Thermodynamics

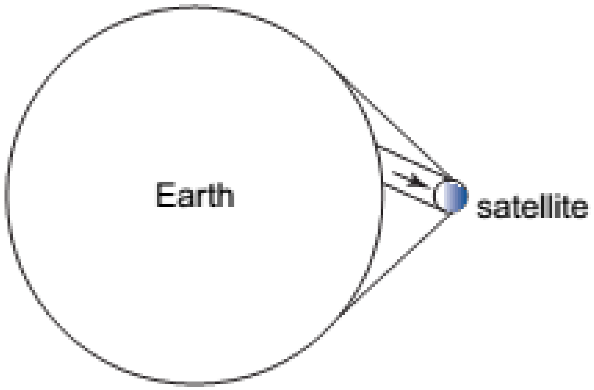
Jintai Lin

Teaching materials are from Michael Wallace and Richard Goody

Outline

- Introduction
- Basics
- First law of thermodynamics
- Second law of thermodynamics
- Static instability
- Heat, work and state functions
- Atmospheric energy budgets

思考题



A. A small, perfectly black, spherical satellite is in orbit around the Earth at an altitude of 2000 km. What angle does the Earth subtend when viewed from the satellite?

B. If the Earth radiates as a blackbody at an equivalent blackbody temperature Te = 255 K, calculate the radiative equilibrium temperature of the satellite when it is in the Earth’s shadow.

思考题

A. Consider two opaque walls facing each other. One of the walls is a blackbody and the other wall is “gray” (i.e.,α_λ independent of λ). The walls are initially at the same temperature T and, apart from the exchange of radiation between them, they are thermally insulated from their surroundings. If α and ε are the absorptivity and emissivity of the gray wall, prove that $\varepsilon = \alpha$.

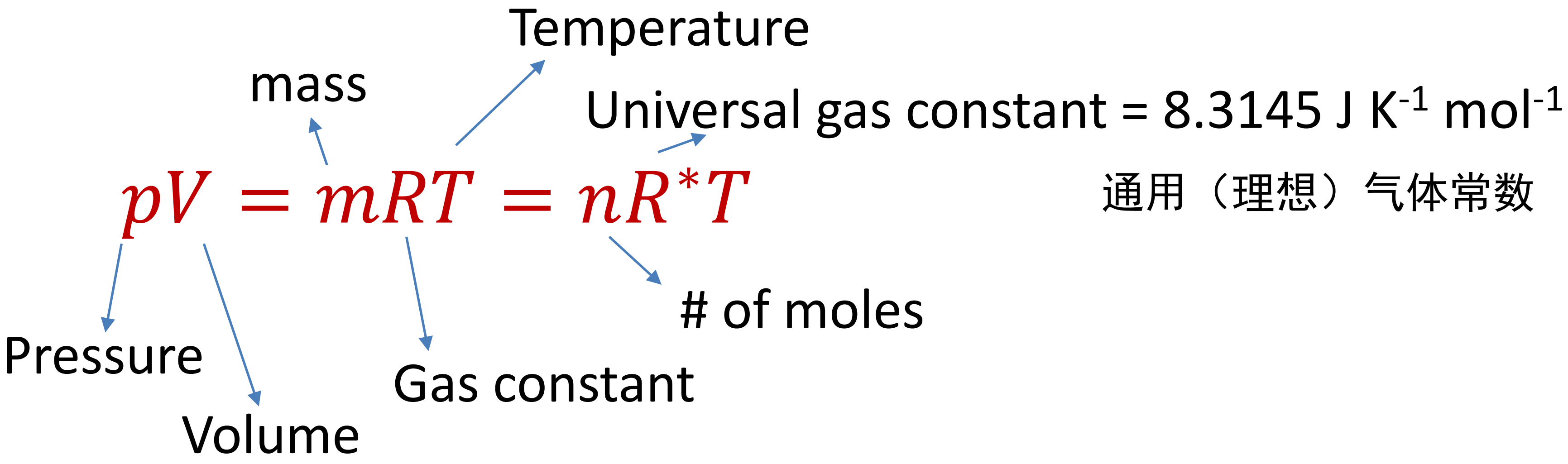
B. Consider the situation where two gray walls are facing each other. One wall has absorptivity α_1 and the other α_2. Prove that

$$\frac{F_1'}{\alpha_1} = \frac{F_2'}{\alpha_2}$$

where F_1' and F_2' are the flux densities of the radiation emitted from the two plates. Make sure of the fact that the two plates are in radiative equilibrium at the same temperature.

Michael Wallace book

Ideal Gas Equation



Temperature

mass

Universal gas constant = 8.3145 J K^{-1} mol^{-1}

$$pV = mRT = nR^*T$$

通用（理想）气体常数

\# of moles

Pressure

Gas constant

Volume

Specific volume

Thus,
$$p = \rho RT \qquad p\alpha = RT$$

- **Ideal gas has negligible molecular size and no interactions except elastic collisions**
- **Ambient air is close to ideal gas, and is treated as so**

Avogadro’s Hypothesis 阿伏加德罗定律

Gram-molar mass M:

$$M = 1000\frac{m}{n}$$ 摩尔质量（g mol^{-1}）

$$R^* = \frac{RM}{1000}$$

Avogadro’s Number N_A: = 6.022x10^{23} per mole

1 mole = N_A molecules

Avogadro’s hypothesis (1811): gases containing the same number of molecules occupy the same volumes at the same temperature and pressure. So:

$$pV = nR^*T$$

Dalton’s Law of Partial Pressures 道尔顿分压定律

John Dalton in 1787:
The total pressure exerted by a mixture of gases that do not interact chemically is equal to the sum of the partial pressures of the gases

Partial pressure of a gas is the pressure it would exert at the same temperature as the mixture if it alone occupied all of the volume that the mixture occupies

$$p = \sum_{i=1}^{I} p_i \boxed{= \sum_{i=1}^{I} \frac{R^*T}{V} n_i}$$

Dry Air

For dry air:

$$p_d \alpha_d = R_d T$$

湍流层顶

- Below turbopause (> 100 km), R is constant (287.0 J kg^{-1} K^{-1})
- Above turbopause, heavier gases decrease with height faster!

Apparent molar mass:

表观摩尔质量

$$M_d = \frac{\sum_i m_i}{\sum_i \frac{m_i}{M_i}} = 28.97 \text{ g mol}^{-1}$$

Therefore:

$$R_d = 1000 \frac{R^*}{M_d} = 287.0 \text{ J K}^{-1} \text{ kg}^{-1}$$

Water Vapor

Water vapor: $e\alpha_v = R_v T$

Therefore: $R_v = 1000\dfrac{R^*}{M_v}$ = 461.51 J K^{-1} kg^{-1}

$$\varepsilon \equiv \frac{R_d}{R_v} = \frac{M_v}{M_d} = 0.622$$

Virtual Temperature 虚温

Virtual temperature:

The temperature that dry air would need to attain in order to have the same (mass) density as the moist air at the same pressure

Density of moist air:

$$\rho = \frac{m_d + m_v}{V} = \rho_d + \rho_v$$

Virtual Temperature

$$p_d = \rho_d R_d T$$

$$e = \rho_v R_v T$$

$$p = p_d + e$$

Dalton's law

$$\rho = \rho_d + \rho_v$$

$$= \frac{p - e}{R_d T} + \frac{e}{R_v T}$$

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

Thus:

$$p = \rho R_d T_v$$

Virtual temperature:

$$T_v = \frac{T}{1 - \frac{e}{p}(1 - \varepsilon)}$$

Water Vapor in the Atmosphere

Mixing ratio:

$$w = \frac{m_v}{m_d} = \frac{q}{1-q}$$

Specific humidity:

$$q = \frac{m_v}{m_d + m_v} = \frac{w}{1+w}$$

Water vapor pressure:

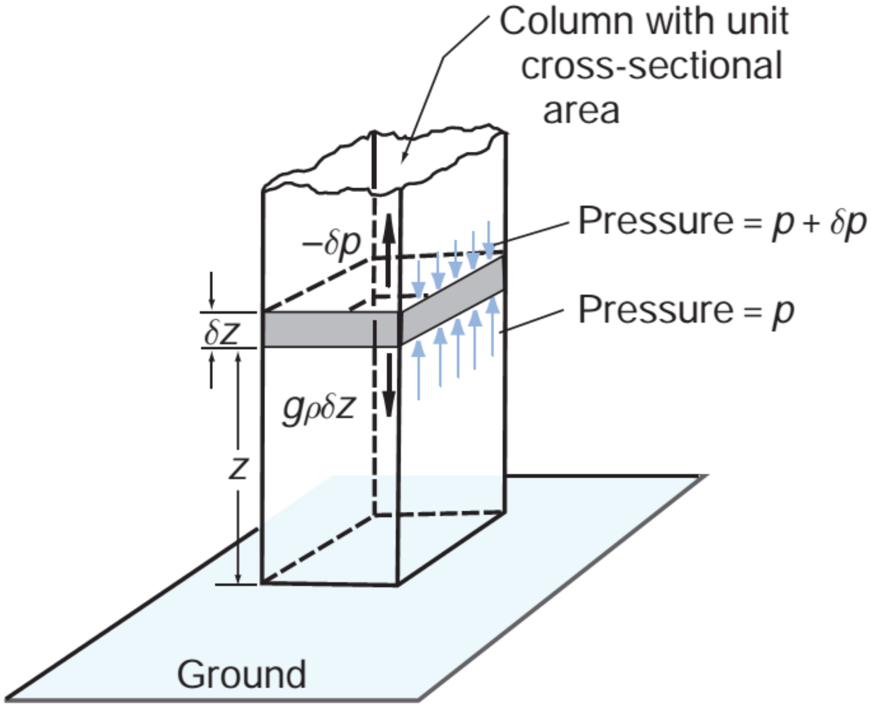
$$e = \frac{w}{w+\varepsilon} p$$

Hydrostatic Equation 静力方程

$$-\delta p = g\rho\delta z$$

Thus:

$$\frac{\partial p}{\partial z} = -g\rho = -\frac{g}{\alpha}$$



Hydrostatic Equation

$$-\delta p = g\rho\delta z$$

$$-\int_{p(z)}^{p(\infty)} dp = \int_{z}^{\infty} g\rho dz$$

Thus: $$p(z) = \int_{z}^{\infty} g\rho dz$$

Atmospheric mass a unit (m^2) of Earth surface

$$Mass = \int_{0}^{\infty} \rho dz = \frac{p_0}{g}$$

Geopotential 位势、Geopotential Height 位势高度

Geopotential:

$$d\phi = g dz$$

$$\phi(z) = \int_0^z g dz \qquad \Phi(z=0)=0$$

Geopotential height:

$$Z = \frac{\phi(z)}{g_0} = \frac{1}{g_0}\int_0^z g dz$$

g_0 is the globally averaged gravity acceleration at the Earth's surface

At hydrostatic state:

$$d\phi = g dz = -\alpha dp$$

Acceleration of Gravity

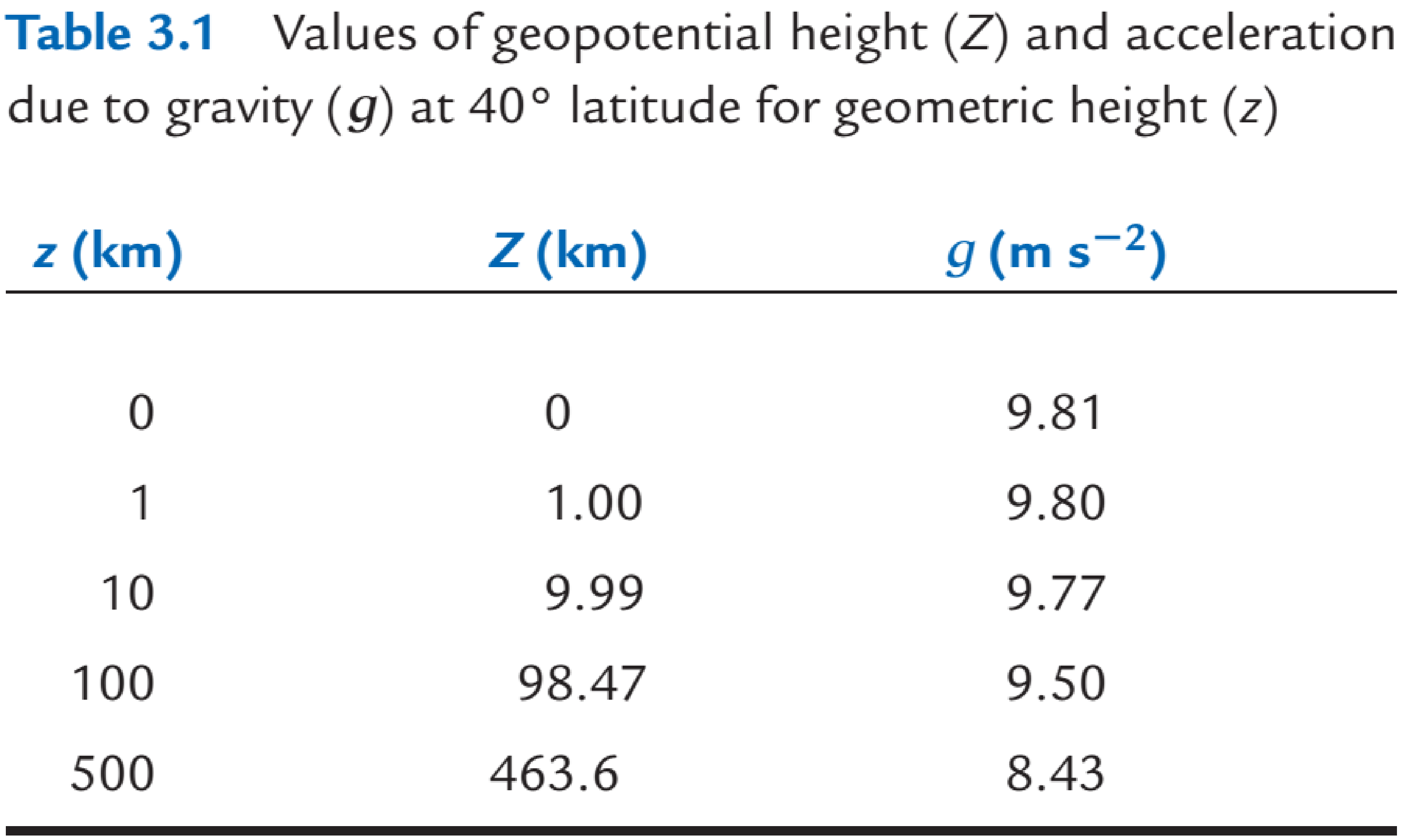


Table 3.1 Values of geopotential height (Z) and acceleration due to gravity (g) at 40° latitude for geometric height (z)

z (km)	Z (km)	g (m s^{-2})
0	0	9.81
1	1.00	9.80
10	9.99	9.77
100	98.47	9.50
500	463.6	8.43

Geopotential Thickness

$$d\phi = -RT\frac{dp}{p} = -R_d T_v \frac{dp}{p}$$

$$\int_{\phi_1}^{\phi_2} d\phi = -\int_{p_1}^{p_2} R_d T_v \frac{dp}{p}$$

$$\phi_2 - \phi_1 = R_d \int_{p_2}^{p_1} T_v \frac{dp}{p}$$

Geopotential thickness:

$$Z_2 - Z_1 = \frac{R_d}{g_0} \int_{p_2}^{p_1} T_v \frac{dp}{p}$$

Scale Height 标高

For isothermal atmosphere with dry air:

$$Z_2 - Z_1 = H \ln(p_1/p_2)$$

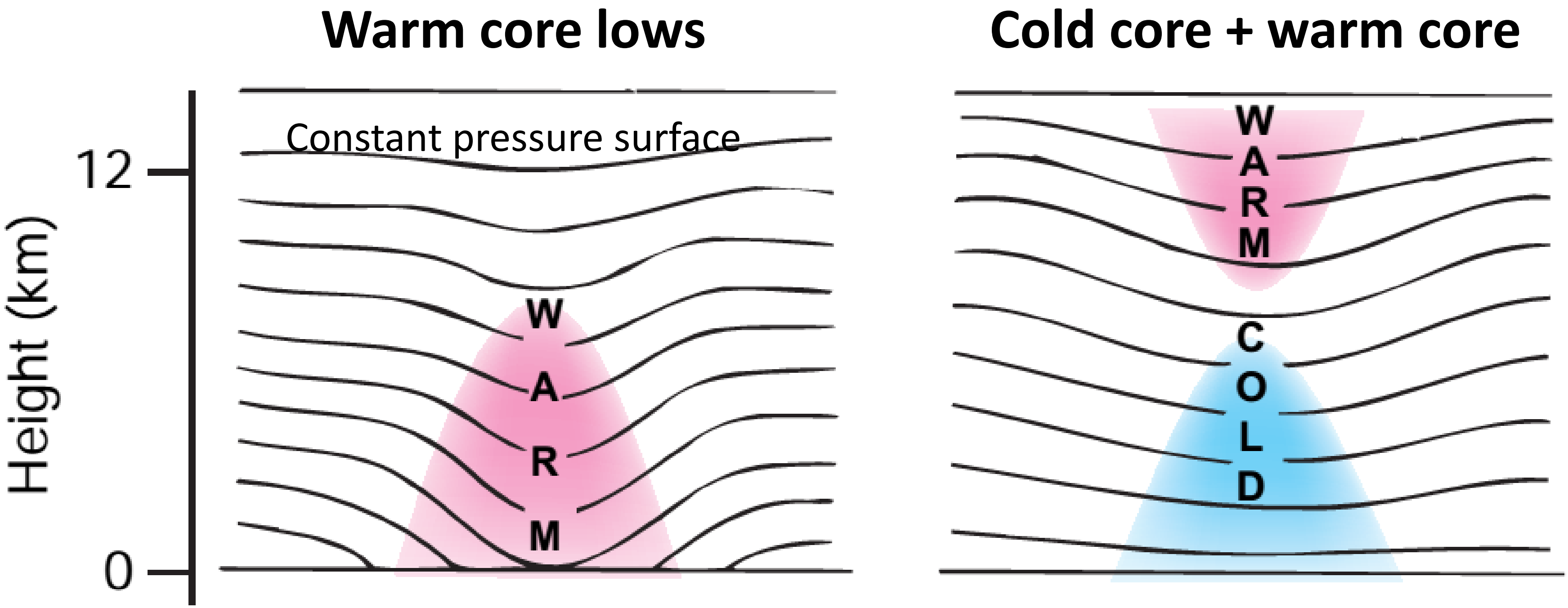
$$p_2 = p_1 e^{-\frac{Z_2 - Z_1}{H}}$$

$$H = \frac{R_d T_v}{g_0} = \frac{R_d T}{g_0} = 29.3T$$

湍流层顶

- Below turbopause (> 100 km), R_d is constant (287.0 J kg^{-1} K^{-1})
- For T = 255 K, we get H ~ 7.5 km
- Above turbopause, concentrations of heavier gases decrease with height faster!

Thickness of Height of Constant Pressure Surfaces



First Law of Thermodynamics

Unless otherwise stated, we only discuss the case in the absence of changes in nuclear energy, internal inter-molecular potential energy, and macroscopic kinetic energy

$$du = \delta q - \delta w$$ **for a unit of mass**

q: heat (interaction, *not transported*)
w: work (interaction, *not transported*)
u: internal kinetic energy (function of state)

Work

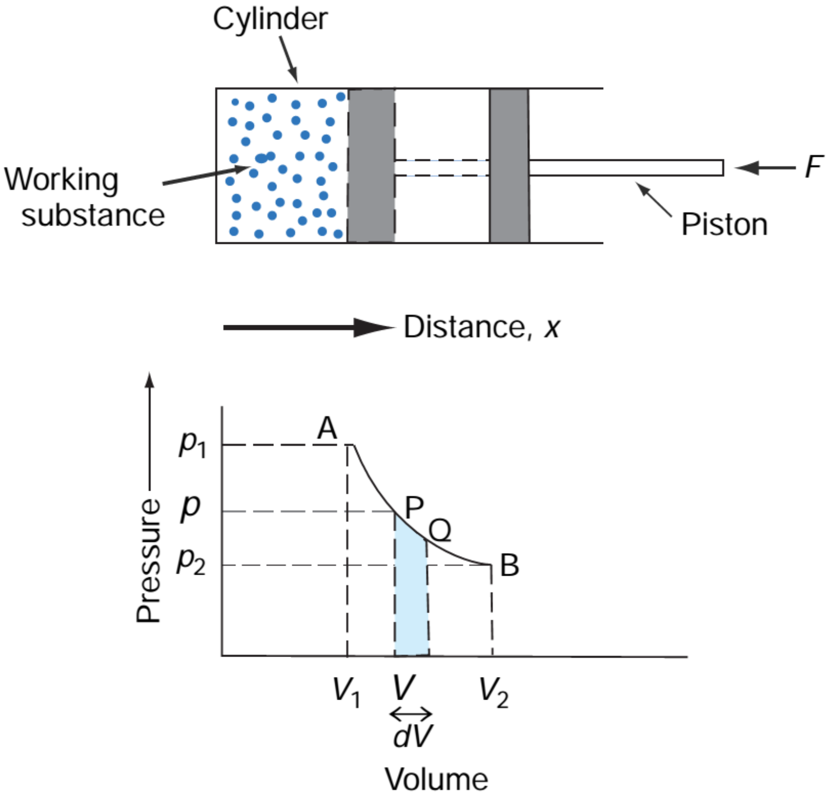
$$dw = Fdx$$

$$= pAdx = pdV$$

体积功

Thus:

$$w = \int_{V_1}^{V_2} pdV$$



Thermodynamic diagram

Specific Heats

Closed system (no phase change) for dry air:

At constant volume:

$$c_v = \left(\frac{\delta q}{\delta T}\right)_{v\ const} = \left(\frac{\partial u}{\partial T}\right)_{v\ const} = \frac{du}{dT}$$

