

Second Law of TD

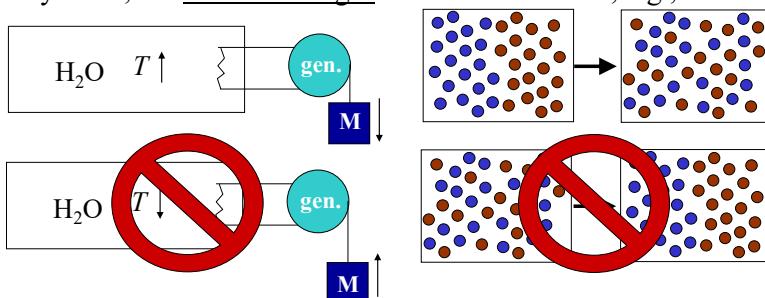
- In classical thermodynamics, the Second Law
 - introduces the concept/property of entropy S
 - provides a basis for determining the possibility/impossibility (or time-direction) of processes

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Second Law-1
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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)

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Postulate: Basis for 2nd Law

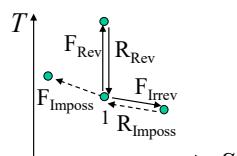
1. \exists an extensive property S , called entropy
 - named by Clausius – Greek for transformation
2. entropy can be produced but never destroyed
 - So for isolated system
 - no flows of energy or matter into or out of system
 - sometimes written as $\Delta S_{isolated} \geq 0$

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

Entropy production

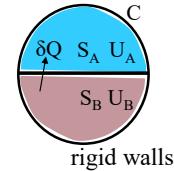
Reversible and Irreversible Processes

- For isolated system, imagine some process F which changes state of system (R would be reverse process)
 - our 2nd Law postulate says S can not be destroyed, and not transferred for isolated system
 - 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 irreversible, though some just slightly – so reversible can be as helpful assumption



TD Definition of Temperature

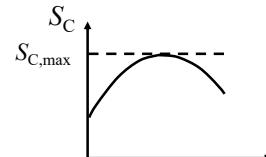
- Consider isolated system C, composed of two closed systems A and B
 - A and B can only exchange energy by heat transfer (V_A, V_B constant)
 - A and B each initially in state of internal TD equilibrium
 - because S extensive



$$S_C = S_A + S_B$$

assume (nonreacting) $= S_A(U_A, V_A) + S_B(U_B, V_B)$
simple compr. subst.

- thermal equilibrium reached when S_C maximized
- ⇒ at that point $T_A = T_B$ from 0th Law



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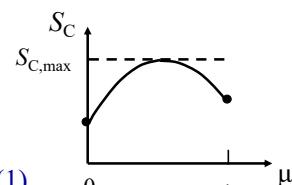
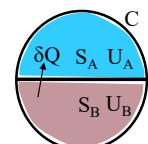
TD Temperature Definition

- 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 $\frac{dS_C}{d\mu} = 0$



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

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

$$*dS_C = \left(\frac{1}{T_A} - \frac{1}{T_B} \right) dU_A > 0 \Rightarrow \checkmark \text{ U}_A \text{ decrease if A hotter} \quad S \text{ has units of energy/temp (J/K)}$$

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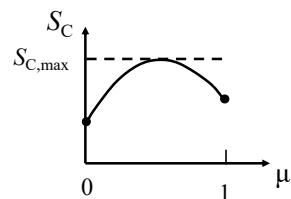
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TD Temperature Definition(con't)

- Is $dS_C/d\mu$ truly a maximum?

