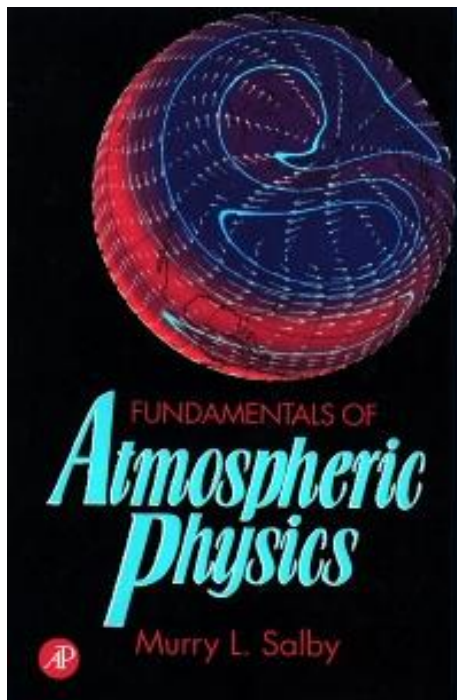


LECTURE OUTLINE

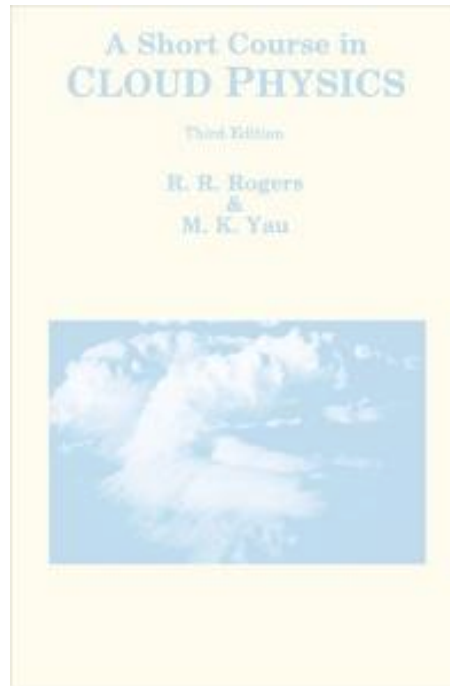
1. The first law of thermodynamics
2. Specific heat capacity
3. Thermodynamic processes
4. Potential temperature
5. Reversible and irreversible processes
6. Entropy



Salby, Chapter 2 and 3

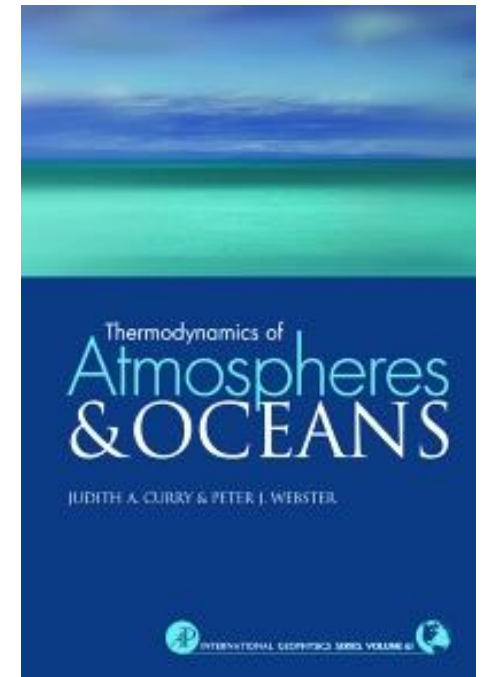


Fundamentals of Atmospheric Physics,
M.L. Salby; [Salby](#)



A Short Course in Cloud Physics,
R.R. Rogers and M.K. Yau; [R&Y](#)

C&W, Chapter 2




Thermodynamics of Atmospheres
and Oceans,
J.A. Curry and P.J. Webster; [C&W](#)

Internal energy

The first law of thermodynamics is inspired by the **observation** that the work performed on an **adiabatic** system is independent of the process, that is, it is independent of the path in state space followed by the system.

The **internal energy** u is defined as the **state variable** whose difference equals the work performed ON the system under adiabatic conditions, or minus the work performed BY the system under adiabatic conditions.

$$\Delta u = -w_{ad} \quad \text{OR} \quad du = -\delta w_{ad}$$


work done BY the system in
adiabatic process

δ depends on the path

d does not depend on the path

If **heat** is exchanged with the environment: $w \neq w_{ad} = -\Delta u$

The work performed by the system w will differ from that performed under adiabatic conditions w_{ad} by an amount q , which equals the energy transferred INTO the system through heat exchange ($w = w_{ad} + q$).

