

Thermodynamics

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Miscellaneous

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Ideal gas law

$$pV = nR^*T \quad (1)$$

where R^* = universal gas constant. Divided by the mass M of the gas:

$$p \frac{V}{M} = p\alpha = \frac{n}{M} R^* T = \frac{1}{m} R^* T \quad (2)$$

where m = molecular weight, α = specific volume, n = number of moles.
With $\rho = \frac{1}{\alpha}$ = air density and $R_d = \frac{R^*}{m_d}$ = gas constant for dry air (287 J kg⁻¹ K⁻¹) and $m_d = 28.96$ g/mole:

$$\frac{p}{\rho} = R_d T \quad (3)$$

And for water vapor:

$$\frac{e}{\rho_v} = R_v T \quad (4)$$

where e = water vapor pressure, $R_v = 461.5$ J kg⁻¹ K⁻¹

Further gas laws

Dalton's law: total pressure = sum of individual partial pressures. Each partial pressure obeys the ideal gas law. Partial pressure of a gas is the pressure it would exert at the same temperature as the mixture if it alone occupied the volume that the mixture occupies. Physical assumption of ideal gases:

- ▶ volume of molecule can be neglected
- ▶ no intermolecular forces (besides collisions)
- ▶ the atmosphere behaves as ideal gas to better than 0.2%
- ▶ breakdown of ideal behavior above 100 km (ionic interactions and breakdown of the local thermodynamic equilibrium)



First law of thermodynamics

- ▶ Heat is a form of energy
- ▶ Energy is conserved

Internal energy u = kinetic and potential energy of a body's molecules or atoms (as opposed to macroscopic kinetic and potential energy). For gases such as air, it's proportional to T .

- ▶ Body of unit mass takes in a certain quantity of heat energy (q) through either thermal conduction or radiation.
- ▶ Body may do a certain amount of external work (w)
- ▶ Excess of energy supplied to body above the external work done is $q - w$
- ▶ If macroscopic kinetic and potential energy of the body remains constant than u must increase by $q-w$

$$dq = du + dw \tag{5}$$



Specific heat

- ▶ work done per unit mass of gas is

$$dw = p d\alpha \tag{6}$$

- ▶ small quantity of heat dq is given to a unit mass of material, so that temp. increases by dT without phase changes. Define the ratio dq/dT = specific heat of the material

$$dq = cdT \tag{7}$$

- ▶ For a gas, c is not constant, but depends upon whether work is done while heat is added. If no work is done, $d\alpha = 0 \rightarrow$

$$c_v = \left(\frac{dq}{dT} \right)_\alpha = \left(\frac{du}{dT} \right)_\alpha \tag{8}$$

where c_v = specific heat at constant volume. If $p = \text{const}$, then

- ▶
- $$c_p = \left(\frac{dq}{dT} \right)_p \tag{9}$$

where c_p = specific heat at constant pressure



First law of thermodynamics

- ▶ $c_p > c_v$, because in a constant pressure process the material is allowed to expand. Thus some added heat will be used in the work term $p d\alpha$, while in the constant volume process all added heat increases T. For dry air:

$$c_p = 1005 \text{ J kg}^{-1} \text{ K}^{-1} \quad (10)$$

$$c_v = 718 \text{ J kg}^{-1} \text{ K}^{-1} \quad (11)$$

- ▶ Of the total heat added, the amount that goes into the internal energy is:

$$du = c_v dT \quad (12)$$

while the rest goes into the work term

First law of thermodynamics

Starting from

$$dq = c_v dT + p d\alpha \quad (13)$$

differentiate the ideal gas law:

$$p d\alpha + \alpha dp = R_d dT \quad (14)$$

so that

$$dq = (c_v + R_d) dT - \alpha dp \quad (15)$$

with $c_p = c_v + R_d$ we get:

$$dq = c_p dT - \alpha dp \quad (16)$$

which is the better form of the 1. law in Atmospheric Science, because T and p can be measured.