At constant pressure:

$$c_p = \left(\frac{\delta q}{\delta T}\right)_{p\ const} = c_v + R$$

In general: $\delta q = du + p d\alpha = c_p dT - \alpha dp$

Enthalpy 焓

$$h = u + p\alpha$$

$$dh = du + d(p\alpha) = c_p dT$$

Enthalpy is a state function, like u, p, v, T

Therefore, under hydrostatic balance:

$$\delta q = d(h + \phi) = d\left(c_p T + \phi\right)$$

h+ϕ: dry static energy

Air Parcel 气块假设

Assuming that a parcel of air is

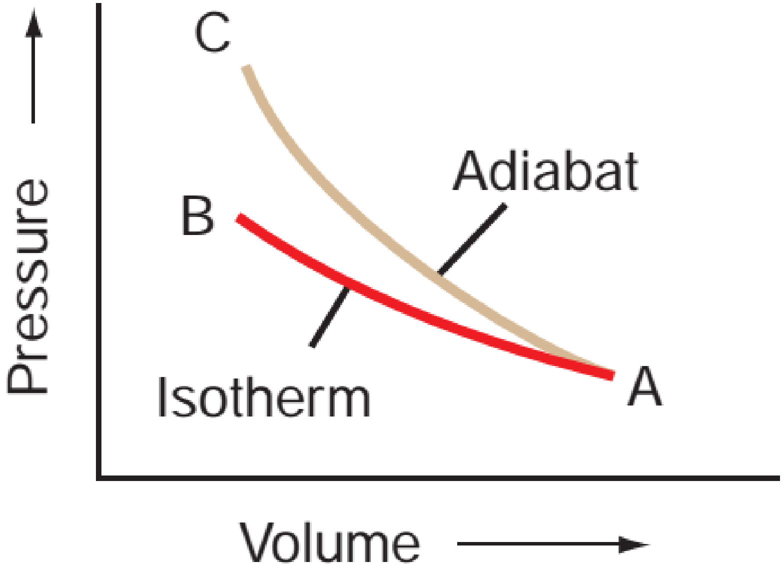
- ✓ Thermally insulated from its environment so that its temperature changes adiabatically as it rises or sinks
- ✓ Always remaining at exactly the same pressure as the environmental air at the same level, which is assumed to be in hydrostatic equilibrium
- ✓ Moving slowing enough that the macroscopic kinetic energy of the air parcel is a negligible fraction of its total energy

Dry Adiabatic Process (Vertical Movement with No Phase Change)

$$\delta q = d\left(c_p T + \phi\right)$$

$$= c_p dT + g dz$$

$$= 0$$



Thus, dry adiabatic lapse rate:

$$\Gamma_d = -\left(\frac{\partial T}{\partial z}\right)_{dry\ parcel} = \frac{g}{c_p}$$

$= 9.8 \text{ K km}^{-1}$

Potential Temperature 位温

Potential temperature of an air parcel:

The temperature θ that the parcel of air would have if it were expanded or compressed (dry) adiabatically from its existing pressure and temperature to a standard pressure p_0 (generally taken as 1000 hPa)

$$\delta q = c_p dT - \alpha dp = 0$$

$$\frac{c_p}{R}\frac{dT}{T} - \frac{dp}{p} = 0$$

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

Thus,

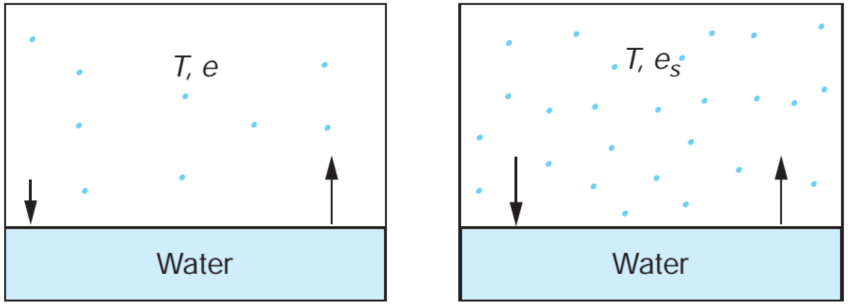
$$\theta = T\left(\frac{p_0}{p}\right)^{R/c_p}$$

Equilibrium (Saturation) Vapor Pressure

e_s: Saturation vapor pressure wrt a plane surface of pure water at T

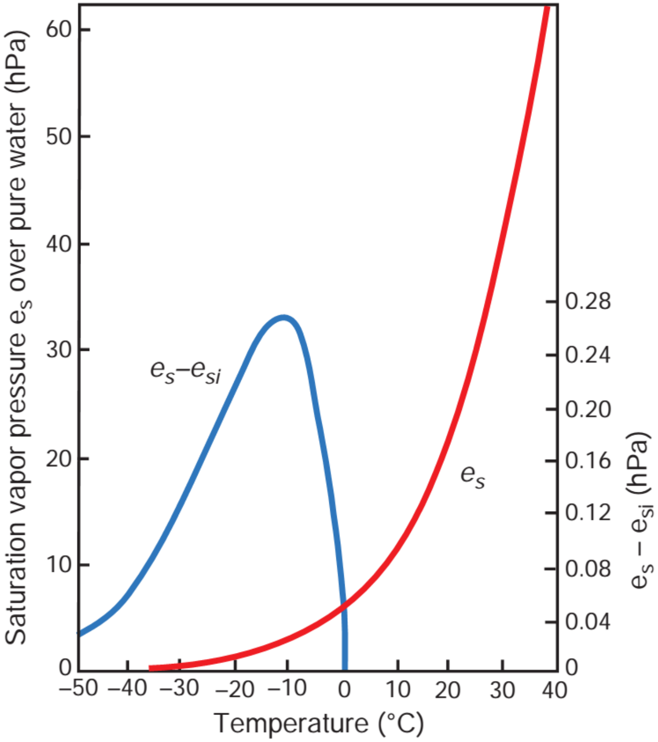
e_{si}: Saturation vapor pressure wrt a plane surface of pure ice at T

贝吉龙过程？



(a) Unsaturated

(b) Saturated



Saturation Mixing Ratio

$$w_s = \frac{m_{vs}}{m_d} = \frac{\rho_{vs}}{\rho_d}$$

$$= \frac{\frac{e_s}{R_v T}}{\frac{p - e_s}{R_d T}} = \varepsilon \frac{e_s}{p - e_s}$$

$$\approx \varepsilon \frac{e_s}{p} = 0.622 \frac{e_s}{p}$$

Relative Humidity

$$RH = 100\frac{e}{e_s} \approx 100\frac{w}{w_s}$$

$$\approx 100\frac{w_s(at\ temperature\ T_d\ and\ pressure\ p)}{w_s(at\ temperature\ T\ and\ pressure\ p)}$$

T_d: Dew point temperature

Latent Heat for Phase Change 潜热

Latent heat of vaporization or evaporation L_v:

The heat that has to be given to a unit of mass of material to convert it from the liquid to the vapor phase without a change in temperature

L_v = 2.5 x 10^6 J kg^{-1} for water at 1 atm and 100^oC

L_v is weakly dependent on T

$\delta q \cong -L_v dw_s$ for a unit mass of moist air (dry + H_2O)

$dw_s > 0$: 蒸发吸热，导致气块的$dq < 0$
$dw_s < 0$: 凝结放热，导致气块的$dq > 0$

Saturated Adiabatic & Pseudoadiabatic Processes

As the air moves upwards, its water vapor becomes saturated and starts to condense to liquid water or deposit to ice

- Saturated adiabatic process: the condensed/deposited water stays in the air parcel, thus the process is adiabatic (no heat interactions with environment) and is reversible
  - ✓ For example, cloud formation without precipitation
- Pseudoadiabatic process: the condensed/deposited water falls out of the air parcel immediately, thus the process is irreversible
  - ✓ For example, precipitation formation
- In both cases, the mass and energy associated with the phase change is small compared to those of the air parcel

Saturated Adiabatic & Pseudoadiabatic Processes

$$\delta q \cong -L_v \cdot dw_s = c_p dT + g dz \quad \Rightarrow \quad \frac{\partial T}{\partial z} = -\frac{L_v}{c_p}\frac{\partial w_s}{\partial z} - \frac{g}{c_p}$$

Note:

$$w_s = \varepsilon \frac{e_s}{p - e_s} = w_s(p, T) \quad \Rightarrow \quad dw_s = \left(\frac{\partial w_s}{\partial p}\right)_T dp + \left(\frac{\partial w_s}{\partial T}\right)_p dT$$

$$\frac{\partial w_s}{\partial z} = \left(\frac{\partial w_s}{\partial p}\right)_T \frac{\partial p}{\partial z} + \left(\frac{\partial w_s}{\partial T}\right)_p \frac{\partial T}{\partial z}$$

Thus:

$$\frac{\partial T}{\partial z}\left[1 + \frac{L_v}{c_p}\left(\frac{\partial w_s}{\partial T}\right)_p\right] = -\frac{g}{c_p}\left[1 + \frac{L_v}{g}\left(\frac{\partial w_s}{\partial p}\right)_T \frac{dp}{dz}\right]$$

$$= -\frac{g}{c_p}\left[1 - \rho L_v \left(\frac{\partial w_s}{\partial p}\right)_T\right]$$

Saturated Adiabatic & Pseudoadiabatic Processes

$$\frac{\partial T}{\partial z}\left[1+\frac{L_v}{c_p}\left(\frac{\partial w_s}{\partial T}\right)_p\right] = -\frac{g}{c_p}\left[1-\rho L_v\left(\frac{\partial w_s}{\partial p}\right)_T\right]$$

Thus, moist adiabatic lapse rate:

$$\Gamma_s = -\left(\frac{\partial T}{\partial z}\right)_{moist\ air} = \Gamma_d \frac{1-\rho L_v\left(\frac{\partial w_s}{\partial p}\right)_T}{1+\frac{L_v}{c_p}\left(\frac{\partial w_s}{\partial T}\right)_p} \approx \frac{\Gamma_d}{1+\frac{L_v}{c_p}\left(\frac{\partial w_s}{\partial T}\right)_p}$$

where: $-\rho L_v\left(\frac{\partial w_s}{\partial p}\right)_T \approx 0.12$ for T = 0°C, p from 1000 to 950 hPa

Saturated Adiabatic & Pseudoadiabatic Processes

$\frac{\delta q}{T} = -\frac{L_v}{T} dw_s = c_p \frac{dT}{T} - R\frac{dp}{p} = c_p \frac{d\theta}{\theta}$ ⇦ $\theta = T\left(\frac{p_0}{p}\right)^{R/c_p}$

