

## 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

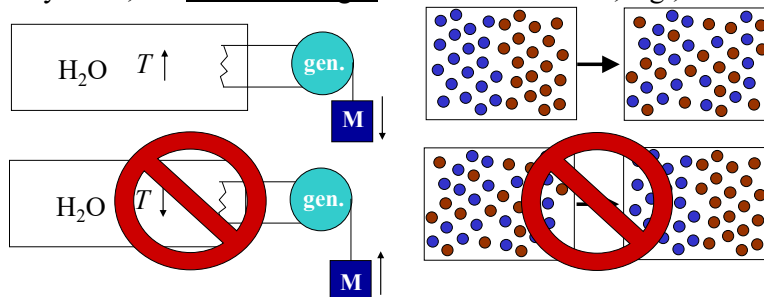
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## Observations

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



- 1<sup>st</sup> 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 2<sup>nd</sup> 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

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

- sometimes written as

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

**Entropy  
production**

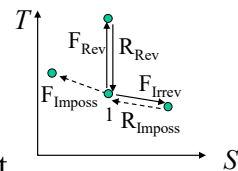
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## Reversible and Irreversible Processes

- For isolated system, imagine some process  $F$  which changes state of system (R would be reverse process)
  - our 2<sup>nd</sup> 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



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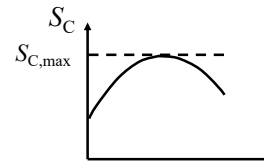
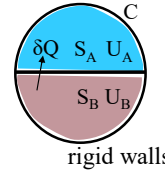
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## TD Definition of Temperature

- 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 equilibrium
  - 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 equilibrium reached when  $S_C$  maximized
  - $\Rightarrow$  at that point  $T_A = T_B$  from 0<sup>th</sup> Law



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## TD Temperature Definition

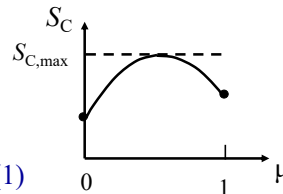
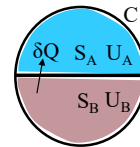
- Consider a “progress” variable to track change in system,  $\mu$ 
  - e.g., fraction of C’s energy that is in A ( $U_A/U_C$ )
  - since  $V_A, V_B$  and  $U_C$  fixed, only free variable is  $\mu$
- From  $S_C = S_A(U_A, V_A) + S_B(U_B, V_B)$ 

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

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

*2<sup>nd</sup> Law Isolated System*  $\frac{dS_C}{d\mu} = 0$

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



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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

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

*intensive*

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

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

✓  $U_A$  decrease if A hotter

$S$  has units of energy/temp (J/K)

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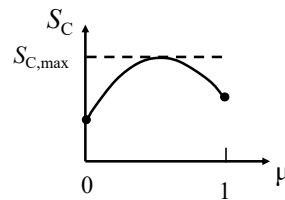
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## TD Temperature Definition(con't)

- Is  $dS_C/d\mu$  truly a maximum?
  - look at 2<sup>nd</sup> derivative
  - result is

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

✓



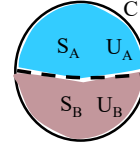
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## TD Definition of Pressure

- 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 ( $\mu_U, \mu_V$ )  
– at TD equilibrium

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

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## TD Definition of Pressure

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

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

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

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

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

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

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## 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./Length<sup>3</sup>
  - units of  $p$ : Force/Length<sup>2</sup> = Energy/Length<sup>3</sup>
- 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  
measurable quantities

– also

$$dU = TdS - pdV$$

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## Example: Gas Diffusion (Mixing)

C

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

$U_A$	$U_B$
$V$	$V$
$T$	$T$
<b>A</b>	<b>B</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  $= \left(\frac{dU}{T}\right)_A + \left(Nk \frac{dV}{V}\right)_A$  # molec.
- Gibbs for B:  $dS_B = \left(\frac{dU}{T}\right)_B + \left(Nk \frac{dV}{V}\right)_B$

