Thermodynamics

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Teaching materials are modified from Michael Wallace and Richard Goody

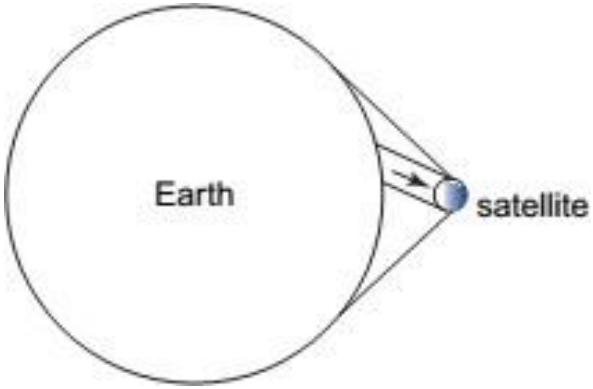


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Outline

- 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.

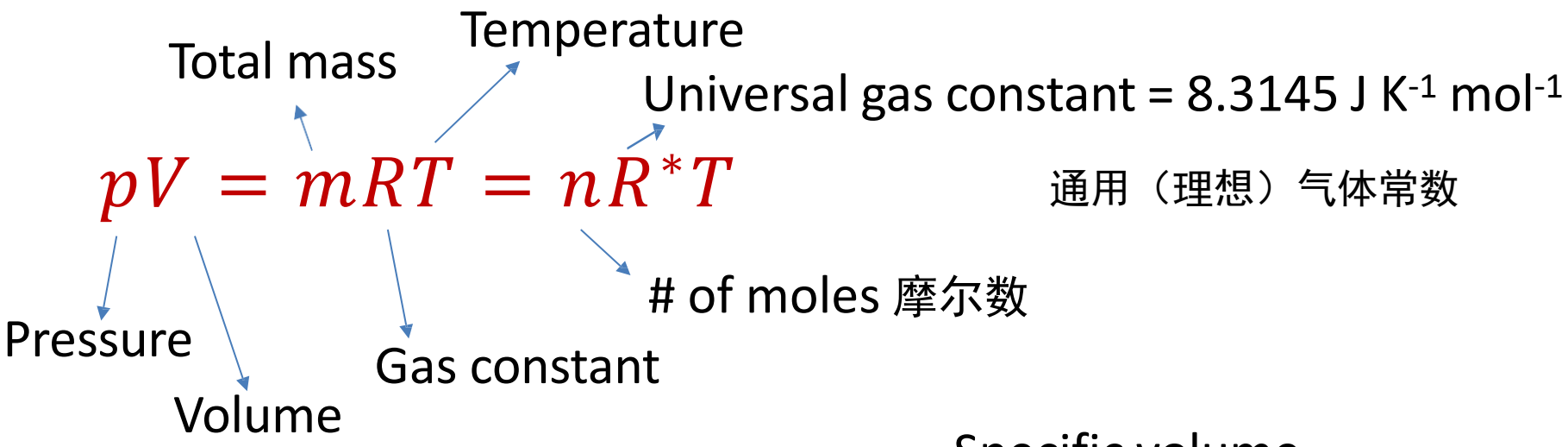
思考题

A. Consider two opaque walls facing one another. One of the walls is a blackbody and the other wall is “gray”. The walls are initially at the same temperature T and, apart from the exchanges of radiation between them, they are thermally insulated from their surroundings. If A and ε are the absorptivity and emissivity of the gray wall, use thermodynamic arguments to prove that $\varepsilon = A$.

B. Consider a similar situation with two “gray” walls, one with absorptivity A_1 and the other with absorptivity A_2. Prove that $\frac{\mathrm{F}_1}{\mathrm{A}_1} = \frac{\mathrm{F}_2}{\mathrm{A}_2}$

where F_1 and F_2 are the flux densities of the radiation emitted from the two walls.

Ideal Gas Equation



Specific volume

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

- Ideal gas has negligible molecular size and no interactions except elastic collisions
- Ambient air is close to ideal gas, and is treated as so
- How to derive the ideal gas equation?

Derivation of Ideal Gas Equation

Probability distribution function of velocity (not speed) in one direction:

$$f(v) = \sqrt{\frac{m}{2\pi kT}}\, e^{-\frac{mv^2}{2kT}}$$

For ideal gas molecules,
with mass m for a molecule

Momentum change of molecules to hit a wall perpendicular to that direction:

$$p \cdot \delta s \cdot \delta t = \int_{v=0}^{\infty} \int_{v'=v}^{\infty} 2 \cdot m \cdot f(v') \cdot v' \cdot dv' \cdot dv \cdot \delta t \cdot \delta s \cdot N$$

Thus, pressure caused by momentum of those molecules:

$$p = \int_{v=0}^{\infty} \int_{v'=v}^{\infty} 2 \cdot m \cdot f(v') \cdot v' \cdot dv' \cdot dv \cdot N$$

$$= NkT = \frac{N}{N_A} \cdot (N_A k) \cdot T = \frac{n}{V} R^* T$$

Gaussian integral

$$\int_{-\infty}^{\infty} e^{-x^2} dx = \sqrt{\pi}$$

Avogadro's Hypothesis 阿伏加德罗定律

Gram-molar mass M:

$$M = 1000\frac{m}{n}$$

Total mass

摩尔质量 $(g\ mol^{-1})$

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

Avogadro's Number: $N_A = 6.022 \times 10^{23}\ per\ mole$

1 mole has N_A molecules

Avogadro's hypothesis (1811): gases containing the same number of molecules occupy the same volume 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 1801:
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 type of gas i is the pressure it would exert at the same temperature as the mixture I if it alone occupied all of the volume that the mixture occupies

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

Dry Air

Specific volume 比容 ($m^3\ kg^{-1}$)

For a unit mass (kg) of dry air: $p_d \alpha_d = R_d T$

Apparent molar mass: 表观摩尔质量

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

Therefore:

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

- Below turbopause (~ 100 km), R_d is constant (287.0 J kg^{-1} K^{-1}) due to high frequency of molecular collision and well mixing of (long-lived) gases
- Above turbopause, heavier gases decrease with height faster, and R_d is no longer constant!

