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Lecture 7

Entropy! (en - trope "inward turning" from Greek)

- This quantity is a measure of $\boxed{\text{disorder}}$ & is used not only in thermodynamics, but many other areas, including communication systems.
- helps for understanding heat engines & efficiency
- Why does time have direction?

  Entropy can help to explain this, & the second law of thermodynamics, which states that entropy is increasing
- eggs crack and do not reassemble, pizza gets baked... cars crash & do not reassemble.

- Entropy helps to understand irreversible thermodynamic processes (Energy does not)

Entropy is denoted by S in thermodynamics

<u>Key postulate of entropy:</u>

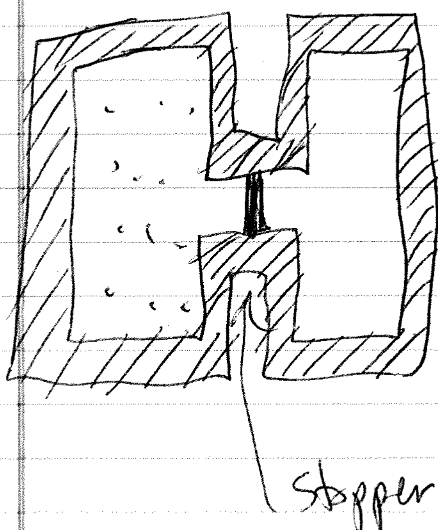
If an irreversible process occurs in a closed system, the entropy S does not decrease. (It always stays the same or increases.)

$$\Delta S \geq 0$$

gives an arrow to time.

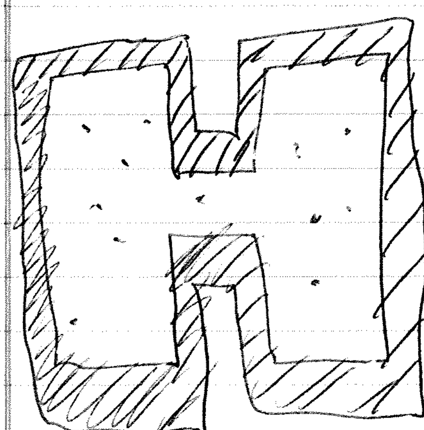
To understand entropy,

consider free expansion:

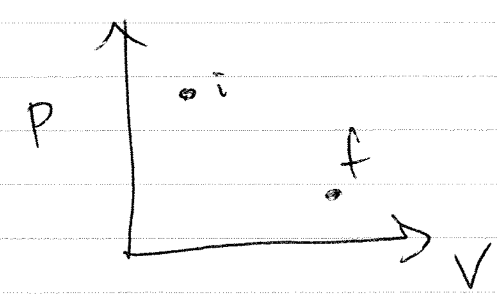


After releasing the stopper, gas expands to other side.

Then picture becomes



Initial & final states on p-V diagram are



However, we cannot define intermediate values b/c there is not a sequence of equilibrium states going from i to f.

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Change in entropy is defined as

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

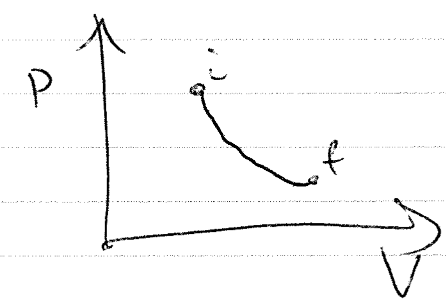
this is a <u>state property</u>,
like temperature, pressure, & volume.

SI unit for entropy is $\frac{J}{K}$.

- For the free expansion, we cannot calculate entropy directly.
- To do so, we use the fact that entropy is a <u>state</u> property, independent of path, & the fact that $T_f = T_i$ for a free expansion.

So to calculate it for free expansion, we instead consider a reversible process w/ well defined set of equilibrium states that gets from initial state to final state.

So i & f lie along an isotherm



$$\Rightarrow \Delta S = S_f - S_i$$
$$= \int_i^f \frac{1}{T}\, dQ$$
$$= \frac{1}{T}\int_i^f dQ = \frac{1}{T}\cdot Q$$

for isothermal process, $\Delta E_{int} = 0$

$\Rightarrow Q = W$ & then we could calculate Q using previous approaches

i.e. $Q = nRT \ln\left(\frac{V_f}{V_i}\right)$

$$\Rightarrow \Delta S = nR \ln\left(\frac{V_f}{V_i}\right)$$

Summarizing what we did:

- To find entropy change for an irreversible process, replace it w/ any reversible process that connects initial & final states.
- Then calculate entropy change for this reversible process using $\int_i^f \frac{dQ}{T}$

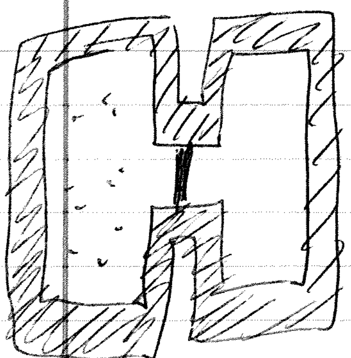
If temp. change ΔT is small relative to temp. of initial & final states, then we can approximate entropy change as

$$\Delta S \approx \frac{Q}{T_{avg.}}$$

For a reversible cyclic process $\Delta S = 0$ (initial & final states are the same)

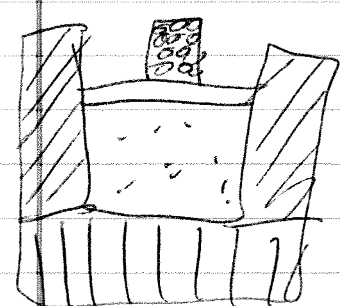
6.5

Question



free expansion process in which there is initial state (T_i, V_i, p_i) + final state (T_f, V_f, p_f)

Another process: isothermal



Same initial + final states as above

Is the change in entropy equal for these?