The first law of thermodynamics

$$\Delta u = q - w$$

δq – the heat transfer INTO the system

$$\underline{du = \delta q - pdv}$$

pdv – the work performed BY the system

The change of internal energy between two states is path independent.

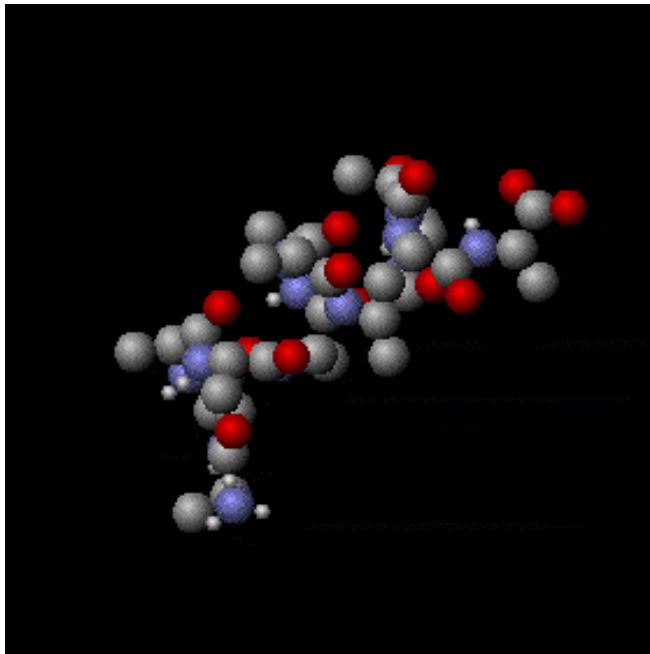
The same is not true of the **work** performed by the system and the **heat** transferred to it.

However the change of internal energy does vanish for a cyclic process i.e. : $\oint pdv = \oint \delta q$

The energy added to the system (work or heat) can:

- increase the velocity of molecules (i.e. increase the temperature of the system)
- create an internal motion in the molecule (rotation, vibration); contribution to the heat capacity
- change the force of attraction between molecules (change of thermodynamic state)

All those forms of energy contribute to the **internal energy** of the system.



A polyatomic molecule (consisting of two or more atoms bound together) can store heat energy in other forms besides its kinetic energy. These forms include rotation of the molecule, and vibration of the atoms relative to its center of mass.

Vibrations of atoms in a molecule consume some of the heat energy that otherwise would contribute to the molecule's kinetic energy.

These extra degrees of freedom contribute to the molar heat capacity of the substance.

Enthalpy $h = u + pv$

We can define any state variable, which is a combination of known state variables. The new variables make easier the analysis of some processes.

Enthalpy $h = u + pv$

is a state variable because it is a combination of: (u, p, v).

In terms of enthalpy the first law of thermodynamics becomes

$$dh = du + pdv + vdp =$$

$$\delta q - \cancel{pdv} + \cancel{pdv} + vdp$$

$$dh = \delta q + vdp$$

Enthalpy is useful for diagnosing processes that occur at constant pressure.

If $dp = 0$ the change of enthalpy equals the heat transferred into the system $dh = \delta q$.

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1. The first law of thermodynamics
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Observations indicate that the heat absorbed by a homogeneous system which is maintained at constant pressure or at constant volume is **proportional to the change of the system's temperature**.

The constant of proportionality between heat absorption and temperature change defines::

the specific heat capacity at constant pressure (c_p): $c_p = \frac{\delta q_p}{dT}$

the specific heat capacity at constant volume (c_v): $c_v = \frac{\delta q_v}{dT}$

where the subscripts denote **isobaric (p=const)** and **isochoric (v=const)** processes, respectively.

The specific heat capacities are related closely to the internal energy and enthalpy of the system.

The internal energy is a state variable; therefore can be expressed in terms of two other state variables.

For instance: $u = u(v, T)$.

$$du = \left(\frac{\partial u}{\partial v} \right)_T dv + \left(\frac{\partial u}{\partial T} \right)_v dT$$

Let's incorporate this into the first law of thermodynamics:

$$du = \delta q - p dv$$

$$\begin{aligned} \delta q - p dv &= \left(\frac{\partial u}{\partial v} \right)_T dv + \left(\frac{\partial u}{\partial T} \right)_v dT \\ \delta q &= \left(\frac{\partial u}{\partial T} \right)_v dT + \left[\left(\frac{\partial u}{\partial v} \right)_T + p \right] dv \end{aligned}$$

For an isochoric process ($v = \text{const}$, $dv = 0$):

$$\left(\frac{\partial u}{\partial T} \right)_v = \frac{\delta q_v}{dT} = c_v$$

The specific heat capacity at constant volume measures the rate internal energy increases with temperature during an isochoric process.