Water Vapor

For a unit mass (kg) of water vapor: $e\alpha_v = R_v T$

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

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

Virtual Temperature 虛温

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

$$p = \rho_d R_d T + \rho_v R_v T = \rho R_d T_v$$

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:

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

$$\approx T\left(1 + 0.378\frac{e}{p}\right)$$

Water Vapor in the Atmosphere

Mass mixing ratio: $w = \frac{m_v}{m_d} = \frac{q}{1-q} < 0.05$ in general

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

Water vapor pressure: $e = \frac{w}{w+\varepsilon} p$

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

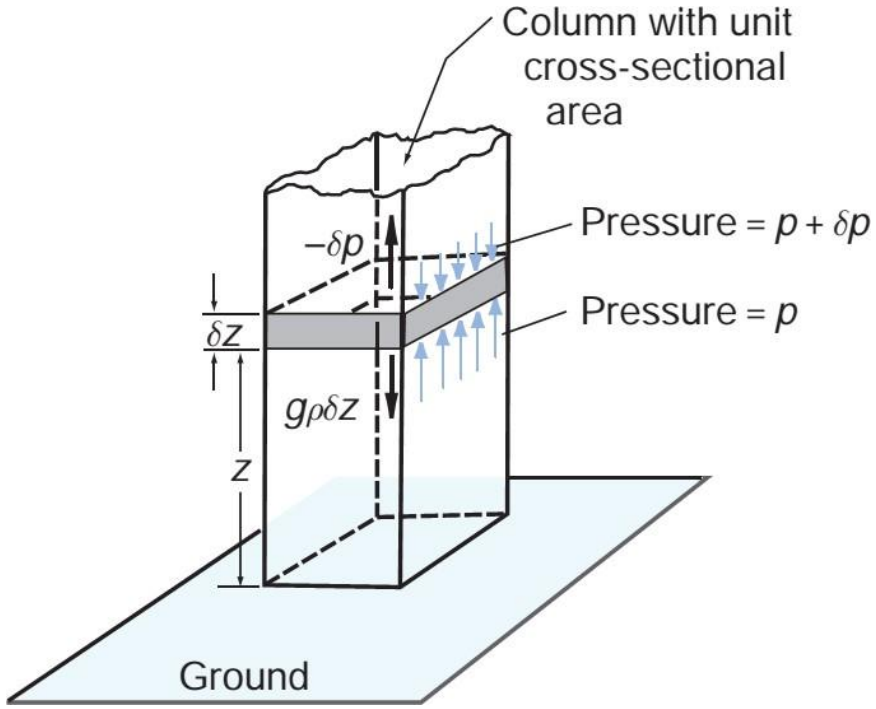
$= T\left(1 + q\frac{1-\varepsilon}{\varepsilon}\right) = T(1 + 0.608q)$

Hydrostatic Equation 静力方程

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

Thus:

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



Under what conditions is the hydrostatic equation valid?

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 above a unit area (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:

$$d\phi = gdz$$

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

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:

$$d\phi = gdz = -\alpha dp$$

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 for Moist Atmosphere

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

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

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

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, dry atmosphere:

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

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

Scale height 标高:

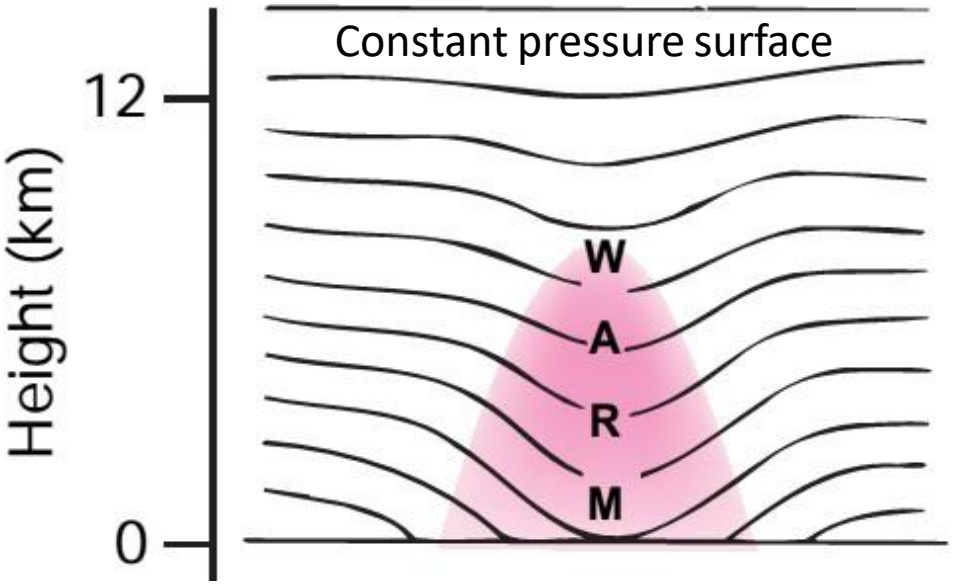
$$H = \frac{R_d T_v}{g_0} = \frac{R_d T}{g_0} = 29.3T$$

For dry air

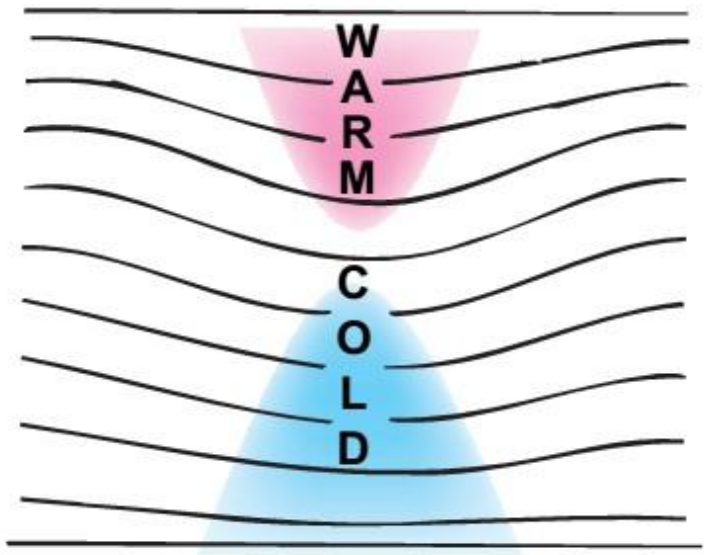
- Below turbopause (~ 100 km), R_d is constant (287.0 J kg^{-1} K^{-1})
- For T = 255 K, we get H ~ 7.5 km
- Above turbopause, concentrations of heavier gases decrease with height faster, and R_d is no longer constant!

Thickness of Height of Constant Pressure Surfaces

Warm core



Cold core below warm core



First Law of Thermodynamics

- Unless otherwise stated, we only discuss the case with no changes in nuclear energy, internal inter-molecular potential energy, chemical reactions, and macroscopic kinetic energy
- By default, we consider a unit mass (kg) of air parcel

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

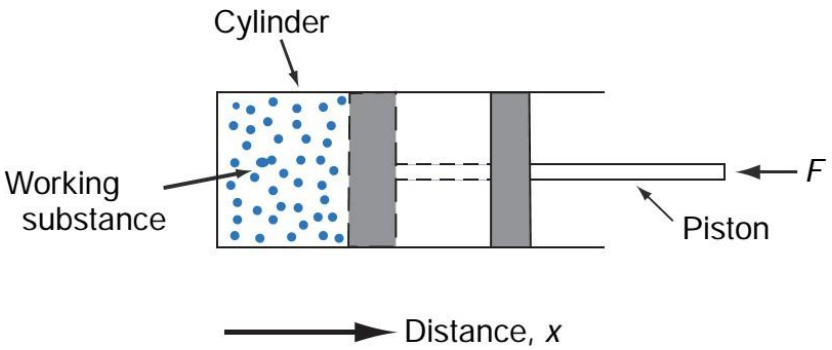
q: heat (interaction, *not transported*)
w: work (interaction, *not transported*)
u: internal kinetic energy (function of state)

