Thermodynamics of the atmosphere

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THERMODYNAMICS
is the link between
the circulation and transfers of heat
(radiative, sensible, and latent)
between the Earth's surface and the atmosphere.

THERMODYNAMICS
deals with
internal transformations of the energy of a system
and exchanges of energy between that system and its environment.

Outline of the course 'Thermodynamics of the Atmosphere'

- Thermodynamics of dry air
- Thermodynamics of moist air
- Processes in the atmosphere
- Thermodynamical diagrams
- Atmospheric stability
  - Dry and moist adiabatic gradients
  - Stability criteria

Textbooks

- *Fundamentals of Atmospheric Physics*, M.L. Salby **(Salby)**
- *A Short Course in Cloud Physics*, R.R. Rogers and M.K. Yau **(R&Y)**
- *Thermodynamics of Atmospheres and Oceanes*, J.A. Curry and P.J. Webster **(C&W)**
- *Microphysics of Cloud and Precipitation*, H. Pruppacher and J. Klett
- *Atmospheric Chemistry and Physics*, J.H. Seinfeld and S.N. Pandis
- *Atmospheric Science. An Introductory Survey*, J. Wallace

Outline of the lecture

1. Composition and structure of the atmosphere
2. Equation of state for dry air
3. Thermodynamic system, state functions

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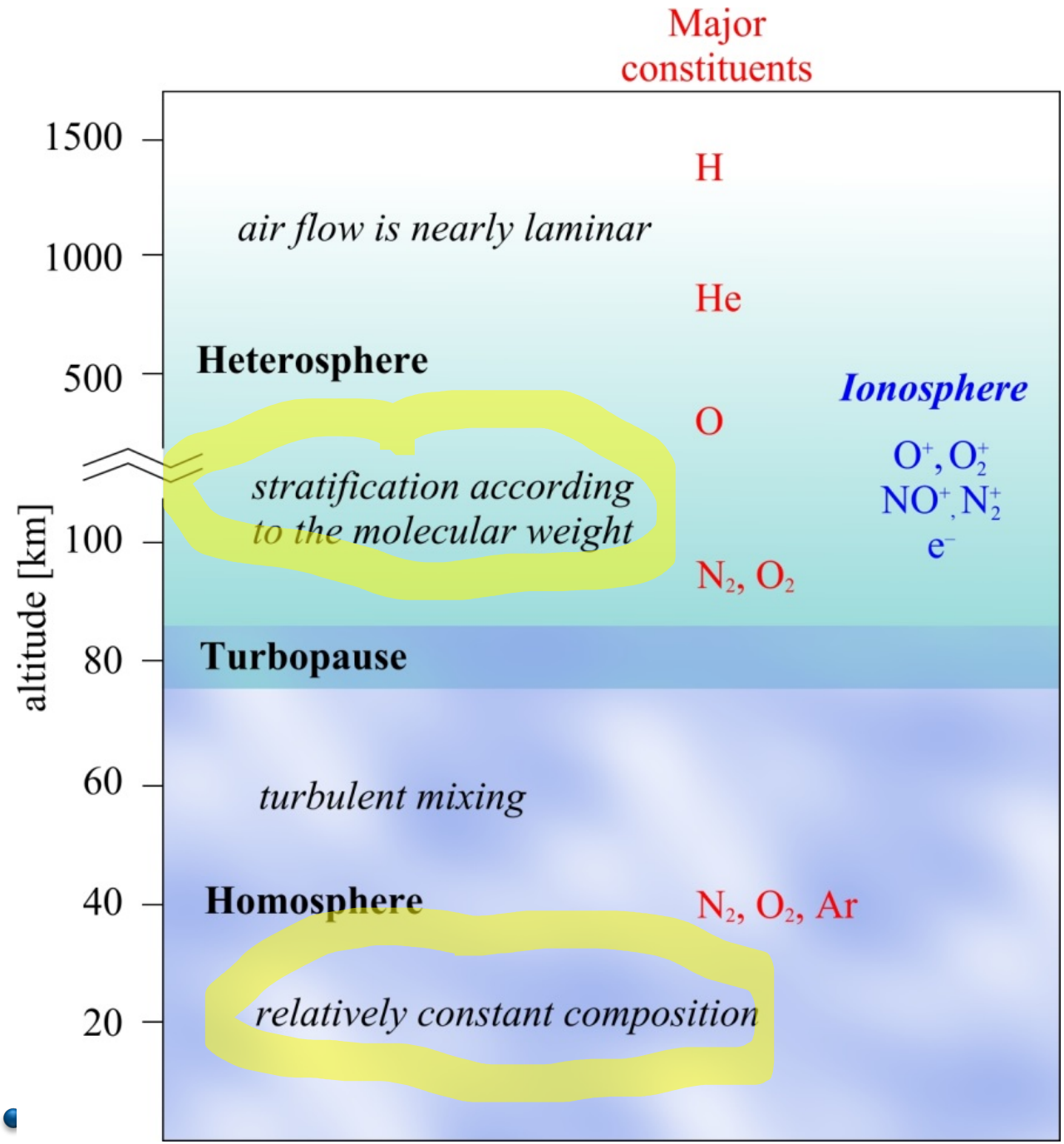
Textbooks