The enthalpy is also a state variable; therefore can be expressed in terms of two other state variables.

For instance $h = h(p, T)$.

$$dh = \left(\frac{\partial h}{\partial p} \right)_T dp + \left(\frac{\partial h}{\partial T} \right)_p dT$$

Let's incorporate this into the first law of thermodynamics:

$$dh = \delta q + v dp$$

$$\begin{aligned} \delta q + v dp &= \left(\frac{\partial h}{\partial p} \right)_T dp + \left(\frac{\partial h}{\partial T} \right)_p dT \\ \delta q &= \left(\frac{\partial h}{\partial T} \right)_p dT + \left[\left(\frac{\partial h}{\partial p} \right)_T - v \right] dp \end{aligned}$$

For an isobaric process ($p = \text{const}$, $dp = 0$):

$$\left(\frac{\partial h}{\partial T} \right)_p = \frac{\delta q_p}{dT} = c_p$$

The specific heat capacity at constant pressure measures the rate enthalpy increases with temperature during an isobaric process.

In a strict sense c_v and c_p are state variables (expressed by two other state variables), so they depend on pressure and temperature.

However, over ranges of pressure and temperature relevant to the atmosphere, the specific heats may be regarded as constant.

Therefore:

the change of internal energy during an isochoric process is proportional to the change of temperature alone:

$$\left(\frac{\partial u}{\partial T}\right)_v = \frac{\delta q_v}{dT} = c_v$$

$$(du)_v = c_v dT$$

similarly the change of enthalpy during an isobaric process is proportional to the change of temperature alone:

$$\left(\frac{\partial h}{\partial T}\right)_p = \frac{\delta q_p}{dT} = c_p$$

$$(dh)_p = c_p dT$$

The internal energy and enthalpy are state variables, therefore their change in a cyclic process doesn't depend on the process.

If the relationships:

$$(du)_v = c_v dT \text{ and } (dh)_p = c_p dT$$

hold for one process, they also hold for any other process.

For an ideal gas the following relationships hold

$$du = c_{vd} dT$$

irrespective of process (subscripts v and p can be removed).

$$dh = c_{pd} dT$$

First law of thermodynamics

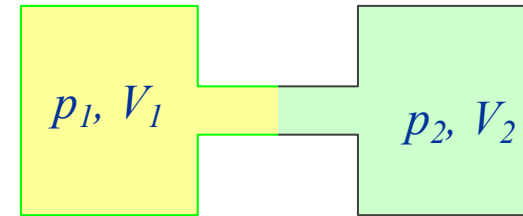
$$\delta q = c_{vd} dT + p dv$$

$$\underline{\delta q = c_{pd} dT - v dp}$$

This is the preferred form of the first law of thermodynamics in atmospheric science because the independent variables on the right-hand side (T, p) can easily be observed.

Joule's experiment

Consider the internal energy of an ideal gas in the form $u(p, T)$.
Joule's experiment demonstrates that u is a function of temperature alone.



Two ideal gases that are initially isolated and at pressures p_1 and p_2 .

- They are brought into contact and allowed to equilibrate, for example, by rupturing a diaphragm that separates them.
- Observations indicate that no heat transfer takes place with the environment during this process.
- Then the first law reduces to the statement that the change of internal energy equals minus the work performed.
- However, the volume of the system (that occupied by both gases) does not change, so the work ($-pdv$) also vanishes and $\Delta u = 0$.
- Yet, the final equilibrated pressure clearly differs from the initial pressures of two gases in isolation.
- Since the total internal energy of the system equals the sum of the contributions from the two cells, it follows that u is not a function of pressure.

It is customary to define u and h so that they vanish at a temperature of absolute zero.

$$u = u(T) = c_v T$$

$$h = h(T) = c_p T$$

$c_p - c_v$ for ideal gas

Subtracting:

$$h = c_{pd}T$$

$$- \quad u = c_{vd}T$$

$$h - u = (c_{pd} - c_{vd})T$$

$$(\cancel{u} + pv) - \cancel{u} = (c_{pd} - c_{vd})T$$

$$\frac{pv}{T} = (c_{vd} - c_{pd}) \quad \Rightarrow \quad c_{pd} - c_{vd} = R_d$$

$$h = u + pv$$

$$\frac{pv}{T} = R_d$$

According to statistical mechanics, the specific heat at constant volume is given by $c_v = 3R_d/2$ for a monoatomic gas and by $c_v = 5R_d/2$ for a diatomic gas.

