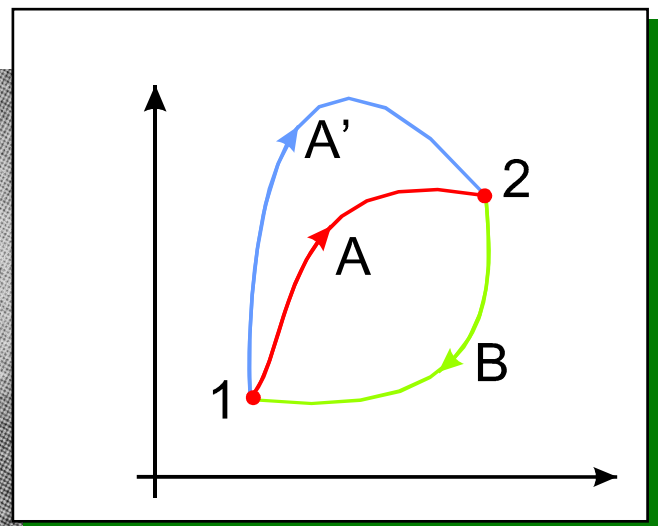
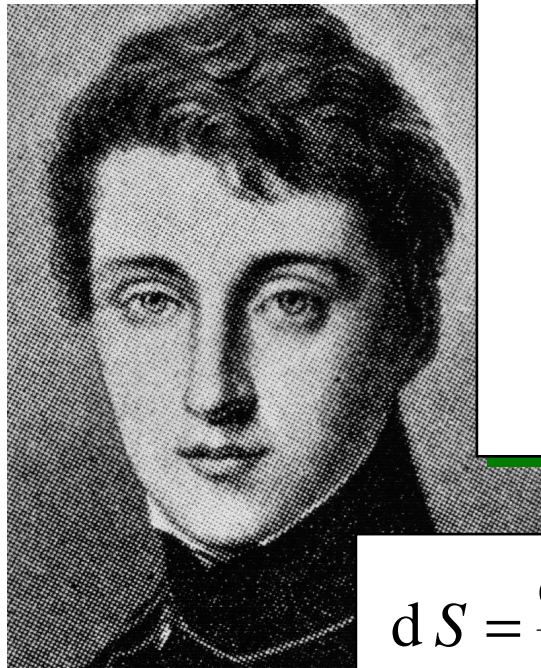


Lecture 2: Entropy

♦ Aims (still revising classical ideas):

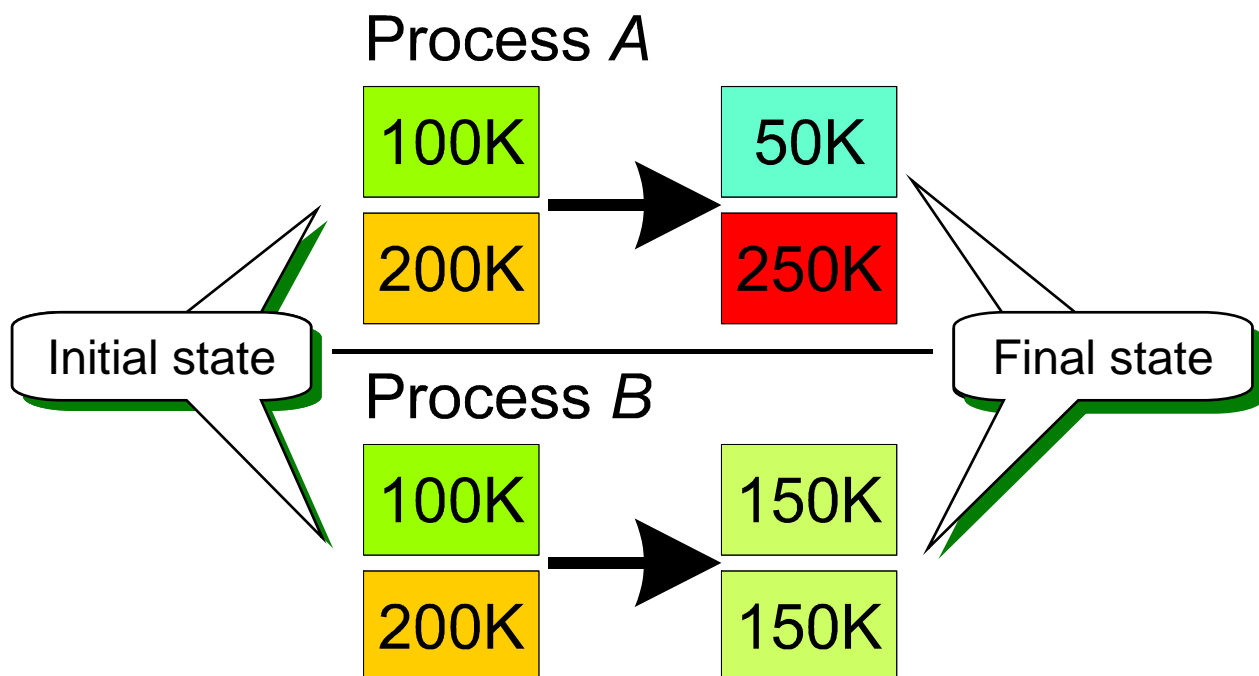
- ▶ Thermodynamic definition of the Entropy,
 - ▣ Deduced from Carnot's theorem.
- ▶ Law of increase of entropy:
 - ▣ Arrow of time.
- ▶ Free energy:
 - ▣ minimised at equilibrium
- ▶ Evaluating entropy changes .