Special processes

$$dq = c_p dT - \alpha dp \quad (17)$$

- ▶ isobaric process: $dp = 0 \rightarrow dq = c_p dT$
- ▶ isothermal process: $dT = 0 \rightarrow dq = -\alpha dp = p d\alpha = dw$
- ▶ isochoric process: $d\alpha = 0 \rightarrow dq = c_v dT = du$
- ▶ adiabatic process: $dq = 0 \rightarrow c_p dT = \alpha dp$

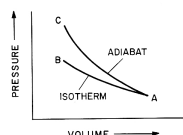


Fig. 2.5 Representation of an isothermal (AB) and an adiabatic (AC) transformation on a p-V diagram.

Adiabatic processes

Adiabatic process (no heat and mass exchange with the environment) is of special significance because many atmospheric processes can be approximated as adiabatic.

From $c_p dT = \alpha dp$ and $\frac{p}{\rho} = R_d T \rightarrow$

$$c_p dT = R_d T \frac{dp}{p} \leftrightarrow \frac{dT}{T} = \frac{R_d}{c_p} \frac{dp}{p} \quad (18)$$

can be integrated to:

$$\frac{T}{T_o} = \left(\frac{p}{p_o} \right)^\kappa \quad (19)$$

where $\kappa = R_d/c_p = 0.286$

With $p_o = 1000$ hPa, define $T_o = \Theta =$ potential temperature (Poisson's equation).

Θ is a conservative quantity for adiabatic transformations

Def: Conserved parameter: Parameter which remains constant during a certain transformation

Entropy

Define entropy:

$$ds = \frac{dq}{T} \quad (20)$$

where ds is the increase in (specific) entropy accompanying the addition of heat to a unit mass of gas at temperature T . Starting from the 1. law (eq 16):

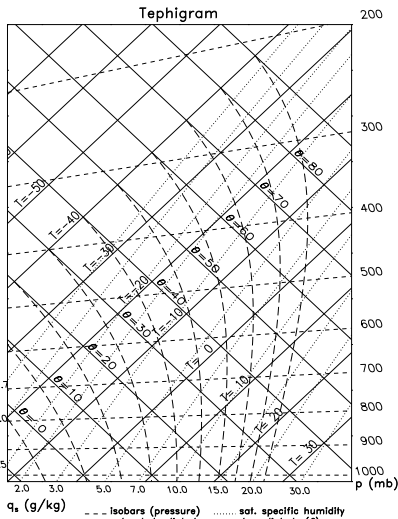
$$ds = \frac{1}{T} [c_p dT - \alpha dp] = c_p \frac{dT}{T} - R_d \frac{dp}{p} = c_p \left[\frac{dT}{T} - \kappa \frac{dp}{p} \right] = c_p \frac{d\Theta}{\Theta} \quad (21)$$

integration gives:

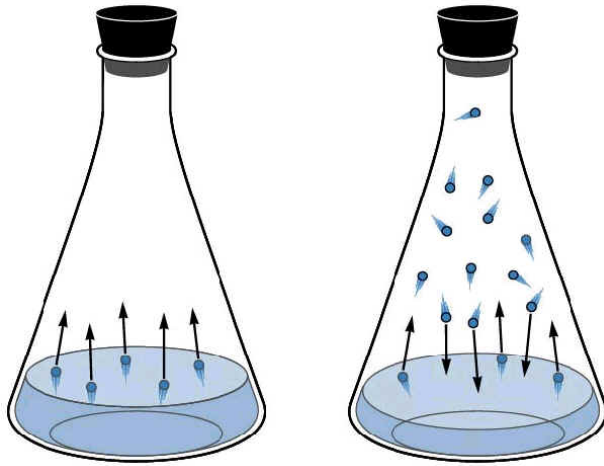
$$s = c_p \ln \Theta + const. \quad (22)$$

which connects entropy with potential temperature. I.e. an adiabatic process ($dq=0$) = isentropic process ($s = const.$).