- Salby, Chapter 1 and 2
- R&Y, Chapter 1


Major constituents
1500
1000
500
100
80
60
40
20
altitude [km]
air flow is nearly laminar
Heterosphere
stratification according to the molecular weight
Turbopause
turbulent mixing
Homosphere
relatively constant composition
H
He
O
N2, O2
Ionosphere
O+, O2+
NO+, N2+
e−
N2, O2, Ar

Processes controlling the stratification of mass and the composition of air

- Molecular diffusion:
  - depends on the mean free path
    - the mean free path varies inversly with air density; it increases exponentially with altitude from about 10^{-7}m at the surface to of order 1m at 100km.
  - the mean free path determines properties of air such as viscosity and thermal conductivity.
  - diffusion of momentum and heat dissipate atmospheric motions by destroying gradients of velocity and temperature.
- Turbulent mixing:
  - stirs different gases with equal efficiency.

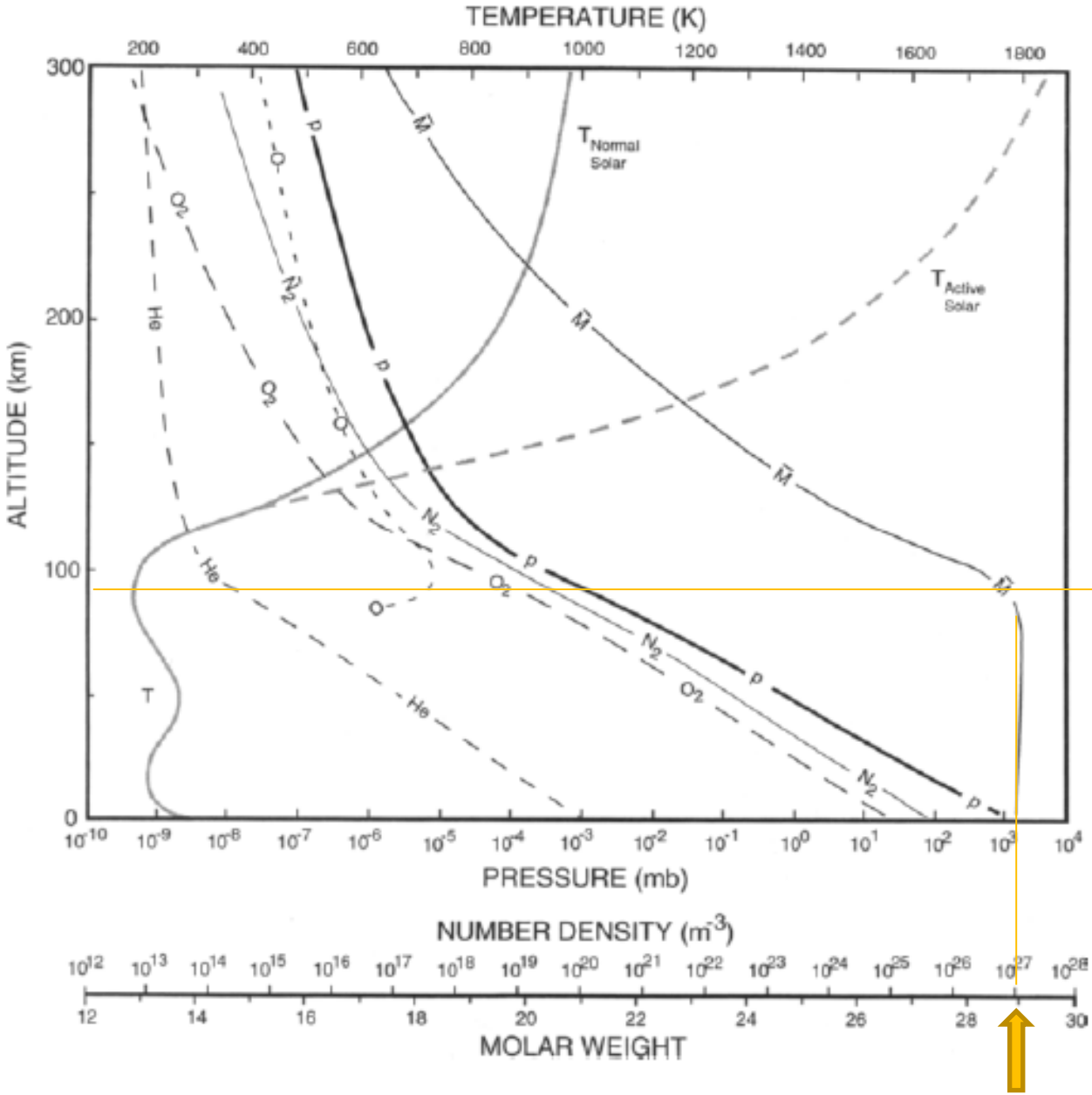
Below 100 km

- The mean free path is small
- Turbulent eddies in the circulation are only weakly damped by molecular diffusion
- Bulk transport by turbulent air motions dominates diffusive transport of atmospheric constituents
- Turbulent air motions stir different gases with equal efficiency
- The components of air are said to be 'well mixed'
- The densities of passive constituents decrease with altitude at the same exponential rate, which gives air a homogeneous composition with constant mixing ratios $r_{N_2} \cong 0.78, \quad r_{O_2} \cong 0.21$