$$dS = \frac{dQ_{rev}}{T}$$

Isolated systems

- ♦ **First law:** defines processes that are allowed. Not all of these can occur; for example,
 - ▶ Consider an isolated system consisting of two equal masses starting at temperatures 100K and 200K:



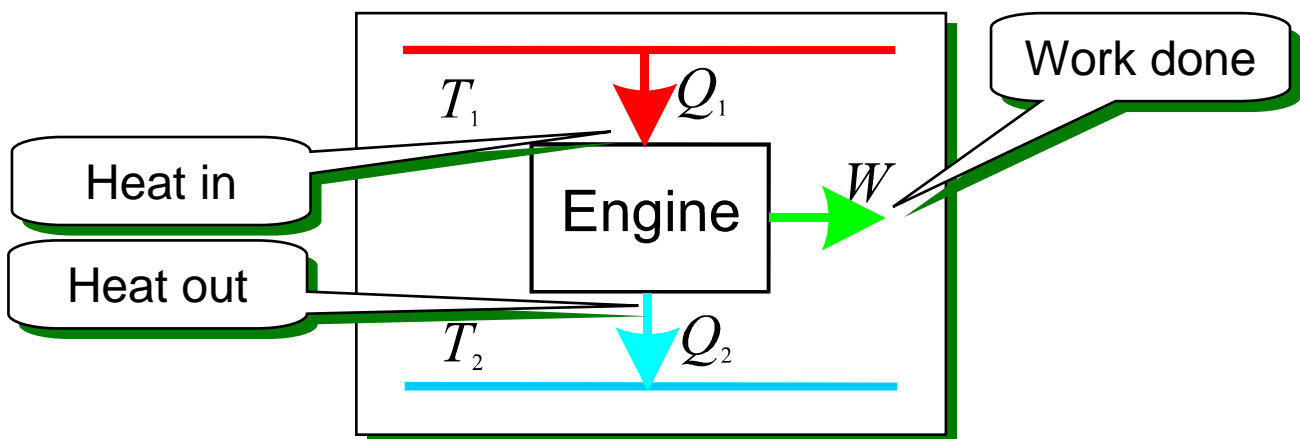
- ▶ The first law allows both processes.
- ▶ Experience (and experiment) show that only process B can happen spontaneously.
- ♦ **Second Law:** defines those processes that can occur.
 - ▶ Related to the nature of irreversible events.

Entropy and heat engines

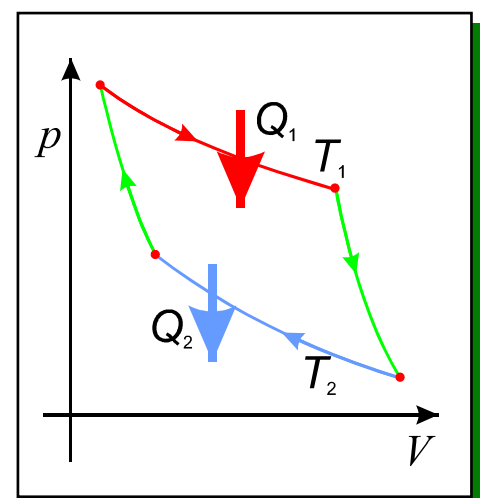
♦ Entropy:

- ▶ Enables us to distinguish states accessible spontaneously from a given initial state.
- ▶ Ideas easiest to grasp from a consideration of reversible heat engines.