Work

$$\delta w = Fdx$$

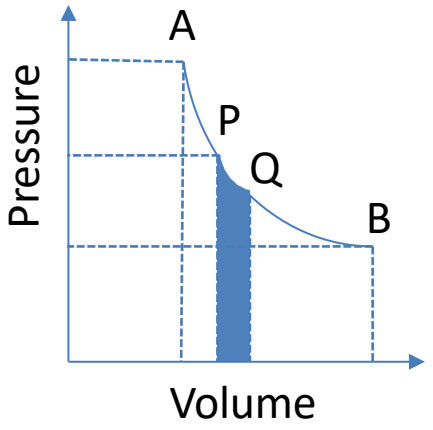
$$= pAdx = pd\alpha$$

体积功



Thus:

$$w = \int_{\alpha_A}^{\alpha_B} pd\alpha$$



Thermodynamic diagram

仅考虑体积功，不考虑相变引起的表面积（表面能）变化等其他做功

Specific Heats

For a closed system of a unit mass of air parcel w/o phase change:

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

At constant volume: $$c_v = \left(\frac{\delta q}{\delta T}\right)_v = \left(\frac{\partial u}{\partial T}\right)_v = \frac{du}{dT}$$

At constant pressure: $$c_p = \left(\frac{\delta q}{\delta T}\right)_p = c_v + R$$

$c_v \approx \frac{5}{2} R$ for the present Earth atmosphere, why?

Enthalpy 焓

Define enthalpy h (a state function, like u, p, v, T):

$$h = u + p\alpha$$

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

Therefore, under hydrostatic equilibrium:

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

Dry static energy $= h + \phi$

Air Parcel 气块假设

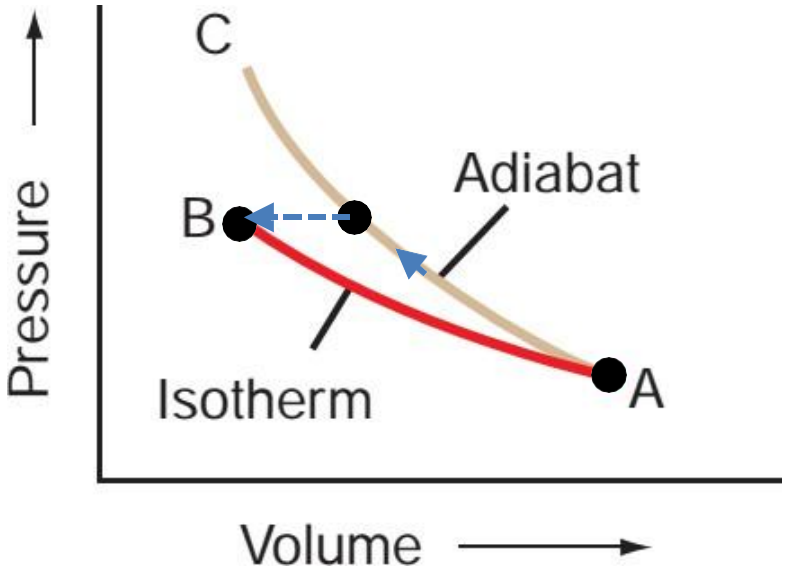
Assuming that a parcel of air is

- ✓ Thermally insulated from its environment, so that its temperature changes adiabatically as it moves vertically
- ✓ Always remaining at exactly the same pressure as the environmental air at the same level, which is assumed to be in hydrostatic equilibrium
- ✓ Moving slowly enough that the macroscopic kinetic energy (and its change) of the air parcel is a negligible fraction of its total (macro + internal) energy

Dry Adiabatic Process
(Vertical Movement with No Phase Change)

Dry static energy is conserved:

$$\delta q = d(h + \phi)$$
$$= d(c_p T + \phi)$$
$$= c_p dT + g dz$$
$$= 0$$



Thus, dry adiabatic lapse rate:

$$\Gamma_d = -\left(\frac{dT}{dz}\right)_{dry\ parcel} = \frac{g}{c_p} = 9.8\ K\ km^{-1}$$

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)

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

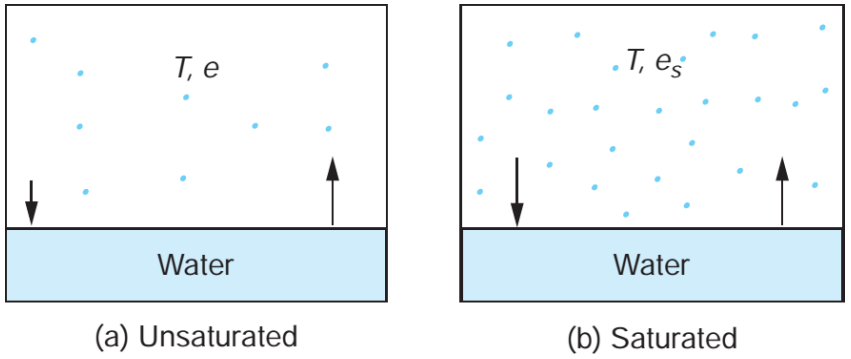
$$\frac{c_p}{R}\frac{dT}{T} - \frac{dp}{p} = 0$$

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

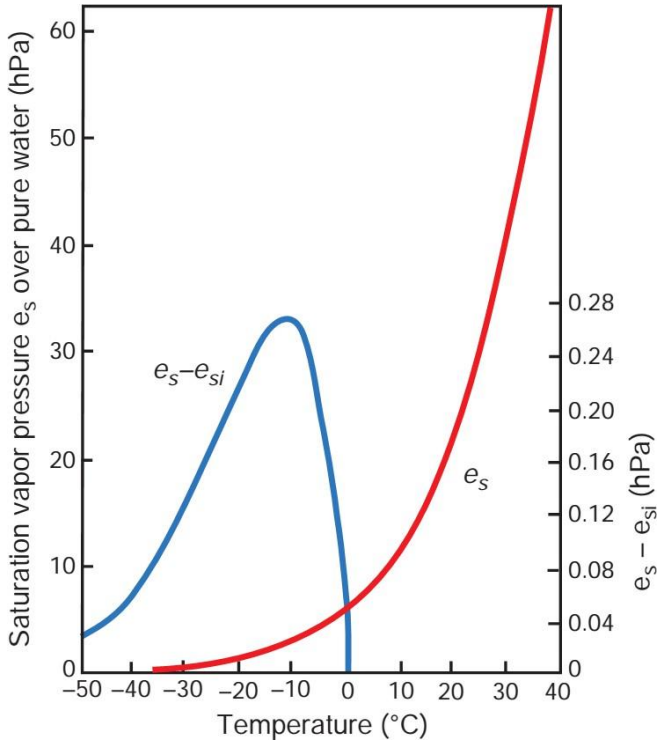
$$\Rightarrow \quad \theta = T\left(\frac{p_0}{p}\right)^{R/c_p}$$

Equilibrium (Saturation) Vapor Pressure

- e_s: Saturation vapor pressure with respect to a plane surface of pure water at T
- e_{si}: Saturation vapor pressure with respect to a plane surface of pure ice at T
- Bergeron process 贝吉龙过程?