- look at 2nd derivative
- result is

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

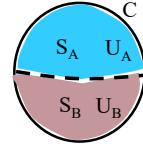


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TD Definition of Pressure

- 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), again



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

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

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

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

TD Definition 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) before, eq. (3) is condition for thermal equilibrium, so $\left(\frac{\partial S_A}{\partial U_A} \right)_{V_A} = \left(\frac{\partial S_B}{\partial U_B} \right)_{V_B} \Rightarrow \left(\frac{\partial S}{\partial U} \right)_V \equiv \frac{1}{T}$
- Then eq. (4) is condition for mechanical equilibrium $\left(\frac{\partial S_A}{\partial V_A} \right)_{U_A} = \left(\frac{\partial S_B}{\partial V_B} \right)_{U_B} \Rightarrow$ TD definition for p

TD Definition of Pressure

- For consistency with other definitions of pressure
 - definition should 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 definition for p agrees with mechanical definition, but only valid in TD equilibrium
 - p intensive ($S/V, T$ both intensive)
 - this result derived for inert, simple compressible substance

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Gibb's Equation

- For simple compressible substance (nonreacting) we have $S = S(U, V)$
- Thus $dS = \left(\frac{\partial S}{\partial U} \right)_V dU + \left(\frac{\partial S}{\partial V} \right)_U dV$
- From p, T definitions

$$dS = \frac{1}{T} dU + \frac{p}{T} dV$$

Gibb's Equation
can determine S from
measureable quantities

– also

$$dU = TdS - pdV$$

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Example: Gas Diffusion (Mixing)

- Two gases (A,B) initially separated in equal volumes that are then allowed to mix, but isolated from surroundings
- What is S_C (total) when system reaches equilibrium (uniformly mixed)?
- Assuming inert $S_C = S_A(U_A, V_A) + S_B(U_B, V_B)$
- Gibbs for A: $dS_A = \left(\frac{dU}{T}\right)_A + \left(\frac{p}{T}dV\right)_A = \left(\frac{dU}{T}\right)_A + \left(\frac{pV}{T}\frac{dV}{V}\right)_A$
– assuming ideal (thermally perfect) gases $= \left(\frac{dU}{T}\right)_A + \left(Nk\frac{dV}{V}\right)_A$
- Gibbs for B: $dS_B = \left(\frac{dU}{T}\right)_B + \left(Nk\frac{dV}{V}\right)_B$ # molec.

U_A	U_B
V	V
T	T
A	B

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Example: Gas Diffusion (Mixing)

- Combine 0, isolated

$$dS_C = dS_A + dS_B = \left(\frac{dU_A}{T} + \frac{dU_B}{T}\right) + k\left(N_A \frac{dV_A}{V_A} + N_B \frac{dV_B}{V_B}\right)$$

U_A	U_B
V	V
T	T
A	B

$$\Delta S_C = k(N_A + N_B) \ln \frac{2V}{V}$$

$\boxed{\Delta S_C = k(N_A + N_B) \ln 2}$ **entropy produced** (due to mixing) with no change in p or T of system (C)

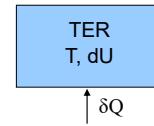
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Heat Transfer and Entropy Transfer

- Consider Thermal Energy Reservoir (TER)
 - CM with fixed volume, only exchanges energy as Q , uniform and constant internal T
 - always in equilibrium
- Since fixed volume, Gibbs $\Rightarrow dS = \frac{1}{T} dU$
- 1st Law $\Rightarrow dU = \delta Q$
- Combine

$$dS = \frac{\delta Q}{T} \quad \text{heat transfer can cause entropy change}$$

- since TER always in equilibrium
heat transfer \Rightarrow entropy transfer



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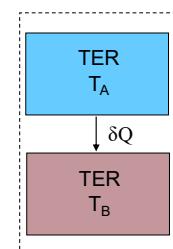
Heat Transfer & Entropy Production

- Now consider two interacting TERs at two T 's, which form isolated system
- From previous result

for δQ shown

$$dS_A = \frac{-\delta Q}{T_A} \quad dS_B = \frac{+\delta Q}{T_B}$$

$$dS_B = -\left(\frac{T_A}{T_B}\right) dS_A$$



- Since overall system isolated $dS_C = \delta P_s \geq 0$

$$dS_A \left(1 - \frac{T_A}{T_B}\right) \geq 0 \quad \text{and if } T_B > T_A \text{ then } dS_A > 0, \text{ so still } dS_C > 0$$