Entropy is a state function 7

We can prove this for an important case in which an ideal gas goes through a reversible process.

Use differential form of 1st law:

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

Since steps of process are reversible, w/ gas in equilibrium states, replace dW w/ $p\,dV$ & dE_{int} w/ $nC_V\,dT$

$\Rightarrow$

$$nC_V\,dT = dQ - p\,dW$$

$\Rightarrow$

$$dQ = p\,dV + nC_V\,dT$$

divide by T

$$\frac{dQ}{T} = \frac{p}{T} dV + n C_V \frac{dT}{T}$$

use ideal gas equation $pV = nRT$

$\Rightarrow p = \frac{nRT}{V}$

$$\Rightarrow \frac{dQ}{T} = nR \frac{dV}{V} + n C_V \frac{dT}{T}$$

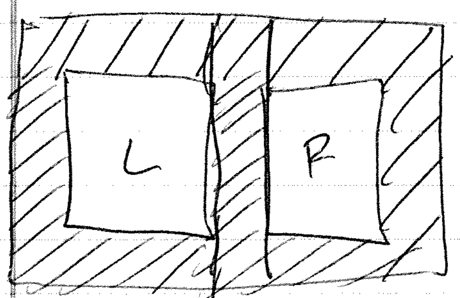
integrate from initial to final state

$$\Delta S = \int_i^f \frac{dQ}{T} = \int_i^f nR \frac{dV}{V} + \int_i^f n C_V \frac{dT}{T}$$

$$\Rightarrow \Delta S = nR \ln \frac{V_f}{V_i} + n C_V \ln \frac{T_f}{T_i}$$

Example:

insulating shutter



two copper blocks surrounded by insulating material

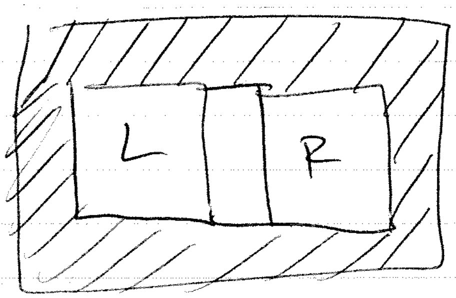
Each have mass

$m = 1.5\,kg$

left block @ temperature $T_{iL} = 60°C$

right block @ " $T_{iR} = 20°C$

insulating shutter is removed to give

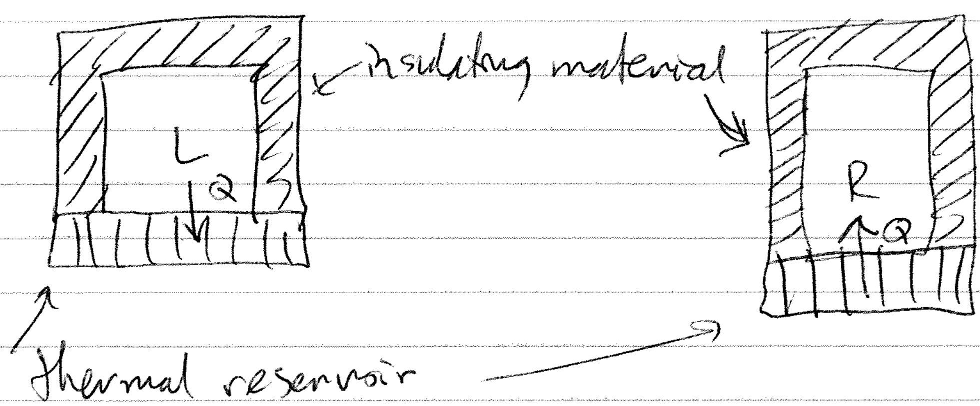


blocks eventually come to equilibrium temp. 40°C

What is net entropy change of two-block system?

1) Figure out entropy change for a reversible process w/ same final states

Replace w/



lower temperature of left reservoir

then $dQ = mc\,dT$

mass of copper

specific heat of copper

then entropy change for left block is

$$\Delta S_L = \int_i^f \frac{dQ}{T} = \int_i^f \frac{mc\,dT}{T}$$

$$= mc \ln(T_f/T_{iL})$$

$$= (1.5 kg)\left(386 \frac{J}{kg \cdot K}\right) \ln\left(\frac{313 K}{333 K}\right)$$

$$= -35.86 \ J/K$$

for right side, similar calculation gives

$$\Delta S_R = mc \ln\left(T_f / T_{iR}\right)$$

$$= (1.5 kg)\left(386 \frac{J}{kg \cdot K}\right) \ln\left(\frac{313 K}{293 K}\right)$$

$$= 38.23 \ J/K$$

$$\Rightarrow \quad \Delta S = \Delta S_L + \Delta S_R$$

$$= -35.86 \ J/K + 38.23 \ J/K$$

$$= 2.4 \ J/K$$

$\Rightarrow$ ΔS for original process is

$$2.4 \ J/K \geq 0.$$