Tephigram



Vapor pressure



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Clausius-Clapeyron-Equation

(= first latent heat equation for the change in saturation vapor pressure (e_s) above a pure liquid water surface with temperature (T)). Heat is required to change phase from liquid to vapor, because the kinetic energy of the vapor molecules exceeds that of liquid molecules at the same T . **Latent heat** per unit mass at constant T , p is required for transition from phase 1 (liquid) to phase 2 (vapor):

$$L = \int_{q_1}^{q_2} dq = \int_{u_1}^{u_2} du + \int_{\alpha_1}^{\alpha_2} pd\alpha = u_2 - u_1 + e_s(\alpha_2 - \alpha_1) \quad (23)$$

e_s is constant throughout this process. Because T is also constant it follows:

$$L = T \int_{q_1}^{q_2} \frac{dq}{T} = T(s_2 - s_1) \quad (24)$$

where s = entropy. Equating results, we find that:

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Gibbs free energy

$$u_1 + e_s\alpha_1 - Ts_1 = u_2 + e_s\alpha_2 - Ts_2 \quad (25)$$

which shows that this particular combination of thermodynamic variables remains constant in an isothermal, isobaric change of phase. This combination is called the Gibbs function of the system (G):

$$G = u + e_s\alpha - Ts \quad (26)$$

Here $G_1 = G_2$. Though it is constant in the phase transition, G varies with T and p . Determine its dependence on these variables by differentiation:

$$dG = du + e_s d\alpha + \alpha de_s - Tds - sdT \quad (27)$$

but $du + e_s d\alpha = dq = Tds$, (27) reduces to:

$$dG = \alpha de_s - sdT \quad (28)$$

because G is the same for both phases, $dG_1 = dG_2 \rightarrow$

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$$\alpha_1 de_s - s_1 dT = \alpha_2 de_s - s_2 dT \quad (29)$$

$$\frac{de_s}{dT} = \frac{s_2 - s_1}{\alpha_2 - \alpha_1} = \frac{L}{T(\alpha_2 - \alpha_1)} \quad (30)$$

because $\alpha_2 \gg \alpha_1$

$$\frac{de_s}{dT} = \frac{L}{T\alpha_2} = \frac{Le_s}{R_v T^2} \text{ (ideal gas law)} \quad (31)$$

As a first approximation, the Clausius-Clapeyron equation can be integrated by regarding $L \sim \text{constant}$. The result is:

$$\ln \frac{e_s(T)}{e_{s0}} = \frac{L}{R_v} \left(\frac{1}{T_0} - \frac{1}{T} \right) \quad (32)$$

where e_{s0} is 611 Pa at $T_0 = 0^\circ\text{C}$. The latent heat of vaporization near 0°C is approximately $2.5 \cdot 10^6 \text{ J/kg}$. This gives, e.g. the Magnus formula:

$$e_s[\text{hPa}] = 6.107 \exp\left(\frac{17.15(T - 273.16)}{T - 38.25}\right) \quad (33)$$

$$e_{si}[\text{hPa}] = 6.1064 \exp\left(\frac{21.88(T - 273.16)}{T - 7.65}\right) \quad (34)$$

Saturation vapor pressure

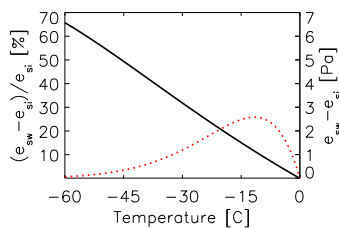
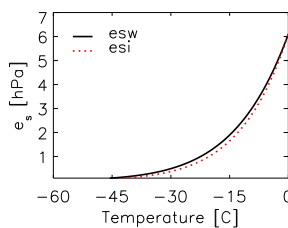
L depends weakly on T , changing by about 6% from -30°C to 30°C . Infer that dependence by noting that L is obtained by:

$$L = u_2 - u_1 + e_s(\alpha_2 - \alpha_1) \quad (35)$$

Table: saturation vapor pressure with respect to water/ice

T (°C)	e_s (Pa)	e_i (Pa)	L_v (J/g)	L_s (J/g)
-40	19.05	12.85	2603	2839
-20	125.63	102.28	2549	2838
0	611.21	611.15	2501	2834
20	2338.5		2453	
40	7381.3		2406	

Saturation vapor pressure



note that $\alpha_2 \gg \alpha_1$ and $e_s \alpha_2 = R_v T$. Differentiate L with respect to temperature

$$\frac{dL}{dT} = \frac{du_2}{dT} - \frac{du_1}{dT} + R_v = c_{vv} - c + R_v = c_{pv} - c \quad (36)$$

where c_{vv} is the specific heat capacity of water vapor at constant volume = $1410 \text{ J kg}^{-1} \text{ K}^{-1}$

c specific heat capacity of liquid water = $4187 \text{ J kg}^{-1} \text{ K}^{-1}$

c_{pv} is the specific heat capacity of water vapor at constant pressure = $1870 \text{ J kg}^{-1} \text{ K}^{-1}$.