These values are confirmed experimentally over a wide range of pressure and temperature relevant in the atmosphere. Taking air to be chiefly diatomic together with the value of R yields the specific heats for dry air:

$$c_{vd} = 5R_d/2 = 717.5 \text{ J kg}^{-1} \text{ K}^{-1}$$

$$c_{pd} = 5R_d/2 + R_d = 1004.5 \text{ J kg}^{-1} \text{ K}^{-1}$$

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Isochoric and isobaric processes

The first law of thermodynamics in internal energy
and enthalpy forms:

$$du = \delta q - p dv$$

$$dh = \delta q + v dp$$

Internal energy and enthalpy:

$$du = c_v dT$$

$$dh = c_p dT$$

$$c_{vd} dT + p dv = \delta q$$

$$c_{pd} dT - v dp = \delta q$$

- Isochoric process ($v = \text{const}, dv = 0$) $\delta q_v = c_{vd} dT$
- Isobaric process ($p = \text{const}, dp = 0$) $\delta q_p = c_{pd} dT$

There are only state variables on the right hand side of these equations; therefore the same should be true for variables on the left hand side of the equations.

The heat transferred in isochoric and isobaric processes is also a state variable!

Adiabatic process

Since heat transfer is slow relative to other dynamical processes affecting a fluid parcel, **adiabatic** behavior ($\delta q = 0$) is frequently a valid approximation.

First law of thermodynamics:

$$\begin{array}{l} du = \cancel{\delta q} - p dv \\ dh = \cancel{\delta q} + v dp \end{array} \quad + \quad \begin{array}{l} du = c_{vd} dT \\ dh = c_{pd} dT \end{array}$$

$$c_{vd} dT + p dv = 0 \quad /T$$

$$c_{pd} dT - v dp = 0 \quad /T$$

$$c_{vd} d \ln T + R_d d \ln v = 0$$

$$c_{pd} d \ln T - R_d d \ln p = 0$$

$$d \ln T^{c_{vd}} + d \ln v^{R_d} = 0$$

$$d \ln T^{c_{pd}} + d \ln p^{-R_d} = 0$$

Poisson's equations

$$T^{c_{vd}} v^{R_d} = \text{const}$$

$$\underline{T^{c_{pd}} p^{-R_d} = \text{const}} \quad \text{commonly used form}$$

