



Chapter 20—Irreversible processes

Physics 2101

Section 3

May 5th: Chap. 20

Announcements:

- **Final Exam: May 11th**
(Tuesday), 7:30 AM at Howe-Russell 130
- **Make up Final: May 15th**
(Saturday) 7:30 AM at Nicholson 119
- **Final Exam for those who need extended time will be at Nicholson 109**

Class Website:

<http://www.phys.lsu.edu/classes/spring2010/phys2101-3/>

<http://www.phys.lsu.edu/~jzhang/teaching.html>

Final Examination

There are two parts:

Part 1: A Cumulative exam from 1-18-6.

Part 2: A special part for these after Exam 4: around 30 to 40%

Part 1 will be entirely from Home Work and the previous examinations.

Remember special cases...

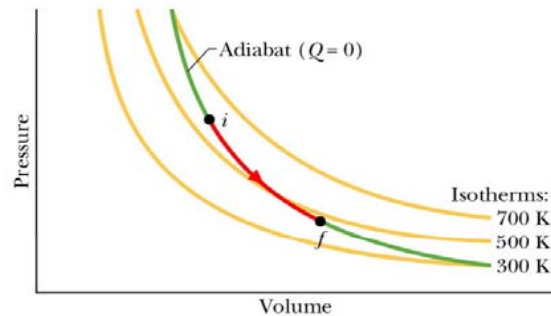
Ideal Gas:

$$PV = nRT$$

$$\Delta E_{\text{int}} = \frac{3}{2} nR(\Delta T)$$

Adiabatic expansion/contraction - NO TRANSFER OF ENERGY AS HEAT $Q = 0$

$$[\Delta E_{\text{int}} = -W]_{\text{adiabatic}}$$



Constant-volume processes (isochoric)-

NO WORK IS DONE $W = 0$

$$\Delta E_{\text{int}} = Q$$

$$W_{\text{by}} = \int_{V_i}^{V_f=V_i} p dV = 0$$

$$Q_{\Delta V=0} = nC_V \Delta T$$

Constant-pressure processes

$$\Delta E_{\text{int}} = Q - p\Delta V$$

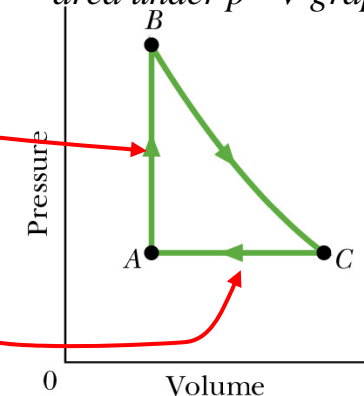
$$C_V = C_P - R$$

$$W_{\text{by}} = \int_{V_i}^{V_f=V_i} p dV = p\Delta V$$

$$Q_{\Delta P=0} = nC_P \Delta T$$

$$W_{\text{by}} = \int p dV$$

= area under $p-V$ graph



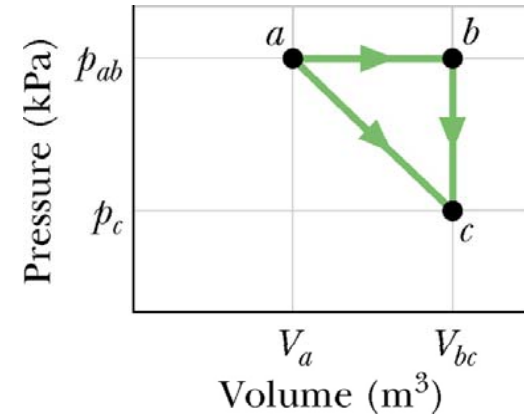
3) Cyclical process (closed cycle)

a) net area in $p-V$ curve is Q

$$\Delta E_{\text{int, closed cycle}} = 0$$

$$\Delta E_{\text{int}} = 0 \Rightarrow Q = W$$

19#46: One mole of an ideal atomic gas goes from a to c along the diagonal path. The scale of the vertical axis is set by $p_{ab}=5.0$ kPa and $p_c=2.0$ kPa, and the scale of the V axis is $V_{bc}4.0$ m³ and $V_a=2.0$ m³. (a) what is the change in the internal Energy? (b) How much Energy is added to the gas? (c) How much heat is required if the gas goes from a to c via abc?



