

# The Basics of Thermodynamic Stability

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# Stability of Thermodynamic Systems

- The 2nd Law implies that since  $S$  is a maximum at equilibrium

$$dS = 0 \quad \underline{\text{and}} \quad d^2S < 0$$

- We have not yet explored the requirement that

$$d^2S < 0$$



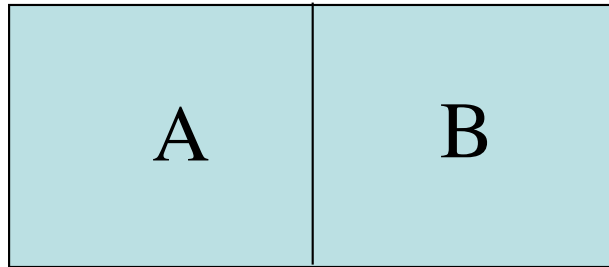
# Problem of Stability

- Mutual Stability - The stability of two systems with respect to each other concerning the partition of energy, volume or mole numbers.
- Intrinsic Stability - The stability of a simple closed system. By dividing the simple system into portions we can treat as a mutual stability problem.



# Stability

- Consider two identical subsystems isolated from the surroundings, and initially isolated from each other



- If the FR for both is the same, then

$$S_{initial} = 2S(U, V, N)$$

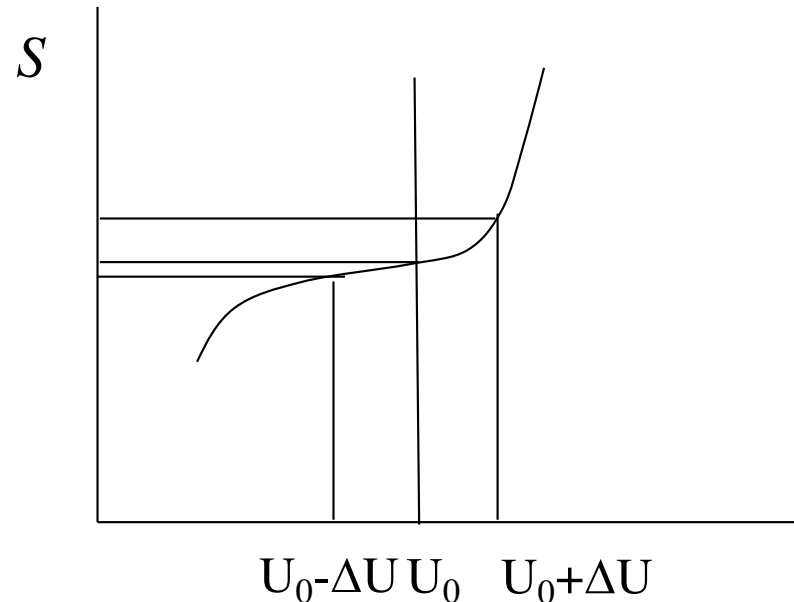
- If we transfer energy from A to B in the amount  $\Delta U$ , then

$$S_{final} = S(U - \Delta U, V, N) + S(U + \Delta U, V, N)$$



# Stability

- Now suppose the entropy is of the form



- Then  $S_{final} > S_{initial}$ . If so, this means that the initial condition was unstable, and if the constraint were removed there would be energy flow across the wall.



# Mutual versus Intrinsic Stability

- We just discussed the case of mutual stability.
- But if in a single system a small local perturbation produces a region with a high entropy, then that system is intrinsically unstable.
- So the criterium is the same.