(a) Unsaturated (b) Saturated



Saturation Mixing Ratio

Mixing ratio of water vapor at the state of saturation:

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

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

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

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

Note that:

$$e = e(\rho_v, T) \qquad w = w(\rho_v, p, T)$$

$$e_s = e_s(T) \qquad w_s = w_s(p, T)$$

Latent Heat for Phase Change 相变潜热

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 0°C

L_v is weakly dependent on T: $L_v = 2.5 \times 10^6 - 2323(T - 273.15)$

$\delta q \approx -L_v dw_s$ for a unit mass of saturated moist air

$dw_s > 0$: evaporation occurs, thus for air parcel, $dq < 0$

$dw_s < 0$: condensation occurs, thus for air parcel, $dq > 0$

Saturated Adiabatic & Pseudoadiabatic Processes

As the air parcel 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
  - ✓ However, the mass and energy of precipitated water is small compared to those of the whole air parcel, why?

Saturated Adiabatic & Pseudoadiabatic Processes

As a unit mass of saturated air parcel moves vertically:

$$\delta q \approx -L_v \cdot dw_s = c_p dT + g dz \quad \Rightarrow \quad \frac{dT}{dz} = -\frac{L_v}{c_p}\frac{dw_s}{dz} - \frac{g}{c_p}$$

Note:

$$w_s = \varepsilon \frac{e_s}{p - e_s} = w_s(p, T)$$

Math

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

Thus:

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

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

Saturated Adiabatic & Pseudoadiabatic Processes

Thus, moist adiabatic lapse rate (with phase change):

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

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

$\Gamma_s \approx 4$ K km^{-1} near the ground in warm, humid air

$\Gamma_s = 6{-}7$ K km^{-1} in the middle troposphere

$\Gamma_s \approx \Gamma_d$ near the tropopause

Saturated Adiabatic & Pseudoadiabatic Processes

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

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

Because: $$\frac{dT}{T} \ll \frac{dw_s}{w_s}$$ Why?

Thus: $$\frac{L_v}{c_p T} dw_s \approx d\left(\frac{L_v w_s}{c_p T}\right)$$

Saturated Adiabatic & Pseudoadiabatic Processes

Thus:

$$-d\left(\frac{L_v w_s}{c_p T}\right) \approx d ln\theta$$

$$-\frac{L_v w_s}{c_p T} \approx ln\theta + constant$$

At low temperature, $w_s/T \to 0$, and thus $\theta \to \theta_e$

Thus, equivalent potential temperature 相当位温 θ_e

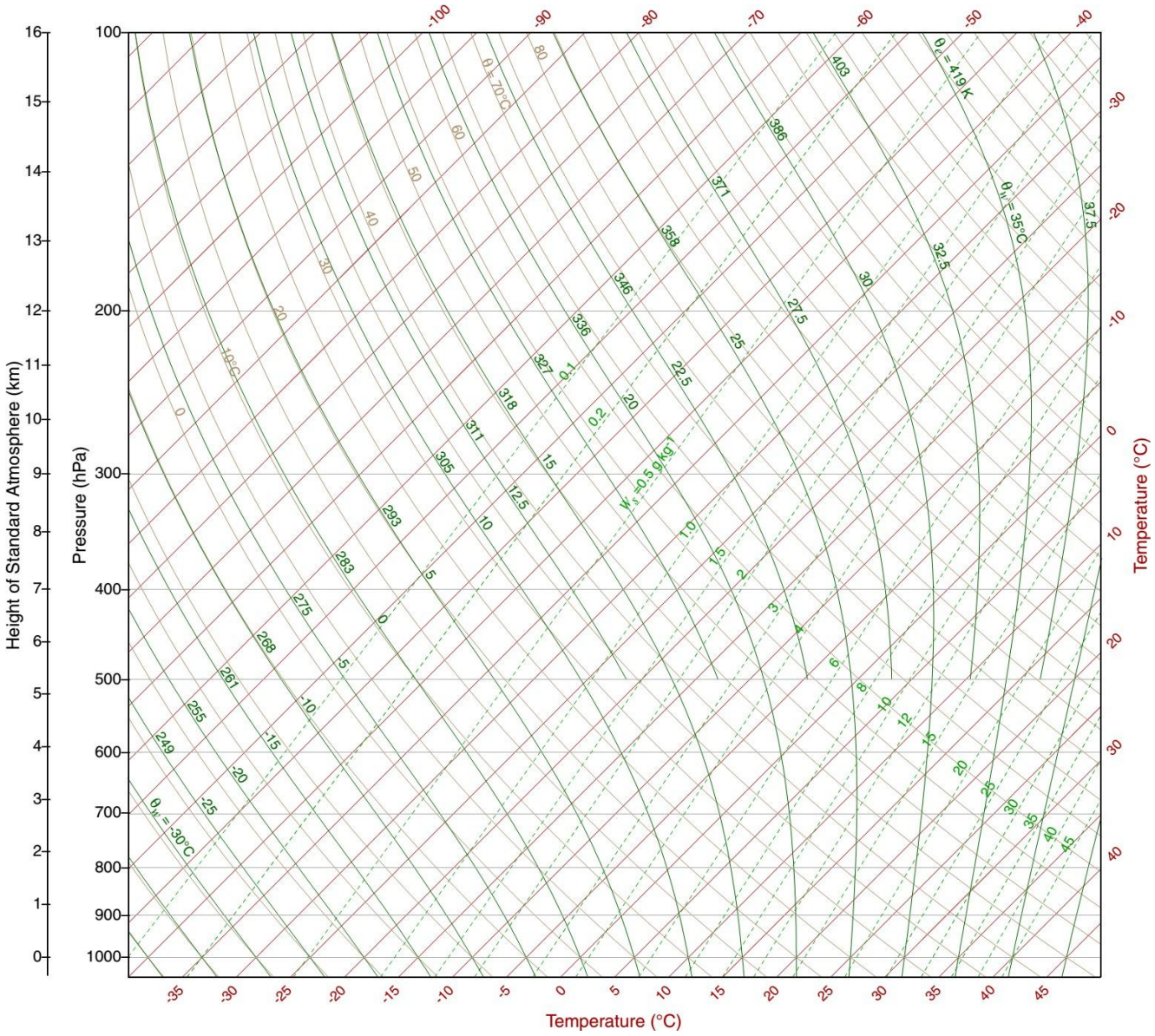
$$-\frac{L_v w_s}{c_p T} \approx ln\frac{\theta}{\theta_e} \quad \Leftrightarrow \quad \theta_e \approx \theta e^{\frac{L_v w_s}{c_p T}}$$