For any straight line on pv plot
it is easy to prove

$$E_{\text{int}} = n \left(\frac{3}{2} \right) RT$$

$$W_{\text{straight}} = \left(\frac{p_f + p_i}{2} \right) \Delta V$$

$$(a) E_{\text{int } c} - E_{\text{int } a} = \left(\frac{3}{2} \right) (T_c - T_a) = \left(\frac{3}{2} \right) (p_c V_c - p_a V_a) = -3000 J$$

$$(b) W = \left(\frac{p_a + p_c}{2} \right) (V_c - V_a) = 7000 J$$

$$Q = \Delta E_{\text{int}} + W = 2000 J$$

(c) ΔE_{int} found in (a)

$$W = (5.0 \times 10^3 Pa) (2 m^3) = 10000 J$$

$$Q = 5000 J$$

Chapter 20: Entropy & the Second law of thermodynamics

0th law Thermal Equilibrium: $A = B$ & $B = C$ then $A = C$

$$Q = nC\Delta T$$

$$Q \rightarrow 0 \text{ as } \Delta T \rightarrow 0$$

1st law Conservation of energy: $\Delta E_{\text{int}} = Q - W$

Change in Internal energy = heat added minus work done b

2nd law **HEAT FLOWS NATURALLY FROM HOT OBJECT TO A COLD OBJECT**

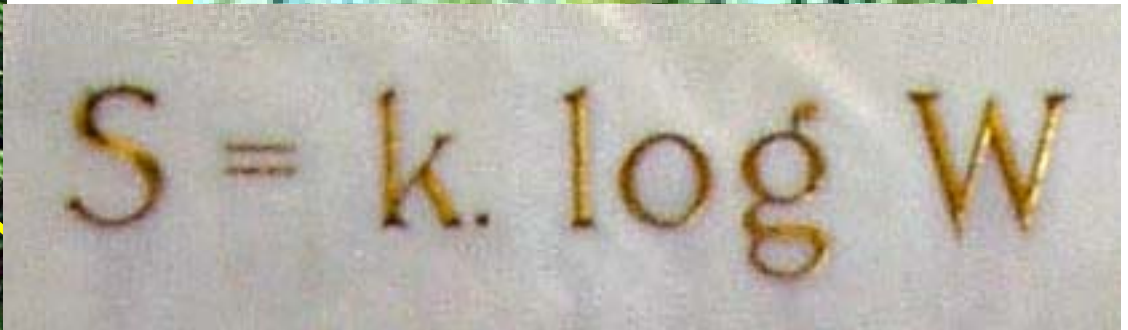
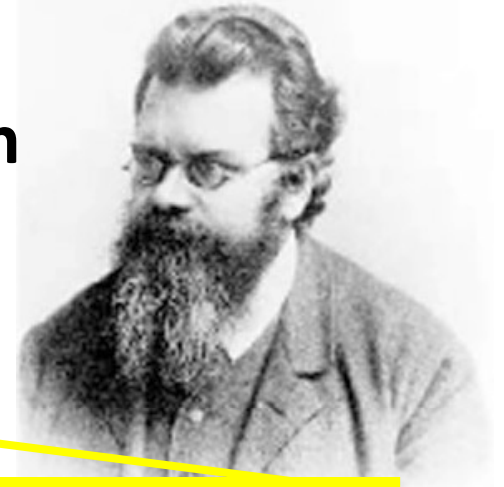
Heat will NOT flow spontaneously from cold to hot



