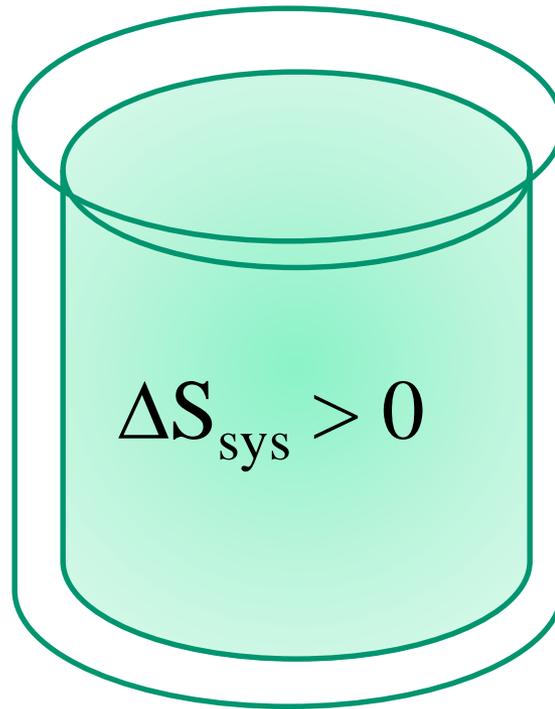


An isolated system requires $\Delta S > 0$

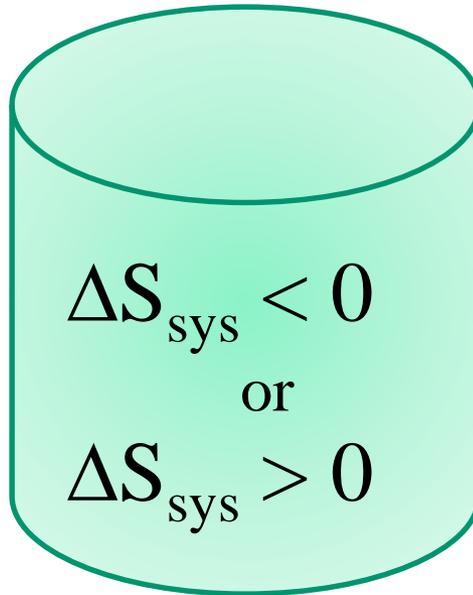


Isolated system:
Entropy increases for any spontaneous process

System and surroundings both play in role in the entropy

$$\Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

$$\Delta S_{\text{surr}} > 0$$



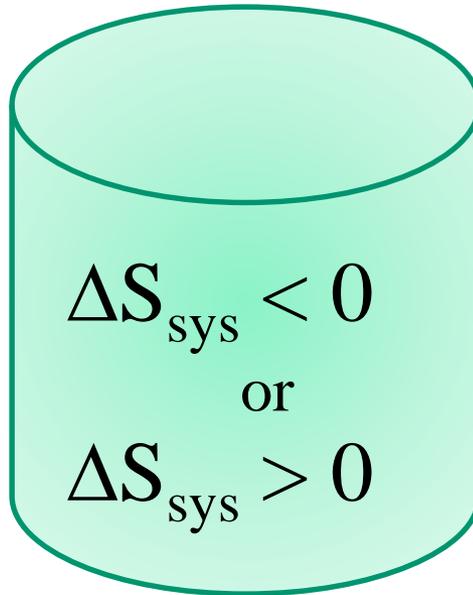
If the system is not isolated, then the entropy can have either sign for the System as long as the surroundings can compensate.

