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

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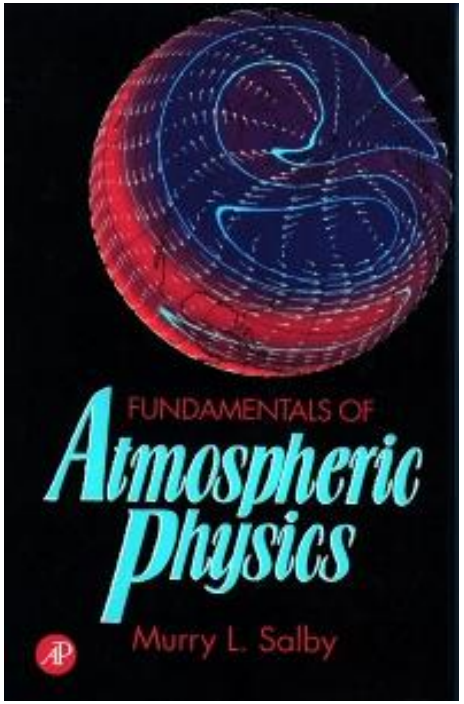
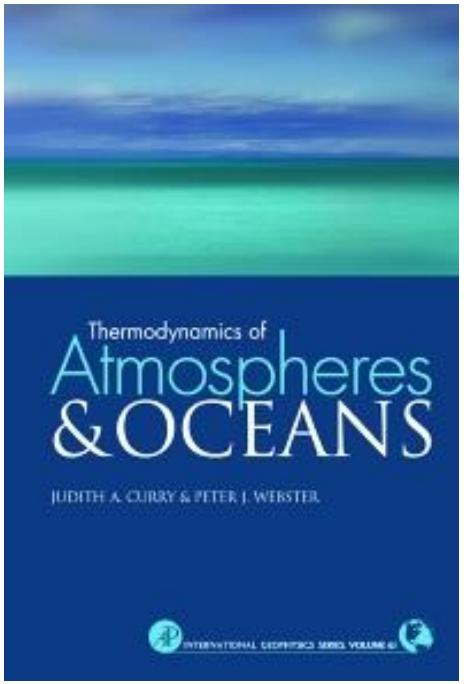
Salby, Chapter 2 and 3



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 Oceanes,
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

$\Delta u = q - w$

$du = \delta q - pdv$

δq – the heat transfer INTO the system

pdv – the work performed BY the system

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

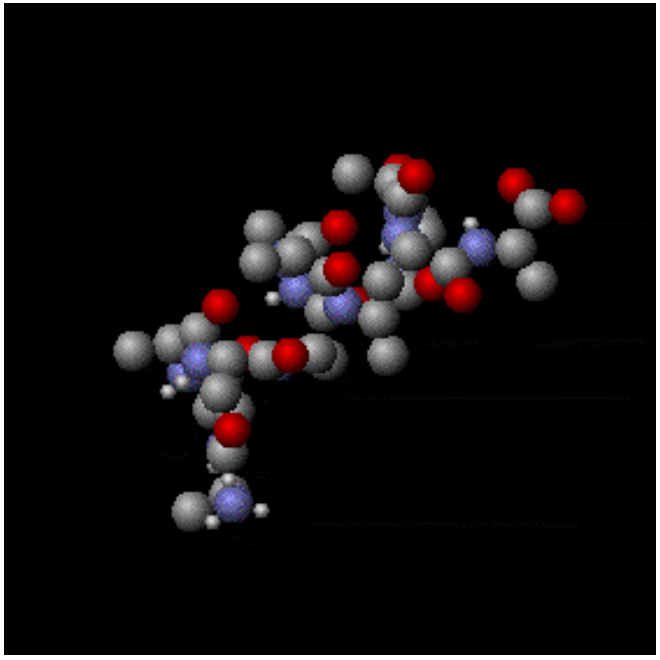
The same is not true of the work performed by the system and the heat transferred to it.

