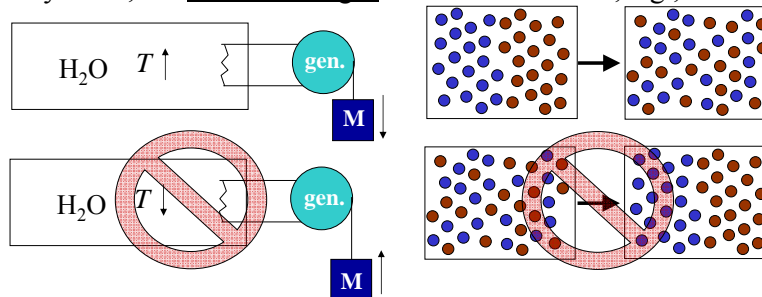


Second Law of TD

- Introduces the concept/property of entropy S
- Provides basis for determining the possibility/impossibility (or time-direction) of processes

Observations

- While certain spontaneous changes in state occur in isolated systems, the reverse changes are never observed, e.g.,



- 1st Law is not sensitive to direction of change
- Suggests there must be some property of system which differentiates what is impossible (direction for change)

Postulate

1. \exists an extensive property S , called entropy
 - named by Clausius – Greek for transformation
 2. entropy can be produced but never destroyed
- So for isolated system
 - no flows of energy or matter into or out of system

$$S_{final} - S_{initial} = \Delta S = \mathcal{P}_s \geq 0$$

- in many texts

$$\Delta S_{isolated} \geq 0$$

Entropy
production

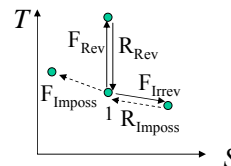
Second Law-3

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Reversible and Irreversible Processes

- For isolated system, imagine some process F which changes state of system (R would be reverse process)
 - 2nd Law says S can not be transferred and not destroyed
 - if S decreases \Rightarrow impossible ($\mathcal{P}_s < 0$)
 - if S constant \Rightarrow reversible ($\mathcal{P}_s = 0$)
 - if S increases \Rightarrow irreversible ($\mathcal{P}_s > 0$)
- Essentially all real processes irrev., though some only slightly – so can use rev. as helpful assumpt.



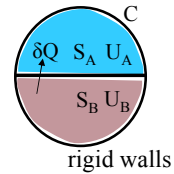
Second Law-4

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TD Definition of Temperature

- Consider isolated system C, composed of two closed systems A and B



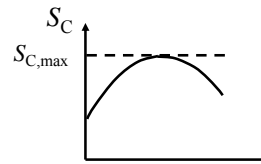
- A and B can only exchange energy by heat transfer (V_A, V_B constant)
- A and B each initially in state of internal TD equil.
- because S extensive

$$S_C = S_A + S_B$$

assume (nonreacting) simple compr. subst.

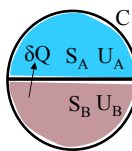
$$= S_A(U_A, V_A) + S_B(U_B, V_B)$$

- thermal equil. reached when S_C maximized
- \Rightarrow at that point $T_A = T_B$ from 0th Law



TD Temperature Definition

- Consider a “progress” variable to track change in system, μ



- e.g., fraction of C’s energy that is in A (U_A/U_C)
- since V_A, V_B and U_C fixed, only free variable is μ

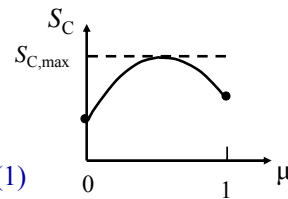
- From $S_C = S_A(U_A, V_A) + S_B(U_B, V_B)$

$$\frac{dS_C}{d\mu} = \left(\frac{\partial S_A}{\partial U_A} \right)_{V_A} \frac{dU_A}{d\mu} + \left(\frac{\partial S_B}{\partial U_B} \right)_{V_B} \frac{dU_B}{d\mu} \quad (1)$$

1st Law Isolated System $dU_C = 0 \Rightarrow \frac{dU_A}{d\mu} = -\frac{dU_B}{d\mu} \quad (2)$