Equivalent Potential Temperature

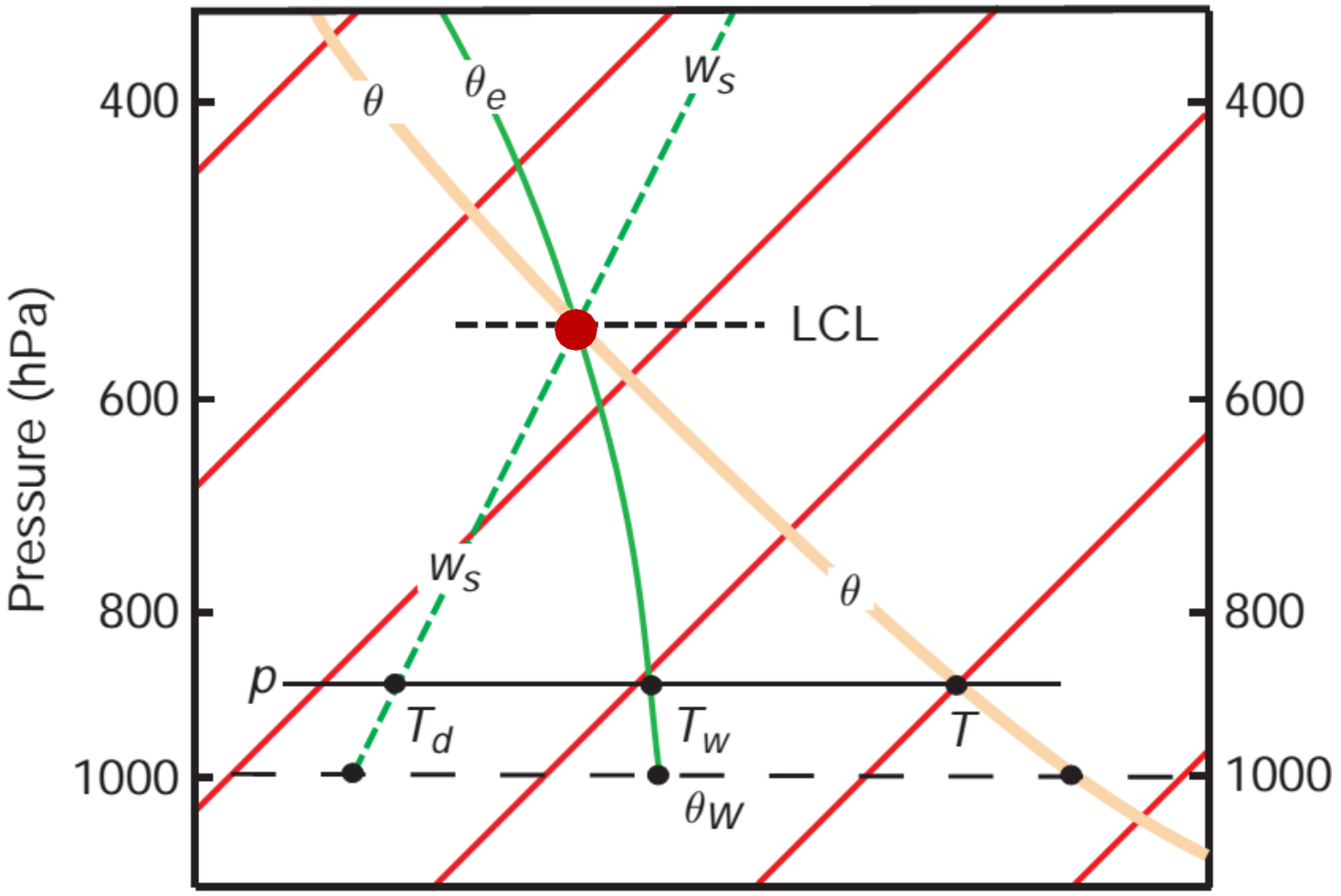
θ_e is the potential temperature θ of a parcel of air when all the water vapor has condensed so that its saturation mixing ratio w_s is zero.

- ✓ The saturated air is lifted adiabatically until all the vapor has condensed, released its latent heat, and fallen out. The air is then compressed dry adiabatically to the standard pressure of 1000 hPa, at which point it will attain the temperature θ_e .
- ✓ If the air is initially unsaturated, w_s and T are the saturation mixing ratio and temperature at the point where the air first becomes saturated after being lifted dry adiabatically.
- ✓ θ_e is conserved during both dry adiabatic and pseudoadiabatic processes as air move vertically.

Skew T-lnP Chart（倾斜T-lnP图）



Normand's Rule 诺曼德法则



Moist Static Energy

Moist static energy is conserved during dry adiabatic or saturated adiabatic ascent or descent with water undergoing transitions between liquid and vapor phases.

Specific humidity

Moist static energy $= h + \phi + L_v q$

$= c_p T + \phi + L_v q$

$$d(h + \phi + L_v q) = c_p dT + g dz + L_v dq = 0$$

Instability of Unsaturated Air Parcel Not In Hydrostatic Equilibrium

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

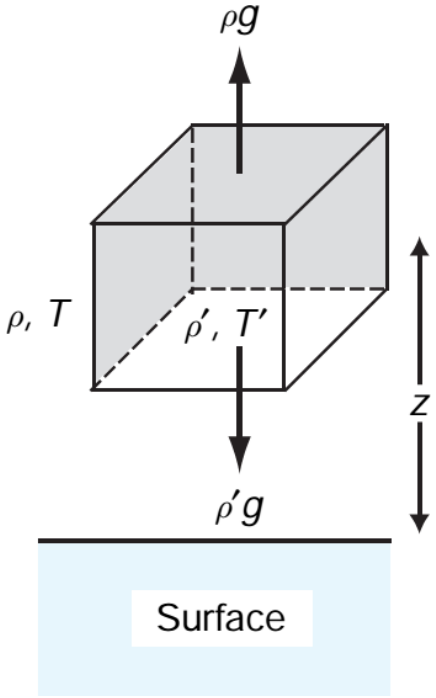
The net upward force acting on a unit of volume of the parcel is:

$$p = \rho RT = \rho' RT' = p'$$

$$F = (\rho - \rho')g \neq 0$$

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

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



Instability of Unsaturated Air Parcel Not In Hydrostatic Equilibrium

If the air parcel is displaced vertically, 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: $$\frac{d^2 z'}{dt^2} = -\frac{g}{T}(\Gamma_d - \Gamma)z'$$

