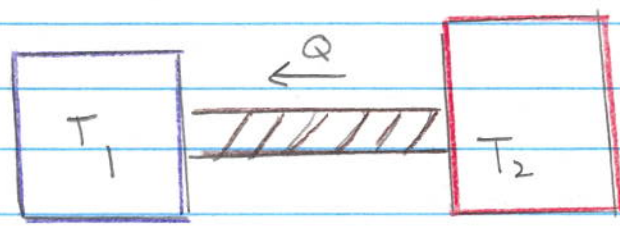
Reversible and Irreversible Processes and Heat

- 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)

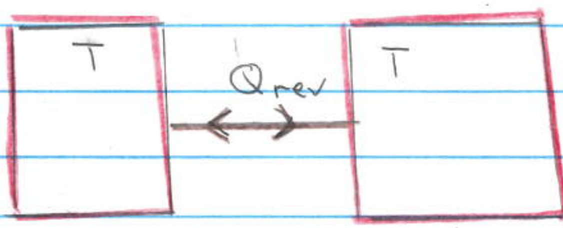
$\Delta S_{bar} = 0$ The bar is in a steady state, nothing has changed about it.

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



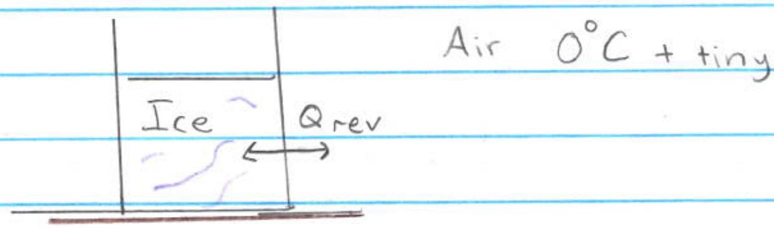
(reversible)

$\Delta S_{univ} = 0$

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

- 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 $0^\circ C$. 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

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

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

$$Q = m L_m$$

mass of ice

- 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.

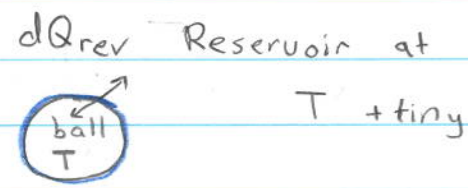
Ex: Ball and Lake

- A ball of iron has specific heat C (C_p and C_v are nearly equal) which is constant. Assume the temperature of the ball is T_S, initially. It is placed into a hot lake at temperature T_R. Through an irreversible transfer of heat the ball will reach equilibrium with the lake (This is a non-equilibrium process).

- Find the change in entropy of the ball

The entropy change ΔS only depends on the states of the ball at the beginning (T_S) and end (T_R) of the process, $S(T_R) - S(T_S)$. Since this is the case, we can replace the real process with an imagined one, where the tempurature of the ball is slowly raised by placing it in contact with reservoirs at temperatures at T between T_S and T_R

$$\boxed{\Delta S_{sys} = \int_{T_S}^{T_R} dS_{sys} = \int_{T_S}^{T_R} \frac{đQ_{rev}}{T} dT}$$



and in each step allow the ball and the reservoir to equilibrate bit by bit. Since $dQ_{rev} = C\,dT$, we have:

$$\Delta S_{sys} = \int_{T_S}^{T_R} C \frac{dT}{T} = C \ln \frac{T_R}{T_S}$$

- Find the entropy change of the lake

The lake is a reservoir its temperature doesn't change

$$\boxed{\Delta S_R = \int \frac{dQ_{in}}{T_R} = \frac{-Q}{T_R}}$$

$Q = -Q_{in}$ is the heat given to ball, i.e. lost by lake.

- Here Q is the heat required to raise the temperature of the ball

$$Q = \int dQ = \int_{T_{sys}}^{T_R} C\,dT = C\left(T_R - T_s\right)$$

So

$$\Delta S_R = -\frac{C\left(T_R - T_s\right)}{T_R}$$

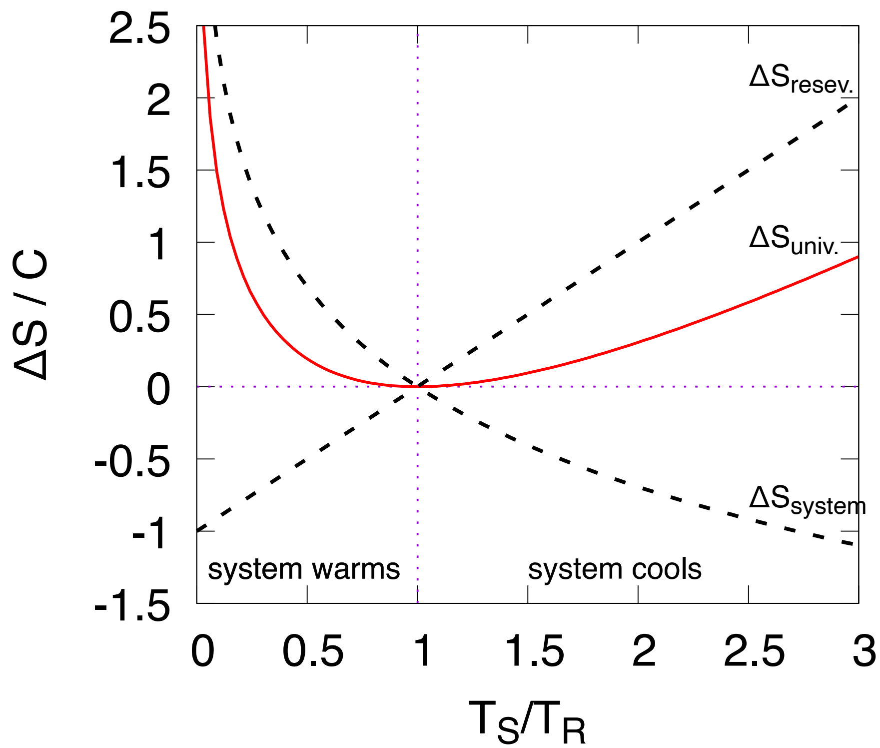
- The total change is entropy of the universe is (see slide)

$$\Delta S_{univ} = \Delta S_{Ball} + \Delta S_R$$

$$= C\ln\left(\frac{T_R}{T_s}\right) - C\left(1 - \frac{T_s}{T_R}\right) \geqslant 0$$

- This is plotted on the next slide. We see that $\Delta S_{univ} > 0$ for all values of T_s / T_R; 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 nicley illustrates the general theorem

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

The entropy change between two equilibrium states can be found by assuming the system is transferred reversibly between the two states using $dS = dQ_{rev}/T$

$$\Delta S_{sys} = \int_{T_S}^{T_R} \frac{dQ_{rev}}{T} = C \ln \frac{T_R}{T_S} \qquad \text{(this case)}$$

This is greater than the (heat)/T given irreversibly by reservoir(s) at temperature(s) T to the the system. In this case there is one reservoir at T_R

$$Q = C(T_R - T_S) \qquad \text{and} \qquad \int \frac{dQ}{T_R} = \frac{Q}{T_R}$$

And so

heat given by reservoir at T_R

$$\boxed{\Delta S_{sys} \geqslant \frac{Q}{T_R}} \qquad \text{(general case for one reservoir)}$$

or

$$C \ln \frac{T_R}{T_S} - \frac{C(T_R - T_s)}{T_R} \geqslant 0 \qquad \text{(see slide again)}$$

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