$$M_d = 28.96\ g\ mol^{-1}$$

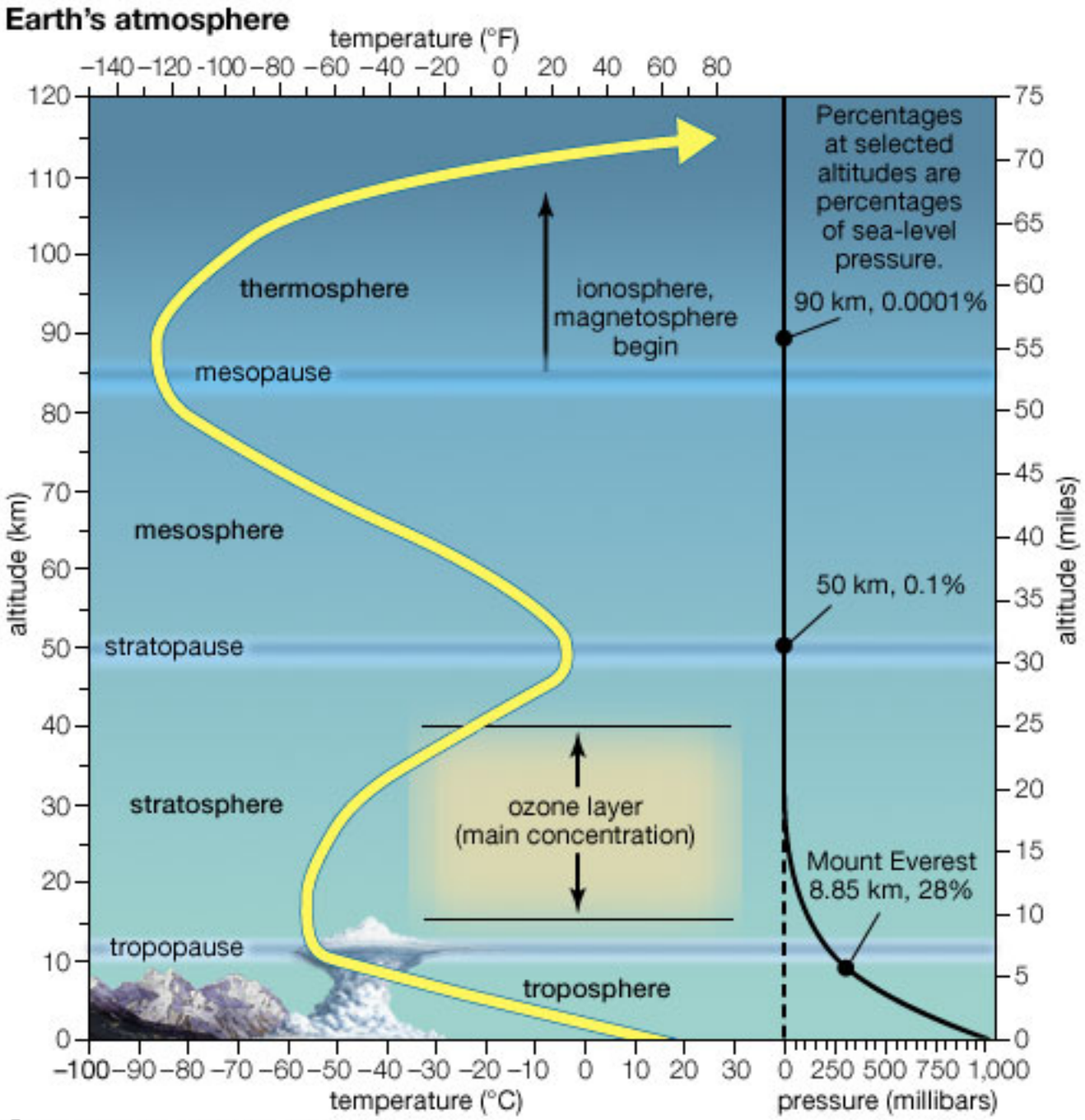
Above 100 km

- The mean free path quickly becomes larger than turbulent displacement of air
- Turbulent air motions are strongly damped by diffusion of momentum and heat
- Diffusive transprt becomes the dominant mechanism for transferring properties vertically
- Molecular diffusion operates on gases according to their molecular weight; it stratifies constituents
- The transition from turbulent transport to diffusive transport occurs at the *homopause* (also known as the *turbopause*)



28.96 g/mol

Figure 1.3 Global–mean pressure (bold), temperature (shaded), mean molar weight (solid), and number densities of atmospheric constituents, as functions of altitude. *Source:* U.S. Standard Atmosphere (1976).



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Why air molecules don't escape from the atmosphere?

In the homosphere and heterosphere, atmospheric molecules interact strongly through frequent collisions.
