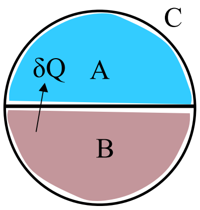
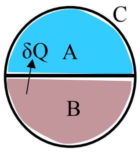
Entropy Approach to 2nd Law for CM

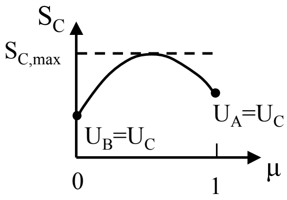
- Start with existence of entropy as a thermodynamic property (measure of microscopic disorder of system, or better, energy states of system)
  - $S=S(U,V)$ function of two indep. variables
- Imagine two systems, A and B, separated by rigid wall (V_A, V_B constant), only exchange is heat transfer, δQ
- Combined system C is isolated
  - no interaction with surroundings
  - total energy U_C fixed
  - 2nd Law, $S_{C,final}-S_{C,initial} = P_s \geq 0$



Equilibrium at Maximum Entropy

- Assume A and B not in equilibrium with each other
- Since entropy is extensive property
  - $S_C=S_A(U_A,V_A) + S_B(U_B,V_B)$
  - valid if A, B individually in equilibrium
  - also, $U_C = U_A + U_B = \mu U_C + (1-\mu)U_C$
- As interaction occurs, S_C will increase until equilibrium achieved ($S_{C,max}$)
- Since V_A, V_B and U_C fixed, only free variable is μ
  - maximize S_C, $dS_C/d\mu=0$





Thermodynamic Def’n. of Temperature

- Taking derivative (using chain-rule)

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

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

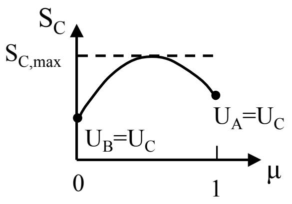
- Equals zero, when $\left(\frac{\partial S_A}{\partial U_A}\right)_{V_A}=\left(\frac{\partial S_B}{\partial U_B}\right)_{V_B}$
- So, two systems are in thermal equilibrium when they have same $\left(\partial S/\partial U\right)_V$
- But, same T also implies thermal equilibrium
- Therefore, let $\boxed{T\equiv\frac{1}{\left(\partial S/\partial U\right)_V}}$ (show reason for 1/ next)

Thermodynamic Def’n. of T (con’t)

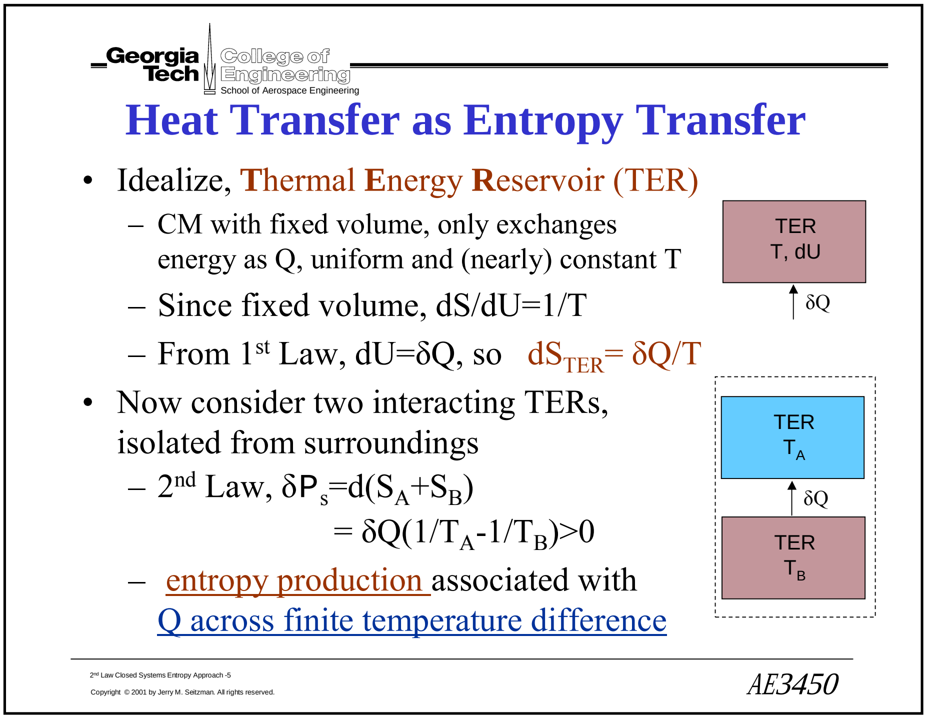
- Need to show thermodynamic def’n. of T consistent with 0th Law of Thermo. (Q from high to low T)