$$\frac{d^2 z'}{dt^2} + N^2 z' = 0$$

$$N = \left[\frac{g}{T}(\Gamma_d - \Gamma)\right]^{1/2}$$

Brunt-Väisälä frequency
浮力（布维）频率

Buoyancy Oscillation

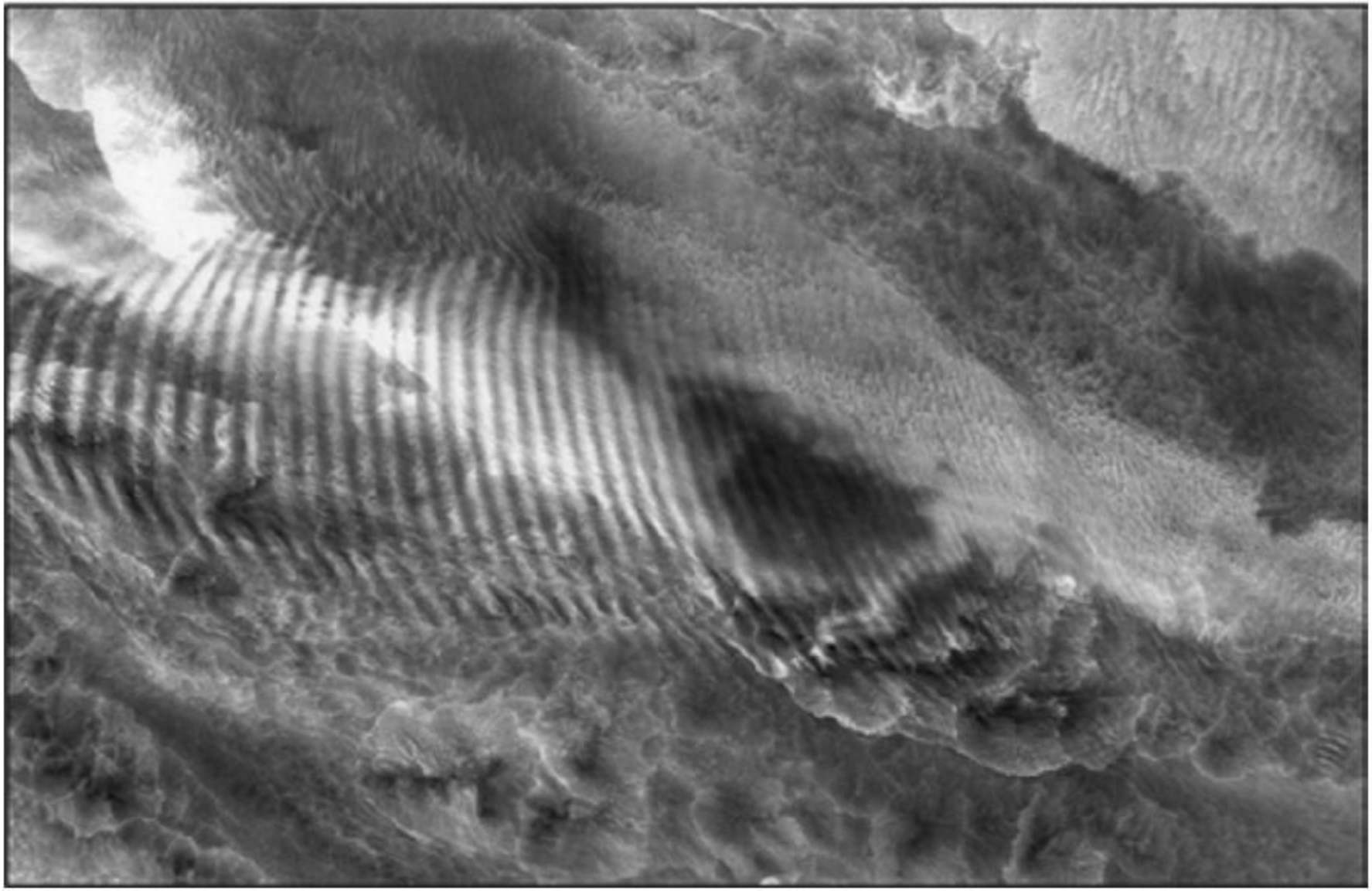
$$\frac{d^2z'}{dt^2} + N^2 z' = 0 \qquad N = \left[\frac{g}{T}(\Gamma_d - \Gamma)\right]^{1/2}$$

Stably stratified atmosphere: $N^2 > 0$ or $\Gamma_d - \Gamma > 0$

Here, air parcel executes a buoyancy oscillation

$$z' = AcosNt + BsinNt$$

Buoyancy Oscillation over Indian Ocean



Static Instability For Unsaturated Air Parcel

Stable: $\Gamma < \Gamma_d$ (θ in env. increases with height)

Neutral: $\Gamma = \Gamma_d$ (θ in env. does not change with height)

Unstable: $\Gamma > \Gamma_d$ (θ in env. decreases 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 Parcel

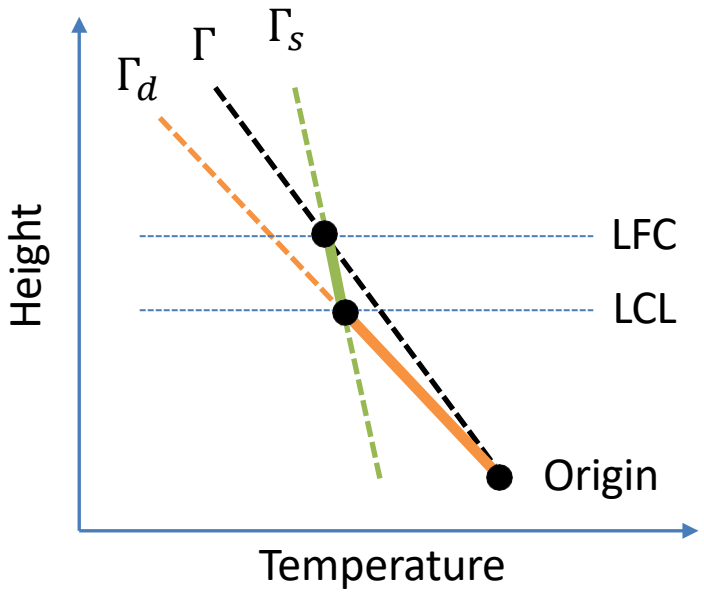
Stable: $\Gamma < \Gamma_s$

Neutral: $\Gamma = \Gamma_s$

Unstable: $\Gamma > \Gamma_s$

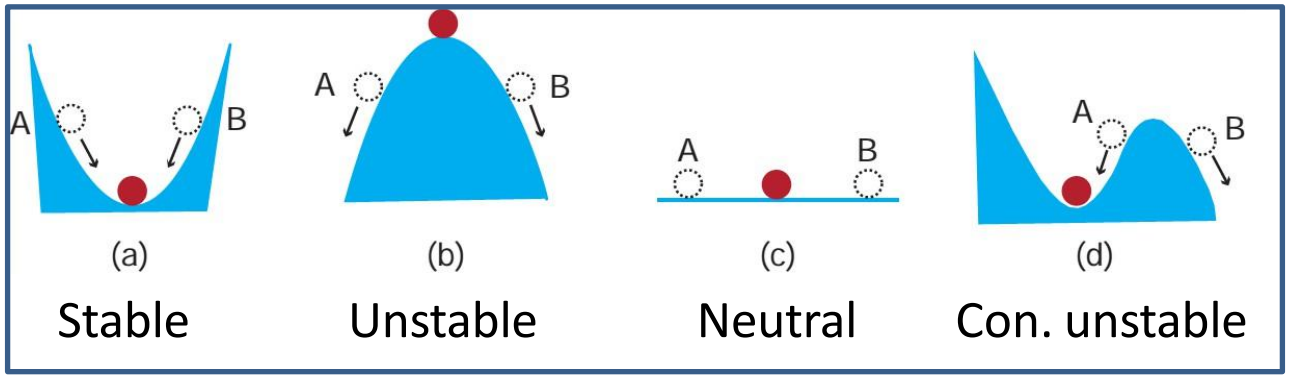
$$\Gamma_s \approx \frac{\Gamma_d}{1 + \frac{L_v}{c_p}\left(\frac{\partial w_s}{\partial T}\right)_p}$$