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 othwerwise would constribute 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

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

$$\delta q - pdv + pdv + vdp$$

$$dh = \delta q + vdp$$

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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   Reversible and irreversible processes

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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 closly 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: $du = \delta q - pdv$

$$\delta q - pdv = \left(\frac{\partial u}{\partial v}\right)_T dv + \left(\frac{\partial u}{\partial T}\right)_v dT$$

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

For an isochoric process ($v = const, dv = 0$):

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

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: $dh = \delta q + v dp$

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

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

For an isobaric process ($p = const, dp = 0$):

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

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:

$(du)_v = c_v dT$ 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

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

$$du = c_{vd} dT$$

$$dh = c_{pd} dT$$

First law of thermodynamics

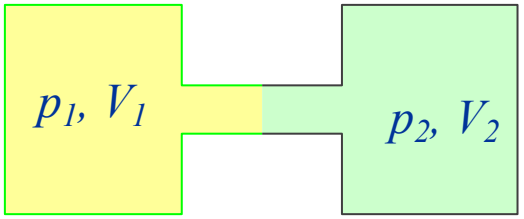
$$\delta q = c_{vd} dT + p dv$$

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

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 indcate 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

Substracting:

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

$$h - u = (c_{pd} - c_v d)T$$
$$(u + pv) - u = (c_{pd} - c_{vd})T$$
$$\frac{pv}{T} = (c_{vd} - c_{pd}) \quad \Rightarrow \quad c_{pd} - c_{vd} = R_d$$

$h = u + pv$

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

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 od 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:

$$du = \delta q - pdv$$
$$dh = \delta q + vdp$$

Internal energy and enthalpy:

$$du = c_v dT$$
$$dh = c_p dT$$

$$c_{vd} dT + pdv = \delta q$$
$$c_{pd} dT - vdp = \delta q$$

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

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 transfered in isochoric and isobaric processes is also a state variable!

Adiabatic process

Because heat transfer is slow compared to other processes influencing a parcel, adiabatic behavior ($\delta q=0$) is a good approximation for many applications.

First law of thermodynamics:

$$du = \cancel{\delta q} - pdv \qquad du = c_{vd}dT$$
$$dh = \cancel{\delta q} + vdp \qquad dh = c_{pd}dT$$

$$c_{vd}dT + pdv = 0 \quad /T$$
$$c_{pd}dT - vdp = 0 \quad /T$$

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

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

Poisson's equations

$$T^{c_{vd}} v^{R_d} = const$$
$$T^{c_{pd}} p^{-R_d} = const$$ commonly used form
$$p^{c_{vd}} v^{dc_p} = const$$