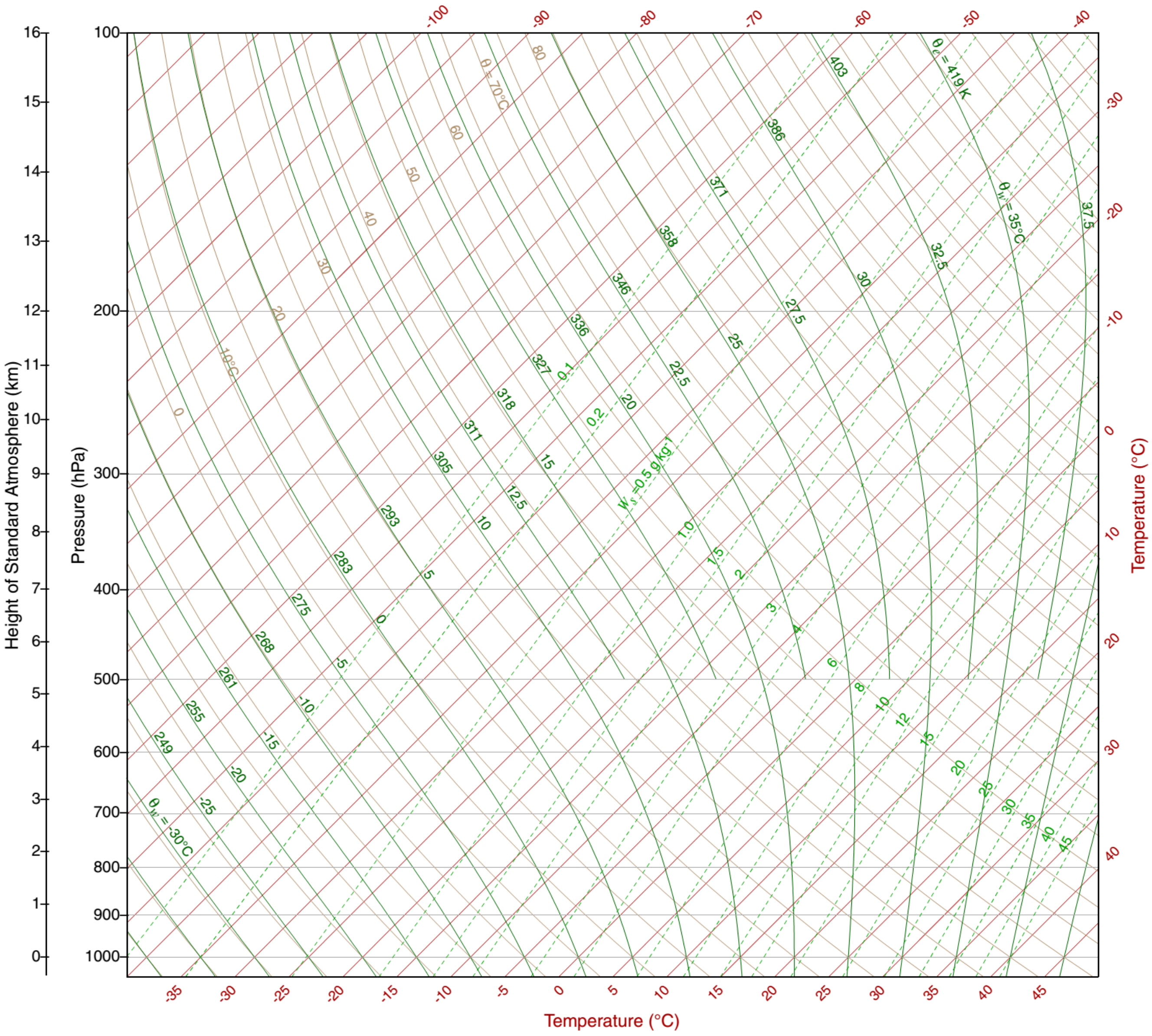
Thus: $-\frac{L_v}{c_p T} dw_s = \frac{d\theta}{\theta}$

Because: $\frac{dT}{T} \ll \frac{dw_s}{w_s}$ ⇨ $\frac{L_v}{c_p T} dw_s \approx d\left(\frac{L_v w_s}{c_p T}\right)$

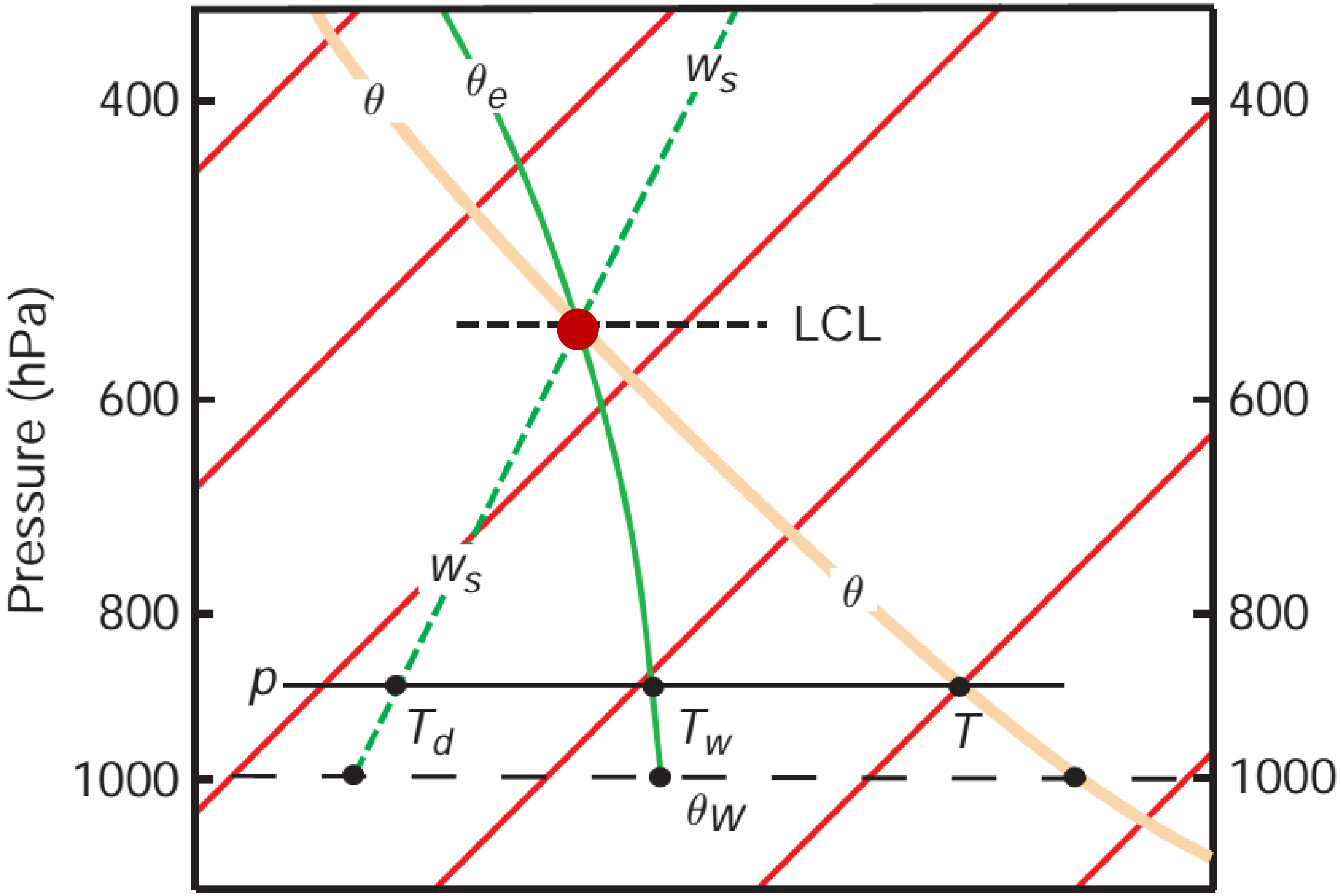
Thus, equivalent potential temperature 相当位温:

$$\theta_e \approx \theta e^{\frac{L_v w_s}{c_p T}}$$

Skew T-lnP Chart（倾斜T-lnP图）



Normand’s Rule 诺曼德法则



Instability of Unsaturated Air Not In Hydrostatic Equilibrium

For an unsaturated air parcel with pressure p’, density ρ’ and temperature T’ (p, ρ and T for environment), & p = p’.

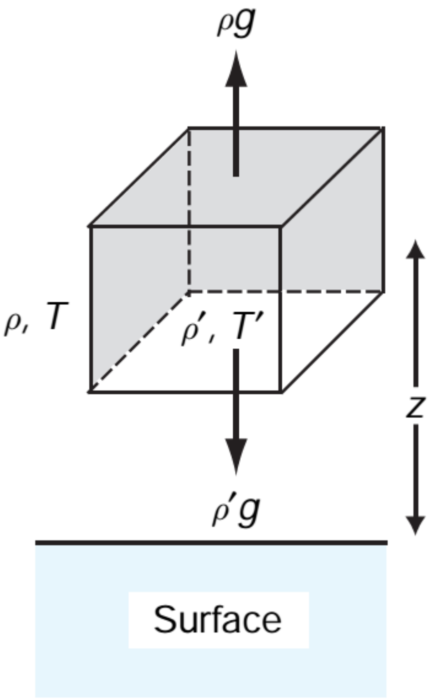
The net upward force acting on a unit of volume of the parcel is:

$$p = \rho R T = \rho' R T'$$

$$F = (\rho - \rho')g$$

$$\frac{d^2 z'}{dt^2} = \frac{F}{\rho'} = \left(\frac{\rho - \rho'}{\rho'}\right) g$$

$$= \left(\frac{T' - T}{T}\right) g$$



Instability of Unsaturated Air: Not In Hydrostatic Equilibrium

If the air parcel is displaced upward, from its equilibrium level at z’ = 0 with the ambient temperature T_0, by a distance z’ to a new level where the ambient temperature is T,

$$T' = T_0 - \Gamma_d z' \qquad T = T_0 - \Gamma z'$$

$$T' - T = -(\Gamma_d - \Gamma) z'$$

Thus: $$\frac{d^2 z'}{dt^2} = -\frac{g}{T}(\Gamma_d - \Gamma) z'$$

$$\frac{d^2 z'}{dt^2} + N^2 z' = 0 \quad \Leftarrow \quad N = \left[\frac{g}{T}(\Gamma_d - \Gamma)\right]^{1/2}$$