♦ Idealised engine:



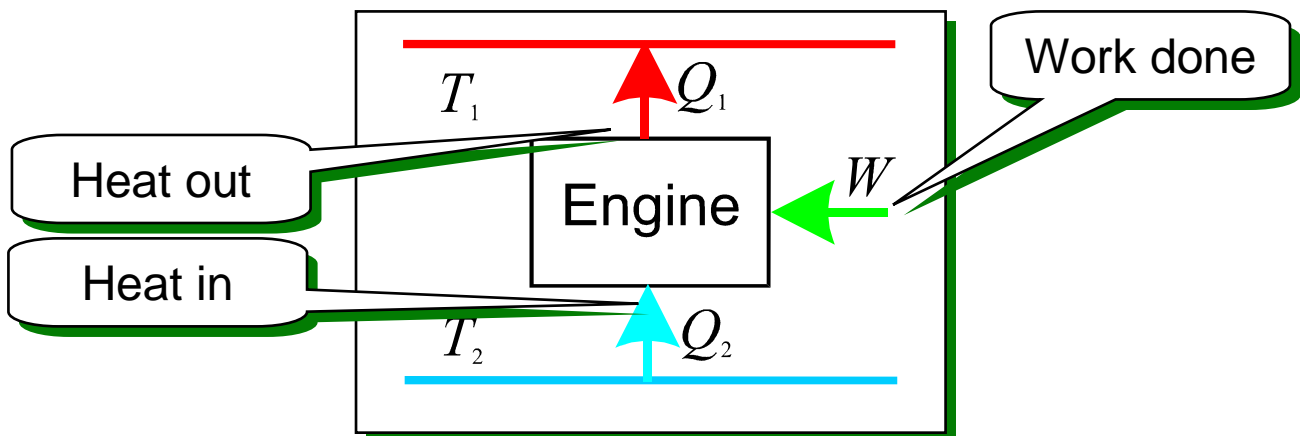
- ▶ Cyclic engines: by executing a cycle, the engine periodically returns to an initial condition; as well as allowing its properties to be explored quantitatively.
- ▶ Details unimportant for this course.



Reversible engines

♦ Reversibility:

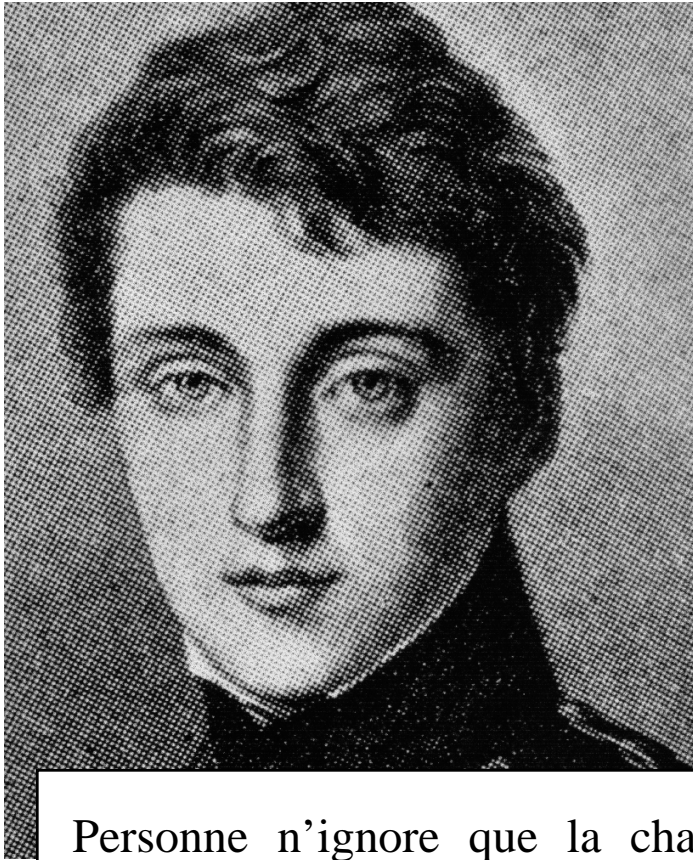
- ▶ Means two (related) things:
 - ▣ All processes are thermodynamically reversible.
 - ▣ The engine itself can be reversed so that work done *on* the engine transfers heat from the “sink” to the “source” (it becomes a refrigerator).