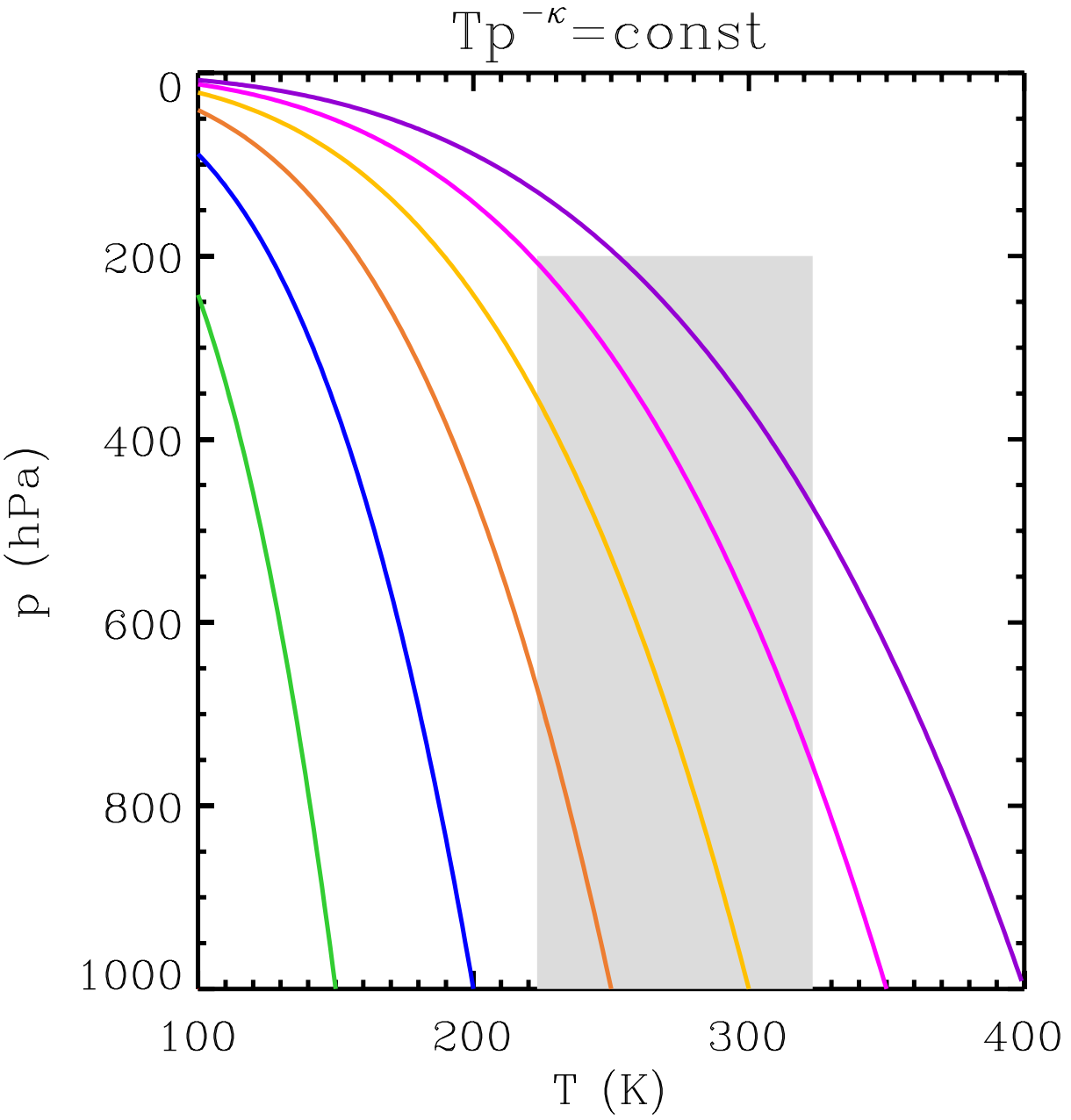
$$T^{c_{pd}} p^{-R_d} = const$$

$$Tp^{-\kappa} = const$$

$$\kappa = \frac{R_d}{c_{pd}} = \frac{R_d}{R_d + c_{vd}}$$

$$= \frac{R_d}{R_d + \frac{5}{2} R_d} = \frac{2}{7}$$

$$\kappa \cong 0.286$$



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Poisson's relation between pressure and temperature motivates the introduction of a new variable that is preserved during an adiabatic process.

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

The potential temperature θ is defined as that temperature assumed by the system when compressed or expanded adiabatically to a reference pressure of p_0=1000 hPa.

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

The unit of potential temperature is K !!!

The potential temperature as a function of temperature and pressure is a state variable. θ is invariant along an adiabatic path in state space.