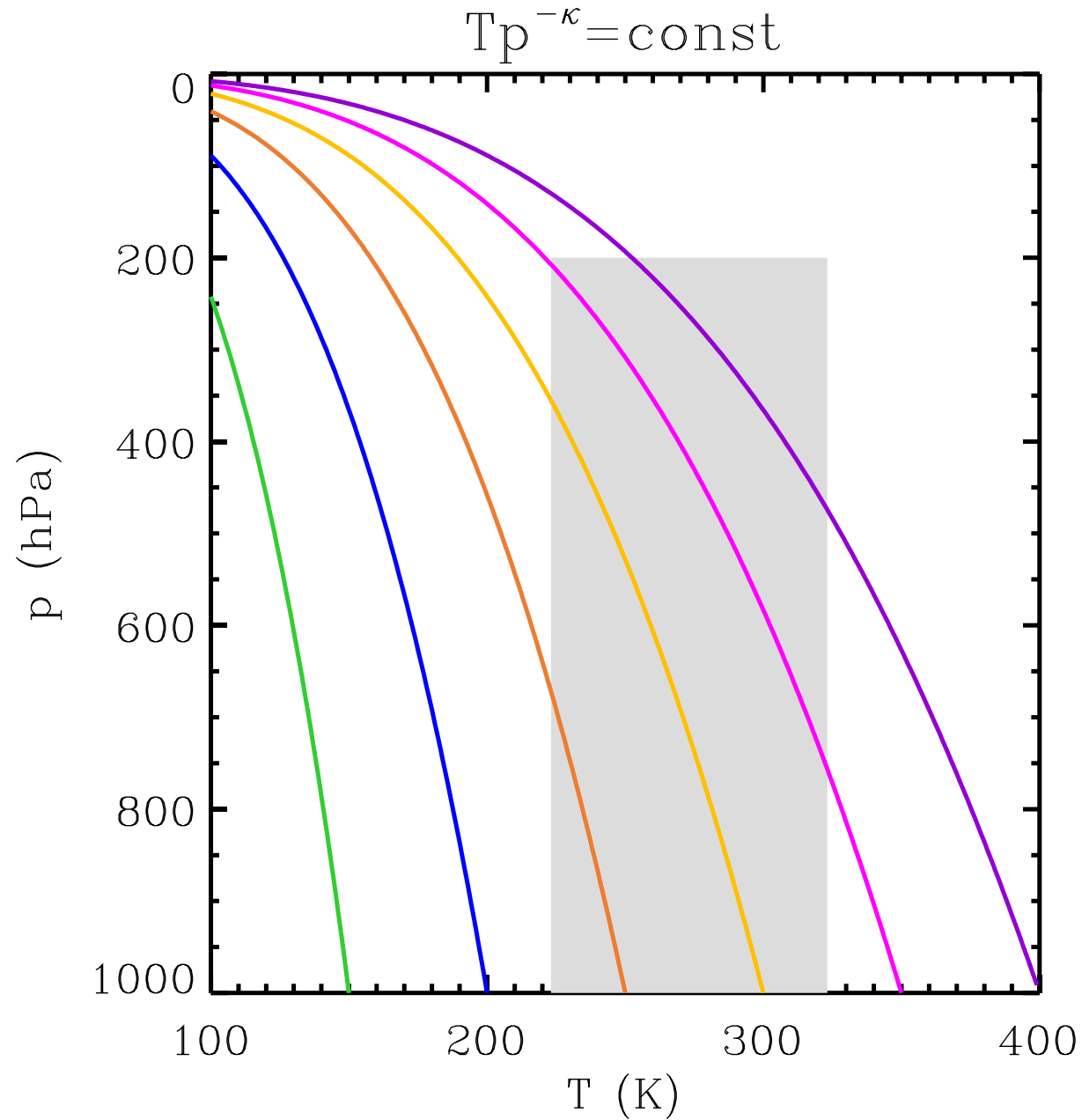
$$p^{c_{vd}} v^{d c_p} = \text{const}$$

$$T^{c_{pd}} p^{-R_d} = \text{const}$$

$$T p^{-\kappa} = \text{const}$$

$$\begin{aligned} \kappa &= \frac{R_d}{c_{pd}} = \frac{R_d}{R_d + c_{vd}} \\ &= \frac{R_d}{R_d + \frac{5}{2}R_d} = \frac{2}{7} \end{aligned}$$

$$\kappa \cong 0.286$$



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Poisson's relation between pressure and temperature suggests introducing a new variable that is conserved in adiabatic processes.

$$Tp^{-\kappa} = \text{const} = \theta p_0^{-\kappa}$$

The **potential temperature**, θ , is defined as the temperature that the system would attain if it were compressed or expanded adiabatically to a reference pressure $p_0 = 1000 \text{ hPa}$.

$$\theta = T \left(\frac{p_0}{p} \right)^\kappa ; \quad \kappa = \frac{R_d}{c_{pd}} \quad \text{The unit of potential temperature is K !!!}$$

Potential temperature is a **state variable** defined as a function of temperature and pressure.

It remains constant along adiabatic paths in state space.

Potential temperature is a more dynamically important quantity than actual temperature.

Under almost all atmospheric conditions, potential temperature increases with height, unlike actual temperature, which may either increase or decrease.

Potential temperature is conserved during all dry adiabatic processes and is therefore an important quantity in the planetary boundary layer, which is often close to dry adiabatic conditions.

The distribution of θ in the atmosphere is determined by the distributions of pressure and temperature.