Closed system in contact with surroundings:
Entropy increases for any spontaneous process

We derive one function that includes both sys and surr

$$\Delta S_{\text{sys}} + \Delta H_{\text{surr}}/T > 0$$

$$\Delta H_{\text{surr}}/T > 0$$

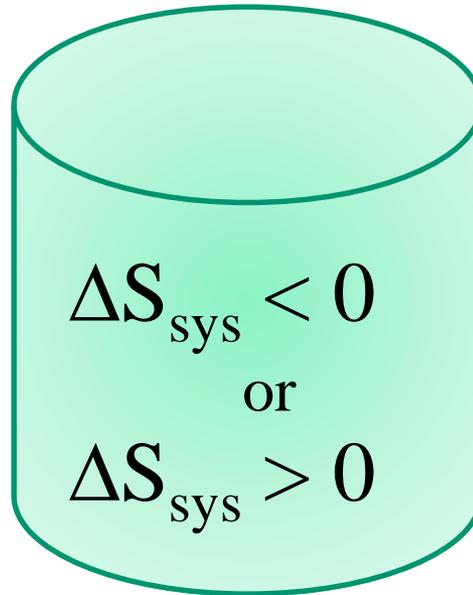


However, if we now turn to a case where the entropy change in the surroundings compensates for a change in the system, we can include the heat flow from surr to sys.

We derive one function that includes both sys and surr

$$\Delta S_{\text{sys}} - \Delta H_{\text{sys}}/T > 0$$

$$-\Delta H_{\text{sys}}/T > 0$$

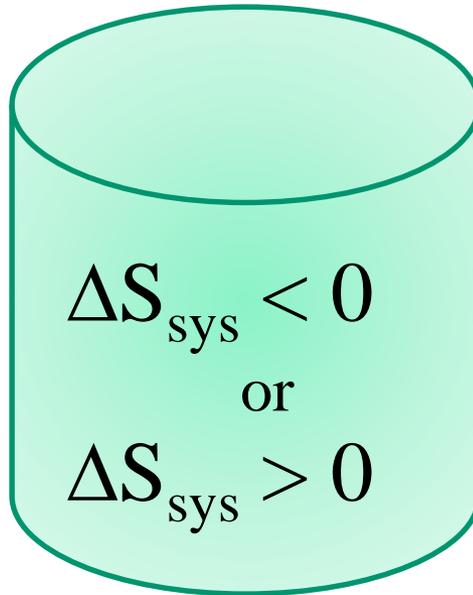


The heat flow to or from the system must opposite to that of the surroundings. Hence, there must be a minus sign In front of the enthalpy term.

We derive one function that includes both sys and surr

$$\Delta H_{\text{sys}} - T\Delta S_{\text{sys}} < 0$$

$$-\Delta H_{\text{sys}}/T > 0$$

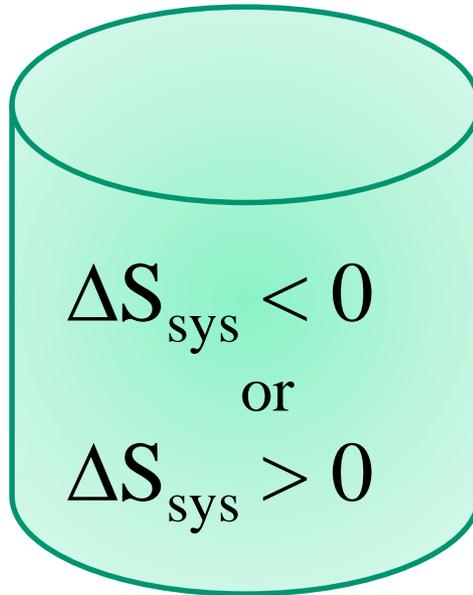


Here we have expressed the total change of system and Surroundings in terms of quantities that relate to the System. Hence, $\Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$ constitutes a new state function

We derive one function that includes both sys and surr

$$\Delta G_{\text{sys}} < 0$$

$$-\Delta H_{\text{sys}}/T > 0$$



Note the sign change when we multiplied by $-T$.

Here we have written the new state function explicitly as the free energy change, ΔG , which is defined for the system.

Definition of Gibbs Free Energy

Reactions will proceed in the direction written if $\Delta G < 0$.

G decreases as shown in the figure below until G is constant.

At equilibrium, $\Delta G = 0$.

$$\Delta G = \Delta G^\circ + RT \ln Q$$

where Q is the reaction quotient. Q changes as the

Reaction proceeds. Finally, at equilibrium $Q = K$. Therefore,

$$\Delta G^\circ = -RT \ln K$$