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## Example: Gas Diffusion (Mixing)

- Combine

0, isolated

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

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

$$\Delta S_C = k(N_A + N_B) \ln 2$$

entropy produced (due to mixing) with  
no change in  $p$  or  $T$  of system (C)

$U_A$	$U_B$
$V$	$V$
$T$	$T$
<b>A</b>	<b>B</b>

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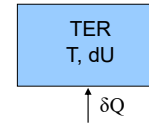
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## Heat Transfer and Entropy Transfer

- 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  $\Rightarrow dS = \frac{1}{T} dU$

- 1<sup>st</sup> 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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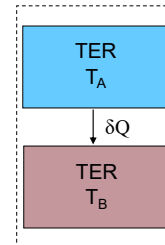
## Heat Transfer & Entropy Production

- Now consider two interacting TERs at two  $T$ 's, which form isolated system

- From previous result

for  $\delta Q$  shown  $\downarrow dS_A = \frac{-\delta Q}{T_A}$   $\uparrow dS_B = \frac{+\delta Q}{T_B}$

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



- Since overall system isolated  $dS_C = \delta \mathcal{P}_s \geq 0$

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

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

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## Second Law for Control Mass

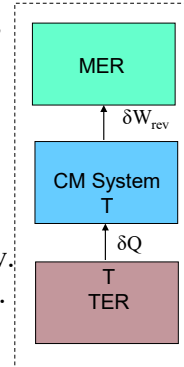
- Consider CM interacting with a TER and a Mechanical Energy Reservoir (MER)
  - CM with no microscopic disorder (no entropy), can only exchange energy as reversible work
- Together they form isolated system

2<sup>nd</sup> Law  $\delta \mathcal{P}_s = d(S_{TER} + S_{MER} + S_{CM})$

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

$$dS_{CM} = \underbrace{\delta Q/T}_{S_{xfer}} + \underbrace{\delta \mathcal{P}_s}_{S_{prod.}} \quad \left\{ \begin{array}{l} > \delta Q/T \text{ irrev.} \\ = \delta Q/T \text{ rev.} \end{array} \right. \text{ inequality}$$

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



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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)

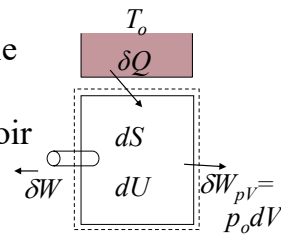
– 1<sup>st</sup> Law  $dU = \delta Q - \delta W - \delta W_{pV}$

– 2<sup>nd</sup> 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 → alt. 2<sup>nd</sup> Law beginning)

## Carnot Efficiency

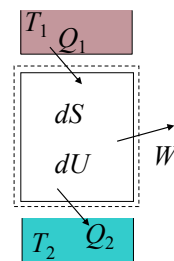
- “**2T Engine**” (Carnot): Heat input from hot reservoir ( $T_1$ ) and heat transfer to colder reservoir ( $T_2$ )

- $W_{max}$ =? for steady-state or cyclic process

– 1<sup>st</sup> Law  $Q_1 = Q_2 + W - \Delta U_{CM} \rightarrow 0$

– 2<sup>nd</sup> Law  $\mathcal{P}_s = Q_2/T_2 - Q_1/T_1 + \Delta S_{CM} \rightarrow 0$

– Combine  $W = Q_1(1 - T_2/T_1) - T_2 \mathcal{P}_s$



- $W_{max}$  if (internally) reversible

• **Cycle efficiency**  $\eta = \frac{W_{out}}{Q_{in}}$ ;  $\eta_{rev} = \frac{W_{max}}{Q_1} = 1 - \frac{T_2}{T_1}$  → 1  $T_1 \gg T_2$   
 $\eta_{act} < \eta_{rev}$

- Clausius Statement: can't have zero-work heat pump (also way to start 2<sup>nd</sup> Law)