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

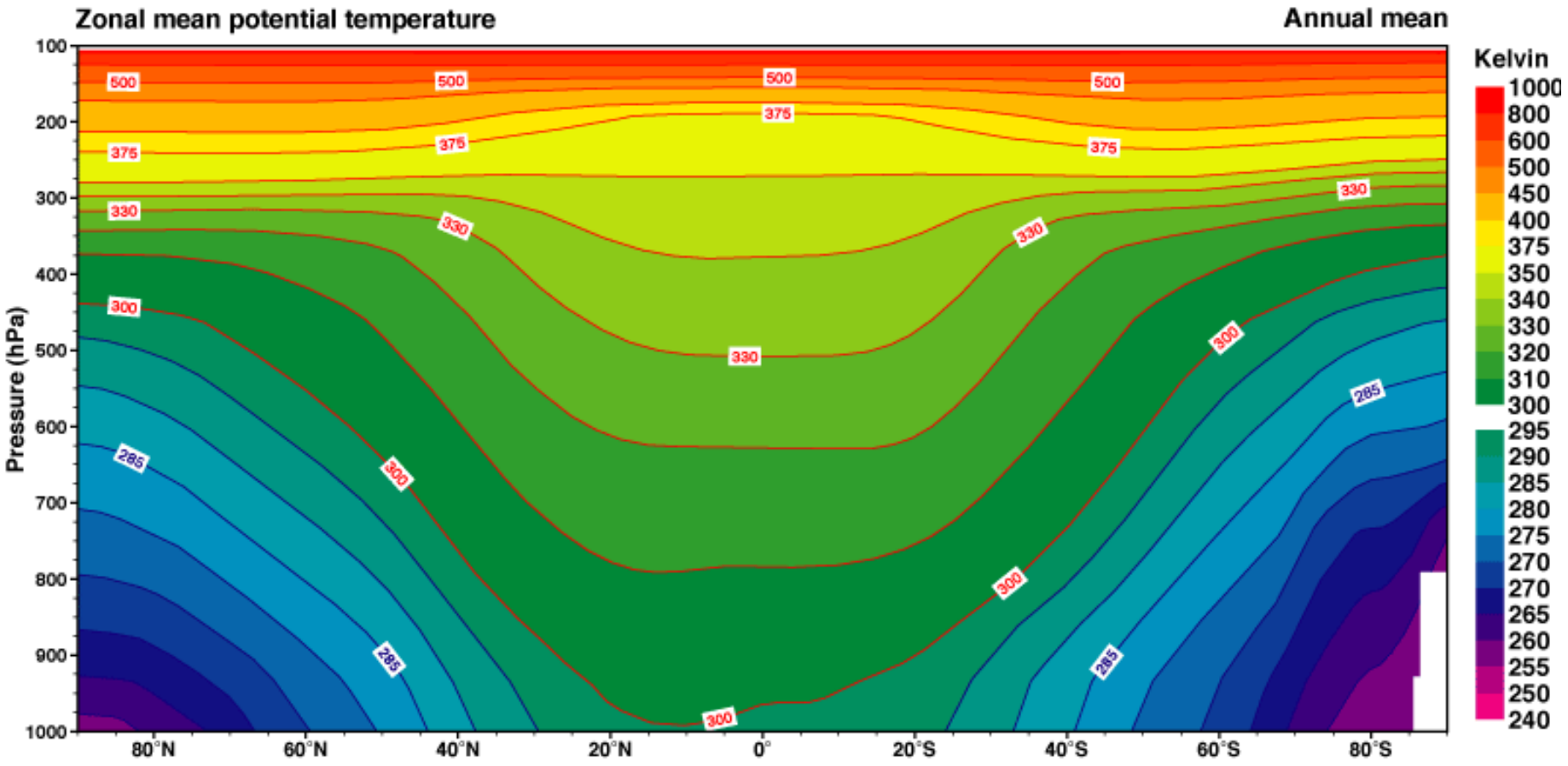
Under almost all circumstances, potential temperature increases upwards in the atmosphere, unlike actual temperature which may increase or decrease.

Potential temperature is conserved for all dry adiabatic processes, and as such is an important quantity in the planetary boundary layer (which is often very close to being dry adiabatic).

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

Because pressure decreases sharply with altitude, $\theta = T(p_0/p)^{\kappa}$ implies that surfaces of constant θ tend to be quasi-horizontal like isobaric surfaces.

Zonal mean potential temperature



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

https://sites.ecmwf.int/era/40-atlas/docs/section_D25/parameter_zmpttp.html#

Adiabatic gradient

The temperature of an air parcel moving vertically changes due to expansion work.

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

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

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

Hydrostatic equation: $dp = -\rho g dz \quad ; \rho = \frac{1}{v}$

$$dp = -\frac{g}{v}dz \implies vdp = -gdz$$

$$c_{pd}dT + gdz = 0$$

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

$$\Gamma_d = \frac{g}{c_{pd}} = \frac{9.81\ \mathrm{m/s^2}}{1004\ \mathrm{J/kgK}} \approx 9.8\frac{\mathrm{K}}{\mathrm{km}}$$

Potential temperature θ:

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

$$d\ln\theta = d\ln T - \kappa d\ln p \qquad \kappa = \frac{R_d}{c_{pd}} \cong 0.286$$

Change of potential temperature with height:

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

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

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

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

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

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

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

Potential temperature does not change in a parcel moving adiabaticly upwards.

Non-adiabatic (diabatic) process

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

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

First law in the form of enthalpy: $dh = \delta q + vdp$ + $dh = c_{pd}dT$

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

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

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

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

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

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

The increase of potential temperature is a direct measure of the heat transferred into the system.

Polytropic processes

Most of the energy exchanged between the earth's surface and the atmosphere and between one atmospheric layer and another is accomplished through radiative transfer.