Above the altitude of about *500km*, which is referred to as the *critical level*, molecular collisions are so rare that a significant fraction of the molecules passes out of the atmosphere without sustaining a single collision.

The escape velocity is determined by the kinetic energy adequate to liberate a molecule from the potential well of the planet's gravitational field.

$$\tfrac{1}{2} m v_e^2 = \int_a^\infty m g_o \left(\frac{a}{r} \right)^2 dr$$

a - is the earth's radius

$$v_e = \sqrt{2 g_o a} \approx 11 \; km s^{-1}$$

Salby, Fundamentals of Atmospheric Physics

Energy is equipartitioned in a molecular ensemble:

→ lighter molecules have greater velocities than heavier ones

→ lighter atmospheric constituents escape to space more readily than the heavier constituents.

At the *critical level* (altitude 500km) the temperature is about 1000K under conditions of normal solar activity, but can reach 2000K during disturbed conditions.

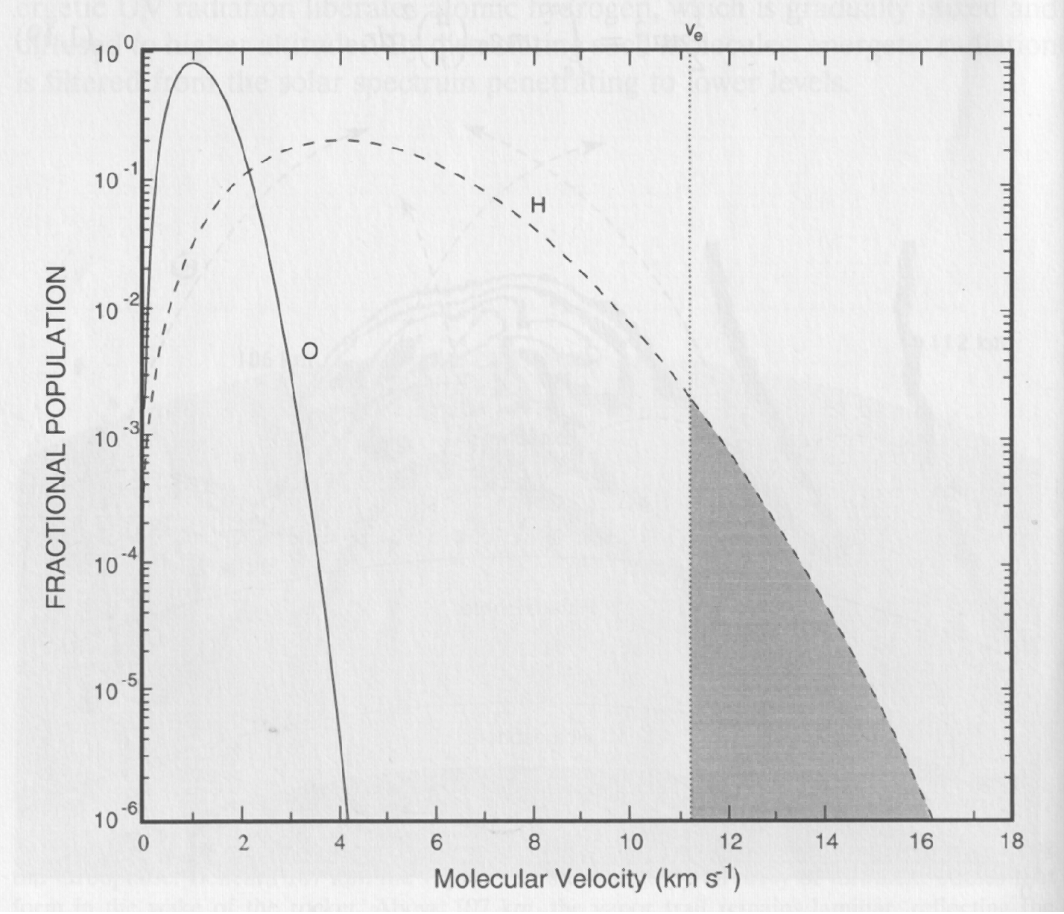
The Boltzmann distributions of a molecular ensemble as function of molecular velocity is:

