

So we can begin total entropy of a parcel. The entropy of a parcel with contributions from water vapor, liquid, and dry air is as follows

$$S = S_d M_d + S_v M_v + S_l M_l \quad (1)$$

Taking the time derivative of equation 1

$$\frac{dS}{dt} = S_d \frac{dM_d}{dt} + M_d \frac{dS_d}{dt} + S_v \frac{dM_v}{dt} + M_v \frac{dS_v}{dt} + S_l \frac{dM_l}{dt} + M_l \frac{dS_l}{dt} \quad (2)$$

Assume that the change of water vapor is equivalent to the the change of liquid and vice versa (i.e., reversible process).

$$\frac{dM_v}{dt} = -\frac{dM_l}{dt} \quad (3)$$

The entropy change between the phase change is as follows

$$\begin{aligned} L_v &= T(S_v - S_l) \\ \frac{L_v}{T} &= S_v - S_l \end{aligned} \quad (4)$$

Subbing equations 3 and 4 we can find the following

$$\begin{aligned} \frac{dS}{dt} &= S_d \frac{dM_d}{dt} + M_d \frac{dS_d}{dt} + S_v \frac{dM_v}{dt} + M_v \frac{dS_v}{dt} + S_l \frac{dM_l}{dt} + M_l \frac{dS_l}{dt} \\ &= S_d \frac{dM_d}{dt} + M_d \frac{dS_d}{dt} + S_v \frac{dM_v}{dt} + M_v \frac{dS_v}{dt} - S_l \frac{dM_v}{dt} + M_l \frac{dS_l}{dt} \\ &= S_d \frac{dM_d}{dt} + M_d \frac{dS_d}{dt} + M_v \frac{dS_v}{dt} + \frac{L_v}{T} \frac{dM_v}{dt} + M_l \frac{dS_l}{dt} \end{aligned} \quad (5)$$

Assume there is no change of dry air with time in the parcel ($\frac{dM_d}{dt} = 0$)

$$\frac{dS}{dt} = M_d \frac{dS_d}{dt} + M_v \frac{dS_v}{dt} + \frac{L_v}{T} \frac{dM_v}{dt} + M_l \frac{dS_l}{dt} \quad (6)$$

Change in Entropy of Dry Air

The entropy of dry air is as follows

$$S_d = c_{pd} \ln T - R_d \ln P_d \quad (7)$$

Taking the time derivative of equation 7

$$\frac{dS_d}{dt} = c_{pd} \frac{1}{T} \frac{dT}{dt} - R_d \frac{1}{P_d} \frac{dP_d}{dt} \quad (8)$$

Change in Entropy of Water Vapor

The entropy of water vapor is as follows

$$S_v = c_{pv} \ln T - R_v \ln e \quad (9)$$

Taking the time derivative of equation 9

$$\frac{dS_v}{dt} = c_{pv} \frac{1}{T} \frac{dT}{dt} - R_v \frac{1}{e} \frac{de}{dt} \quad (10)$$

Change in Entropy of Liquid

The entropy of liquid water is as follows

$$S_l = c_l \ln T \quad (11)$$

Taking the time derivative of equation 11

$$\frac{dS_l}{dt} = c_l \frac{1}{T} \frac{dT}{dt} \quad (12)$$

Putting them together

Now subbing equations 8, 10, and 12 into equation 6

$$\begin{aligned} \frac{dS}{dt} &= M_d \frac{dS_d}{dt} + M_v \frac{dS_v}{dt} + \frac{L_v}{T} \frac{dM_v}{dt} + M_l \frac{dS_l}{dt} \\ &= M_d \left(c_{pd} \frac{1}{T} \frac{dT}{dt} - R_d \frac{1}{P_d} \frac{dP_d}{dt} \right) + M_v \left(c_{pv} \frac{1}{T} \frac{dT}{dt} - R_d \frac{1}{e} \frac{de}{dt} \right) + \frac{L_v}{T} \frac{dM_v}{dt} + M_l c_l \frac{1}{T} \frac{dT}{dt} \\ &= (M_d c_{pd} + M_v c_{pv} + M_l c_l) \frac{1}{T} \frac{dT}{dt} - \frac{M_d R_d}{P_d} \frac{dP_d}{dt} - \frac{R_v M_v}{e} \frac{de}{dt} + \frac{L_v}{T} \frac{dM_v}{dt} \end{aligned} \quad (13)$$

Now we can define the total mass of water and the change of enthalpy via Kirchoffs relations between vapor and liquid phases.