$$\Delta S_{\text{total}} \geq 0$$

Hall of fame

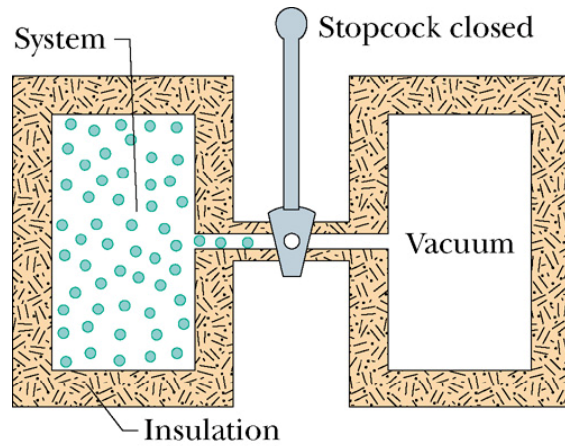
Ludwig Boltzmann
(1844-1906)



Boltzmann constant

$$k = 1.38 \times 10^{-23} \text{ J/K}$$

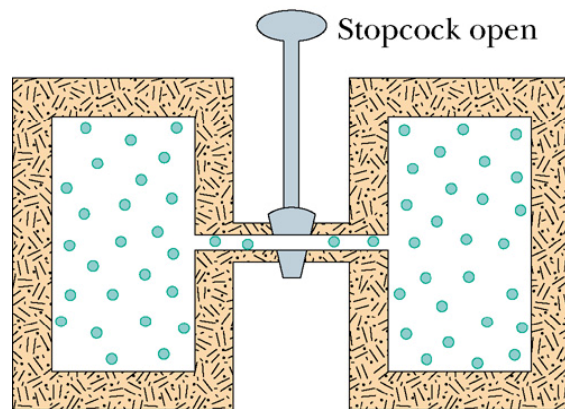
Irreversible Processes



(a) Initial state i



Irreversible process

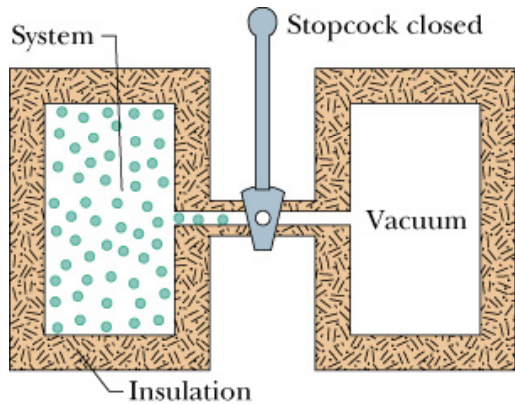


(b) Final state f

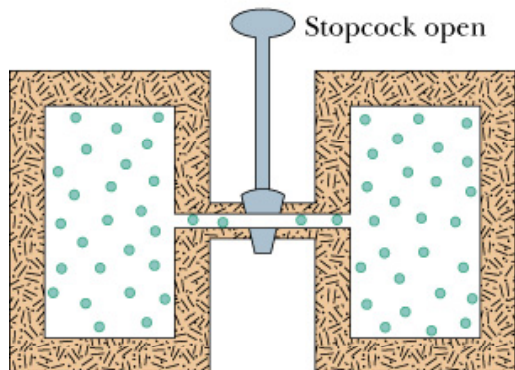


20-3 Change in Entropy

Consider the free expansion of a gas shown in the figure. The initial and final states (P_i, V_i) and (P_f, V_f) are shown on the $P-V$ diagram below. Even though the initial and final states are well defined, we do not have intermediate equilibrium states that take us from (P_i, V_i) to (P_f, V_f) .