$$\frac{dS_C}{d\mu}=\left(\frac{\partial S_A}{\partial U_A}\right)_{V_A}U_C+\left(\frac{\partial S_B}{\partial U_B}\right)_{V_B}(-U_C)$$

$$dS_C=\left(\frac{1}{T_A}-\frac{1}{T_B}\right)U_C d\mu$$



- If $T_B>T_A$, $\left(\frac{1}{T_A}-\frac{1}{T_B}\right)>0$
- 2nd Law⇒$dS_C>0$, so $d\mu>0$ energy flowing from B to A
- For $dS_C/d\mu$ to truly be maximum, then $d^2S_C/d\mu^2<0$
  - result, $\left(\partial^2 S/\partial U^2\right)_V<0\Rightarrow\left(\partial T/\partial U\right)_V>0$ U increases with T



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Heat Transfer as Entropy Transfer

- Idealize, **T**hermal **E**nergy **R**eservoir (TER)
  - CM with fixed volume, only exchanges energy as Q, uniform and (nearly) constant T
  - Since fixed volume, $dS/dU=1/T$
  - From 1st Law, $dU=\delta Q$, so $dS_{TER}=\delta Q/T$
- Now consider two interacting TERs, isolated from surroundings
  - 2nd Law, $\delta P_s = d(S_A+S_B)$
    $= \delta Q(1/T_A - 1/T_B) > 0$
  - entropy production associated with Q across finite temperature difference

2nd Law Closed Systems Entropy Approach -5

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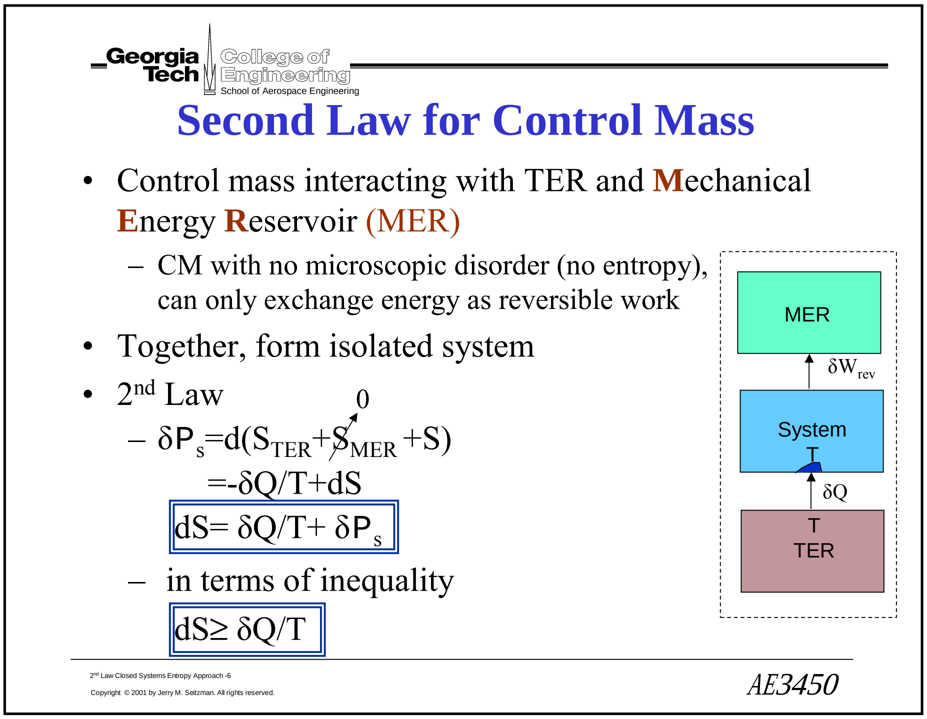

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Second Law for Control Mass

- Control mass interacting with TER and **M**echanical **E**nergy **R**eservoir (MER)
  - CM with no microscopic disorder (no entropy), can only exchange energy as reversible work
- Together, form isolated system
- 2nd Law
  - $\delta P_s = d(S_{TER} + \cancelto{0}{S_{MER}} + S)$
    $= -\delta Q/T + dS$
    $\boxed{dS = \delta Q/T + \delta P_s}$
  - in terms of inequality
    $\boxed{dS \geq \delta Q/T}$

2nd Law Closed Systems Entropy Approach -6

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