- **entropy production** occurs when there is *heat transfer across a finite temperature difference*

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Second Law for Control Mass

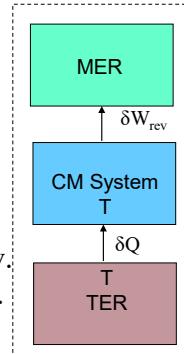
- Consider CM interacting with a TER and a **Mechanical Energy Reservoir (MER)**
 - CM with no microscopic disorder (no entropy), can only exchange energy as reversible work
- Together they form isolated system

$$\text{2nd Law} \quad \delta\mathcal{P}_s = d(S_{TER} + S_{MER}^0 + S_{CM})$$

$$= -\delta Q/T + dS_{CM} \quad \text{inequality}$$

$$\boxed{dS_{CM} = \delta Q/T + \delta\mathcal{P}_s} \quad \begin{array}{l} dS_{CM} \left\{ \begin{array}{l} > \delta Q/T \\ = \delta Q/T \end{array} \right. \end{array} \quad \begin{array}{l} \text{irrev.} \\ \text{rev.} \end{array}$$

$$\Delta S_{CM} = \int_1^2 \frac{\delta Q}{T} + \mathcal{P}_s \quad \begin{array}{l} \text{adiab.+rev.} \\ \text{one way to get isentropic} \end{array}$$



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Availability Analysis

- What is the maximum work obtainable from a system?
- “**1T Engine**”: Heat input from reservoir at T_o with work output (pV + shaft)
 - 1st Law $dU = \delta Q - \delta W - \delta W_{pV}$
 - 2nd Law $\delta\mathcal{P}_s = dS - \delta Q/T_o$
 - combine $\delta W = -dU - p_o dV + T_o dS - T_o \delta\mathcal{P}_s$

$$\delta W = -\underbrace{(dU + p_o dV - T_o dS)}_{\text{all state variables}} - \underbrace{T_o \delta\mathcal{P}_s}_{\geq 0}$$

– (shaft) work done \leq function of state (**availability**)

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Optimum Work

$$\delta W = -(dU + p_o dV - T_o dS) - T_o \delta \mathcal{P}_s$$

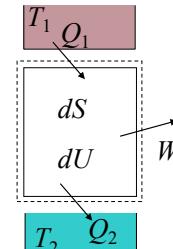
- W_{max} : when no entropy production (reversible); maximum use of “available” energy
- For given state change, less work output means less heat intake

$$dU + p_o dV = \delta Q - \delta W$$
- Converse also true
 - work done on system to produce given state change is minimized if reversible and produces more heat if irreversible
- 1T engine can not be run in steady-state or cycle
(Kelvin Planck Statement \rightarrow alt. 2nd Law beginning)

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Carnot Efficiency

- “**2T Engine**” (Carnot): Heat input from hot reservoir (T_1) and heat transfer to colder reservoir (T_2)
- $W_{max}=?$ for steady-state or cyclic process
 - 1st Law $Q_1 = Q_2 + W - \Delta U_{CM,0}$
 - 2nd Law $\mathcal{P}_s = Q_2/T_2 - Q_1/T_1 + \Delta S_{CM,0}$
 - Combine $W = Q_1(1 - T_2/T_1) - T_2 \mathcal{P}_s$
- W_{max} if (internally) reversible
- **Cycle efficiency** $\eta = \frac{W_{out}}{Q_{in}}; \eta_{rev} = \frac{W_{max}}{Q_1} = 1 - \frac{T_2}{T_1} \rightarrow 1 T_1 \gg T_2$ $\eta_{act} < \eta_{rev}$
- Clausius Statement: can’t have zero-work heat pump (also way to start 2nd Law)



Carnot Effic.

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