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

It is sometimes convenient to model radiative transfer as a politropic process wherein the heat transferred into the system is proportional to the system's change of temperature. The constant of proportionality, c, is the polytropic specific heat capacity.

$$\delta q = c dT$$

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

$$du = \delta q - pdv \qquad c_{vd} dT = cdT - pdv$$

$$dh = \delta q + vdp \qquad c_{pd} dT = cdT + vdp$$

$$\delta q = c dT$$

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

Equations resemble the first law for an adiabatic process, but with modified specific heats.

Formulas valid for an adiabatic process hold for a polytropic process with the transformation:

$$c_{pd} \longrightarrow (c_{pd} - c)$$
$$c_{vd} \longrightarrow (c_{vd} - c)$$

In terms of potential temperature, the first law becomes:

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

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

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   Reversible and irreversible processes

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- The first law of thermodynamics describes how the state of a system changes in response to work it performs and heat absorbed by it.
  - The first law of thermodynamic places NO limitations on the transformation between heat and work.
- It says nothing about a feasibility of a thermodynamic proces.
- The second law of thermodynamics limits both the amount and the direction of heat transfer.
  - The second law alows definition of the stability of thermodynamic equilibrium.
- Thermodynamic processes:
  - natural process is one that proceeds freely; inherently ‚irreversible'
  - reversible
  - impossible

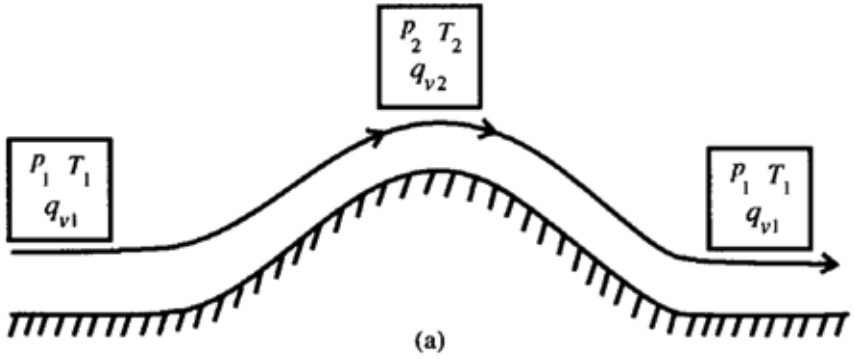
Reversible and irreversible processes

In all thermodynamic processes, the changes that occur in the environment must be considered in conjunction with the changes that occur in the thermodynamic system.

- A reversible process
  - is one in which the system is in an equilibrium state throughout the process
  - the system passes at an infinitesimal rate through a continuous succession of balanced states that are infinitesimally different from each other
  - the process can be reversed, and the system and its environment will return to the initial state.
- Irreversible processes
  - proceed at finite rates
  - if the system is restored to its initial state, the environment will have changed from its initial state
  - the term 'irreversible' does not mean that a system cannot return to its original state, but that the system plus its environment cannot be restored.

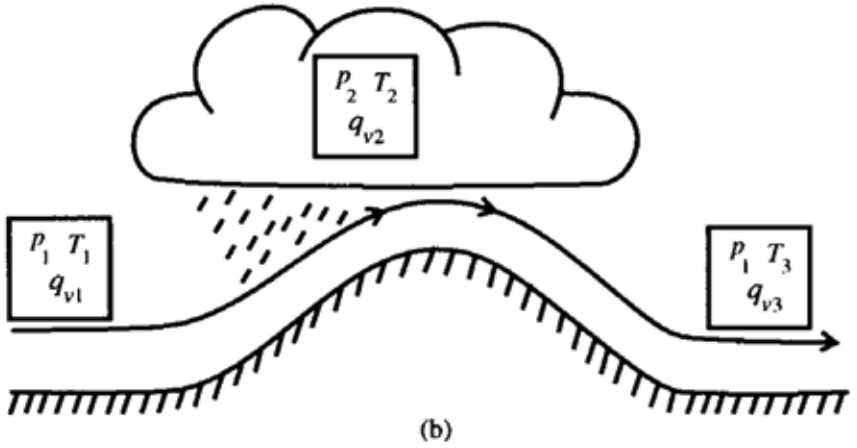
Reversible process:

- moist air initially at pressure p_1 and having 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 process of passing over the mountain was done reversibly and adiabatically, the temperature and specific humidity are restored to their initial values.



