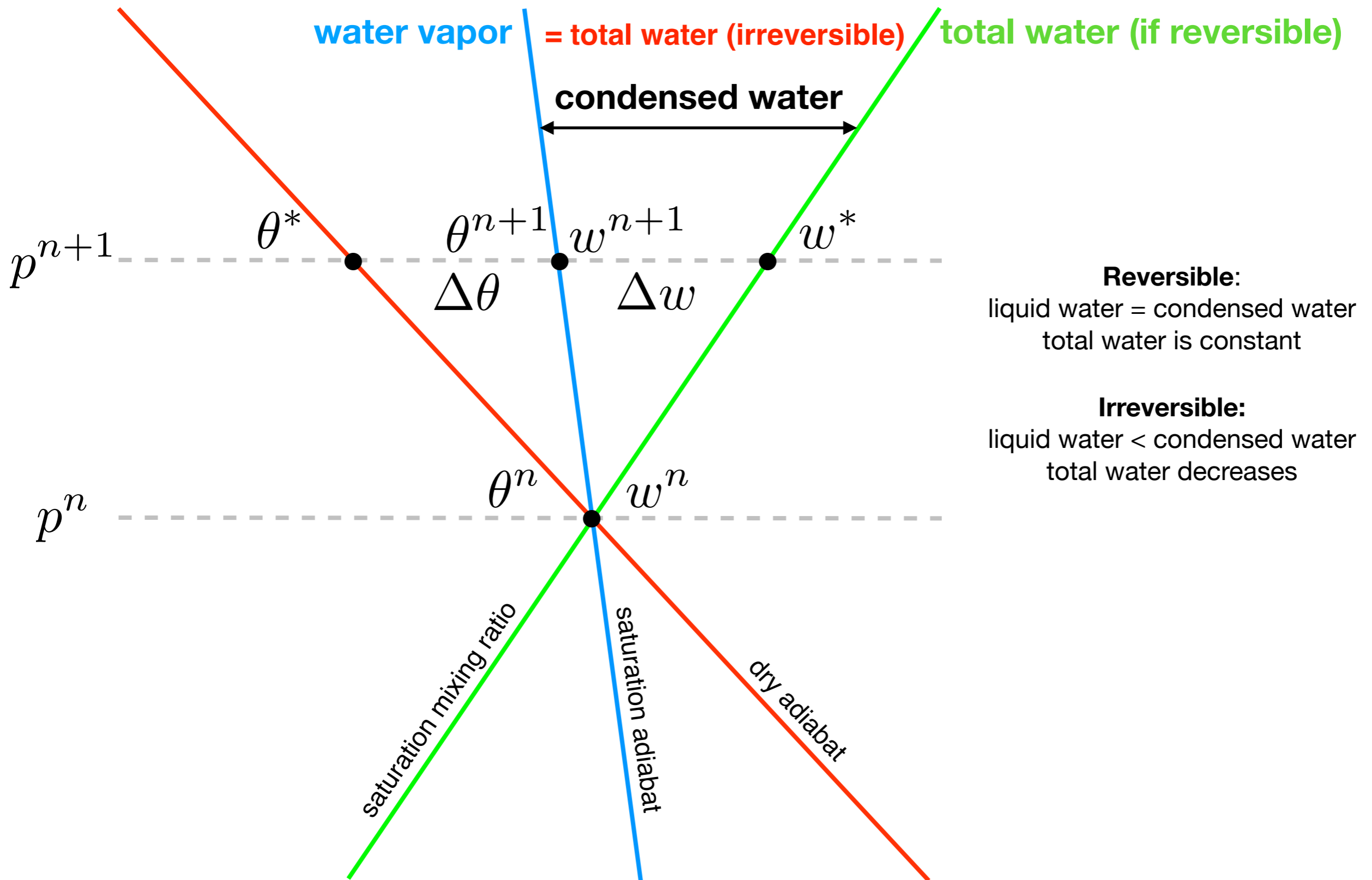
- During a *reversible* process, the *total water mixing ratio* $(w_t = w + w_l)$ in a parcel remains constant.

- During a *pseudo-adiabatic* process, any condensed water immediately falls out of the parcel (as precipitation) so that the *liquid water mixing ratio* (w_l) is always zero.

Saturated Adiabatic Ascent

water vapor = total water (irreversible) total water (if reversible)

condensed water

p^{n+1} θ^* θ^{n+1} w^{n+1} w^*

$\Delta\theta$ Δw

θ^n w^n

p^n

saturation mixing ratio

saturation adiabat

dry adiabat

Reversible:
liquid water = condensed water
total water is constant

Irreversible:
liquid water < condensed water
total water decreases

- Naturally occurring processes are usually neither exactly reversible nor pseudo-adiabatic, but somewhere in between:

  Some, but not all, of the condensed water falls out of the parcel as precipitation so that the *liquid water mixing ratio* may be greater than zero, but the *total water mixing ratio* is reduced by the loss due to precipitation.

- Naturally occurring processes are usually neither exactly reversible nor pseudo-adiabatic, but somewhere in between:

  Some, but not all, of the condensed water falls out of the parcel as precipitation so that the *liquid water mixing ratio* may be greater than zero, but the *total water mixing ratio* is reduced by the loss due to precipitation.

- Given the *total water mixing ratio,* one can then determine the remaining unknown mixing ratios:

  – We will assume that the parcel is either exactly saturated, or unsaturated with no liquid water.

  – If a parcel is exactly saturated: $w = w_s(T, p)$, so $w_l = w_t - w_s(T, p)$.

  – If a parcel is unsaturated with no liquid water: $w_l = 0$, so $w = w_t$.