Picture taken from https://phys.org/news/2015-09-fate-universeheat-death-big-rip.html

Heat death of the Universe

Law of increase of entropy

Reversible adiabatic changes

1st and 2nd law combined

* https://en.wikipedia.org/wiki/Graphical_timeline_from_Big_Bang_to_Heat_Death

The Universe is dying!

View universe as closed system

Systems are driving towards thermal equilibrium

Once reached there can no longer be any heat flow (0^{th} law)

$\Rightarrow$ No work will be done (2^{nd} law)

1^{st} law states conservation of energy and hence there can be no new energy supplied to system

How long have we got? 10^{1000} years (Wikipedia*)

However…

Modern big-bang theory says that T_{universe} is continually changing

Continual expansion - never reaches true thermodynamic equilibrium

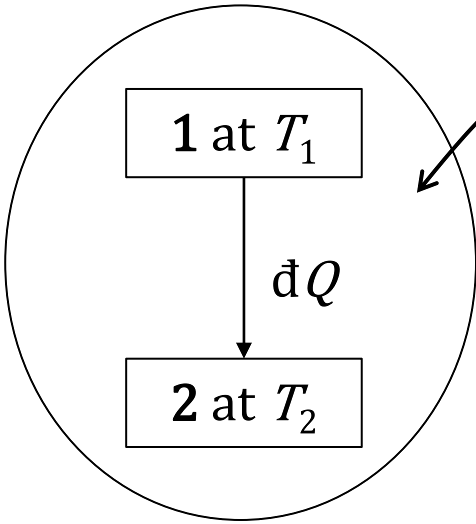
T_{universe} is never constant

Death is avoided.

Yet, expansion can in principle be purely adiabatic

Entropy constant: Death!

Law of increase of entropy



$đQ = 0$ from outside: isolated

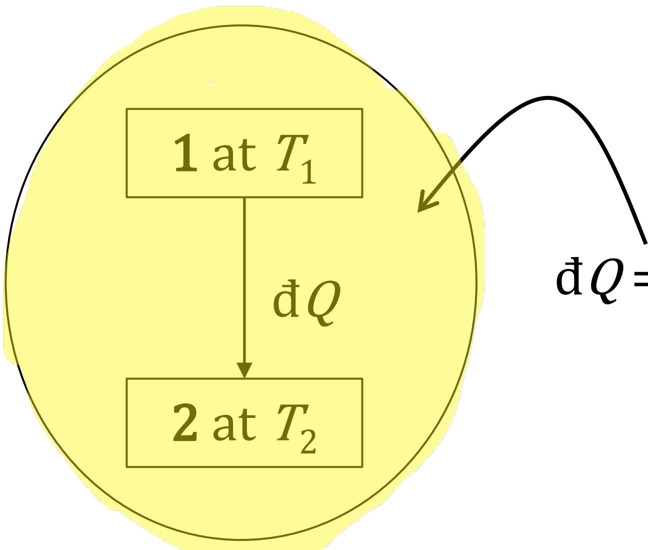
$T_1 > T_2$ so $đQ > 0$

0th law: **1** & **2** are not in equilibrium

1st law: $-đQ_1 = đQ_2$

2nd law: irreversible & spontaneous; heat flow from **2** to **1** impossible

Law of increase of entropy



$đQ = 0$ from outside: isolated

$T_1 > T_2$ so $đQ > 0$

$$\mathrm{d}S_1 = -\frac{đQ}{T_1}$$

(Clausius)

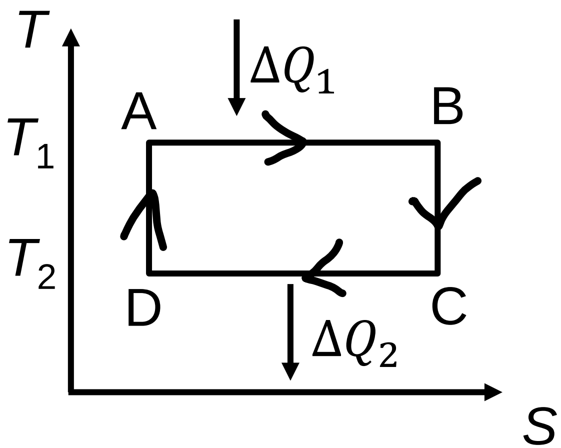
$$\mathrm{d}S_2 = +\frac{đQ}{T_2}$$

$$\mathrm{d}S_{\text{total}} = đQ\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$ positive because $T_1 > T_2$

$$\mathrm{d}S_{\text{total}} > 0$$

Reversible adiabatic changes

Carnot cycle in different coordinates:



$$\Delta Q_1 = T_1 \int_A^B \mathrm{d}S = T_1(S_B - S_A)$$

$$\Delta Q_2 = T_2 \int_C^D \mathrm{d}S = T_2(S_D - S_C)$$

$$\oint \mathrm{d}U = 0 = \Delta Q + \Delta W$$

work out:

- heat?
- work done

$$\oint T\mathrm{d}S = \Delta Q = \text{area enclosed}$$

$$\therefore \text{w.d. by system } \Delta W' = -\Delta W = \Delta Q = \text{area enclosed}$$

Combined statement of 1st and 2nd law

$\mathrm{d}U = đQ + đW$ 1st law

$đW = -p\mathrm{d}V$ for a reversible change of V

$đQ = T\mathrm{d}S$ for a reversible change (2nd law)

Hence $dU = TdS - pdV$ true for reversible AND irreversible changes

All variables are FoS (path independent)

Restrictions: closed system

work done by volume change only (otherwise additional terms needed)

Combined statement of 1st and 2nd law

from $dU = TdS - pdV$ we see that $U = U(S,V)$

$$\therefore \mathrm{d}U = \left(\frac{\partial U}{\partial S}\right)_V \mathrm{d}S + \left(\frac{\partial U}{\partial V}\right)_S \mathrm{d}V$$

Comparing these two equations:

$$T = \left(\frac{\partial U}{\partial S}\right)_V \text{ and } p = -\left(\frac{\partial U}{\partial V}\right)_S$$

Now recall that if *f*(*x*,*y*) is FoS then

$$\mathrm{d}f = \left(\frac{\partial f}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial f}{\partial y}\right)_x \mathrm{d}y \equiv X\mathrm{d}x + Y\mathrm{d}y \text{ where } \left(\frac{\partial X}{\partial y}\right)_x = \left(\frac{\partial Y}{\partial x}\right)_y$$

since dU is exact: $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$ a Maxwell relation (more later)