Since pressure decreases rapidly with height,

$$\theta = T \left(\frac{p_0}{p} \right)^\kappa$$

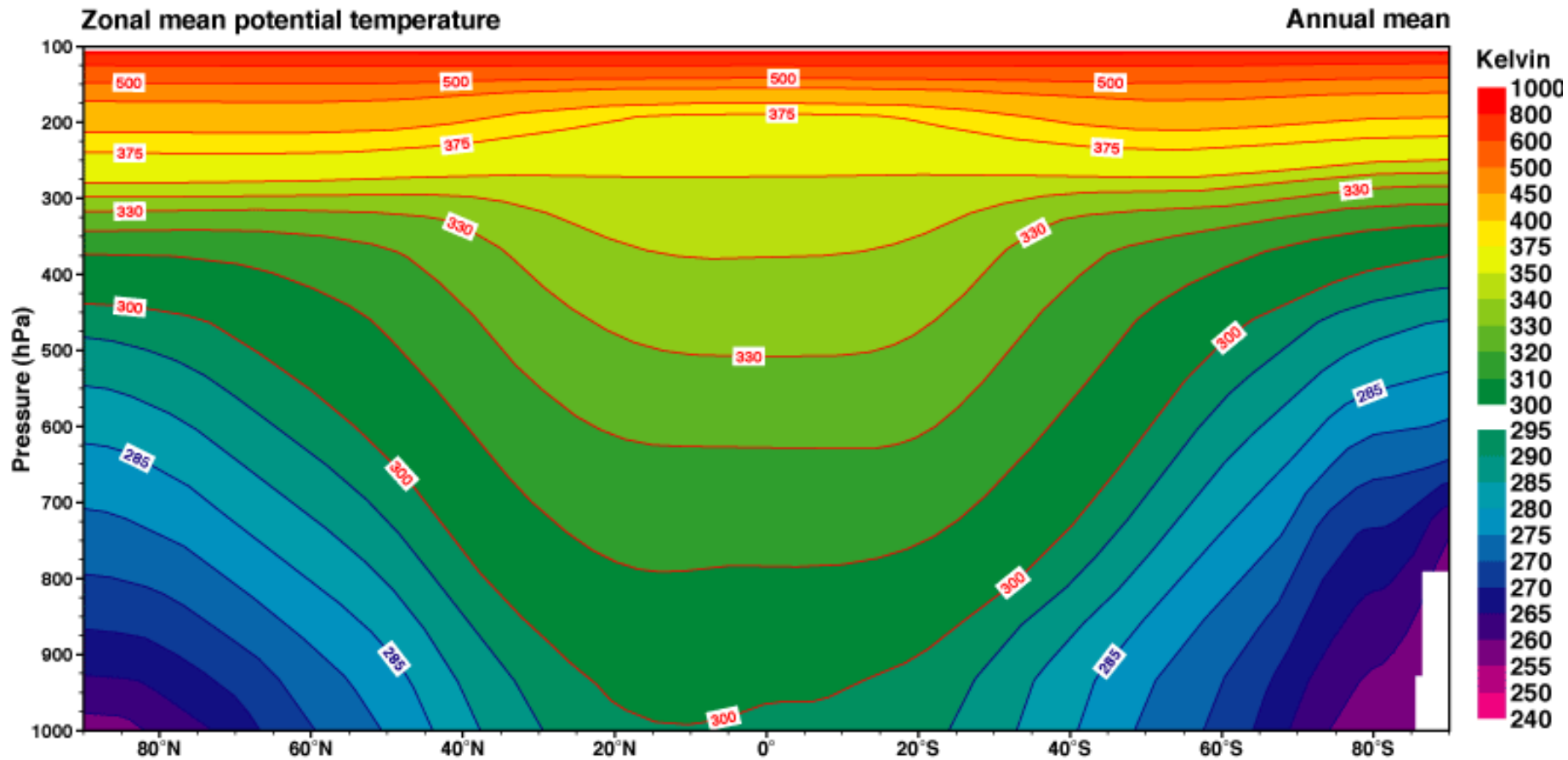
implies that surfaces of constant θ tend to be quasi-horizontal, similarly to isobaric surfaces.

Under almost all atmospheric conditions:

$$\frac{d\theta}{dz} > 0$$

which means the atmosphere is stably stratified.

Zonal mean potential temperature



ECMWF : ERA-40 Atlas : Pressure level climatologies (latitude-pressure projections) : Zonal mean potential temperature - tropospheric perspective, Latitude-Height, Annual mean

Adiabatic gradient

The temperature of an air parcel moving vertically changes due to expansion (or compression) work.

It is useful to write the first law in terms of enthalpy.

$$dh = c_{pd}dT = \cancel{\delta q} + vdp \quad \text{in adiabatic process } \delta q = 0$$

$$c_{pd}dT - vdp = 0$$

Hydrostatic equation:

$$dp = -\rho g dz \quad ; \quad \rho = \frac{1}{v}$$
$$dp = -\frac{g}{v} dz \quad \Rightarrow \quad vdp = -g dz$$

$$c_{pd}dT + g dz = 0$$

$$\Gamma_a = -\frac{dT}{dz} = \frac{g}{c_{pd}} \qquad \Gamma_a = \frac{g}{c_{pd}} = \frac{9.81 \text{ m/s}^2}{1004 \text{ J/kgK}} \approx 9.8 \frac{\text{K}}{\text{km}}$$