# Stability Condition

- The condition for stability of the initial state is

$$S_{final} < S_{initial}$$

- In the limit as  $\Delta U$  goes to zero

$$\left. \frac{d^2 S}{dU^2} \right)_{V,N} \leq 0$$



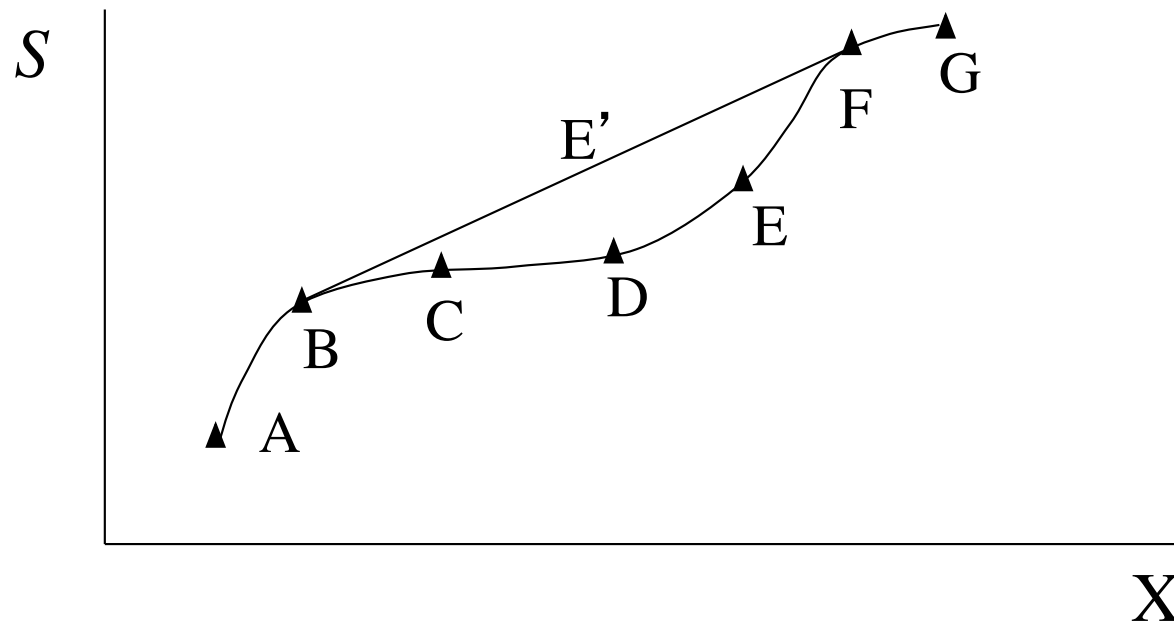
- Likewise

$$\left. \frac{d^2 S}{dV^2} \right|_{U,N} \leq 0$$

- These require the FR to be concave in the region of interest.
- Note, these are a local criterion.



- One might have a FR that looks like



- CDE is locally unstable
- BCDEF is globally unstable
- However,  $BE'F$  is stable and will represent the FR in this region as states along BCDEF will not occur as equilibrium states.



# More Generally

- If both  $U$  and  $V$  vary, the stability criterion becomes

$$\frac{\partial^2 S}{\partial U^2} \frac{\partial^2 S}{\partial V^2} - \left( \frac{\partial^2 S}{\partial U \partial V} \right)^2 \geq 0$$



# For the Potentials

- U: 
$$\frac{\partial^2 U}{\partial S^2} \frac{\partial^2 U}{\partial V^2} - \left( \frac{\partial^2 U}{\partial S \partial V} \right)^2 \geq 0$$

- F: 
$$\left. \frac{\partial^2 F}{\partial T^2} \right)_{V,N} \leq 0 \qquad \left. \frac{\partial^2 F}{\partial V^2} \right)_{T,N} \geq 0$$

- H: 
$$\left. \frac{\partial^2 H}{\partial T^2} \right)_{P,N} \geq 0 \qquad \left. \frac{\partial^2 H}{\partial P^2} \right)_{S,N} \leq 0$$

- G: 
$$\left. \frac{\partial^2 G}{\partial T^2} \right)_{P,N} \leq 0 \qquad \left. \frac{\partial^2 G}{\partial P^2} \right)_{T,N} \leq 0$$



# Maxwell's Relations can be used to explore the consequences

- Local stability requires that

$$\kappa_T \geq \kappa_S \geq 0$$

$$c_p \geq c_v \geq 0$$

$$\left( \frac{\partial P}{\partial v} \right)_T = -\frac{1}{\kappa_T} \leq 0$$

( $\kappa_T$  isothermal compressibility,  $\kappa_S$  adiabatic compressibility)

