

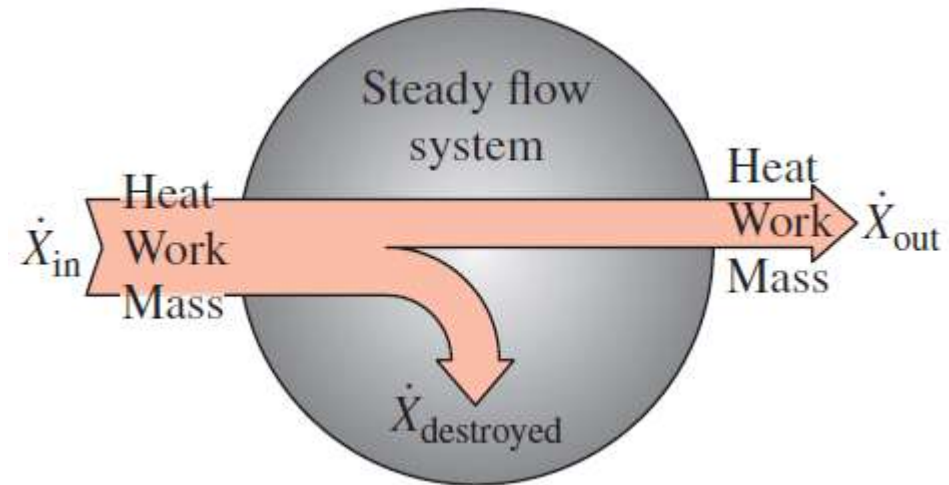
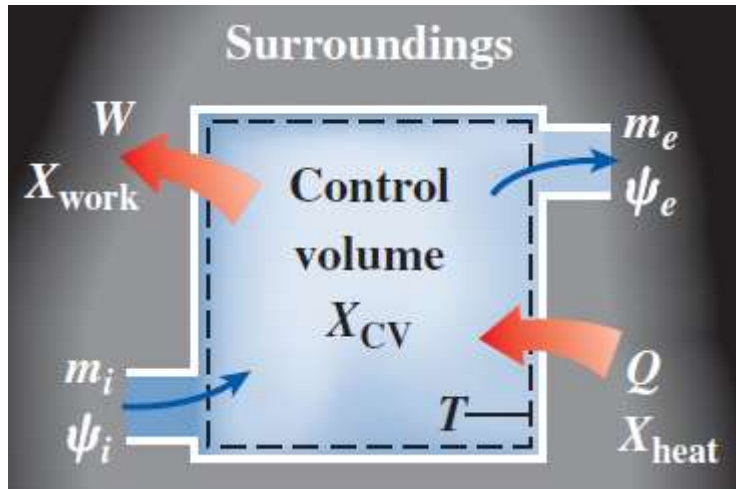
*Extremal Thermodynamic Functions  
 $S$ ,  $U$ ,  $H$ ,  $A$  &  $G$  for different  
Experimental conditions*

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## Previously: Exergy Balances



$$X_{heat} - X_{work} + X_{mass,in} - X_{mass,out} - X_{destroyed} = (X_2 - X_1)_{CV}$$

$$\sum \left( 1 - \frac{T_0}{T_k} \right) \dot{Q}_k - \left( \dot{W} - P_0 \frac{dV_{CV}}{dt} \right) + \sum_{in} \dot{m}\psi - \sum_{out} \dot{m}\psi - \dot{X}_{destroyed} = \frac{dX_{CV}}{dt}$$

Single-stream: 
$$\sum \left( 1 - \frac{T_0}{T_k} \right) \dot{Q}_k - \dot{W} + \dot{m}(\psi_1 - \psi_2) - \dot{X}_{destroyed} = 0$$

$$\eta_{II} = \frac{\dot{W}_{out}}{\dot{W}_{rev,out}}$$

$$\dot{X}_{destroyed} = \dot{W}_{rev,out} - \dot{W}_{out}$$

$$\eta_{II,mix} = 1 - \frac{T_0 \dot{S}_{gen}}{\dot{m}_1 \psi_1 + \dot{m}_2 \psi_2}$$

## *Flashback & flashforward: Extremum principles*

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

	$-TS$ →	
$+PV$ ↓	$U$ (or $E$ )	$A$ (or $F$ ) $= U - TS$
	$H$ $= U + PV$	$G$ $= U + PV - TS$

- Differences in experimental conditions lead to representation of extremum conditions via different thermodynamic potentials/functions



***+PV***

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

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

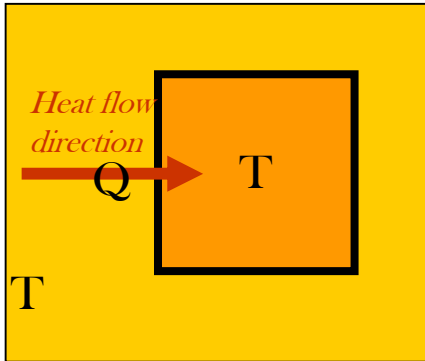
$$dA = -SdT - PdV$$

$$dG = -SdT + VdP$$

	Constant V	Constant P
Constant S	U	H
Constant T	F	G

- $\delta S (U,V,N) \geq 0$ ;  $\delta U (S,V,N) \leq 0$ ;  $\delta H (S,P,N) \leq 0$ ;
- $\delta A (T,V,N) \leq 0$ ;  $\delta G (T,P,N) \leq 0$ ;

# What is controlled in experiments determines the relevant TD extremum fxn-2



Combined (bath+system) is Isolated:  $\Delta U_{\text{bath}} + \Delta U_{\text{system}} = 0$

$$\Delta S - \frac{Q_{\text{rev}}}{T} \geq 0$$

$$\Delta S - \frac{\Delta U}{T} \geq 0$$

$$T\Delta S - \Delta U \geq 0 \quad \text{or equivalently} \quad \Delta U - T\Delta S \leq 0$$

$$A = U - TS \quad \Delta A = \Delta U - (T\Delta S + S\Delta T)$$

*Zero at constant T*

$$\Delta A = \Delta U - (T\Delta S) \leq 0$$

- $\delta S (U,V,N) \geq 0$ ;  $\delta U (S,V,N) \leq 0$ ;  $\delta H (S,P,N) \leq 0$ ;
- $\delta A (T,V,N) \leq 0$ ;  $\delta G (T,P,N) \leq 0$ ;

## *What's next?*

- Maxwell relations & Clapeyron equation