Potential temperature θ :
$$\frac{\theta}{T} = \left(\frac{p_0}{p} \right)^\kappa$$

$$d \ln \theta = d \ln T - \kappa d \ln p$$

Change of potential temperature with height:

$$\frac{d \ln \theta}{dz} = \frac{d \ln T}{dz} - \frac{R_d}{c_{pd}} \frac{d \ln p}{dz}$$

$$\frac{1}{\theta} \frac{d\theta}{dz} = \frac{1}{T} \frac{dT}{dz} - \frac{R_d}{c_{pd}} \frac{1}{p} \frac{dp}{dz}$$

$$\frac{1}{\theta} \frac{d\theta}{dz} = -\frac{1}{T} \frac{g}{c_p} + \frac{R_d}{c_{pd}} \frac{1}{p} \rho g$$

$$\frac{1}{\theta} \frac{d\theta}{dz} = -\frac{1}{T} \frac{g}{c_p} + \frac{R_d}{c_{pd}} \frac{g}{R_d T}$$

$$\frac{d\theta}{dz} = 0$$

$$\kappa = \frac{R_d}{c_{pd}} \cong 0.286$$

$$\frac{dT}{dz} = -\Gamma_d = -\frac{g}{c_{pd}} \quad \frac{dp}{dz} = -\rho g$$

$$p = R_d T \rho \Rightarrow \frac{\rho}{p} = \frac{1}{R_d T}$$

Potential temperature does not change in a parcel moving adiabatically with height.

Non-adiabatic (diabatic) process

Potential temperature θ :
$$\frac{\theta}{T} = \left(\frac{p_0}{p} \right)^\kappa \quad \kappa = \frac{R_d}{c_{pd}}$$

Natural logarithm of the equation:
$$d\ln\theta = d\ln T - \kappa d\ln p$$

The first law in terms of enthalpy:
$$dh = \delta q + v dp \quad + \quad dh = c_{pd} dT$$

$$c_{pd} dT - v dp = \delta q \quad /T$$

$$c_{pd} \frac{dT}{T} - \frac{v}{T} dp = \frac{\delta q}{T}$$

$$c_{pd} d\ln T - R_d d\ln p = \frac{\delta q}{T} \quad /c_{pd}$$

$$d\ln T - \kappa d\ln p = \frac{\delta q}{c_{pd} T}$$

$$\frac{v}{T} = \frac{R_d}{p}$$

$$d\ln\theta = \frac{\delta q}{c_{pd} T}$$

An increase in potential temperature is a direct measure of the heat added to the system.

Polytropic processes

Most of the energy exchanged between the Earth's surface and the atmosphere, as well as between different atmospheric layers, occurs through radiative transfer.

Radiative transfer is the primary diabatic process outside the boundary layer and clouds.

It is sometimes convenient to model radiative transfer as a polytropic process, in which the heat added to the system is proportional to the system's temperature change. The constant of proportionality, c , is called the polytropic specific heat capacity.

$$\delta q = c dT$$

For a polytropic process, the first law can be written in the form:

$$du = \delta q - p dv$$

$$dh = \delta q + v dp$$



$$c_{vd} dT = c dT - p dv$$

$$c_{pd} dT = c dT + v dp$$

$$\delta q = c dT$$

$$(c_{vd} - c)dT + pdv = 0$$

$$(c_{pd} - c)dT - vdp = 0$$

The equations resemble those for an adiabatic process, but with modified specific heats.

Formulas valid for an adiabatic process also hold for a polytropic process, provided that the specific heats are appropriately modified:

$$c_{pd} \rightarrow (c_{pd} - c)$$

$$c_{vd} \rightarrow (c_{vd} - c)$$

In terms of potential temperature, the first law becomes:

$$d\ln\theta = \frac{\delta q}{c_{pd}T}$$



$$\delta q = cdT$$

$$d\ln\theta = \frac{cdT}{c_{pd}T}$$

$$d\ln\theta = \frac{c}{c_{pd}} d\ln T$$

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1. The first law of thermodynamics
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- **The first law of thermodynamics** describes how the state of a system changes in response to the work it performs and the heat it absorbs.
- The first law places **no limitations** on the transformation between heat and work.
- It says nothing about the feasibility or direction of a thermodynamic process.

- **The second law of thermodynamics** introduces fundamental constraints on natural processes.
- It specifies the direction of spontaneous change and limits the efficiency of heat-to-work conversion.

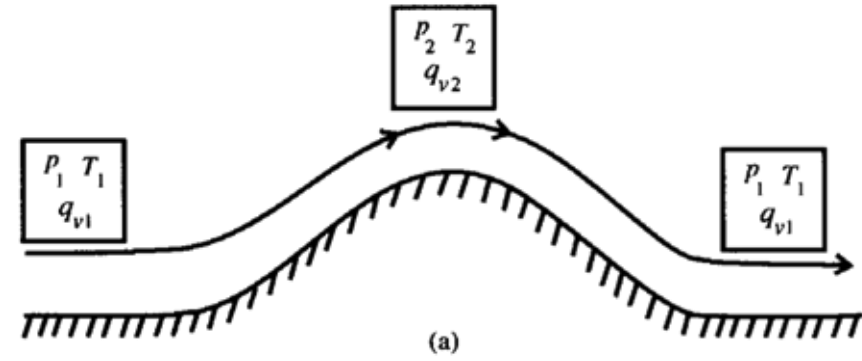
Reversible and irreversible processes

In any thermodynamic process, the changes occurring in the environment must be considered alongside those occurring in the system.