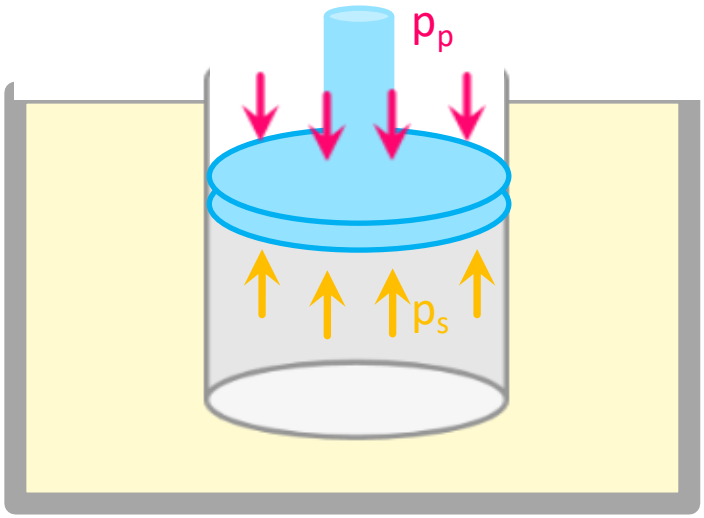
Irreversible process:

- clouds formas the mass of moist air rises, and some of the cloud water rains out
- when the mass of air descends on the other side to its initial pressure, p_1, its specific humidity is lower and its temperature is higher than the original values
- the total water content of the atmosphere decreases irreversibly and the atmosphere is warmed irreversibly.