Regard c_{vv} , c and c_{pv} as constant. Then

$$L = (c_{pv} - c)(T - T_o) + L_o \quad (37)$$

introduce that into the Clausius-Clapeyron equation and compare the results. c_{pv} varies more slowly with temp. It is only 2% larger at 30°C than at -30°C .

Saturation with respect to ice

for temperatures $< 0^\circ\text{C}$

$$\frac{e_i(T)}{e_{s0}} = \exp \left\{ \frac{L_s}{R_v} \left(\frac{1}{T_o} - \frac{1}{T} \right) \right\}$$

$$\frac{e_s(T)}{e_i(T)} = \exp \left\{ \frac{L_f}{R_v T_o} \left(\frac{T_o}{T} - 1 \right) \right\} \quad (38)$$

in the vicinity of 0°C :

$$\frac{e_s(T)}{e_i(T)} \approx \left(\frac{T_o}{T} \right)^{2.66} \quad (39)$$

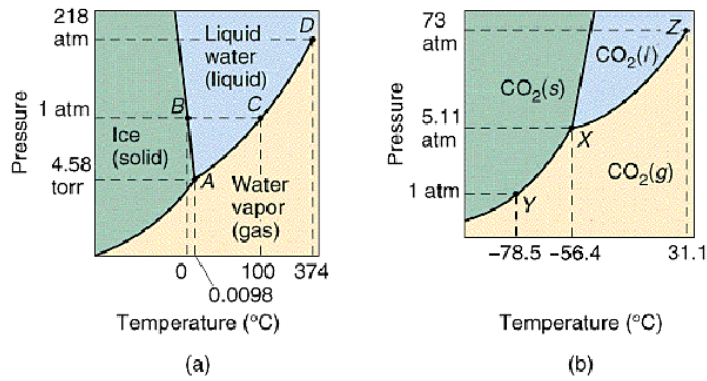
$\rightarrow e_s > e_i$ for $T < 0^\circ\text{C}$. e_s/e_i steadily increases as T decreases.

Any atmosphere saturated with respect to water is supersaturated with respect to ice.

Importance of water vapor

- ▶ water vapor is clear, colorless, odorless gas making up 0 to 4% of surface air
- ▶ water vapor behaves as an ideal gas
- ▶ average water vapor declines rapidly with height; strong sources and sinks near the ground; maximum water vapor strong function of temperature
- ▶ lifetime of water vapor in troposphere about 1 week
- ▶ oceans cover 71% of Earth's surface
- ▶ appears in all three phases
- ▶ large latent heat (phase change energy). Because of the large phase change energies it dominates the energy fluxes in the Earth/atmosphere system.
- ▶ transports heat vertically and poleward - help balance radiative forcing
- ▶ dominant greenhouse gas - emits and absorbs infrared radiation. Water absorbs in all parts of the radiation spectrum with the exception of parts in the visible and in the UV.
- ▶ forms clouds - influences albedo and greenhouse effect
- ▶ needed for agriculture, life \rightarrow hydrological cycle
- ▶ evaporation and precipitation affects ocean salinity - helps drive ocean circulations
- ▶ ice less dense than liquid - hydrogen bonding \rightarrow ice floats on lakes in winter
- ▶ supercooled water can exist in clouds \rightarrow influences precipitation production

Phase diagram for water and carbon dioxide



Phase diagram of water

- ▶ lines are the phase transition curves between phases (at equilibrium)
- ▶ phase transition curves meet at the triple point (273.16K, 6.107 hPa). This is the only condition when all three phases can exist in equilibrium.
- ▶ Phases can coexist at other conditions, but then a net flux is occurring between phases
- ▶ At 1013 hPa, the freezing point is 273.15K (0C). The 0.01K depression is due to the solubility effects of air in water and the external pressure exerted by dry air
- ▶ vapor-liquid transition curve terminates at the critical point (647K, 218.8 atm)
- ▶ note the negative slope of the fusion curve (most substances have a positive slope)
- ▶ ice can be melted by increasing the pressure (skating)
- ▶ also related to ice density being lower than liquid density (ice on top of lakes)