$$\frac{dn}{n} = \frac{4}{\sqrt{\pi}} \frac{\upsilon^2}{\upsilon_0^3} \exp\left[-\left(\frac{\upsilon}{\upsilon_0} \right)^2 \right] d\upsilon , \quad \upsilon_0 = \sqrt{\frac{2kT}{m}}$$

dn/n – the fractional number of molecules having velocities in the range (v, v+dv)

υ_o – the most probably velocity, m is the mass of the molecules, and k is the Bolzmann constant

Bolzmann distribution of velocities



$$\frac{dn}{n} = \frac{4}{\sqrt{\pi}} \frac{v^2}{v_0^3} \exp\left[-\left(\frac{v}{v_0}\right)^2\right] dv, \quad v_0 = \sqrt{\frac{2kT}{m}}$$

$$k = 1{,}381 \cdot 10^{-23} \frac{J}{K}$$

$$m_H = 1u = \frac{1}{N_A}(g) = \frac{1}{N_A \cdot 1000}(kg)$$

$$1u = 1{,}66053 \cdot 10^{-27}\, kg$$

$$T = 1000K$$

The fraction of molecules with velocitues exeeding the escale velocity, v_e

$$\frac{\Delta n_e}{n} = \int_{v_e}^{\infty} \frac{4}{\sqrt{\pi}} \frac{v^2}{v_0^3} \exp\left[-\left(\frac{v}{v_0}\right)^2\right] dv$$

$$\cong \frac{2}{\sqrt{\pi}} \left(\frac{v_e}{v_0}\right) \exp\left[-\left(\frac{v_e}{v_0}\right)^2\right]$$

For atomic oxygen: $v_0 = 1.02\, km\, s^{-1}$, $\frac{\Delta n_e}{n} = 10^{-45}$

The fraction of O molecules having velocities greater than v_e is 10^{-45}.

A lower bound on the time to deplete all O molecules initially at the critical level is given by the mean time between collisions divided by the fraction of molecules moving upward with $v > v_e$. Near 500km, the mean time between collisions is of order of 10s.

The time for all O molecules initially at the critical level to escape the earth's gravitational field is greater than **10^{46}s**, far greater than the four billion years the planet has existed.

The population of hydrogen (H) is distributed over much higher velocities, so many more molecules exeed the escape velocity v_e

For hydrogen: $v_0 = 4.08\,km\,s^{-1}$, $\frac{\Delta n_e}{n} = 10^{-4}$ Time = **10^5 s = 1 day**

During conditions of disturbed solar activity, temperatures at the critical level are substantially higher, so hydrogen molecules are boild off the atmosphere even faster.

The rapid escape of atomic hydrogen from the planet's gravitational field explains why H is found only in small abundances in the earth's atmosphere, despite its continual production by photodissociation of H_2O.

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The equation of state for a perfect gas in thermal equilibrium: $pV = CT$

C depends upon the particular gas.

Avogadro's Law:

At the same pressure and temperaturę one mole of any gas occupies the same volume V^* ($V^*=V/n$, n – the numer of moles):

$$pV = CT \quad / n$$
$$pV^* = C'T$$

C' is the same constant for all gases.

C' is called the universal gas constant, denoted by R^*: $R^* = 8.314\ J\,mol^{-1}K^{-1}$

$$pV = nR^*T$$

The volume (V) and the numer of moles (n) are not convenient paremeters to describe the state of atmosphere.