(a) Initial state i

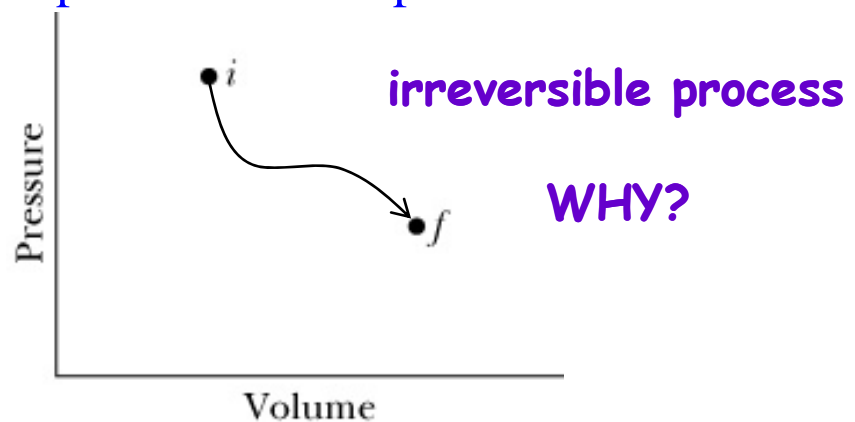


(b) Final state f

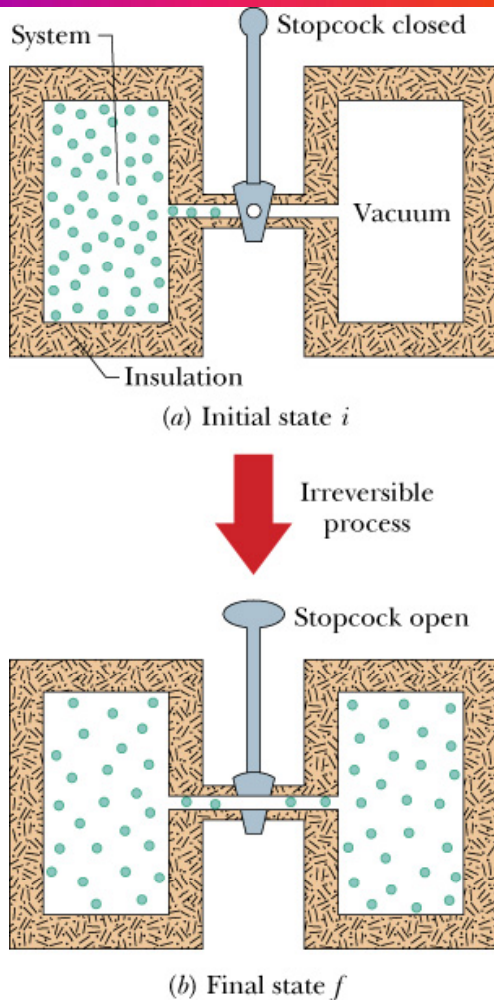
The pressure, temperature, and volume of the gas fluctuate unpredictably in the process --- Can't do the integral!!

During the free expansion the temperature does not change:

$$T_i = T_f.$$



20-3 Change in Entropy



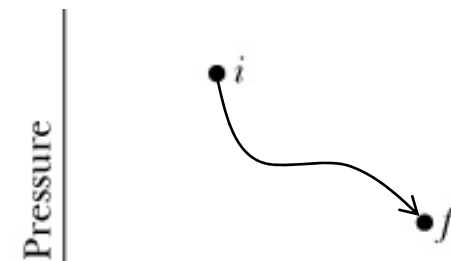
$$\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T}$$

In order to define the entropy change ΔS for an irreversible process that takes us from an initial state i to a final state f of a system, we find a reversible process that connects states i and f .

We can then calculate :

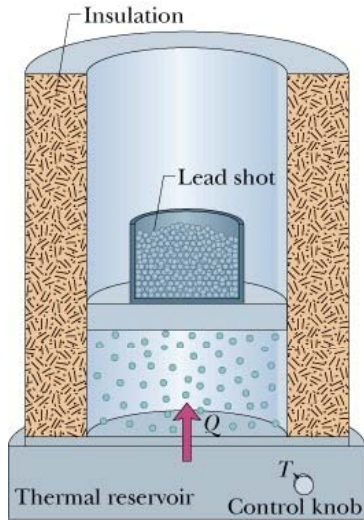
$$\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T}$$