N is Brunt-Väisälä frequency 浮力（布维）频率

Buoyancy Oscillation

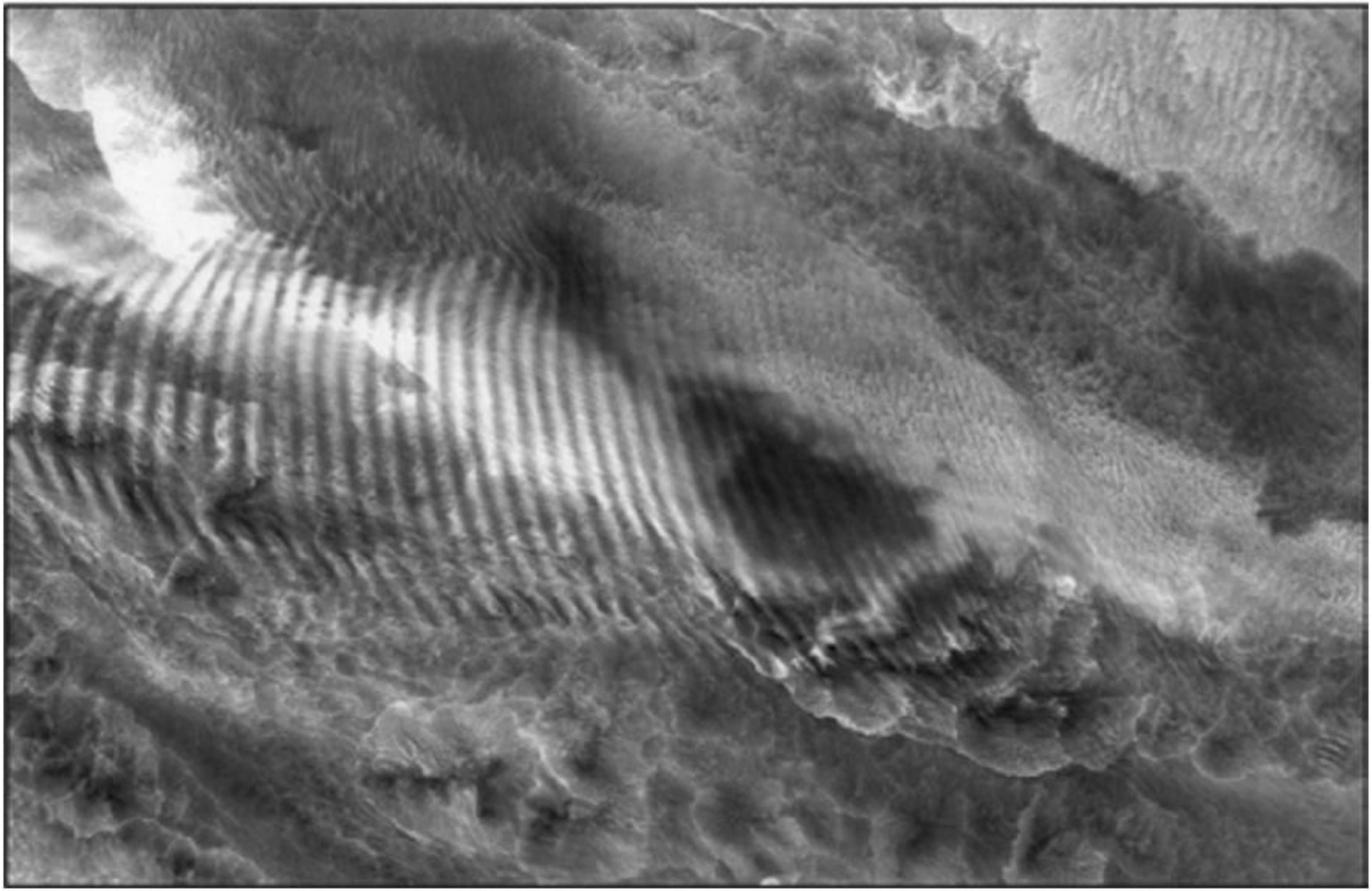
$$\frac{d^2 z'}{dt^2} + N^2 z' = 0 \qquad N = \left[\frac{g}{T}(\Gamma_d - \Gamma)\right]^{1/2}$$

Stably stratified atmosphere: N > 0, or $\Gamma_d - \Gamma > 0$

Air parcel executes a buoyancy oscillation

$$z' = A\cos Nt + B\sin Nt$$

Buoyancy Oscillation over Indian Ocean



Static Instability For Unsaturated Air

Stable: $\Gamma < \Gamma_d$ (i.e., θ increases with height)
Neutral: $\Gamma = \Gamma_d$ (i.e., θ increases with height)
Unstable: $\Gamma > \Gamma_d$ (i.e., θ increases with height)

From:

$$\theta = T\left(\frac{p_0}{p}\right)^{R/c_p}$$

We get:

$$\frac{1}{\theta}\frac{\partial\theta}{\partial z} = \frac{1}{T}(\Gamma_d - \Gamma)$$

Static Instability For Saturated Air

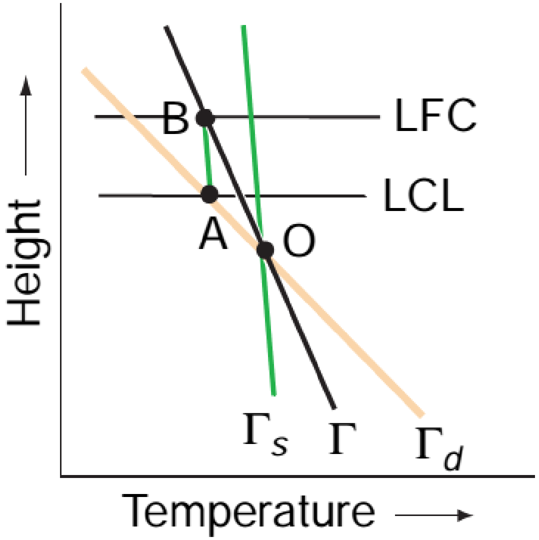
Stable: $\Gamma < \Gamma_s$

Neutral: $\Gamma = \Gamma_s$

Unstable: $\Gamma > \Gamma_s$

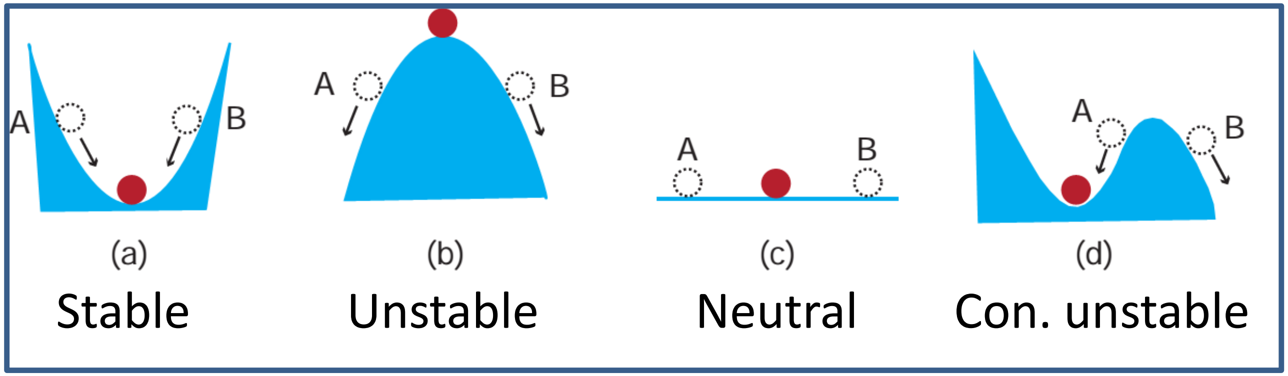
$$\Gamma_s \approx \frac{\Gamma_d}{1 + \frac{L_v}{c_p}\left(\frac{\partial w_s}{\partial T}\right)_p}$$

Conditional and Convective Instability



Conditionally unstable:

$\Gamma_s < \Gamma < \Gamma_d$



(a) Stable

(b) Unstable

(c) Neutral

(d) Con. unstable

Heat Engine and Its Efficiency

Efficiency of a (heat) engine:

- Absorb heat (energy) Q_1 at high temperature T_1
- Release heat (energy) Q_2 at low temperature T_2
- Do work provided by the energy difference W
- *Could dissipate heat (energy) for irreversible transformation*

Definition:

Thermal efficiency $$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1}$$

Carnot Cycle and Carnot’s Theorem

Carnot’s theorem:

- **No engine can be more efficient than a reversible engine working between the same limits of temperature**
- **All reversible engines working between the same limits of temperature have the same efficiency**

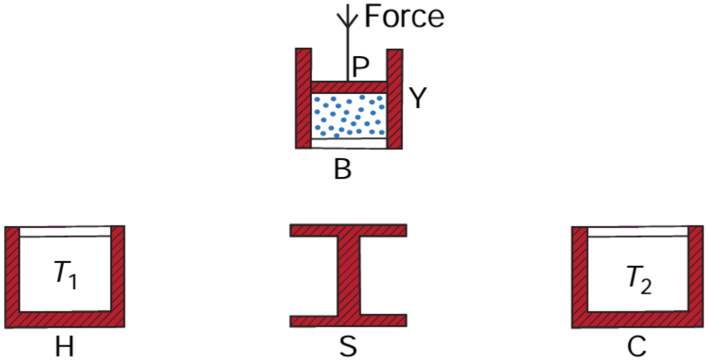
- ***Reversible transformation can be reversed at any point by making an infinitesimal change in the surroundings***
- ***Irreversible (spontaneous) transformation***

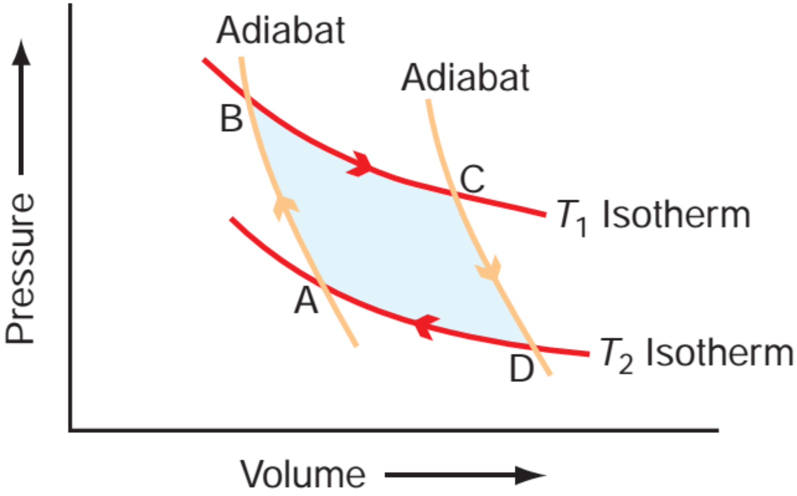
Confined by the Second Law of Thermodynamics

克劳修斯表述：不可能把热量从低温物体传递到高温物体而不产生其他影响

开尔文表述：不可能从单一热源吸收能量，使之完全变为有用功而不产生其他影响

Carnot Cycle and Carnot's Theorem





Carnot cycle (reversible):

1. **A → B: Adiabatic**
2. **B → C: Isothermal expansion (absorbing heat)**
3. **C → D: Adiabatic**
4. **D → A: Isothermal compression (releasing heat)**

Carnot Cycle and Carnot's Theorem

A → B: adiabatic

For a unit of mass

$$\begin{aligned}\delta q &= du + pd\alpha \\ &= c_p dT - \alpha dp \\ &= \frac{c_p}{R} d(p\alpha) - \alpha dp \\ &= \frac{c_p}{R} pd\alpha + \frac{c_v}{R} \alpha dp \\ &= 0\end{aligned}$$