When applying the ideal gas law to the atmosphere it is convenient to write the equation in terms of intensive variables.

We divide both sides of the ideal gas equation by mass m :

$$pV = nR^*T \quad / m$$

$$p\upsilon = \frac{1}{M} R^*T$$

$$\frac{V}{m} = \upsilon = \frac{1}{\rho} \qquad \frac{m}{n} = M$$

υ - *specific volume*
ρ - *density*
M - *molecular weight of the gas*

$$R = R^* / M \qquad \textit{individual gas constant}$$

$$p\upsilon = RT \qquad p = RT\rho$$

Strictly speaking, air does not have a molecular weight, since it is a mixture of gases and there is no such thing as an „air molecule”. Composition of the air is constant up to ~100 km.

Dalton's law states that:

the total pressure (p) exerted by a mixture of gases is equal to the sum of the partial pressures (p_i) that would be exerted by each constituent alone if it filled the entire volume at the temperature of the mixture.

$$p = \sum_i p_i \,, \qquad p_i V = m_i R_i T \qquad R_i = R^* / M_i$$

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$$R = \frac{\sum_i m_i R_i}{\sum_i m_i} = \frac{\sum_i m_i \frac{R^*}{M_i}}{\sum_i n_i M_i} = \frac{R^* \sum_i n_i}{\sum_i n_i M_i} = \frac{R^*}{\bar{M}}$$

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$$R = \frac{\sum_i m_i R_i}{\sum_i m_i} = \frac{\sum_i m_i \frac{R^*}{M_i}}{\sum_i n_i M_i} = \frac{R^* \sum_i n_i}{\sum_i n_i M_i} = \frac{R^*}{\bar{M}}$$

$$\boxed{pV = mRT}$$

$$pV = mRT$$

$$p = RT\rho$$

For dry air the individual gas constant is denoted by R (or R_d).

The mean molecular weight for dry air gases is determined to be 28.96 g/mol:

the weighted mean: 78% nitrogen (M_{N2} = 28g), 21% oxygen (M_{O2}=32g), 0.9% argon.

$$R = \frac{R^*}{\bar{M}} = \frac{8.314 \frac{J}{mol\ K}}{28.96 \frac{g}{mol}} = 287 \frac{J}{kg\ K}$$

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A **thermodynamic system** is a defined quantity of matter which can exchange energy with its surroundings

- by performing mechanical work or
- by transferring heat across the boundary.

A system may be *open* or *closed*, depending on whether or not it exchanges matter with its environment.

A system is said to be *isolated* if it does not exchange any kind of energy with its environment.

The *environment* comprises the surroundings of the thermodynamic system.

The **thermodynamic system** addressed in this course is a portion of air undergoing transformations; it is an *open system*.

We will sometimes treat portions of the atmosphere as *closed system*, which is a reasonable approximation:

- if the volumes are large enough to neglect exchanges with the surroundings or
- if the surroundings have the same properties as the system.

A system is said to be *homogeneous* if its properties do not vary in space, and *heterogeneous* otherwise.

Because an air parcel is of infinitesimal dimension, it is by definition homogeneous so long as it involves only gas phase.

On the other hand, stratification of density and pressure make the ***atmosphere as a whole a heterogeneous system.***

In the atmosphere the exchange of mass is due to:

- entrainment of mass from the environment and subsequent mixing
- diffusion (some constituents, e.g. water vapor)

Above the planetary boundary layer and outside regions close to deep convective clouds the exchange of mass is slow comparing to other processes;

The *atmosphere* can be considered as a *closed system*.

The system can exchange energy with its surroundings through two fundamental mechanisms:

- it can perform ***work*** on the surrounding (a mechanical exchange of energy)
- ***heat*** can be transferred across the control surface (a thermal exchange of energy between the system and its environment)

Work: the atmosphere is a compressible gas, perhaps containing an aerosol of liquid and solid particles.

The primary mechanism means of exchanging energy with the environment is expansion work.

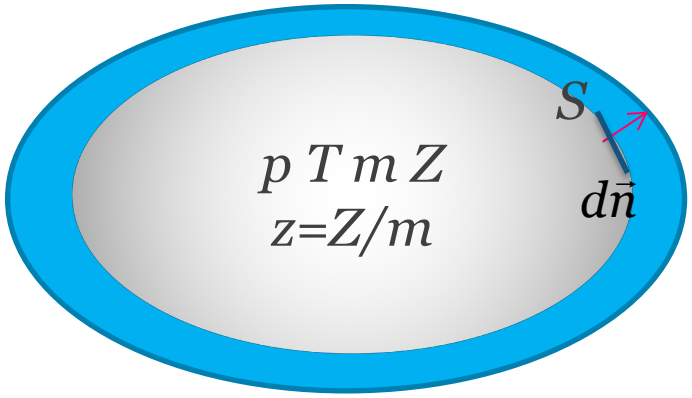
Another form of work is linked with turbulence

Heat: diffusion or thermal conduction.