Conditional and Convective Instability



Conditionally unstable:

$$\Gamma_s < \Gamma < \Gamma_d$$



Heat Engine and Its Efficiency

A heat engine undergoes thermodynamic cycles that:

- 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*

Thermal efficiency of a heat engine:

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

A thermodynamic cycle consists of linked sequences of thermodynamic processes that involve transfer of heat and work into and out of the system, while varying pressure, temperature, and other state variables within the system, and that eventually return the system to its initial state

Carnot's Theorem

Carnot's theorem:

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

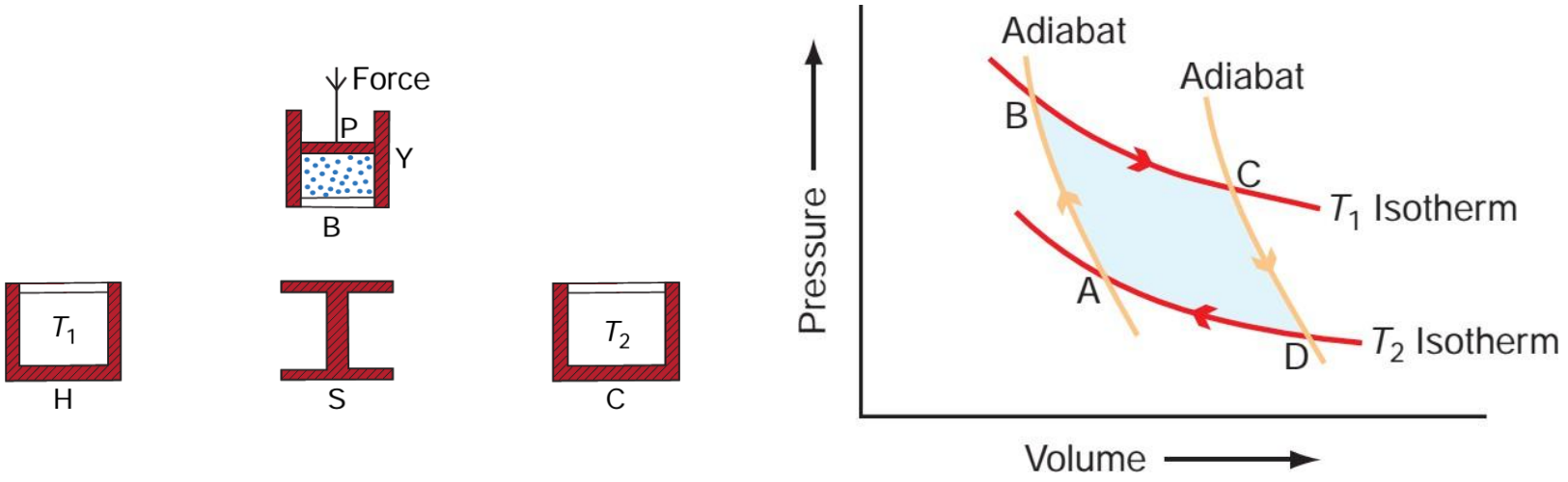
- *Reversible transformation can be reversed at any point by making an infinitesimal change in the surroundings*
- *Irreversible (spontaneous) transformation*

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: A Special, Simple Reversible Thermodynamic Cycle



Carnot cycle (reversible, with no phase change):

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

Carnot Cycle: Relationship between Pressure and Volume

A → B: adiabatic

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

For a unit of mass

Thus: $\gamma dln\alpha + dlnp = 0$

$\gamma = c_p/c_v = 1.4$

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

Carnot Cycle

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

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

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

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

Carnot efficiency: the maximum thermal efficiency

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

Entropy 熵

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

For a unit of mass

For reversible heat exchange: $$ds \equiv \frac{\delta q_{\text{rev}}}{T}$$

In this case:

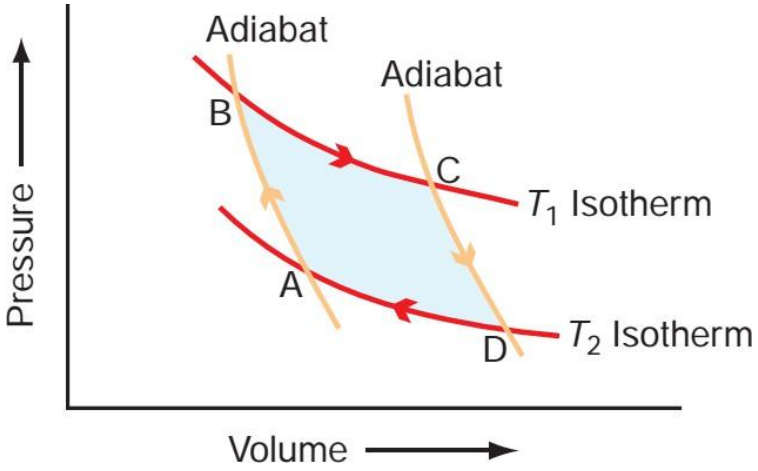
First Law of Thermodynamics: $$Tds = du + pd\alpha$$