SI units for S : J/K

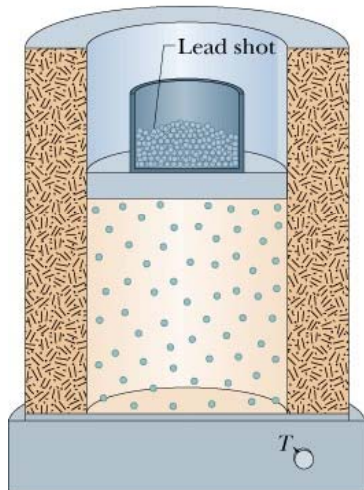


A lucky thing!

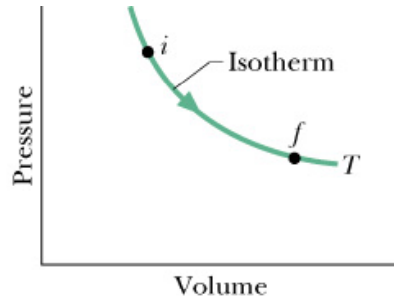
However, S is still a state function though Q depends on details of process!



(a) Initial state i



(b) Final state f



In the free expansion of the example, $T_i = T_f$.

We thus replace the free expansion with an isothermal expansion that connects states

(P_i, V_i) and (P_f, V_f) .

A trick!

From the first law of thermodynamics we have:

$$dE_{\text{int}} = dQ - dW \rightarrow dQ = dE_{\text{int}} + dW = nC_v dT + PdV \rightarrow$$

$$\frac{dQ}{T} = P \frac{dV}{T} + nC_v \frac{dT}{T}.$$

From ideal gas law we have: $pV = nRT \rightarrow p \frac{dV}{T} = nR \frac{dV}{V}$.

$$\Delta S = \int_i^f \frac{dQ}{T} = nR \int_i^f \frac{dV}{V} + nC_v \int_i^f \frac{dT}{T} = nR \ln \frac{V_f}{V_i} + nC_v \ln \frac{T_f}{T_i}$$

The change in entropy depends only on the properties of the initial and final states. It does not depend on

how the system changes from the initial to the final state.

How to understand this: Entropy

How to describe a system:
P, T, V, E_{int} , and n

Entropy, S, like T, V, P, E_{int} , and n is
state variable

The **entropy** of a **closed system** (no energy and mass comes in and out) never decreases.
It either stays constant (**reversible process**) or increases (**irreversible process**).

-----2nd –Law of Thermodynamics

How to define **entropy**? Easier to define **Change of entropy** during a process.



$$0 \leq \Delta S_{total} \\ \text{system}$$

$$\Delta S_{part} = S_f - S_i = \int_i^f \frac{dQ}{T}$$

Temp in Kelvin
Units: [J/K]

where Q is energy transferred to or from a system during a process

What is a process? expansion, compression, temperature rise, add mass

[Note: since $T > 0$, if Q is positive (negative) the ΔS is positive (negative)]

Reversible vs irreversible

{Reversible processes are those which can be done infinitely slowly to ensure thermal equilibrium at the end of each step during the process}

Entropy: Different processes

1) For reversible process: $\Delta S_{\text{cycle,rev}} = 0 = \oint \frac{dQ}{T}$

2) For isothermal process:

$$\Delta S_{\text{isothermal}} = \frac{Q}{T}$$

Q is total energy transferred as heat during the process (note: heat must be transferred from reservoir to keep temperature constant)

3) In general for a “small” change in temperature:

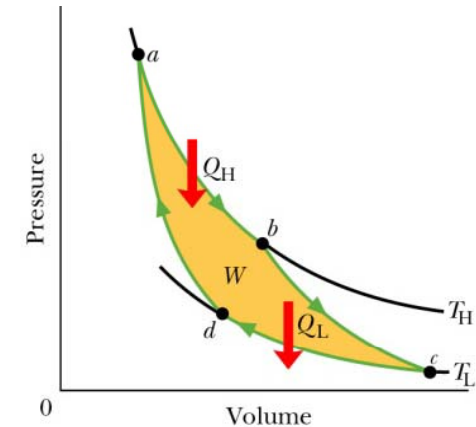
$$\Delta S = S_f - S_i \approx \frac{Q}{T_{\text{ave}}}$$

Checkpoint 1: Water is heated on a stove. Rank the entropy changes of the water as its temperature rises (a) from 20° C to 30° C , (b) 30° C to 35° C, and (c) 80° C to 85° C, greatest first .