Thus: $\gamma d \ln \alpha + d \ln p = 0$

$\gamma = c_p / c_v = 1.4$

$$p_A \alpha_A^{\gamma} = p_B \alpha_B^{\gamma}$$

Carnot Cycle and Carnot's Theorem

A → B: $p_A\alpha_A^\gamma = p_B\alpha_B^\gamma$ adiabatic

B → C: $p_B\alpha_B = p_C\alpha_C$ isothermal

C → D: $p_C\alpha_C^\gamma = p_D\alpha_D^\gamma$ adiabatic

D → A: $p_D\alpha_D = p_A\alpha_A$ isothermal

Thus:

$$\frac{\alpha_C}{\alpha_B} = \frac{\alpha_D}{\alpha_A}$$

Carnot Cycle and Carnot's Theorem

$$Q_1 = \int_{\alpha_B}^{\alpha_C} p\,d\alpha = \int_{\alpha_B}^{\alpha_C} \frac{nR^*T_1}{\alpha}\,d\alpha = nR^*T_1 \int_{\alpha_B}^{\alpha_C} \frac{d\alpha}{\alpha} = nR^*T_1 \ln\left(\frac{\alpha_C}{\alpha_B}\right)$$

$$Q_2 = nR^*T_2 \ln\left(\frac{\alpha_D}{\alpha_A}\right)$$

Thus:

$$\frac{Q_1}{Q_2} = \frac{T_1 \ln\left(\frac{\alpha_C}{\alpha_B}\right)}{T_2 \ln\left(\frac{\alpha_D}{\alpha_A}\right)} = \frac{T_1}{T_2}$$

$$\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}$$

Carnot efficiency

(maximum thermal efficiency)

Entropy 熵

Entropy is a state function, like u, h, p, v, T

For reversible heat exchange:

$$ds \equiv \frac{\delta q_{rev}}{T}$$

First Law of Thermodynamics:

$$Tds = du + pd\alpha$$

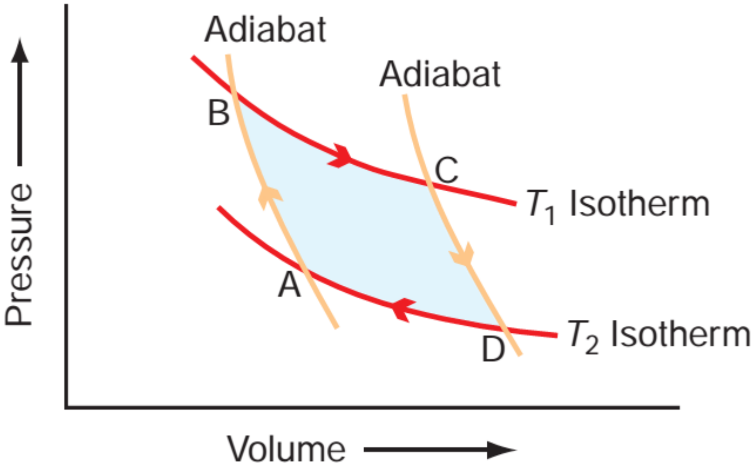
Adiabatic = Isentropic

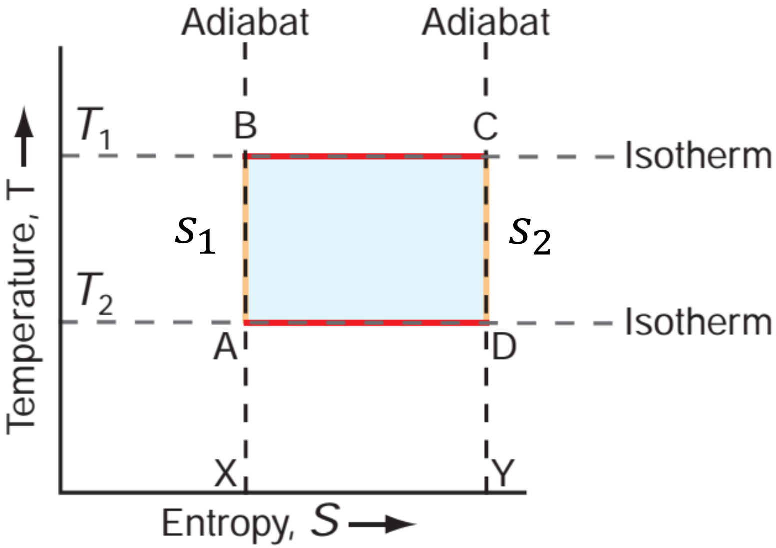
$$ds = c_p \frac{d\theta}{\theta}$$

$$s = c_p \ln \theta + constant$$

Entropy

Temperature-entropy diagram



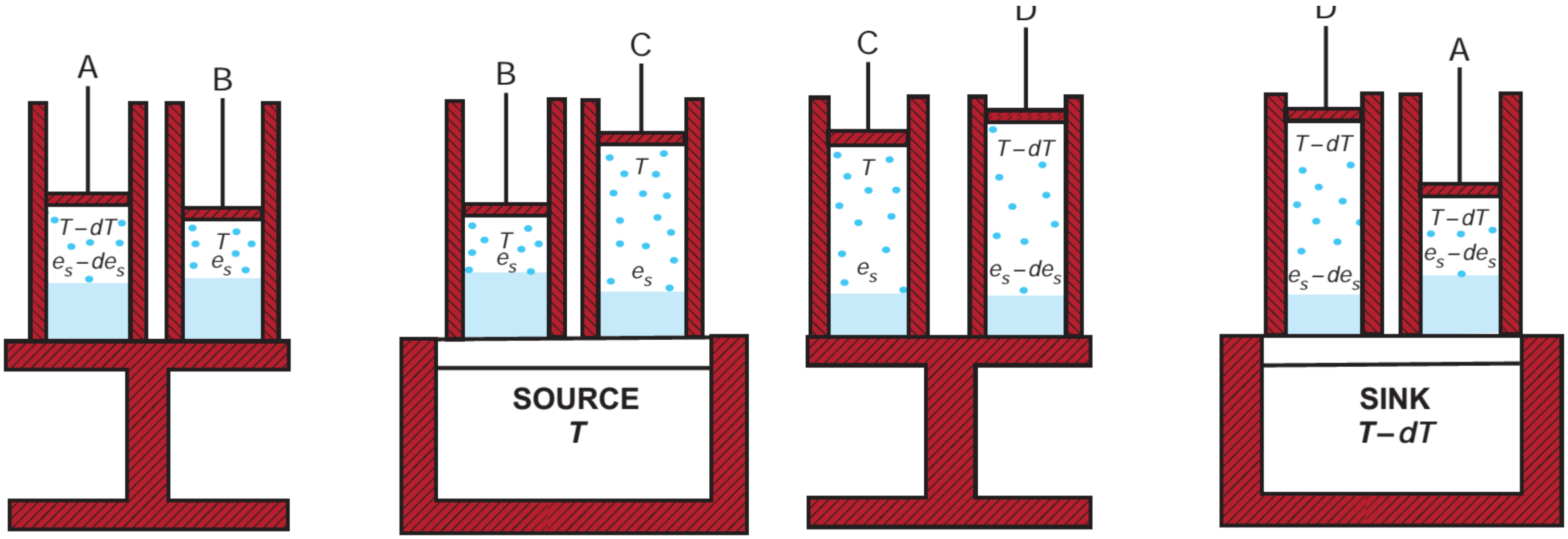


$$w = (T_1 - T_2)(s_2 - s_1) = \Delta T \cdot \Delta s$$

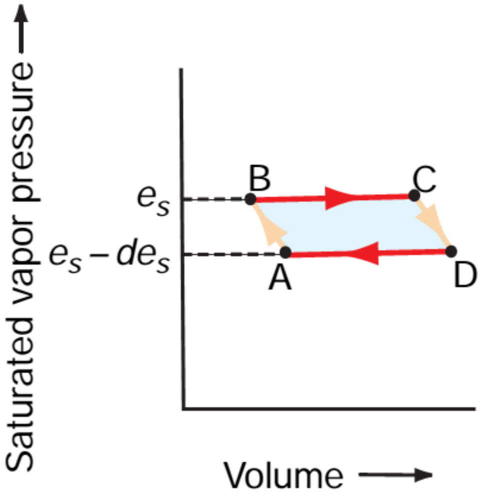
Clausius-Clapeyron Equation

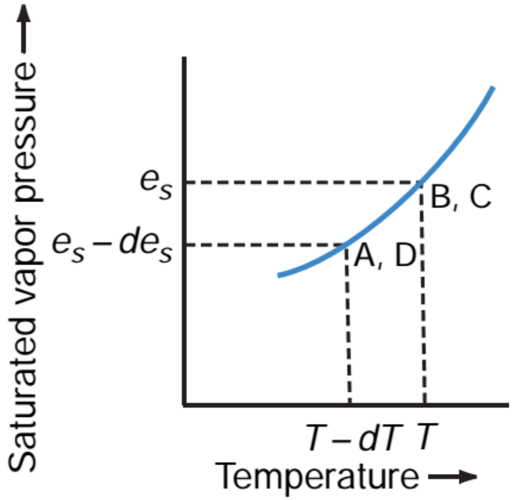
a.k.a. first latent heat equation

绝热，无相变 ➡ 吸热，蒸发 ➡ 绝热，无相变 ➡ 放热，凝结



Clausius-Clapeyron Equation





- Adiabatic at A→B and C→D
- Phase change at B→C and D→A

$$\frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1} \Rightarrow \frac{Q_1}{T_1} = \frac{Q_2}{T_2} = \frac{Q_1 - Q_2}{T_1 - T_2}$$

Clausius-Clapeyron Equation

Converting a unit of mass from liquid to vapor:

$$Q_1 - Q_2 = (\alpha_C - \alpha_B)de_s = (\alpha_2 - \alpha_1)de_s$$

$$Q_1 = L_v, \qquad T_1 = T, \qquad T_1 - T_2 = dT$$

Thus:

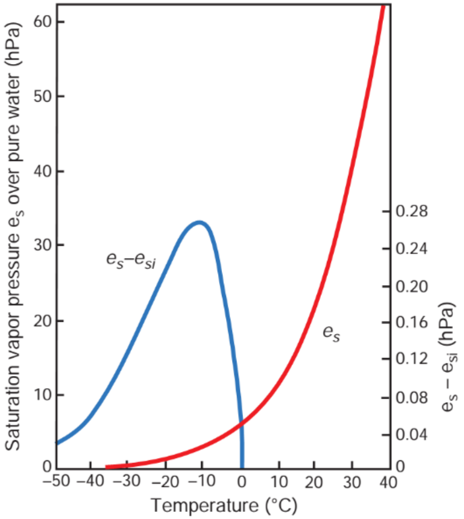
$$\frac{L_v}{T} = \frac{(\alpha_2 - \alpha_1)de_s}{dT}$$

α_1: Specific volume of liquid

α_2: Specific volume of vapor

C-C Eq.

$$\left\{ \begin{aligned} &\frac{de_s}{dT} = \frac{L_v}{T(\alpha_2 - \alpha_1)} \approx \frac{L_v}{T\alpha_2} = \frac{L_v e_s}{R_v T^2} \\ &\frac{1}{e_s}\frac{de_s}{dT} \approx \frac{L_v}{R_v T^2} = \frac{L_v M_v}{1000 R^* T^2} \end{aligned} \right.$$



Entropy and Second Law of Thermodynamics

Second Law of Thermodynamics:

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

$$\Delta S_{\text{universe}} = 0 \text{ for reversible (equilibrium) transformations}$$

$$\Delta S_{\text{universe}} > 0 \text{ for irreversible (spontaneous) transformations}$$

- ***Reversible transformation can be reversed at any point by making an infinitesimal change in the surroundings***
- ***Irreversible (spontaneous) transformation***

思考题

Derive a relationship for the height of a given pressure surface (p) in terms of the pressure p_0 and temperature T_0 at sea level, assuming that the temperature decreases uniformly with height at a rate of Γ K km^{-1}

$$z = \frac{T_0}{\Gamma}\left[1 - \left(\frac{p}{p_0}\right)^{R\Gamma/g}\right]$$

高度计

This is the basis for the calibration of aircraft altimeters

思考题

Lifting all assumptions for air parcel, except that the environment is still in hydrostatic equilibrium.