If the system is open, the energy exchange can occur through the absorption of water vapor from the surroundings, condensation and the release of latent heat, and precipitation out of the system of the condensed water.

Radiative transfer.

Work



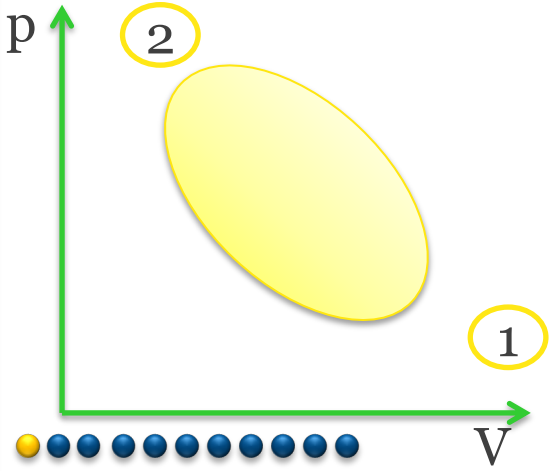
If a pressure imbalance exists across the control surface, it is out of equilibrium.

The system will then expand or contract to relieve the mechanical imbalance.

By adjusting to the environmental pressure, the system performs expansion work or has such work performed on it.

The incremental expansion work δW performed by displacing a section of control surface $\boldsymbol{S}$ $(=S d\boldsymbol{n})$, with unit normal $\boldsymbol{n}$, perpendicular to itself by $\boldsymbol{dn}$ is:

$$\delta W = \left(p\, d\vec{S} \right) \cdot d\vec{n} = p dV$$



The cyclic work is represented in the area enclosed by the path of the system in *p*-*v* plane.
Although the system is restored to its initial state, namely, the net change of properties is zero, the same is not true of the work performed during the cycle.
Net work is performed during a cyclic variation.

Heat transfer

For many applications, heat transfer is secondary to processes introduced through motion.

It is especially true above the boundary layer, where turbulent mixing between bodies of air is relatively weak.

In the free atmosphere and away from clouds, the prevailing form of heat transfer is radiative → a timescale (τ_c) of order of 2 weeks.

The timescale of expansion work (τ_m) is of order of 1 day.

If no heat is exchanged between a system and its environment, the control surface is said to be *adiabatic*, and *diabatic* otherwise.

Because heat transfer is slow compared to other processes influencing a parcel, *adiabatic* behavior is a good approximation for many applcations.

Heat transfer must be central to processes that operate on long timescales since it is ultimately responsible for driving the atmosphere.

Timescales

$\tau_c = 2$ weeks

$\tau_m = 1$ day

$\tau_c >> \tau_m$

Thermodynamic properties

Two types of properties characterize the state of a system:

- *intensive, z,* (does not depend on the mass of the system); e.q. pressure, temperature
- *extensive, Z,* (depends on the mass); e.g. volume

An intensive property z may be defined from an extensive property Z, by referencing the latter to the mass of the system $z=Z/m$

The intensive property is referred to as a specific property.

The specific volume is an example:

V- volume, v=V/m – specific volume

$$pV = mRT \;/\; m$$
$$pv = RT$$

Describing the thermodynamic state of a system requires us to specify **all** of its properties.

That requirement can be relaxed for gases and other substances at normal temperatures and pressures.

A *pure* substance is one whose thermodynamic state is uniquely determined by any *two intensive properties (z_1, z_2),* , which are then referred to as ***state variables***.

A third variable (z_3) can be determined through an equation of ***state*** of the form :

$$f(z_1, z_2, z_3) = 0$$
$$z_3 = g(z_1, z_2)$$

A pure substance (gas) has two thermodynamic degrees of freedom.

An ideal gas is a pure substance that has as its equation of state the ***ideal gas law***.

$$p = p(v, T)$$

Thermodynamic equilibrium

A homogeneous system is said to be **thermodynamic equilibrium** if it is in mechanical and in thermal equilibrium.

A local state of thermodynamic system is described by its *intensive parameters*, like pressure and temperature.