Moist air: its vapor content

- ▶ vapor pressure e = partial pressure of water vapor
- ▶ vapor density ρ_v = absolute humidity
- ▶ mixing ratio w = mass of water vapor per unit mass of dry air

$$w = \frac{\rho_v}{\rho_d} = \frac{\frac{e}{R_v T}}{\frac{p-e}{R_d T}} = \frac{\epsilon e}{p-e} \sim \epsilon \frac{e}{p} \quad (40)$$

where $\epsilon = \frac{R_d}{R_v} = \frac{m_w}{m_d} = 0.622$

- ▶ specific humidity q , mass of water vapor per unit mass of moist air:

$$q = \frac{\rho_v}{\rho} = \frac{\rho_v}{\rho_v + \rho_d} = \frac{\frac{e}{R_v T}}{\frac{p-e}{R_d T} + \frac{e}{R_v T}} = \frac{\epsilon e}{p-e+\epsilon e} \sim \epsilon \frac{e}{p} \quad (41)$$

- ▶ relative humidity

$$f = \frac{w}{w_s(\rho, T)} \sim \frac{e}{e_s} \quad (42)$$

Virtual temperature

- ▶ Is introduced to avoid using a gas constant for moist air because density of moist air is lower than for dry air
- ▶ e.g. mixture of 4% (per volume) of water vapor and 96% dry air
 $m_d=28.96 \text{ g/mole}$, $m_w=18 \text{ g/mole}$, $\rightarrow m_m=28.526 \text{ g/mole}$
 $v \text{ (ideal gases)} = 22.4 \text{ l/mole}$

$$\rho_d = \frac{m}{V} = \frac{M_d}{v} = \frac{28.96 \text{ g/mole}}{22.4 \text{ l/mole}} = 1.29 \text{ g/l} = 1.29 \text{ kg/m}^3 \quad (43)$$

$$\rho_m = \frac{m}{V} = \frac{M_m}{v} = \frac{28.53 \text{ g/mole}}{22.4 \text{ l/mole}} = 1.27 \text{ g/l} = 1.27 \text{ kg/m}^3 \quad (44)$$

- ▶ In general: Consider a volume V of moist air at temperature T and total pressure p which contains mass M_d of dry air and mass M_v of water vapor. The density ρ of the moist air is given by:

$$\rho = \frac{M_d + M_v}{V} = \rho'_d + \rho'_v \quad (45)$$

Virtual temperature

where ρ'_d is the density which the same mass of dry air would have if it alone occupied the volume V and ρ'_v is the density which the same mass of water vapor would have if it alone occupied the volume V (*partial densities*). Note that ρ'_d is less than the true density of dry air.

Applying the ideal gas equation to water vapor and dry air, we have

$$e = R_v \rho'_v T \quad (46)$$

$$p'_d = R_d \rho'_d T \quad (47)$$

$$\rho = \rho'_d + \rho'_v = \frac{p'_d}{R_d T} + \frac{e}{R_v T} \quad (48)$$

Applying Dalton's law of partial pressures:

$$p = p'_d + e \quad (49)$$

yields:

Virtual temperature

$$\rho = \frac{p - e}{R_d T} + \frac{e \epsilon}{R_d T} = \frac{1}{R_d T} (p - e + \epsilon e) \quad (50)$$

$$\rho = \frac{p}{R_d T} [1 - e/p(1 - \epsilon)] \quad (51)$$

$$(52)$$

Add term in brackets to temperature to obtain:

$$p = R_d \rho T_v \text{ where} \quad (53)$$

$$T_v = \frac{T}{1 - e/p(1 - \epsilon)} \approx T(1 + 0.61w) \quad (54)$$

$T_v \equiv$ virtual temperature: moisture content added to temperature

$T_v =$ temperature dry air must have in order to have the same density as moist air $T_v > T_d$, because $\rho_m < \rho_d$ and $\rho(T_{high}) < \rho(T_{low})$ for const. p