(a) Show that when a parcel of dry air at temperature T' moves adiabatically in ambient air with temperature T, the temperature lapse rate of the air parcel is given by

$$\Gamma = -\frac{\partial T'}{\partial z} = \frac{T'}{T}\frac{g}{c_p}$$

(b) Explain why the lapse rate in this case differs from the dry adiabatic lapse rate (g/c_p)

思考题

- Assuming the truth of the second law of thermodynamics, prove that an isolated ideal gas can expand spontaneously (e.g., into a vacuum) but cannot contract spontaneously

- One kilogram of ice at 0^{o}C is placed in an isolated container with 1 kg of water at 10^{o}C and 1 atm. (a) How much of the ice melts? (b) What change is there in the entropy of the universe due to the melting of the ice? (specific heat of water is 4218 J K^{-1} kg^{-1})

思考题

By differentiating the enthalpy function (h = u + pα), show that

$$\left(\frac{\partial p}{\partial T}\right)_s = \left(\frac{\partial s}{\partial \alpha}\right)_p$$

where s is entropy.

Note：

$$dh = Tds + \alpha dp$$

$$\frac{\partial}{\partial x_j}\left(\frac{\partial y}{\partial x_i}\right) = \frac{\partial}{\partial x_i}\left(\frac{\partial y}{\partial x_j}\right)$$

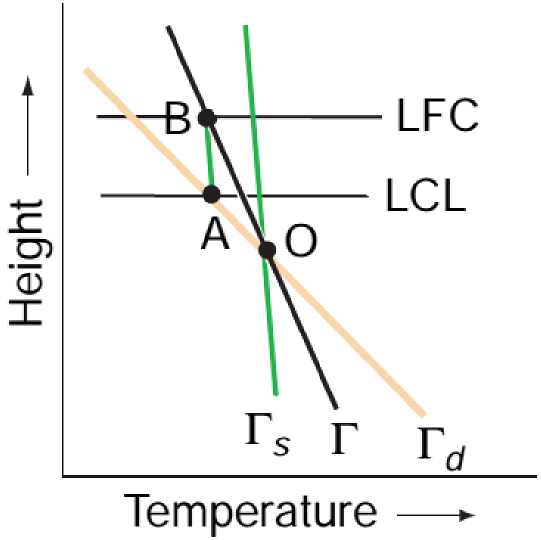
Show that this is equivalent to the Clausius-Clapeyron Equation.

This is one of the Maxwell’s four thermodynamic equations.

Conditional and Convective Instability

Conditionally unstable:

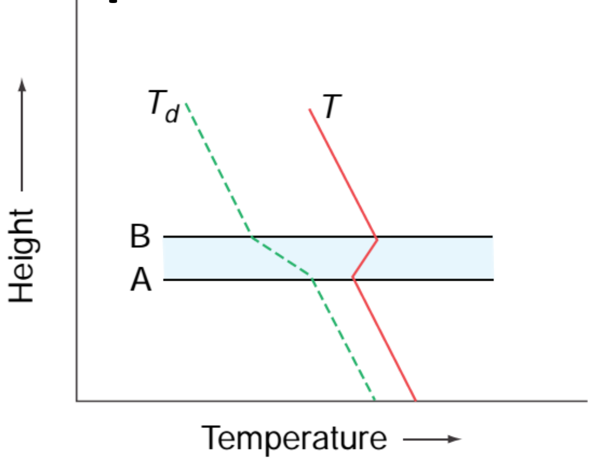
$\Gamma_s < \Gamma < \Gamma_d$

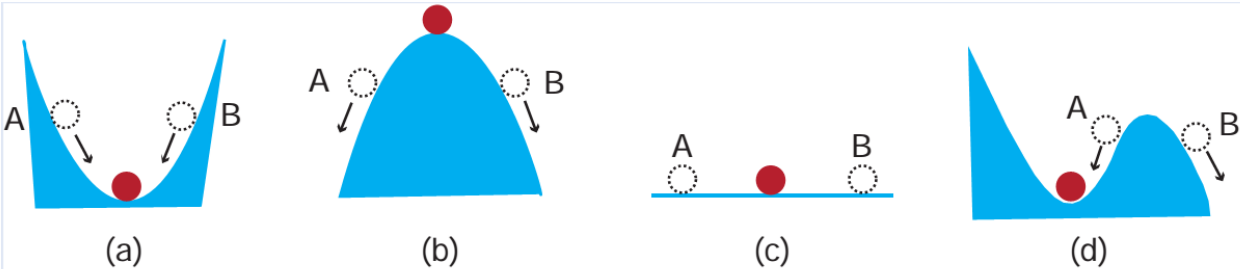


Convective instability:

θ_e decreases with height

Occurs often in tropics, albeit with only occasional deep convection





Stable Unstable Neutral Con. unstable

Heat

Heating rate per unit volume:

$$\rho\dot{q} = -\nabla \cdot \vec{F}_q$$

$$\vec{F}_q = \vec{F}_{rad} + \vec{F}_{dif}$$

$\vec{F}_{dif}$ **Flux of molecular diffusion (thermal conductivity)**
Only important in the thin layer above the surface called molecular diffusion layer

$\vec{F}_{rad}$ **Flux of radiation**

Work

Rate of working by fluid on surface dA (normal = n_j):

$$u_i \sigma_{ij} n_j dA$$

Work on surface

$$\sigma_{ij} = -p\delta_{ij} + \tau_{ij}$$

Stress tensor

$$\approx -p\delta_{ij} + \nu \frac{\partial u_i}{\partial x_j}$$

Work

$$\int_A u_i \sigma_{ij} n_j dA = \int_V \frac{\partial u_i \sigma_{ij}}{\partial x_j} dV$$

Gauss' Theorem

$$\rho \dot{\phi} = \frac{\partial u_i \sigma_{ij}}{x_j} = \sigma_{ij} \frac{\partial u_i}{\partial x_j} + u_i \frac{\partial \sigma_{ij}}{\partial x_j} = -p \nabla \cdot \vec{u} + \tau_{ij} \frac{\partial u_i}{\partial x_j} + u_i \frac{\partial \sigma_{ij}}{\partial x_j}$$

可逆做功

$$\rho \dot{\phi}_{rev} = -p \nabla \cdot \vec{u} = \frac{p}{\rho} \frac{d\rho}{dt} = -\rho p \frac{dv}{dt}$$

Continuity Equation

不可逆做功
（耗散项）

$$\rho \dot{\phi}_{irr} = \tau_{ij} \frac{\partial u_i}{\partial x_j} \approx p \nu \left(\frac{\partial u_i}{\partial x_j} \right)^2 \geq 0$$

平移项
（可逆+不可逆）

$$\rho \dot{\phi}_{tran} = u_i \frac{\partial \sigma_{ij}}{\partial x_j}$$

Energy

Kinetic energy:

$$k = \frac{1}{2} u_i u_i = \frac{1}{2} \vec{u} \cdot \vec{u}$$

$$\rho \frac{dk}{dt} = -\rho g w + u_i \frac{\partial \sigma_{ij}}{\partial x_j} = -\rho g w + \dot{\phi}_{trans}$$

Potential (geopotential) energy:

$$\pi(z) = \int_0^z g(z')dz'$$

$$\rho \frac{d\pi}{dt} = \rho g \frac{dz}{dt} = \rho g w$$

$$\frac{d\pi}{\mathrm{dz}} = g(z)$$

$$g(z)dz = g_0 d\tilde{z}$$

Energy and Enthalpy

(kinetic)

Internal energy:

$$\rho\frac{de}{dt}=\rho(\dot{q}+\dot{\phi}_{irr})+\rho\dot{\phi}_{rev}=\rho(\dot{q}+\dot{\phi}_{irr})+\frac{dp}{dt}-\rho r\frac{dT}{dt}$$

Enthalpy 焓 :

$$h=e+pv$$

$$\rho\frac{dh}{dt}=\rho\frac{d(e+pv)}{dt}=\rho\frac{d(e+rT)}{dt}=\rho(\dot{q}+\dot{\phi}_{irr})+\frac{dp}{dt}$$

Total energy:

$$total\quad energy=k+\pi+e$$

$$\rho\frac{d(k+\pi+e)}{dt}=\rho\dot{q}+\rho(\underline{\dot{\phi}_{trans}+\dot{\phi}_{rev}+\dot{\phi}_{irr}})$$

Total work

Energy + enthalpy:

$$energy+enthalpy=k+\pi+h$$

$$\rho\frac{d(k+\pi+h)}{dt}=\rho\dot{q}+\underline{\frac{\partial(\tau_{ij}u_i)}{\partial x_j}}+\frac{\partial p}{\partial t}$$

Viscous work

Entropy

$$\rho \frac{ds}{dt} = \frac{\rho}{T}(\dot{q} + \dot{\phi}_{irr})$$

Consequences of Hydrostatic Constraints

$$d\pi = gdz = -\frac{dp}{\rho}$$

$$Total \quad potential \quad energy = e + \pi$$

$$\rho \frac{d(e+\pi)}{dt} \approx \rho(\dot{q} + \dot{\phi}_{irr}) - \rho r \frac{dT}{dt}$$

$$Static \quad energy = h + \pi$$

$$d(h+\pi) \approx \rho(\dot{q} + \dot{\phi}_{irr}) = Tds$$

The first and second laws are the same for a system with one or two degrees of freedom

Consequences of Hydrostatic Constraints

Kinetic energy:

$$\rho \frac{dk}{dt} = -\rho g w - \vec{u} \cdot \nabla p + u_i \frac{\partial \tau_{ij}}{\partial x_j}$$

$$= -\rho g w - (w \frac{\partial p}{\partial z} + \vec{u} \cdot \nabla_h p) + u_i \frac{\partial \tau_{ij}}{\partial x_j}$$

$$= -\vec{u} \cdot \nabla_h p + u_i \frac{\partial \tau_{ij}}{\partial x_j}$$

Where: $\nabla_h = \frac{\partial}{\partial x} + \frac{\partial}{\partial y}$

This separates horizontal pressure force (directly measured) from vertical pressure force (approximated)

Energy Inventories

Definition:

$$\{\chi\} = \int_{system} \rho\chi dV$$

$$\left\{\frac{d\chi}{dt}\right\} = \int_{surface} F_n(\chi)dA + \frac{\partial\{\chi\}}{\partial t} = \tilde{F}(\chi) + \frac{\partial\{\chi\}}{\partial t}$$