$$M_{H_2O} = M_v + M_l \quad (14)$$

$$\begin{aligned} \frac{dL_v}{dT} &= c_{pv} - c_l \\ c_{pv} &= \frac{dL_v}{dT} + c_l \end{aligned} \quad (15)$$

Subbing equations 14 and 15 into equation 13

$$\begin{aligned} \frac{dS}{dt} &= \left(M_d c_{pd} + M_v \left(\frac{dL_v}{dT} + c_l \right) + M_l c_l \right) \frac{1}{T} \frac{dT}{dt} - \frac{M_d R_d}{P_d} \frac{dP_d}{dt} - \frac{R_v M_v}{e} \frac{de}{dt} + \frac{L_v}{T} \frac{dM_v}{dt} \\ &= \left(M_d c_{pd} + M_{H_2O} c_l + M_v \frac{dL_v}{dT} \right) \frac{1}{T} \frac{dT}{dt} - \frac{M_d R_d}{P_d} \frac{dP_d}{dt} - \frac{R_v M_v}{e} \frac{de}{dt} + \frac{L_v}{T} \frac{dM_v}{dt} \\ &= (M_d c_{pd} + M_{H_2O} c_l) \frac{1}{T} \frac{dT}{dt} + M_v \frac{dL_v}{dT} \frac{1}{T} \frac{dT}{dt} - \frac{M_d R_d}{P_d} \frac{dP_d}{dt} - \frac{R_v M_v}{e} \frac{de}{dt} + \frac{L_v}{T} \frac{dM_v}{dt} \\ &= (M_d c_{pd} + M_{H_2O} c_l) \frac{1}{T} \frac{dT}{dt} + \frac{M_v}{T} \frac{dL_v}{dT} - \frac{M_d R_d}{P_d} \frac{dP_d}{dt} - \frac{R_v M_v}{e} \frac{de}{dt} + \frac{L_v}{T} \frac{dM_v}{dt} \end{aligned} \quad (16)$$

Relative Humidity and Water Vapor

Now we can define the parcel's water vapor as having some sort of relative humidity with respect to saturation vapor pressure. Then, we will take the time derivative of this relation. Finally, we

will expand the derivative of saturation vapor pressure to accomodate changes in temperature.

$$\begin{aligned}
 H_l &= \frac{e}{e_s} \\
 e &= e_s H_l \\
 \frac{de}{dt} &= H_l \frac{de_s}{dt} + e_s \frac{dH_l}{dt} \\
 &= H_l \frac{de_s}{dT} \frac{dT}{dt} + e_s \frac{dH_l}{dt}
 \end{aligned} \tag{17}$$

Since we know the Clausius-Clayperon relation, we can place this into equation 17

$$\begin{aligned}
 \frac{1}{e_s} \frac{de_s}{dT} &= \frac{L_v}{R_v T^2} \\
 \frac{de_s}{dT} &= \frac{e_s L_v}{R_v T^2} \\
 \frac{de}{dt} &= H_l \frac{de_s}{dT} \frac{dT}{dt} + e_s \frac{dH_l}{dt} \\
 &= H_l \frac{e_s L_v}{R_v T^2} \frac{dT}{dt} + e_s \frac{dH_l}{dt}
 \end{aligned} \tag{18}$$

Accounting for Saturation

Now we can sub in equation 18 into 16

$$\begin{aligned}
 \frac{dS}{dt} &= (M_d c_{pd} + M_{H_2O} c_l) \frac{1}{T} \frac{dT}{dt} + \frac{M_v}{T} \frac{dL_v}{dt} - \frac{M_d R_d}{P_d} \frac{dP_d}{dt} - \frac{R_v M_v}{e} \left(H_l \frac{e_s L_v}{R_v T^2} \frac{dT}{dt} + e_s \frac{dH_l}{dt} \right) + \frac{L_v}{T} \frac{dM_v}{dt} \\
 &= (M_d c_{pd} + M_{H_2O} c_l) \frac{1}{T} \frac{dT}{dt} + \frac{M_v}{T} \frac{dL_v}{dt} - \frac{M_d R_d}{P_d} \frac{dP_d}{dt} - \frac{R_v M_v}{e} H_l \frac{e_s L_v}{R_v T^2} \frac{dT}{dt} - \frac{R_v M_v}{e} e_s \frac{dH_l}{dt} + \frac{L_v}{T} \frac{dM_v}{dt} \\
 &= (M_d c_{pd} + M_{H_2O} c_l) \frac{1}{T} \frac{dT}{dt} + \frac{M_v}{T} \frac{dL_v}{dt} - \frac{M_d R_d}{P_d} \frac{dP_d}{dt} - \frac{M_v L_v}{T^2} \frac{dT}{dt} - \frac{R_v M_v}{H_l} \frac{dH_l}{dt} + \frac{L_v}{T} \frac{dM_v}{dt}
 \end{aligned} \tag{19}$$