Thermodynamic equilibrium:

- mechanical equilibrium (at most an infinitisemal pressure difference between the system and its surroundings : p_s-p_e=δp)
- thermal equilibrium (at most an infinitisemal temperature difference between the system and its surroundings : T_s-T_e= δT)

In an isolated system all internal differences of parameters disappear. The temperature and pressure become equal; the same concerns the density.

A system in which all internal differences disappear is in a state of thermodynamic equilibrium. Its thermodynamic properties don't vary in time.

A system in thermodynamic equilibrium is easier to understand that a non equilibriated system.

In analysing thermodynamic processes we often assume that every intemediate state of the process is an equilibrium state.

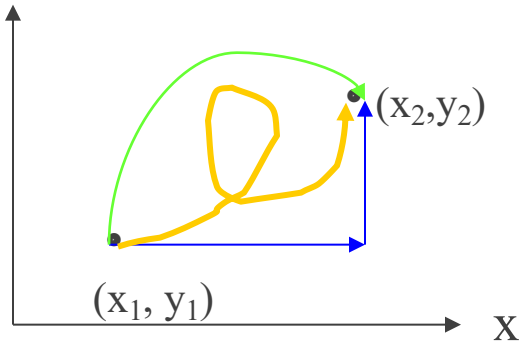
A thermodynamic process that proceeds so slowly that every intermediate state is in thermodynamic equilibrium is said a *reversible* process.

Thermodynamics addresses how a system evolves form one state to another. The transformation of a system between two states describes a path in state space (→ ***thermodynamic process***).

Infinitely many paths connect two states.

Thus, a ***thermodynamic process*** depends on the particular path in state space followed by the system.

The change of a state variable depends only on the initial and final states of the system, namely, it is *path independent*.



The cyclic integral of a state variable vanishes:

$$\oint dz = 0$$

The incremental change of a quantity *z(x,y)* may be represented as an exact differential:

$$dz = \frac{\partial z}{\partial x}dx + \frac{\partial z}{\partial y}dy$$

where *x* and *y* are independent variables of the system. It is true only under certain conditions.

If the exact differential is written as *dz=Mdx+Ndy*, where *M(x,y)* and *N(x,y)* are continuously differentiable functions, we obtain *Euler's relation*:

$$\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}$$

Under these circumstances, the quantity: $M(x,y)dx + N(x,y)dy = dz$

represents an exact differential. That is there exists a function z such that

$$M(x,y) = \frac{\partial z}{\partial x}, \quad N(x,y) = \frac{\partial z}{\partial y} \quad , \quad \left[\frac{\partial M}{\partial y} = \frac{\partial^2 z}{\partial x \partial y}, \frac{\partial N}{\partial x} = \frac{\partial^2 z}{\partial x \partial y} \right]$$

in which case:

$$\int_{z(x_0,y_0)}^{z(x,y)} dz = z(x,y) - z(x_0,y_0) = \Delta z$$

$$z = z(x,y) + c$$

The variable *z* is a *point function*: it depends only on the evaluation point *(x,y)*, and its net change along a contour depends only on the initial and final points of the contour.

Point function is also referred to as a *potential function* $z(x,y)$ defines an irrotational vector field

$$\vec{v} = \nabla z = M(x,y)\vec{i} + N(x,y)\vec{j}$$

which satisfies

$$\nabla \times \vec{v} = 0$$

Conversely, an irrotational vector field may be represented as the gradient of a scalar potential z.

Gravity $\vec{g}$ is an irrotational vector field: $\nabla \times \vec{g} \equiv 0$. The work performed to displace a unit mass between two points in a gravitational field is independent of path and defines the gravitational potential Φ.

Thermodynamic state variables are point functions.

As properties of the system, they depend only on the system's state but not on its history.

By contrast, the *work* performed by the system and the *heat* transferred into it during a thermodynamic process *are not properties of the system*.

Work and *heat* transfer are, in general, *path functions*.

They depend on the path in state space followed by the system. The thermodynamic process must be specified to define those quantities unambiguously.

Path-dependent, *work* and *heat* transfer can differ along the forward and reverse legs of a cyclic process.

Consequently, the net *work* and *heat* transfer during a cyclic variation of the system need not vanish, as does the net change of a state variable.

During a cyclic variation of the system, the cumulative work and heat

$$w = \oint \delta w \quad and \quad q = \oint \delta q$$

do not return to their original positions after the system has been restored to its initial state.

Under special circumstances, the *work* performed by a system or the *heat* transferred into it **IS** independent of path.

Because it is then a point function, the special form of work or heat transfer can be used as a state variable.

→ the displacement work in gravitational field is path independent (the gravitational potential Φ is then a property of the system).

→ adiabatic process.