Potential Energy:

$$\{\pi\} = \int_{atmos} \rho\pi dV$$

$$= \int_0^\infty \rho gzdz$$

$$= \int_0^{p_0} zdp$$

Hydrostatic

$$= \int_0^\infty pdz + [(pz)_\infty - (pz)_0]$$

$$= r\int_0^\infty \rho Tdz$$

Energy Inventories

$$\{h\} = \{c_p T\} + \{m_v l\}$$

$$\{e\} = \{c_v T\} + \{m_v l\}$$

$$\{h_{dry}\} = \{c_p T\} = c_p \int_0^\infty \rho T dz$$

$$\{e_{dry}\} = \{c_v T\} = c_v \int_0^\infty \rho T dz$$

$$\{c_p T\} : \{c_v T\} : \{\pi\} \approx 7 : 5 : 2$$

$$\{h\} = \{e + \pi\}$$

Hydrostatic

Energy Inventories

$$\{e+\pi+k\}=\{c_vT+lm+\pi+k\}\approx 1.3\times 10^{24}\,J$$

$$\{c_pT\}=97.5\%$$

$$\{c_vT\}=70.4\%$$

$$\{\pi\}=27.1\%$$

$$\{k\}=0.05\%$$

Kinetic energy is very small compared to internal and potential energy

Kinetic Energy

Rate of change:

$$\frac{\partial\{k\}}{\partial t}=\left\{\frac{u_i}{\rho}\frac{\partial\sigma_{ij}}{\partial x_j}\right\}-\{gw\}$$

No surface flux

$$=-\left\{\frac{\vec{u}}{\rho}\cdot\nabla_h p\right\}+\left\{\frac{u_i}{\rho}\frac{\partial\tau_{ij}}{\partial x_j}\right\}-\{gw\}$$

Because:

$$\left\{\frac{u_i}{\rho}\frac{\partial\tau_{ij}}{\partial x_j}\right\}=\left\{\frac{1}{\rho}\frac{\partial u_i\tau_{ij}}{\partial x_j}\right\}-\{\dot{\phi}_{irr}\}=-\int_{surface}u_i\tau_{iz}dA-\{\dot{\phi}_{irr}\}$$

We thus get:

$$\frac{\partial\{k\}}{\partial t}=\underbrace{-\int_{surface}u_i\tau_{iz}dA}_{\text{Wind Stress}}\underbrace{-\left\{\frac{\vec{u}}{\rho}\cdot\nabla_h p\right\}}_{\text{Generation}}\underbrace{-\{\dot{\phi}_{irr}\}}_{\text{Dissipation by friction}}$$

Total Potential Energy

$$p\rho\frac{dv}{dt} = -\frac{p}{\rho}\frac{dp}{dt} = p\nabla\cdot\vec{u} = \nabla\cdot p\vec{u} - \vec{u}\cdot\nabla p$$

$$\rho\frac{d\pi}{dt} = \rho g w = -w\frac{\partial p}{\partial z}$$

Hydrostatic

Thus:

$$\rho\frac{d\,(e+\pi)}{dt} = \rho(\dot{q} + \dot{\phi}_{irr}) + \vec{u}\cdot\nabla_h p - \nabla\cdot p\vec{u}$$

$$\frac{\partial\{e+\pi\}}{\partial t} = -\tilde{F}(e+\pi) + \{\dot{q}\} + \left\{\frac{\vec{u}}{\rho}\cdot\nabla_h p\right\} + \{\dot{\phi}_{irr}\}$$

Where:

$$\int_{atmos}\nabla\cdot p\vec{u}\,dV = -\int_{surface} pw\,dA = 0$$

Conservation of Energy

For a long-term average over the entire atmosphere, net surface fluxes must be zero if we are to maintain a steady state. In the absence of heat interaction:

$$\int_{surface} u_i \tau_{iz} dA = 0$$

$$\tilde{F}(e + \pi) = 0$$

$$\{\dot{q}\} = 0$$

Therefore:

$$\frac{\partial\{e + \pi\}}{\partial t} = -\frac{\partial\{k\}}{\partial t}$$

Surface Heat and Entropy Fluxes

Surface flux is a result of molecular diffusion through a very thin molecular diffusion layer

We have:

$$\tilde{F}(e+\pi) = \tilde{F}(e)$$

$$= \tilde{F}([1-m]e_{dry}) + \tilde{F}(m_v l) + \tilde{F}(mcT)$$

$$\approx \tilde{F}(e_{dry}) + l \cdot \tilde{F}(m_v) + cT \cdot \tilde{F}(m)$$

Where:

$$\tilde{F}(\pi) = F_z(\pi) = w\pi(\varepsilon) = wg\varepsilon \to 0$$

$\tilde{F}(m) = 0$	**Steady state**
$\tilde{F}(e_{dry}) =$	**Flux of sensible heat**
$l \cdot \tilde{F}(m_v) =$	**Flux of latent heat**

Surface Heat and Entropy Fluxes

Because:

$$\tilde{F}(h_{dry},\varepsilon) = \frac{c_p}{c_v} F_z(e_{dry},\varepsilon)$$

Flux divergence:

$$\rho \frac{d\varepsilon}{dt} = \frac{\partial \rho\varepsilon}{\partial t} + \nabla \cdot \vec{F}$$

$$\vec{F} = \vec{u}\rho\varepsilon$$

Assumptions: Hydrostatic, steady state, weak water vapor divergence, divergence of diffusive heat flux F(diff) much larger than dissipation work and divergence of radiation flux

$$\frac{\partial F_z(h_{dry})}{\partial z} \approx -\frac{\partial F(diff)}{\partial z}$$

Thus:

$$F_z(h_{dry}+\pi,\varepsilon) = F_z(h_{dry},\varepsilon) = F(diff,0)$$

$$F_z(e_{dry}+\pi,\varepsilon) = F_z(e_{dry},\varepsilon) = \frac{c_v}{c_p} F(diff,0)$$

$$F_z(s_{dry},\varepsilon) = \frac{F(diff,0)}{T_g}$$

Molecular entropy diffusion

Carnot Efficiency of Atmosphere

- Warm reservoir: 0-35° lat.
  Cool reservoir: 35-90° lat.: 15 K cooler
- Warm reservoir: Surface
  Cool reservoir: 5km (emis level): 25 K cooler
- Total temperature difference: 40 K
- Mean atmospheric temperature ~ 250 K

Carnot efficiency: 40/250 = 0.16

In steady state, efficiency of atmosphere is zero (kinetic energy is a small factor of total energy!)

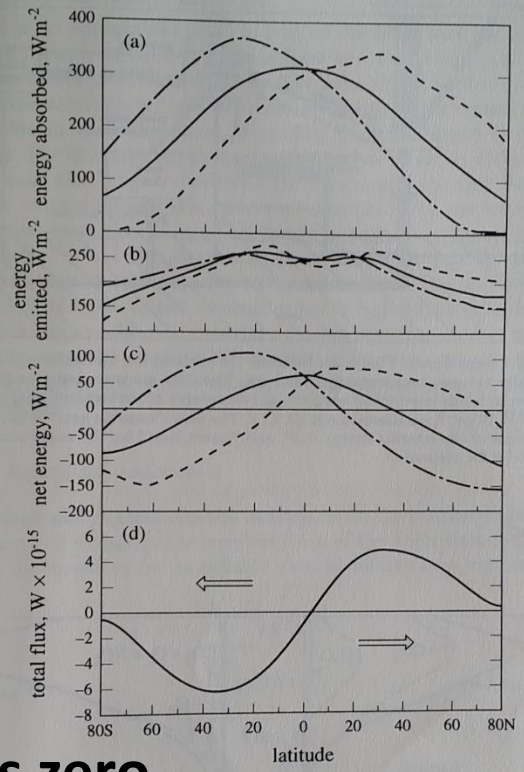


Figure 2.2 Latitude distribution of radiation fluxes. The first three panels give time-and-longitude averages of the radiation fluxes at the top of the atmosphere, as might be measured from a satellite. (a) is the net solar flux, incident less reflected. (b) is the outgoing flux of thermal radiation, and (c) is the balance, (a)−(b). (d) is the horizontal flux that must be carried across latitude circles by motions in the atmosphere-ocean system (northward positive) required to balance (c). Heavy, full lines are annual averages; dash-dot lines are averages over the three northern winter months; broken lines are averages over the three northern summer months.

Carnot Efficiency of Atmosphere

Heat flux: $$\dot{\varphi} = \dot{q}_1 - r\dot{\phi}_{irr}$$

Dissipation: $$\dot{\phi}_{irr} = \dot{q}_1 - \dot{q}_2$$

Carnot's theorem:

$$\frac{\dot{q}_1}{T_1} = \frac{\dot{q}_2}{T_2}$$

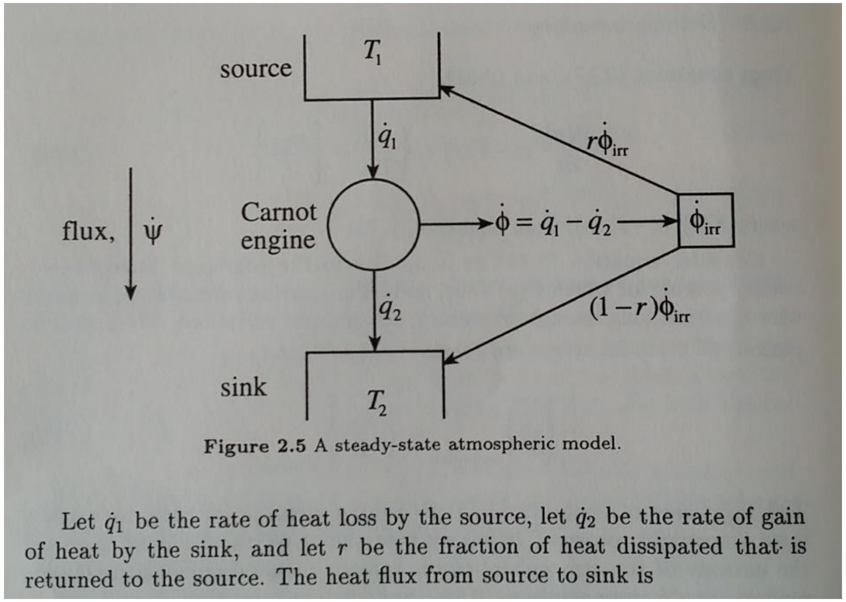


Figure 2.5 A steady-state atmospheric model.

Let $\dot{q}_1$ be the rate of heat loss by the source, let $\dot{q}_2$ be the rate of gain of heat by the sink, and let r be the fraction of heat dissipated that is returned to the source. The heat flux from source to sink is

Thus: $$\frac{\dot{\phi}_{irr}}{\dot{\varphi}} = \frac{T_1 - T_2}{T_1 + r(T_2 - T_1)} \approx \frac{T_1 - T_2}{T_1 \quad or \quad T_2} \approx 0.16$$

Last figure: **Maximum poleward heat flux by motion: $4.5\text{x}10^{15}$ W**
Average dissipation: 2.5 W m^{-2}, thus $\frac{\dot{\phi}_{irr}}{\dot{\varphi}}$ is 0.14

The atmosphere is efficient in dissipating mechanical energy in friction and returning work partly to heat source and sink