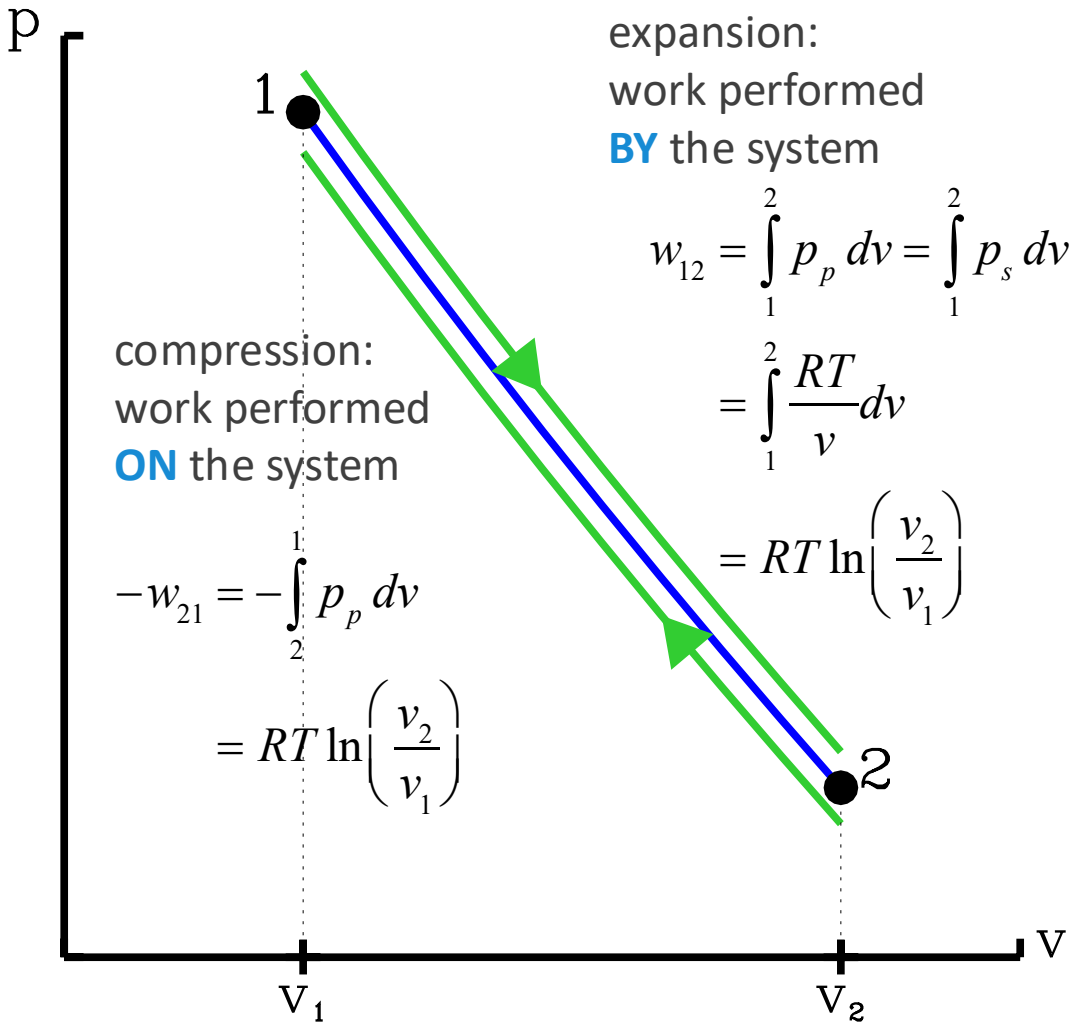


Curry&Webster, Thermodynamics of Atmospheres & Oceans. Fig. 2.4

Isothermal reversible process



- The gas is acted on by a piston and is maintained at a constant temperature, T, through contact with a heat reservoir.
- The gas is expanded isothermally at constant temperature, T, from state 1 to state 2 and subsequently restored to state 1 through isothermal compression.
- If the cycle is executed very slowly and without friction, the system pressure, p_s, is uniform throughout the gas and equals that exerted by the piston, p_p ($p_p = p_s$).



expansion:
work performed
BY the system

$$w_{12} = \int_1^2 p_p\, dv = \int_1^2 p_s\, dv$$

$$= \int_1^2 \frac{RT}{v} dv$$

$$= RT \ln\left(\frac{v_2}{v_1}\right)$$

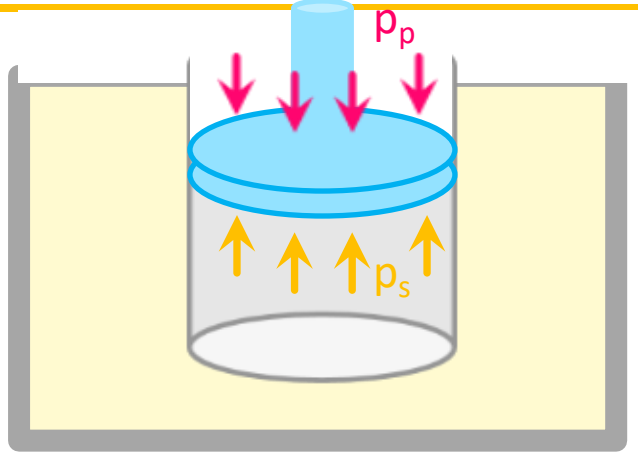
compression:
work performed
ON the system

$$-w_{21} = -\int_2^1 p_p\, dv$$

$$= RT \ln\left(\frac{v_2}{v_1}\right)$$

The net work performed during the cycle wanishes.
Since $\oint du = 0$ we have $\oint \delta q = \oint p dv = 0$.

Isothermal irreversible process



If the cycle is executed rapidly, some of the gas is accelerated. Pressure is no longer uniform across the system and p_s does not equal p_p.

During rapid compression the piston must exert a pressure that exceeds that exerted when the compression is executed slowly.

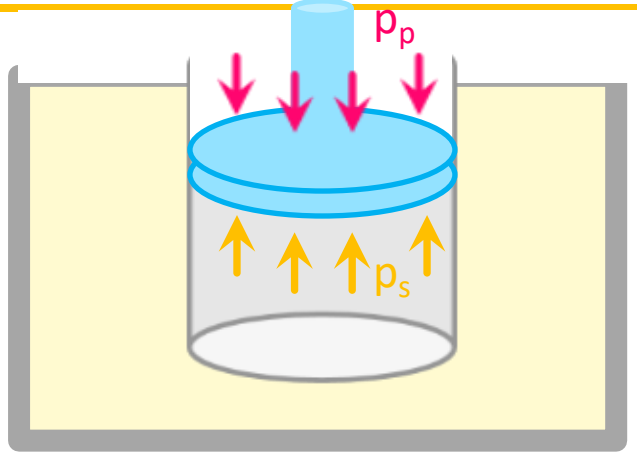
The work performed **ON** the system exceeds that performed under reversible conditions.