2nd Law Isolated System $\frac{dS_C}{d\mu} = 0$

$$\left(\frac{\partial S_A}{\partial U_A} \right)_{V_A} = \left(\frac{\partial S_B}{\partial U_B} \right)_{V_B}$$



TD Temperature Definition

- So, two systems are in thermal equilibrium when they have same $(\partial S / \partial U)_v$
 - but, thermal equilibrium implies systems have the same T
- Therefore, we can use $(\partial S / \partial U)_v$ to DEFINE T
 - to maintain heat transfer from high to low T ,*

we choose

$$T \equiv \frac{1}{(\partial S / \partial U)_v}$$

intensive ↗

TD defn. for T of a simple comp. substance (in equilibrium)

$$* dS_C = \left(\frac{1}{T_A} - \frac{1}{T_B} \right) dU_A > 0 \Rightarrow dU_A < 0 \text{ if } T_A > T_B$$

✓ U_A decrease if A hotter
S has units of energy/temp (J/K)

Second Law-7

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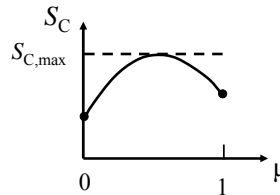
TD Temperature Definition(con't)

- Is $dS_C/d\mu$ truly a maximum, look at 2nd deriv.

– result,

$$\left(\partial^2 S / \partial U^2 \right)_v < 0 \Rightarrow \left(\partial T / \partial U \right)_v > 0$$

✓



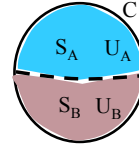
Second Law-8

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TD Def'n. of Pressure

- Isolated system C composed of two closed subsystems A & B, which can exchange energy by heat and pdV (mechanical) work



- For simple compressible substance (nonreacting)

$$S_C = S_A(U_A, V_A) + S_B(U_B, V_B)$$

$$U_C = U_A + U_B \quad V_C = V_A + V_B$$

- U, V independent variables \Rightarrow can define two progress (linear combination) variables (μ_U, μ_V)

– at TD equilibrium

$$\frac{dS_C}{d\mu_U} = 0; \frac{dS_C}{d\mu_V} = 0$$

Second Law-9

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TD Def'n. of Pressure

- So,
$$\frac{dS_C}{d\mu_U} = \left(\frac{\partial S_A}{\partial U_A} \right)_{V_A} \frac{dU_A}{d\mu_U} + \left(\frac{\partial S_B}{\partial U_B} \right)_{V_B} \frac{dU_B}{d\mu_U} = 0 \quad (3)$$

$$\frac{dS_C}{d\mu_V} = \left(\frac{\partial S_A}{\partial V_A} \right)_{U_A} \frac{dV_A}{d\mu_V} + \left(\frac{\partial S_B}{\partial V_B} \right)_{U_B} \frac{dV_B}{d\mu_V} = 0 \quad (4)$$

- Like eq. (1), eq. (3) is condition for thermal equilibrium, so

$$\left(\frac{\partial S_A}{\partial U_A} \right)_{V_A} = \left(\frac{\partial S_B}{\partial U_B} \right)_{V_B} \Rightarrow \boxed{\left(\frac{\partial S}{\partial U} \right)_V \equiv \frac{1}{T}}$$

- Then eq. (4) is condition for mechanical equilibrium

$$\left(\frac{\partial S_A}{\partial V_A} \right)_{U_A} = \left(\frac{\partial S_B}{\partial V_B} \right)_{U_B} \Rightarrow \text{TD defn. for } p$$

Second Law-10

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TD Def'n. of Pressure

- For consistency with other definitions of pressure
 - definition show allow sub-system with higher pressure to expand and increase S_C
 - units of S/V : Energy/Temp./Length³
 - units of p : Force/Length² = Energy/Length³
- Leads to $\frac{p}{T} \equiv \left(\frac{\partial S}{\partial V} \right)_U$ TD defn. for p agrees with mechanical def'n., but only valid in TD equil.
 - p intensive (S/V , T both intensive)
 - this result derived for inert simple compressible substance