In equation 19, we can see the following from a chain rule...

$$\frac{d}{dt} \left(\frac{M_v L_v}{T} \right) = \frac{M_v}{T} \frac{dL_v}{dt} - \frac{M_v L_v}{T^2} \frac{dT}{dt} + \frac{L_v}{T} \frac{dM_v}{dt} \tag{20}$$

Subbing in equation 20 into 19

$$\frac{dS}{dt} = (M_d c_{pd} + M_{H_2O} c_l) \frac{1}{T} \frac{dT}{dt} + \frac{d}{dt} \left(\frac{M_v L_v}{T} \right) - \frac{M_d R_d}{P_d} \frac{dP_d}{dt} - \frac{R_v M_v}{H_l} \frac{dH_l}{dt} \tag{21}$$

Now divide equation 21 by the mass of dry air to yield mixing ratios.

$$\begin{aligned}
 \frac{1}{M_d} \frac{dS}{dt} &= (c_{pd} + r_t c_l) \frac{1}{T} \frac{dT}{dt} + \frac{d}{dt} \left(\frac{r_v L_v}{T} \right) - \frac{R_d}{P_d} \frac{dP_d}{dt} - \frac{r_v R_v}{H_l} \frac{dH_l}{dt} \\
 r_v &= \frac{M_v}{M_d} \\
 r_t &= \frac{M_{H_2O}}{M_d}
 \end{aligned} \tag{22}$$

Adding in a Type of Potential Temperature

Now define a new potential temperature (derivation elsewhere) for dry air with an adjustment for the specific heat.

$$\theta_d = T \left(\frac{P_{sfc}}{P_d} \right)^{\kappa^*} \quad (23)$$

$$\kappa^* = \frac{R_d}{c_{pd} + r_t c_l}$$

Now taking the natural log of both sides and then taking time derivative of equation 23

$$\begin{aligned} \ln(\theta_d) &= \ln \left(T \left(\frac{P_{sfc}}{P_d} \right)^{\kappa^*} \right) \\ &= \ln(T) + \kappa^* (\ln(P_{sfc}) - \ln(P_d)) \\ \frac{d(\ln(\theta_d))}{dt} &= \frac{1}{T} \frac{dT}{dt} + \kappa^* \left(\frac{1}{P_{sfc}} \frac{dP_{sfc}}{dt} - \frac{1}{P_d} \frac{dP_d}{dt} \right) \\ \frac{1}{\theta_d} \frac{d\theta_d}{dt} &= \frac{1}{T} \frac{dT}{dt} - \kappa^* \frac{1}{P_d} \frac{dP_d}{dt} \end{aligned} \quad (24)$$

Multiply both sides of equation 24 by the specific heat and rearrange for the temperature derivative

$$\begin{aligned} (c_{pd} + r_t c_l) \frac{1}{\theta_d} \frac{d\theta_d}{dt} &= (c_{pd} + r_t c_l) \frac{1}{T} \frac{dT}{dt} - \frac{R_d}{P_d} \frac{dP_d}{dt} \\ (c_{pd} + r_t c_l) \frac{1}{T} \frac{dT}{dt} &= (c_{pd} + r_t c_l) \frac{1}{\theta_d} \frac{d\theta_d}{dt} + \frac{R_d}{P_d} \frac{dP_d}{dt} \end{aligned} \quad (25)$$

Putting it all together

Now substitute in equation 25 into equation 22

$$\begin{aligned} \frac{1}{M_d} \frac{dS}{dt} &= (c_{pd} + r_t c_l) \frac{1}{\theta_d} \frac{d\theta_d}{dt} + \frac{R_d}{P_d} \frac{dP_d}{dt} + \frac{d}{dt} \left(\frac{r_v L_v}{T} \right) - \frac{R_d}{P_d} \frac{dP_d}{dt} - \frac{r_v R_v}{H_l} \frac{dH_l}{dt} \\ &= (c_{pd} + r_t c_l) \frac{1}{\theta_d} \frac{d\theta_d}{dt} + \frac{d}{dt} \left(\frac{r_v L_v}{T} \right) - \frac{r_v R_v}{H_l} \frac{dH_l}{dt} \end{aligned} \quad (26)$$

Now during the time of our parcel we can assume a reversible process, which implies that total entropy of a parcel is conserved.