♦ The Carnot engine:

- ▶ Both a concept and a specific “realisation” of a reversible cyclic engine. It is based on adiabatic and isothermal processes using an ideal gas.
 - ▣ Concept also used more generally for any reversible cyclic system.

Sadi Carnot (1796-1832)



RÉFLEXIONS SUR LA PUISSANCE MOTRICE DU FEU.

Personne n'ignore que la chaleur peut être la cause du mouvement, qu'elle possède même une grande puissance motrice: les machines à vapeur, aujourd'hui si répandues, en sont une preuve parlante à tous les yeux.

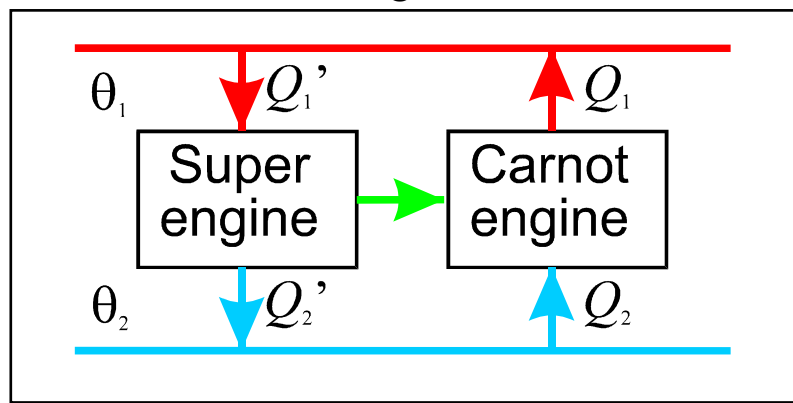
C'est à la chaleur que doivent être attribués les grands mouvemens qui frappent nos regards sur la terre; c'est à elle que sont dues les agitations de l'atmosphère, l'ascension des nuages, la chute des pluies et des autres météores, les courans d'eau qui sillonnent la surface du globe et dont l'homme est parvenu à employer pour son usage une faible partie....

Carnot's theorem

♦ Carnot's theorem

- ▶ Of all heat engines working between two given temperatures none can be more efficient than a reversible heat engine.

- Proof: If a super engine exists use it to drive the reversible engine backwards:



- If super engine has greater efficiency:

$$Q_1' < Q_1$$

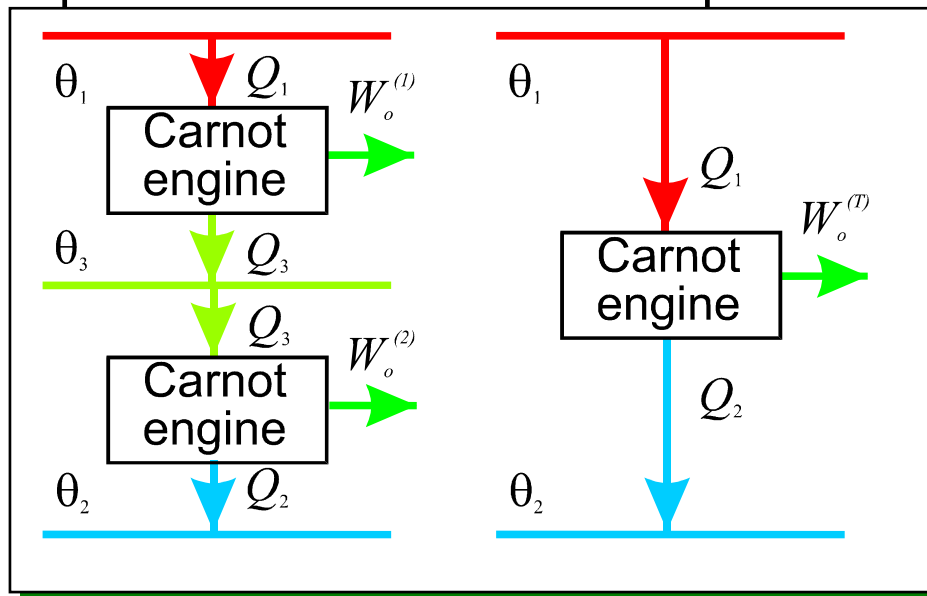
- Thus heat $Q_1 - Q_1' > 0$ has been delivered from the cold to the hot reservoirs.
- Violates our knowledge of the world, and what we now call the “Second Law”.
- ▶ Clausius statement of the second law.
 - No process is possible whose sole purpose is the transfer of heat from a colder to a hotter body.