Dew point temperature

- ▶ Dew point temperature (T_d) = temperature to which moist air must be cooled with p and w held constant, for it to reach saturation with respect to water ($w = w_s(p, T_d)$). Starting from $e_s(T) = A \exp(-B/T)$ with $A = 2.53 \cdot 10^9$ hPa and $B = 5420$ K.

$$T_d = T_d(w, p) = -\frac{B}{\ln(e_s/A)} = \frac{B}{\ln \frac{Ae}{wp}} \quad (55)$$

- ▶ Frost point: as dew point, but with saturation with respect to ice
- ▶ At Earth's surface pressure varies only slightly \Rightarrow dew point is a good indicator of moisture content of air.
- ▶ In warm humid weather, T_d is a better indicator for human discomfort than RH, e.g. $T_d > 20^\circ\text{C}$ uncomfortable, $T_d > 24^\circ\text{C}$ sticky.
- ▶ Example: a) snow storm: Air temp: -2°C , Dew point -2°C and a b) desert: Air temp: 35°C , Dew point 5°C . Which one has higher RH, which one contains more water?



Wet bulb temperature

- ▶ T to which a parcel of air is cooled by evaporation with $p = \text{const}$, but $w \neq \text{const}$ until air is saturated with respect to water
- ▶ T_w is measured directly with a thermometer, the bulb of which is covered with a moist cloth. The heat required to evaporate water from the bulb is supplied by cooling of the air which comes into contact with it. When air is saturated, the temperature of the wet bulb reaches a steady value.
- ▶ evaporation of cloud droplets are at wet-bulb-temp.
- ▶ T_w similar to T_d . Unsaturated air approaching wet bulb has mixing ratio w , T_d is temperature to which air must be cooled with $p = \text{const}$. to become saturated. Air leaving wet bulb has mixing ratio w' at temperature T_w . If air approaching wet-bulb is not saturated, than $w' > w$, because of evaporation, and $\Rightarrow T_w > T_d$.

$$T_d \leq T_w \leq T \quad (56)$$

where equal sign only applies under saturated conditions



Equivalent and isentropic condensation temperature

Equivalent temperature $T_e = T$ that a parcel of moist air would attain if all the moisture were condensed out at constant pressure:

$$T_e = T + \frac{Lw}{c_p} \quad (57)$$

Isentropic condensation temperature $T_c = T$ at which saturation is reached when moist air is cooled adiabatically with w held constant (i.e. the temperature at the lifting condensation level (LCL)):

$$T_c = T_o \left(\frac{p_c}{p_o} \right)^{\kappa} \quad (58)$$

Determination of different temperatures

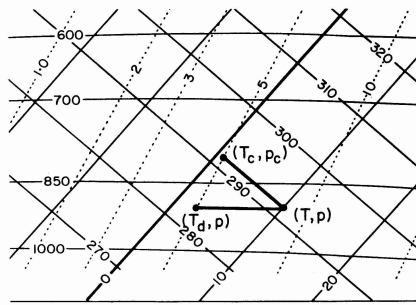


FIG. 2.2. Temperature, dew point, and isentropic condensation temperature, indicated on a tephigram. In the example shown the sample of air at 10°C, 900 mb, is assumed to have a mixing ratio of 5 g/kg. Its dew point, found from the intersection of the 900 mb isobar and the 5 g/kg vapor line, is 2.2°C. Its isentropic condensation point, found from the intersection of the adiabat through (T, p) with the 5 g/kg vapor line, is at 0.7°C and approximately 800 mb.

Pseudoadiabatic process

- ▶ Examples for the pseudoadiabatic process: Foehn wind, Chinook on the eastern slopes of the Rocky Mountains, or Santa Ana winds (desert wind in California).
- ▶ calculate changes in p, T and w_s from 1. law of thermodyn.

$$dT = \frac{1}{\rho c_p} dp - \frac{L}{c_p} dw_s \quad (59)$$

(mathematical description of the pseudoadiabatic process).
Calculate adiabatic liquid water content from $dw_l = -dw_s$

- ▶ w_l is the liquid water produced by the pseudoadiabatic expansion beyond the condensation point.
- ▶ during the **pseudoadiabatic process** condensed water precipitates, while it remains in the air during the **reversible saturated process** accounting for the latent heat absorbed by the water substance.