Dry adiabatic = Isentropic $$ds = c_p \frac{d\theta}{\theta}$$

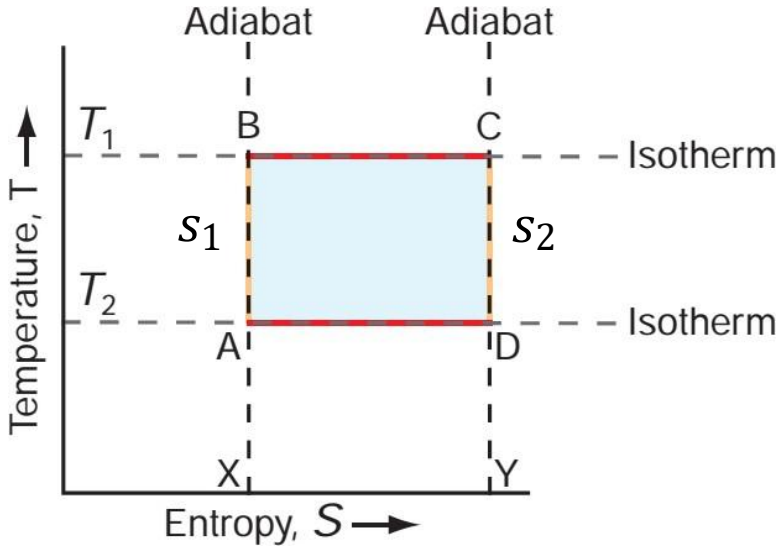
$$s = c_p ln\theta + constant$$

Entropy and Work in a Carnot Cycle

Pressure-volume diagram



Temperature-entropy diagram

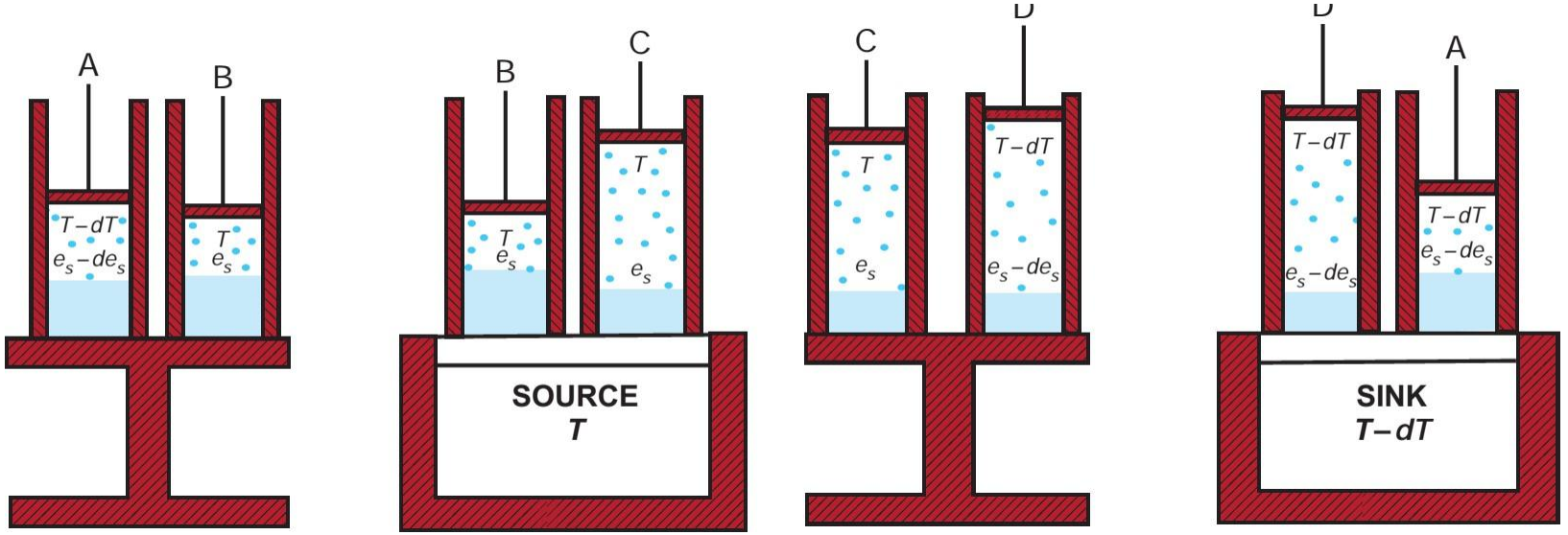


$$W = (T_1 - T_2)(s_2 - s_1) = \Delta T \cdot \Delta s$$

Clausius-Clapeyron Equation: The First Latent Heat Equation

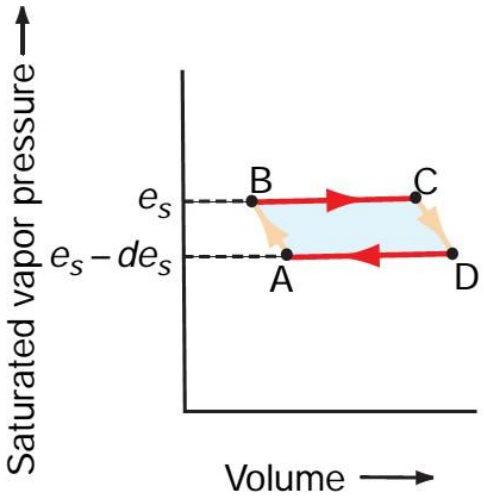
为了推导C-C方程，构建一个可逆、有相变（蒸发/凝结）的热力学循环，即系统中的成分发生相变（比如水的相变）

绝热，无相变 ➡ 等温吸热，蒸发 ➡ 绝热，无相变 ➡ 等温放热，凝结

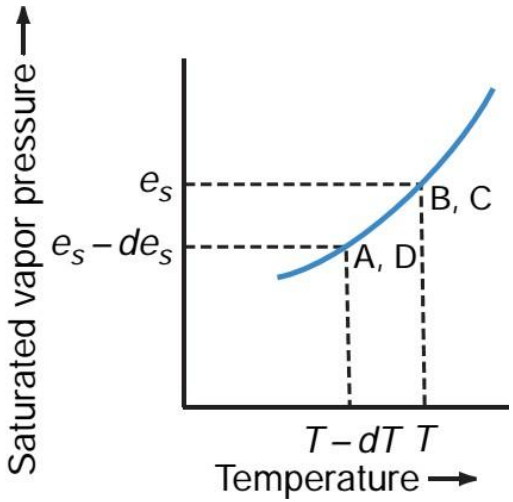


Clausius-Clapeyron Equation

P-V diagram



P-T diagram



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

Carnot's theorem: All reversible engines working between the same limits of temperature have the same efficiency. Thus,

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

Clausius-Clapeyron Equation

Converting a unit of mass from liquid to vapor:

$$Q_1 - Q_2 = (\alpha_C - \alpha_B)de_s = (\alpha_{vapor} - \alpha_{liquid})de_s$$

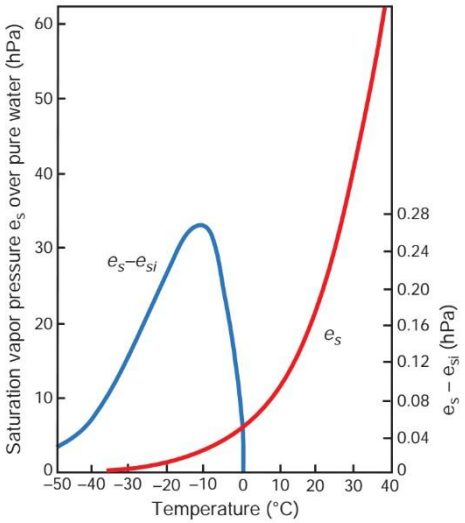
$$Q_1 = L_v, \qquad T_1 = T, \qquad T_1 - T_2 = dT$$

Thus: $$\frac{L_v}{T} = \frac{(\alpha_{vapor} - \alpha_{liquid})de_s}{dT} \approx \frac{\alpha_{vapor} de_s}{dT}$$

C-C Eq.

$$\frac{de_s}{dT} \approx \frac{L_v}{T\alpha_{vapor}} = \frac{L_v e_s}{R_v T^2}$$

$$\frac{1}{e_s}\frac{de_s}{dT} \approx \frac{L_v}{R_v T^2} = \frac{L_v M_v}{1000 R^* T^2}$$



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 T 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

$$\Gamma = -\frac{dT'}{dz} = \frac{T'}{T}\frac{g}{c_p}$$

(b) Explain why the lapse rate in this case differs from the dry adiabatic lapse rate $\Gamma_d = \frac{g}{c_p}$

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

A. By differentiating the enthalpy function ($h = u + p\alpha$), show that

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

where s is entropy

Note:

$$dh = Tds + \alpha dp$$

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

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

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