Connection to Entropy

- Question? How are Q and T related?

$$\frac{Q_1}{Q_2} = f(T_1, T_2)$$

- Consider 2 engines in tandem. No heat deposited at intermediate temperature



- Two in tandem are equivalent to one (on right).

$$\frac{Q_1}{Q_2} = \frac{Q_1}{Q_3} \cdot \frac{Q_3}{Q_2} \Rightarrow f(T_1, T_2) = f(T_1, T_3) \cdot f(T_3, T_2)$$

satisfied if

$$f(T_1, T_2) = \frac{T_1}{T_2} \Rightarrow \boxed{\frac{Q_1}{T_1} = \frac{Q_2}{T_2}}$$

Entropy

♦ A new function of state;

- ▶ Previous argument leads us to the conclusion that the quantity Q/T , or more generally,

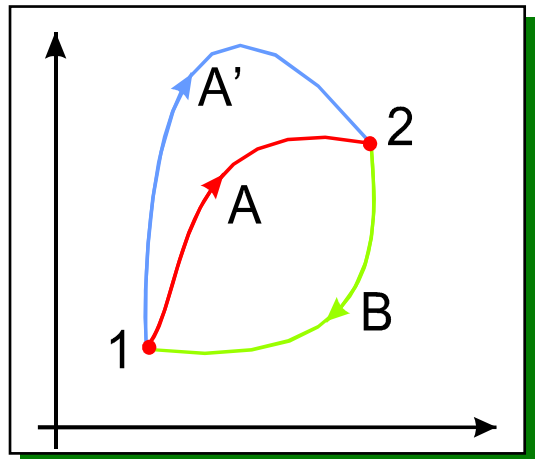
$$dS = \frac{dQ_{rev}}{T}$$

is conserved in the reversible changes of a Carnot cycle. i.e.:

$$\Delta S = \oint \frac{dQ_{rev}}{T} = 0$$

- ▶ S is a function of state (even though dQ is an imperfect differential).

- Proof:
Split a reversible loop, into 2 paths A & B.
Integrate S round the loop.



$$\oint \frac{dQ_{rev}}{T} = \int_A \frac{dQ_{rev}}{T} + \int_B \frac{dQ_{rev}}{T} = 0$$

The answer does not depend on path (both A and A' give the same result) so S depends only on the end points.

Calculating entropy

♦ Entropy;

- ▶ Entropy S is a function of state.
- ▶ Change in entropy between states 1 and 2

is $\Delta S = \int_1^2 \frac{dQ_{rev}}{T}$ independent of path.

Note, heat supplied reversibly

♦ Example:

♦ Heating a solid

- ▶ Heat from $T_1 \rightarrow T_2$, heat capacity C , neglect volume change, $p dV = 0$.

$$dQ = c dT = T dS$$

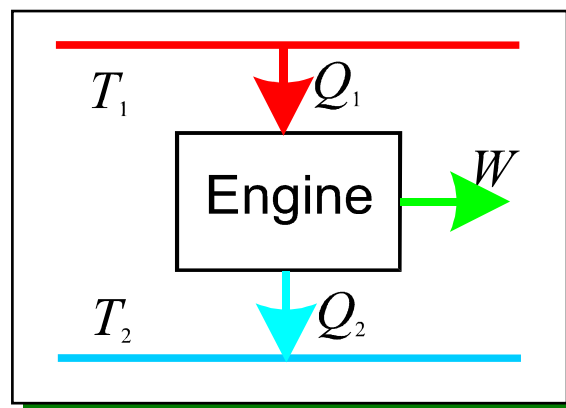
$$\Delta S = \int_{T_1}^{T_2} \frac{C dT}{T} = C \ln(T_2/T_1)$$

See Examples 1, Q. 3

Irreversible changes

♦ Irreversible cycles:

- Recall Carnot's theorem



Carnot engine : Less efficient engine

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

Carnot Theorem

\Rightarrow

$$\frac{Q_1}{T_1} < \frac{Q_2}{T_2}$$

$$Q'_2 > Q_2$$

- Generalising to any cycle:

$$\Delta S = \oint \frac{dQ_{rev}}{T} = 0$$

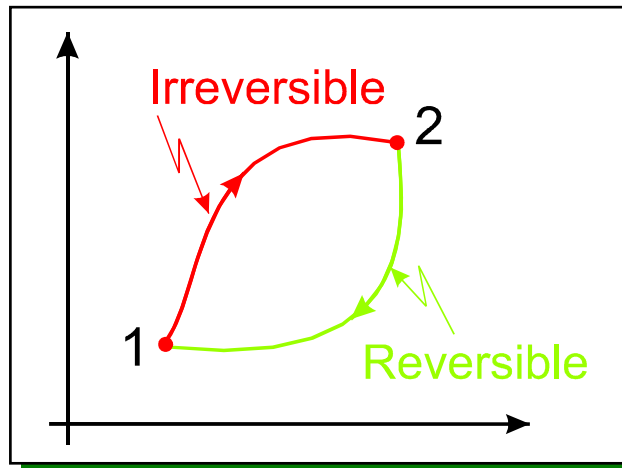
$$\oint \frac{dQ}{T} < 0$$

- i.e. in any cycle,

$$\oint \frac{dQ}{T} \leq 0$$

The Second Law

- ♦ What happens to S in an irreversible change?



- ▶ Going round the partly reversible loop:

$$\int_1^2 \frac{dQ_{irrev}}{T} + \int_2^1 \frac{dQ_{rev}}{T} \leq 0$$

$$\int_1^2 \frac{dQ_{irrev}}{T} \leq \int_1^2 \frac{dQ_{rev}}{T} = \Delta S$$

$$dS \geq \frac{dQ}{T}$$

The second law

- ▶ For an isolated system $dQ=0$, $dS \geq 0$.

- ▶ The entropy of an isolated system cannot decrease

- ▶ Gives us the arrow of time.

Free Energy

- ♦ **Free energy** is another function of state useful in bridging to statistical mechanics (see later lectures).

$$\text{▶ } F = U - TS$$

(evidently a fn. of state since U , T & S are fns. of state).

- ▶ For a system that can exchange heat with its surroundings but do no work ($p dV=0$, constant volume)

$$dQ_{\text{surroundings}} = -dU_{\text{system}}$$

$$dQ_{\text{system}} = dU_{\text{system}}$$

$$\int \frac{dQ_{\text{system}}}{T} = \frac{\Delta U_{\text{system}}}{T}$$

$$\leq \Delta S_{\text{system}}$$

$$\Delta(U_{\text{system}} - TS_{\text{system}}) = \Delta F_{\text{system}} \leq 0$$

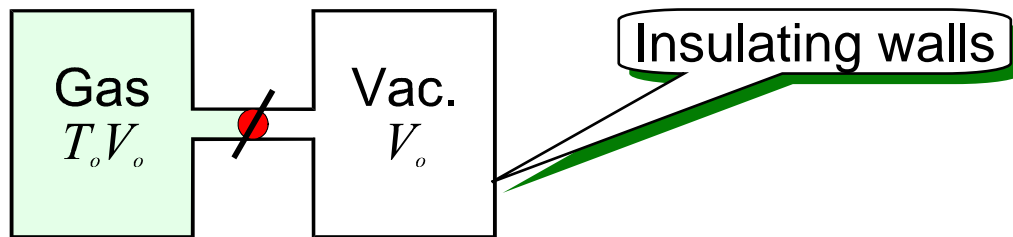
- ▶ The free energy decreases in any spontaneous, irreversible change, as the system moves towards equilibrium.

▶ **The Free Energy is a minimum at equilibrium.**

- ▶ A Thermodynamic Potential.

Entropy and configuration

- ♦ **Joule expansion:** Irreversible expansion of a perfect gas into a vacuum.



- ▶ We can work with the **initial and final states** (common strategy in problem solving) when dealing with functions of state.
- ▶ What is the final state, T_f, p_f ?
 - ▣ Use the first law:

$$\Delta U = \Delta Q + \Delta W$$

- ▣ Consider the system as a whole
 - ▣ $\Delta W=0$, no work done on (or by) the universe
 - ▣ $\Delta Q=0$, isolated adiabatic change.
 - ▣ First Law gives $\Delta U=0$.
- ▶ For a perfect gas: $U=3RT/2$.
- ▶ $T_f = T_i$.
- ▶ p follows from gas laws $p_1 V_1 = p_2 V_2$.