Foehnmauer (Karlsruhe)

Equivalent temperature T_e

adiabatic definition: follow the pseudoadiabat from a given p to very low p , thus condensing out all the water vapor, and then returning to the original p along the dry adiabat:

$$T_e = T \exp\left(\frac{LW_s}{c_p T_c}\right) \quad (60)$$

equivalent potential temperature Θ_e is obtained from taking T_e to 1000 hPa. It is conserved over phase changes as long as the system is not precipitating, i.e. in a **reversible saturated adiabatic process**.

Determination of different temperatures

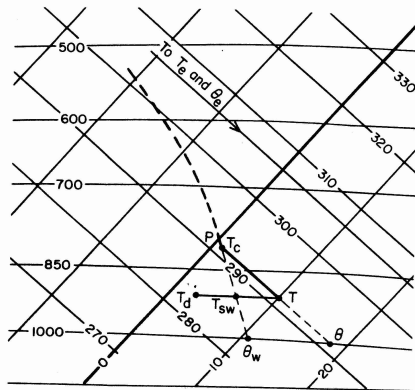


FIG. 2.3. Continued expansion of the air sample of Fig. 2.2 beyond point P , the isentropic condensation point. The dashed line is the pseudoadiabat through P . This diagram indicates the graphical determination of some of the important theoretical temperatures that characterize an air sample.

Hydrostatic equation

Vertical pressure gradient force on the air exactly balances the force of gravity:

$$\frac{\partial p}{\partial z} = -g\rho \quad (61)$$

Integration shows that the hydrostatic pressure at any level in the atmosphere is equal to the weight of an air column with unit cross-sectional area extending upwards from that level. Substituting for ρ from the equation of state gives:

$$\frac{dp}{p} = -\frac{g}{R_d \bar{T}_v} dz \quad (62)$$

Integration yields:

$$p = p_o \exp\left[-\frac{g}{R_d \bar{T}_v}(z - z_o)\right] \quad (63)$$

= **hypometric equation**. Here p is the pressure at height z and \bar{T}_v is the mean virtual temperature over the pressure interval from p_o to p , given by:

$$\bar{T}_v = \frac{\int_{\ln p_o}^{\ln p} T_v d(\ln p)}{\ln p - \ln p_o} \quad (64)$$

Concept of an air parcel

- ▶ **air parcel:** An imaginary volume of air to which may be assigned any or all of the basic dynamic and thermodynamic properties of atmospheric air
- ▶ A parcel is large enough to contain a very great number of molecules, but small enough so that the properties assigned to it are approximately uniform within it and so that its motions with respect to the surrounding atmosphere do not induce marked compensatory movements.
- ▶ No precise numerical definition, but a good visualization is a cubic foot of air when discussing static stability.
- ▶ thermally insulated from its environment so that its temperature changes adiabatically as it rises or sinks
- ▶ always at the same pressure as the environmental air at the same level, which is assumed to be in hydrostatic equilibrium

Dry adiabatic lapse rate

Air parcel undergoes adiabatic transformations ($dq=0$) and the atmosphere is in hydrostatic equilibrium, for a unit mass of air in the parcel we have:

$$dq = 0 = -\alpha dp + c_p dT \quad (65)$$

$$c_p dT = \alpha dp = \frac{1}{\rho} dp = -gdz \text{ (hydrostatic equation)} \quad (66)$$

$$dT = -\frac{g}{c_p} dz \leftrightarrow -\left(\frac{dT}{dz}\right)_{dry\ parcel} = \frac{g}{c_p} \equiv \Gamma_d \quad (67)$$

$\Gamma_d \equiv$ dry adiabatic lapse rate ~ 9.8 K/km. Normally the atmospheric lapse rate is 6-7 K/km.

Buoyant force on a parcel of air

Buoyancy force per unit mass is:

$$F_B = g \left(\frac{\rho' - \rho}{\rho} \right) = g \left(\frac{T - T'}{T'} \right) \quad (68)$$

This force is positive when the parcel is warmer than ambient air, negative when the parcel is cooler than ambient.

For moist air, replace T by T_v .