Entropy: Gas processes

1) For reversible process:

$$\Delta S_{\text{cycle,rev}} = 0 = \oint \frac{dQ}{T}$$



2) For isothermal process:

$$\Delta S_{\text{rev,isothermal}} = \frac{Q}{T}$$

$$\Delta E_{\text{int}} = 0 \Rightarrow Q = W$$

$$W = nRT \ln\left(\frac{V_f}{V_i}\right) \Rightarrow \Delta S_{\text{isothermal}} = nR \ln\left(\frac{V_f}{V_i}\right)$$

3) In general process for gas, using 1st law:

$$dE_{\text{int}} = dQ - dW$$

$$\frac{nC_V dT}{T} = \frac{dQ}{T} - \frac{pdV}{T} \quad \& \quad p = \frac{nRT}{V} \quad \Rightarrow \quad \int \frac{dQ}{T} = \int \left(\frac{nRT}{V}\right) \frac{dV}{T} + \int \frac{nC_V dT}{T}$$

Now integrate:

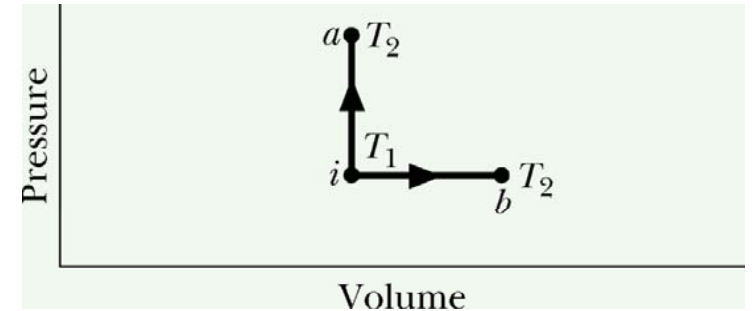
$$\Delta S_{\text{rev,gas}} = S_f - S_i = nR \ln\left(\frac{V_f}{V_i}\right) + nC_V \ln\left(\frac{T_f}{T_i}\right) \quad \Leftarrow \quad [pV = nRT]_{\text{reversible}}$$

4) For adiabatic (reversible) adiabatic compression/expansion:

$$\Delta S_{\text{rev,adiabatic}} = 0$$

Entropy is a State Function

Checkpoint 2: An ideal gas has a temperature T_1 at the initial state I shown in the p-V diagram. The gas has a higher temperature T_2 at the final states a and b, which it can reach along the paths shown. Is the entropy change along the path to state a larger than, smaller than, or the same as that along path to state b?



$$\Delta S = S_f - S_i = nR \ln \frac{V_f}{V_i} + nC_V \ln \frac{T_f}{T_i}. \quad (20-4)$$

From I to a:
$$\Delta S = nC_V \ln \frac{T_2}{T_1}$$

From I to b:
$$\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_b}{V_a}$$

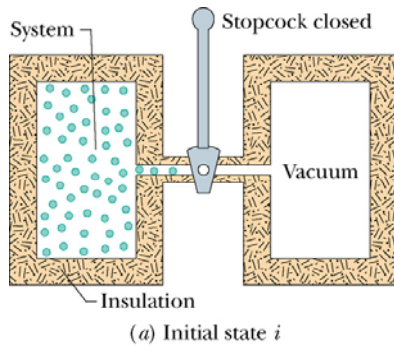
Entropy change in phase transition: Liquid/solid processes