Joule expansion: Entropy change

♦ Entropy change:

- ▶ To calculate the entropy change, we need a reversible route from initial to final state.

- ▣ Initially: $p_o V_o T_o$

- ▣ Finally: $p_1 V_1 T_1$ or, if volume doubles, $p_o/2, 2V_o, T_o$.

- ▶ Choose an isothermal expansion

$$dU = dQ + dW$$

$$\Delta T = 0 \rightarrow \Delta U = 0$$

$$0 = T dS - P dV$$

$$T dS = \frac{RT}{V} dV$$

$$\int dS = R \int \frac{dV}{V}$$

For 1 mole

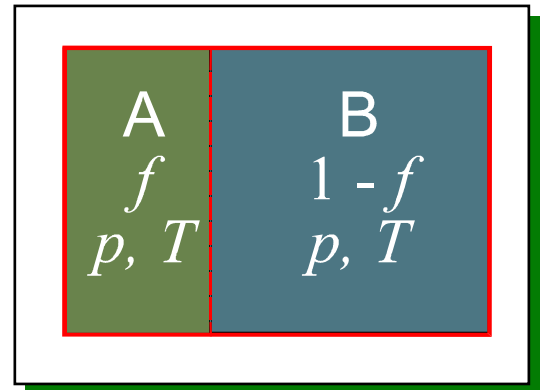
$$\Delta S = R \ln(V_1/V_o)$$

- ▶ In the case above $V_o \rightarrow 2V_o$
 - ▣ $\Delta S = R \ln 2 > 0$
- ▶ Note: entropy increases without heat input.
- ▶ Leads to the notion that entropy is related to configuration (disorder).

Entropy of mixing

♦ Change in entropy on mixing

- ▶ A and B are two components separated by a partition.
- ▶ Mixing is irreversible so expect entropy to increase when the partition is removed.



- ▶ For f moles, $S \rightarrow f S$, when only V changes:
- ▶ Gas A:

$$\Delta S_A = f R \ln(V/fV)$$

- ▶ Gas B:

$$\Delta S_B = (1-f) R \ln(V/(1-f)V)$$

$$\Delta S_{mix} = \Delta S_A + \Delta S_B = R \left(f \ln \left(\frac{1}{f} \right) + (1-f) \ln \left(\frac{1}{1-f} \right) \right)$$

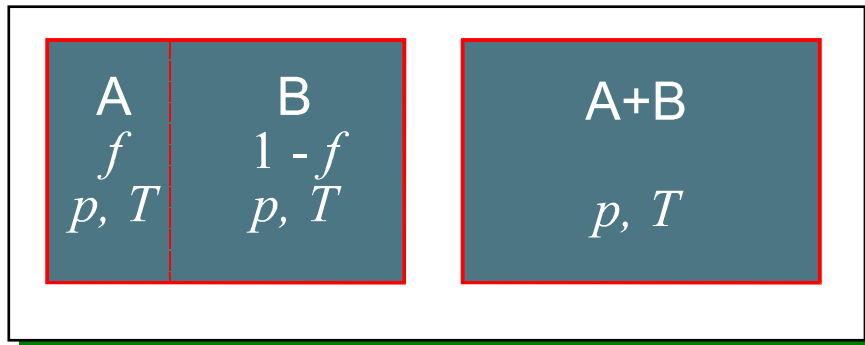
$$\Delta S_{mix} = -R(f \ln(f) + (1-f) \ln(1-f)) > 0$$

- ▶ $\Delta S > 0$, an irreversible process

- ▶ Note: final state is more disordered

Gibbs' Paradox

♦ What if the 2 gases are identical?



- ▶ There can be no increase in entropy since initial and final states are identical.

$$\Delta S_{mix} = 0.$$

- ▶ Particles are **indistinguishable** (impossible to separate them even in principle).
- ▶ If the particles are distinguishable, no matter how small the difference between A and B there is a finite entropy change.
- ▶ To understand the paradox we need a microscopic view of entropy.
- ▶ We start on such an approach next lecture.

Corrections 2004

♦ Slide 10

- ▶ ΔS removed from last two equations.