# 3.020 Lecture 5

Prof. Rafael Jaramillo

# 1 Entropy and the 2$^{\text{nd}}$ law of thermodynamics

1. Clausius theorem
2. Reversible processes and entropy
3. Reversible & irreversible processes
4. Entropy maximization

a play in 4 acts

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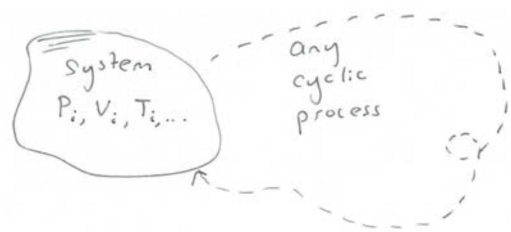
## 1.1 Clausius theorem (stated without proof)

$$\underbrace{\oint} \frac{\delta Q}{T} \leqslant 0$$

Cyclic process = state variables return to their starting value

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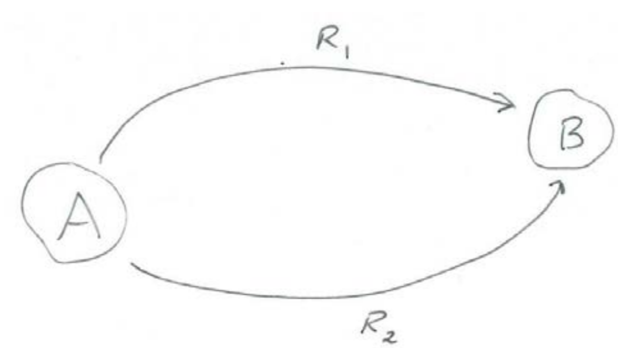
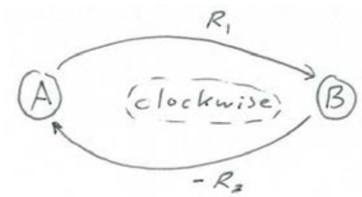
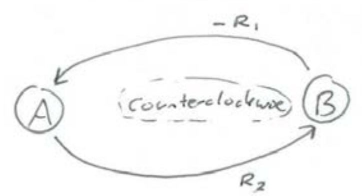
## 1.2 Reversible processes and entropy

- Hypothesize that there exist type of processes for which every step is reversible
- Consider a cyclic process along two reversible paths, $R_1$ & $R_2$






$$\oint \frac{\delta Q}{T} = \int_A^B \frac{\delta Q}{T}\Big|_{R_1} + \int_B^A \frac{\delta Q}{T}\Big|_{-R_2} = \int_A^B \frac{\delta Q}{T}\Big|_{R_1} - \int_A^B \frac{\delta Q}{T}\Big|_{R_2} \leqslant 0$$




$$\oint \frac{\delta Q}{T} = \int_A^B \frac{\delta Q}{T}\Big|_{R_2} + \int_B^A \frac{\delta Q}{T}\Big|_{-R_1} = \int_A^B \frac{\delta Q}{T}\Big|_{R_2} - \int_A^B \frac{\delta Q}{T}\Big|_{R_1} \leqslant 0$$

"$\leqslant$" is guaranteed by Clausius theorem

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- Compare results for clockwise & counterclockwise circuits

$$\int_A^B \frac{\delta Q}{T}\Big|_{R_1} - \int_A^B \frac{\delta Q}{T}\Big|_{R_2} = 0 \quad \Rightarrow \text{Entropy (S), a new state function}$$
$$\int_A^B \frac{\delta Q}{T}\Big|_{R_1} = \int_A^B \frac{\delta Q}{T}\Big|_{R_2} = S(B) - S(A) \quad \Rightarrow dS = \frac{\delta Q}{T}\Big|_{rev.}$$

"rev." : along any reversible path

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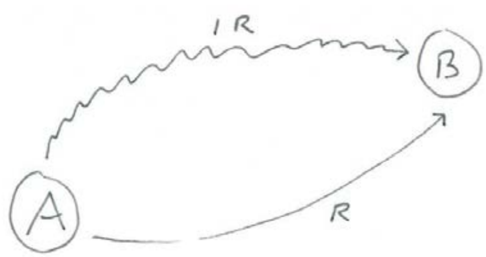
## 1.3 Reversible & irreversible processes

- Hypothesize that there exist processes that are irreversible
- Consider states A & B, which are connected by reversible & irreversible processes




$$\oint \frac{\delta Q}{T} = \int_A^B \frac{\delta Q}{T}_{IR} + \underbrace{\int_B^A \frac{\delta Q}{T}_{-R}}_{\text{run the reversible process backwards to complete the cycle}} \leqslant 0$$

$$\text{Use} \quad \int_A^B \frac{\delta Q}{T} \underbrace{\leqslant}_{\text{equality for reversible process}} S(B) - S(A)$$

### 1.4 Entropy maximization in an isolated system

$$\int_A^B \frac{\delta Q}{T} \leqslant S(B) - S(A)$$

Now isolate s.t. $\delta Q = 0$

$$S(A) \leqslant S(B) \quad \Rightarrow$$

Entropy never decreases for <u>any</u> process in an isolated system

$\Uparrow$

a form of the 2nd law of thermodynamics

## 2 Combined statement of 1st and 2nd laws

$$dU = \delta Q + \delta W + \mu dN \quad \leftarrow \quad 1^{\text{st}} \text{ law}$$

$$\text{Work done on system} \quad \delta W = -PdV$$

$$\text{Heat received by system} \quad \delta Q = TdS \quad \leftarrow \quad \text{for a reversible process}$$

$$\underbrace{dU = TdS - PdV + \mu dN}_{\text{all state functions}}$$

# 3 Equilibrium

- State of rest - state functions aren't changing.
- State of balance - molecular-scale changes average to zero

see Wiki entry on defin of thermo equilibrium

| $t = 0$ | | $t = \infty$ |
|---|---|---|
| Prepare system, incl. its boundary conditions | $\xrightarrow{Wait}$ | equilibrium when all macroscopic changes are finished |

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Q: What happens while we wait?
A. All spontaneous processes happen eventually.
@ equilibrium, all possible spontaneous processes have already happened

* For an isolated system, the relation $S(A) \leqslant S(B)$ - a ratchet effect - means that equilibrium is a state of maximum entropy

⇒ For an isolated system, equilibrium is the state of max. entropy, given the boundary conditions.