- 1) For phase changes:
Temperature = constant

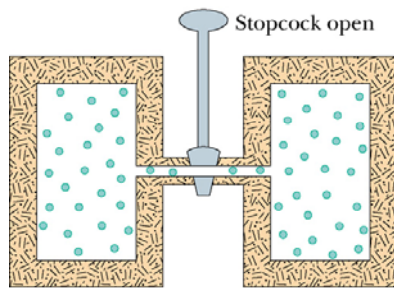
$$\begin{aligned}\Delta S_{\text{phase change}} &= \int \frac{dQ}{T} \\ &= \frac{Q_{\text{phase change}}}{T} \\ &= \frac{mL}{T}\end{aligned}$$

- 2) For temperature changes:

$$\begin{aligned}\Delta S_{\text{liquid / solid}} &= S_f - S_i = \int \frac{dQ}{T} \\ &= \int \frac{mcdT}{T} \\ &= mc \ln\left(\frac{T_f}{T_i}\right)\end{aligned}$$



(a) Initial state i



(b) Final state f

Sample problem 20-1: Suppose 1.0 mol of nitrogen gas is confined to the left side of the container in the figure. You open the stop-cock and the volume of the gas doubles. What is the entropy change of the gas for this irreversible process?

Free Expansion so

$$\Delta T = 0$$

Back to Ch. 19

$$Q = nrT \ln \frac{V_f}{V_i}$$

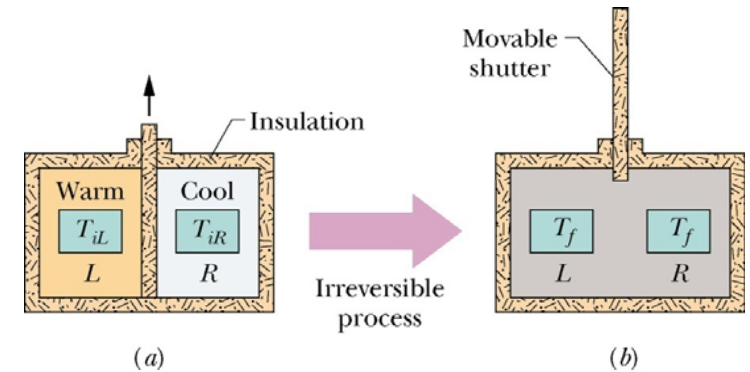
$$\Delta S = S_f - S_i = \frac{Q}{T} \quad (\text{change in entropy, isothermal process}). \quad (20-2)$$

$$\Delta S = \frac{Q}{T} = \frac{nRT \ln(V_f / V_i)}{T} = nR \ln \frac{V_f}{V_i}$$

Put in numbers

$$\Delta S = +5.76 \text{ J / K}$$

Sample Problem 20-2: Two identical copper blocks of mass $m=1.5\text{kg}$: Block L is at $T_{iL}=60^\circ\text{C}$ and block R is at $T_{iR}=20^\circ\text{C}$. The blocks are in a thermally insulated box and are separated by an insulating shutter. When we lift the shutter, the blocks come to equilibrium with $T_f=40^\circ\text{C}$. What is the entropy of this irreversible process? Specific heat of Cu is 386 J/KgK .



We can only do this if we treat it as a reversible process. So let's create a thermal reservoir. Start with a reservoir at 60°C and put L in contact with it. Lower the reservoir temperature slowly to 40°C . Heat is transferred from the block to the reservoir.

$$dQ = mcdT \quad \Delta S_L = \int_i^f \frac{dQ}{T} = \int_{T_{iL}}^{T_f} \frac{mcdT}{T} = mc \ln \frac{T_f}{T_{iL}} = -35.86\text{ J / K}$$

Now set reservoir at 20°C and put in contact with R. Raise the temperature slowly to 40°C .

$$\Delta S_R = 38.23\text{ J / K}$$

$$\Delta S_{rev} = \Delta S_R + \Delta S_L = 2.4\text{ J / K}$$