- **A reversible process**
 - is one in which the system remains in thermodynamic equilibrium throughout the process;
 - proceeds infinitesimally slowly through a continuous succession of equilibrium states that differ only infinitesimally from one another;
 - can be reversed without leaving any net change in either the system or its surroundings.
- **Irreversible processes**
 - proceed at finite rates;
 - if the system is restored to its initial state, the surroundings will have undergone a change;
 - do not imply that the system itself cannot return to its original state, but rather that the combined system and surroundings cannot be restored to their initial conditions.

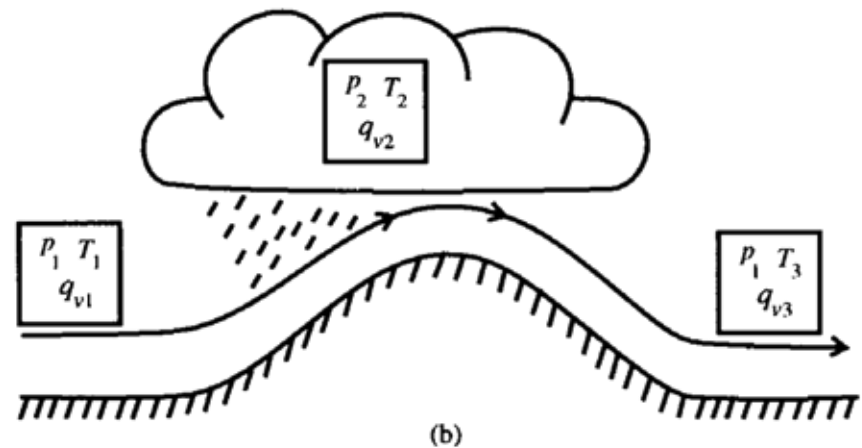
Reversible process:

- Moist air initially at pressure p_1 , temperature T_1 , and specific humidity q_1 rises adiabatically to the top of a mountain.
- It then descends adiabatically on the other side to the initial pressure p_1 .
- Because the passage over the mountain occurs both reversibly and adiabatically, the temperature and specific humidity are restored to their initial values.



Irreversible process:

- Clouds form as the moist air mass rises, and part of the condensed water precipitates out.
- When the air mass descends on the lee side to its initial pressure p_1 , its specific humidity is lower and its temperature is higher than their original values.
- The total water content of the atmosphere decreases irreversibly, and the atmosphere is warmed irreversibly.



Consider a reversible heating process. If it proceeds infinitesimally slowly, the ideal gas law is satisfied at all times.

The first law:

$$dh = \delta q + v dp$$

$$\delta q = c_p dT - v dp$$

$$v = \frac{RT}{p}$$

$$\delta q = c_p dT - RT \frac{dp}{p} \quad /T$$

$$\frac{\delta q}{T} = c_p d \ln T - R d \ln p$$

The two terms on the right-hand side are, by definition, exact differentials (since they depend only on intensive variables), and therefore their sum must also be an exact differential.

Dividing heat by temperature converts the inexact differential δq into an exact differential.

$$\oint \left(\frac{\delta q}{T} \right)_{rev} = 0$$

Entropy (with units $\text{J K}^{-1} \text{kg}^{-1}$) is defined so that the entropy change between two states corresponds to a reversible process connecting them.

$$ds = \left(\frac{\delta q}{T} \right)_{rev}, \quad ds = c_p d \ln T - R d \ln p$$

When the entropy change between two given states occurs via an irreversible process, the change in entropy is exactly the same as for a reversible process.

Because entropy is a state variable and ds is an exact differential

$$ds = c_p d \ln T - R d \ln p ,$$

the integration of ds does not depend on the path of integration; it depends only on the initial and final states.

Although the change in entropy between two states is independent of the path, the integral $\int \delta q/T$ depends on the path and therefore differs for reversible and irreversible processes.

$$\int \left(\frac{\delta q}{T} \right)_{rev} > \int \left(\frac{\delta q}{T} \right)_{irev} \quad ds = \left(\frac{\delta q}{T} \right)_{rev}$$

$$ds > \left(\frac{\delta q}{T} \right)_{irev}$$

For a given entropy change, an irreversible process requires more heat input than a reversible one; the excess heat is ultimately rejected to the surroundings.