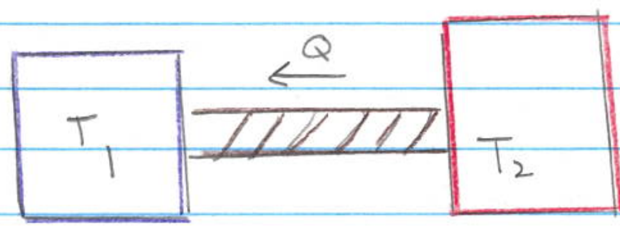
Reversible and Irreversible Processes and Heat

- We have said that heat flows inevitably from hot to cold. We have similarly said that the total number of possible configurations inevitably increases, $\Delta S > 0$, until equilibrium.

Heat flowing from hot to cold is irreversible; it will not spontaneously flow from cold to hot. All irreversible processes are associated with an increase in entropy

$\boxed{\text{Ex: An irreversible processes; } \Delta S_{univ} > 0}$

- Consider heat flowing from a large hot object to a large cold object through a conducting bar. After a while a steady state is reached and a heat Q passes through the system



(irreversible)
$T_1 < T_2$

- The change in entropy of our universe is

$$\Delta S_{univ} = \Delta S_1 + \Delta S_{bar} + \Delta S_2$$

$$\Delta S_1 = \frac{Q}{T_1}$$

(system one has absorbed heat Q and rethermalized it. It is so large its temperature doesn't change significantly. It is a "reservoir")

$\Delta S_2 = -\frac{Q}{T_2}$ (System has lost heat Q at temperature T_2)

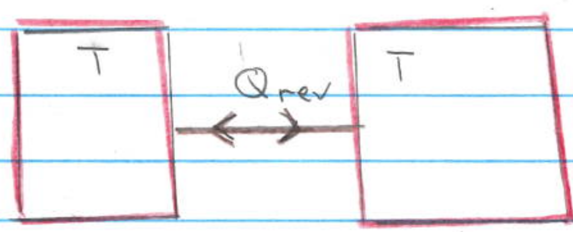
$\Delta S_{bar} = 0$ The bar is in a steady state, nothing has changed about it.

So

$$\boxed{\Delta S_{univ} = \frac{Q}{T_1} - \frac{Q}{T_2} > 0}$$

this process is irreversible!

- When two bodies are in equilibrium and at the same temperature, or infinitessimally close, heat can either way without an entropy increase, i.e. it is reversible



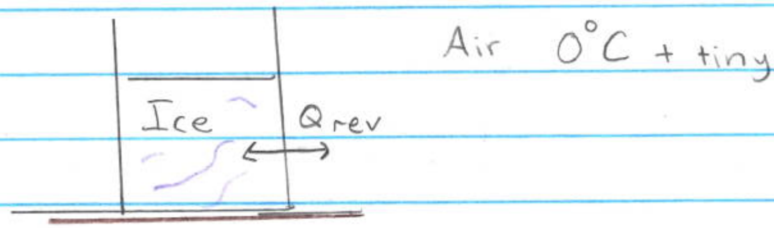
(reversible)

$\Delta S_{univ} = 0$

$$\Delta S_{univ} = \frac{Q}{T} - \frac{Q}{T} = 0$$

- We call the equilibrium transfer of heat a reversible transfer, and have $\Delta S_{univ} = 0$

Ex: A cup of ice is in contact with air at $0^\circ C$ plus a tiny bit



- As heat flows into the ice it will melt and become water at 0° C. The amount of heat required to melt the ice is the latent heat of fusion $L_m = 334\ J/kg$. So for 1kg of ice it takes 334 J. In general

$$Q = m L_m$$

mass of ice

$$\Delta S_{\substack{ice \\ water}} = \frac{Q_{rev}}{T}$$

$$\Delta S_{air} = \frac{-Q_{rev}}{T}$$

- The change in entropy of the universe is zero

$$\boxed{\Delta S_{univ} = \Delta S_{\substack{ice \\ water}} + \Delta S_{air} = 0}$$

(reversible exchange of heat)

- In general if the ambient air is right at freezing the system (ice+water) has a hard time deciding which way the heat will flow; the transfer of heat is reversible.