$$-w_{irev} > -w_{rev}$$

$$\Delta u = 0 \quad \rightarrow \quad q_{irev} - w_{irev} = q_{rev} - w_{rev}$$

$$q_{irev} < q_{rev}$$

Isothermal irreversible process



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$$\Delta u = 0 \rightarrow q_{irev} - w_{irev} = q_{rev} - w_{rev}$$

$$q_{irev} < q_{rev}$$

During rapid expansion the piston must exert a pressure that is smaller that that exerted when the expansion is executed slowly.

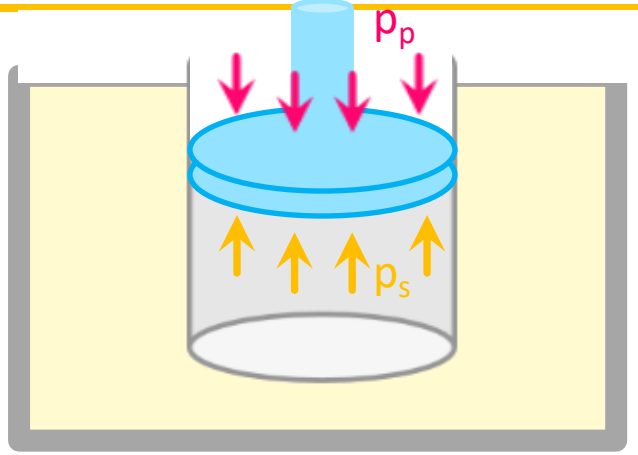
The work performed **BY** the system is less than that performed under reversible conditions.

$$w_{irev} < w_{rev}$$

$$\Delta u = 0 \rightarrow q_{irev} - w_{irev} = q_{rev} - w_{rev}$$

$$q_{irev} < q_{rev}$$

Isothermal irreversible process



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The work performed **ON** the system exceeds that performed under reversible conditions.

$$-w_{irev} > -w_{rev}$$

$$\Delta u = 0 \rightarrow q_{irev} - w_{irev} = q_{rev} - w_{rev}$$

$$q_{irev} < q_{rev}$$

During rapid expansion the piston must exert a pressure that is smaller that that exerted when the expansion is executed slowly.

The work performed **BY** the system is less than that performed under reversible conditions.

$$w_{irev} < w_{rev}$$

$$\Delta u = 0 \rightarrow q_{irev} - w_{irev} = q_{rev} - w_{rev}$$

$$q_{irev} < q_{rev}$$

The work performed by the system is less than that performed under reversible conditions. In a closed cycle $\oint pdv < 0$ (in reversible conditions: $\oint pdv = 0$).

$$\oint du = 0 \quad \longrightarrow \quad \oint dq = \oint pdv < 0$$

Net work is performed on the system, which must be compensated by net rejection of heat to the environment.

Consider a reversible heating process. If the process occurs infinitesimally slowly the ideal gas law is always fullfiled.

The first law:

$$dh = \delta q + vdp$$

$$\delta q = c_p dT - vdp \qquad v = \frac{RT}{p}$$

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

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

The two terms on the right-hand side are by definition exact differentials (they depend only on intensive variables), and 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 J K^{-1} kg^{-1}) is defined so that the change in entropy from one state to the another is associated with a reversible process connecting the two states.

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

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

This is because entropy is a state variable and ds is an exact differential ($ds=c_p dlnT\text{-}Rdlnp$), which means that integration of ds does not depend on the path of integration; it depends only on the initial and final state.

Although the change in entropy is exactly the same for reversible and irreversible processes that have the same initial and final states , the integral of $\delta q/T$ is not the same for reversible and irreversible processes.

$$\delta q_{irev} < \delta q_{rev}$$

$$\left(\frac{\delta q}{T}\right)_{irev} < \left(\frac{\delta q}{T}\right)_{rev} \qquad ds = \left(\frac{\delta q}{T}\right)_{rev}$$

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

To accomplish a given change of entropy (or state) by an irreversible process, more heat is required than when a reversible process is involved.