$$\frac{dS}{dt} = 0 \quad (27)$$

Substituting equation 27 into 26

$$0 = (c_{pd} + r_t c_l) \frac{1}{\theta_d} \frac{d\theta_d}{dt} + \frac{d}{dt} \left(\frac{r_v L_v}{T} \right) - \frac{r_v R_v}{H_l} \frac{dH_l}{dt} \quad (28)$$

Now we can see the relationship between the three values.

$$\begin{aligned} 0 &= (c_{pd} + r_t c_l) \frac{d\theta_d}{\theta_d} + d \left(\frac{r_v L_v}{T} \right) - \frac{r_v R_v}{H_l} dH_l \\ - (c_{pd} + r_t c_l) \frac{d\theta_d}{\theta_d} &= d \left(\frac{r_v L_v}{T} \right) - \frac{r_v R_v}{H_l} dH_l \end{aligned} \quad (29)$$

Now we can integrate this relationship in equation 29.

$$\begin{aligned}
0 &= (c_{pd} + r_t c_l) \frac{d\theta_d}{\theta_d} + d \left(\frac{r_v L_v}{T} \right) - \frac{r_v R_v}{H_l} dH_l \\
&- (c_{pd} + r_t c_l) \int_{\theta_{d,s}}^{\theta_{d,f}} \frac{d\theta_d}{\theta_d} = \int_{T_s}^{T_f} d \left(\frac{r_v L_v}{T} \right) - \int_{H_{l,s}}^{H_{l,f}} \frac{r_v R_v}{H_l} dH_l \\
&- (c_{pd} + r_t c_l) (\ln(\theta_{d,f}) - \ln(\theta_{d,s})) = \left(\frac{r_{v,f} L_v(T_f)}{T_f} - \frac{r_{v,s} L_v(T_s)}{T_s} \right) - (r_{v,f} R_v \ln(H_{l,f}) - r_{v,s} R_v \ln(H_{l,s})) \\
&(c_{pd} + r_t c_l) \ln \left(\frac{\theta_{d,f}}{\theta_{d,s}} \right) = - \left(\frac{r_{v,f} L_v(T_f)}{T_f} - \frac{r_{v,s} L_v(T_s)}{T_s} \right) + (r_{v,f} R_v \ln(H_{l,f}) - r_{v,s} R_v \ln(H_{l,s}))
\end{aligned} \tag{30}$$

Now in equation 30, we should assume that at final temperature is what the parcel would be if all of the water vapor would be instantly condensed, but no fallout. This implies the following

$$r_{v,f} = 0 \tag{31}$$

Placing this assumption into equation 30

$$\begin{aligned}
(c_{pd} + r_t c_l) \ln \left(\frac{\theta_{d,f}}{\theta_{d,s}} \right) &= - \left(\frac{0 L_v(T_f)}{T_f} - \frac{r_{v,s} L_v(T_s)}{T_s} \right) + (0 R_v \ln(H_{l,f}) - r_{v,s} R_v \ln(H_{l,s})) \\
(c_{pd} + r_t c_l) \ln \left(\frac{\theta_{d,f}}{\theta_{d,s}} \right) &= \frac{r_{v,s} L_v(T_s)}{T_s} - r_{v,s} R_v \ln(H_{l,s}) \\
\ln \left(\frac{\theta_{d,f}}{\theta_{d,s}} \right) &= \frac{r_{v,s} L_v(T_s)}{(c_{pd} + r_t c_l) T_s} - \frac{r_{v,s} R_v}{(c_{pd} + r_t c_l)} \ln(H_{l,s})
\end{aligned} \tag{32}$$

If we define the temperature, relative humidity, moisture content and dry potential temperature at the level of the parcel, then we find the equivalent potential temperature

$$\begin{aligned}
\left(\frac{\theta_e}{\theta_d} \right) &= e^{\frac{r_{v,s} L_v(T_s)}{(c_{pd} + r_t c_l) T_s} - \frac{r_{v,s} R_v}{(c_{pd} + r_t c_l)}} H_{l,s} \\
\theta_e &= \theta_d e^{\frac{r_v L_v(T)}{(c_{pd} + r_t c_l) T} - \frac{r_v R_v}{(c_{pd} + r_t c_l)}} H_l \\
&= T \left(\frac{P_{sf} c}{P_d} \right)^{\frac{R_d}{c_{pd} + r_t c_l}} e^{\frac{r_v L_v(T)}{(c_{pd} + r_t c_l) T} - \frac{r_v R_v}{(c_{pd} + r_t c_l)}} H_l
\end{aligned} \tag{33}$$