A ball and a lake

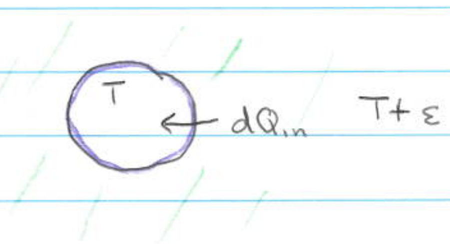
- A cold ball of iron has specific C (C_p and C_V are nearly equal) which is constant. It is thrown into a hot lake. The initial temperature of the ball (the system) is T_S. The temperature of the lake is T_R. The lake is a reservoir. $T_S < T_R$

- The ball will reach equilibrium with the lake. This is an irreversible process. Calculate ΔS for the ball, and lake, and the universe

The Ball

- The entropy change ΔS depends only on its state at the beginning (T_S) and end (T_R) of the process $\Delta S = S(T_R) - S(T_S)$. Since

- Since this is so, we can replace the real process with an imagined one where the temperature of the ball is slowly raised by placing it in contact with reservoirs between T_S and T_R. Then



$$dS = \frac{dQ_{rev}}{T} = C\frac{dT}{T}$$

dS for ball

intermediat temperature of ball

Integrating we find

$$\Delta S_s = \int_{T_S}^{T_R} C \frac{dT}{T} = C \ln T_R / T_S$$

The lake

- The lake is a reservoir: its temperature is constant

$$\Delta S_R = \int \frac{dQ_{in}}{T_R} = -\frac{Q}{T_R} \leftarrow Q \text{ is amount of heat given to ball i.e. lost by lake}$$

- This is the heat required to raise the temperature of the ball is:

$$Q = \int dQ = \int_{T_S}^{T} C \, dT = C(T_R - T_S)$$

So

$$\Delta S_R = -C(T_R - T_S)/T_S$$

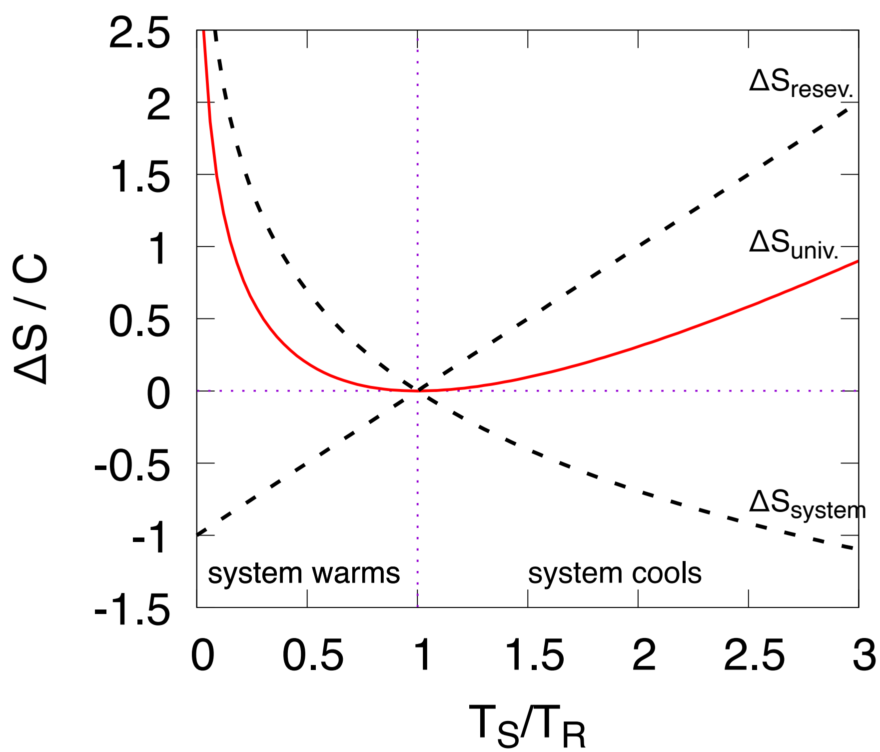
The total

- The sum is $\Delta S_{univ} = \Delta S_{ball} + \Delta S_R$ or

$$\Delta S_{univ} = C \ln (T_R/T_S) - C(1 - T_R/T_S) \geq 0$$

- This is plotted on the next slide and is positive. Since, $\ln x - (1-x) \geq 0$, It is irreversible.

Change in Entropy Ball in Lake: Blundell Example 14.1



System = Ball

The ball has (initial) temperature T_S

Reservoir = Lake

The reservoir has constant temperature T_R

Universe is the ball and lake

The problem nicely illustrates the general theorem

$$\boxed{\Delta S = S_B - S_A = \int_A^B \frac{đQ_{rev}}{T} \geqslant \frac{Q}{T_R}}$$

- The entropy change between two equilibrium states (A and B) can be found by assuming the heat is transferred reversibly so that $đS = dQ_{rev}/T$ in each step:

$$\Delta S = \int_{T_S}^{T_R} \frac{dQ_{rev}}{T} = C \ln\left(\frac{T_R}{T_S}\right)$$

- This is greater than the (heat)/T actually given irreversibly by reservoir(s) in contact with the system. Here there is one reservoir with temperature T_R

$$Q = C(T_R - T_S) \quad \text{and} \quad \frac{Q}{T_R} = C(1 - T_S/T_R)$$

and so

$$\boxed{\Delta S_{sys} \geqslant Q/T_R}$$

means that

$$C \ln \frac{T_R}{T_S} - C(1 - T_S/T_R) \geqslant 0$$