Thermodynamics

I. Internal Energy
- energy of atoms and molecules
- thermal equilibrium
- ideal gas law
- temperature & kinetic theory

II. Heat
- thermal conductivity
- 1st law of thermodynamics
- heat engines & cycles
- **2nd law of thermodynamics**

	The student will be able to:	HW:
1	Define and apply concepts of internal energy, thermal equilibrium, zeroth law of thermodynamics, and temperature.	✓ 1 – 3
2	State and apply the ideal gas law in terms of Boltzmann's constant and solve related problems with variables pressure, volume, and temperature.	✓ 4 – 7
3	State and apply the stipulations of the kinetic theory of gases and solve related problems involving pressure, force, kinetic energy, Boltzmann's constant, temperature, and speed distributions of particles	✓ 8 – 13
4	Define and apply the concept of thermal conductivity and solve related problems involving heat flow.	✓ 14 – 19
5	State and apply the first law of thermodynamics and solve related problems including work, heat, heat engines & cycles, *P*-*V* diagrams.	✓ 20 – 26
6	Define and describe entropy; state and apply qualitatively the second law of thermodynamics.	27 – 30

Entropy

Entropy is a measure of a system's state. Greater entropy indicates more randomness and disorder in the system. Change in entropy at a constant temperature is given by:

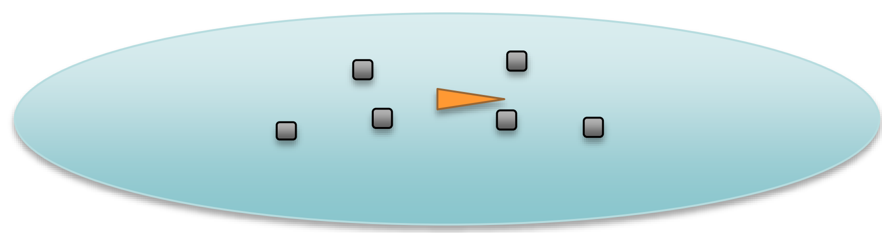
$$\Delta S = \frac{Q}{T}$$

where: S = entropy of a system
Q = heat (into the system)
T = temperature

Oh look, a cute snowman.
But wait, oh no, he’s melting!

Before

Aww, poor little guy!



After

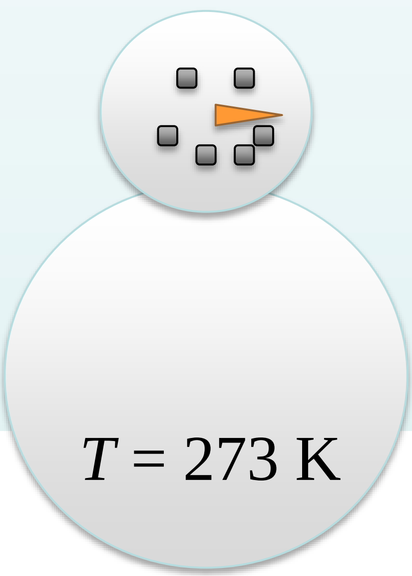
Heat of fusion, Q, with snow at melting point:

$$Q = mL$$

$$Q = (100\ \text{kg})(334\ \text{kJ/kg})$$

$$Q = 33400\ \text{kJ}$$

$T = 275$ K



Before

$$\Delta S = Q/T$$

$$\Delta S = (33400\ \text{kJ})/273\ \text{K}$$

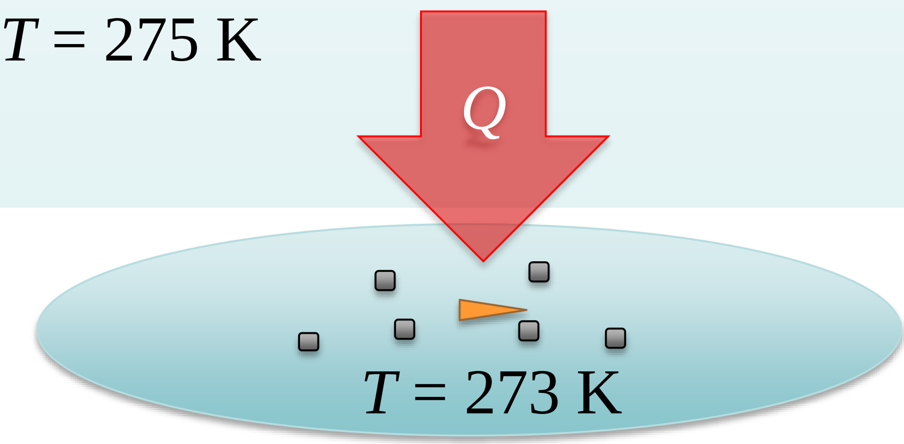
$$\Delta S_{\text{snowman}} = 122\ \text{kJ/K}$$

$$\Delta S = Q/T$$

$$\Delta S = (-33400\ \text{kJ})/275\ \text{K}$$

$$\Delta S_{\text{surroundings}} = -121\ \text{kJ/K}$$

$T = 275$ K

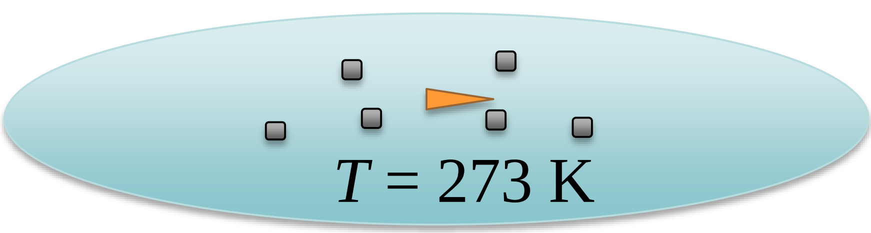


After

No temperature change in snowman or surroundings…

Now night has fallen and the puddle starts to freeze…

T = 271 K



Before

$$\Delta S = Q/T$$

$$\Delta S = (-33400 \text{ kJ})/273 \text{ K}$$

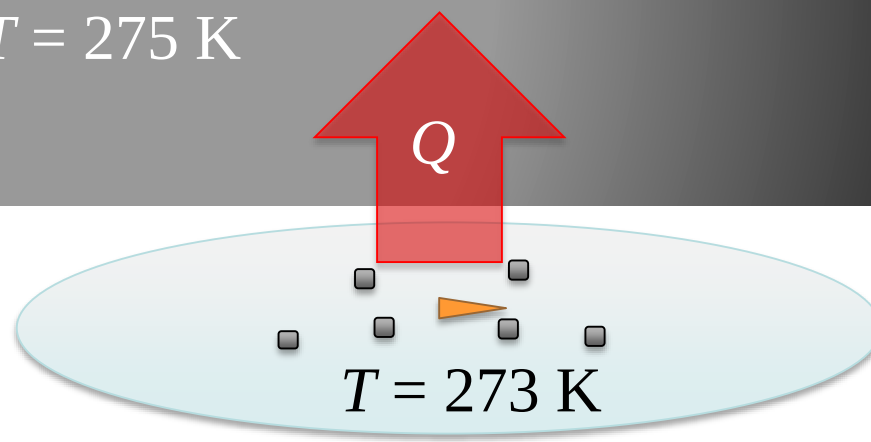
$$\Delta S_{remains} = -122 \text{ kJ/K}$$

$$\Delta S = Q/T$$

$$\Delta S = (33400 \text{ kJ})/271 \text{ K}$$

$$\Delta S_{surroundings} = 123 \text{ kJ/K}$$

T = 275 K

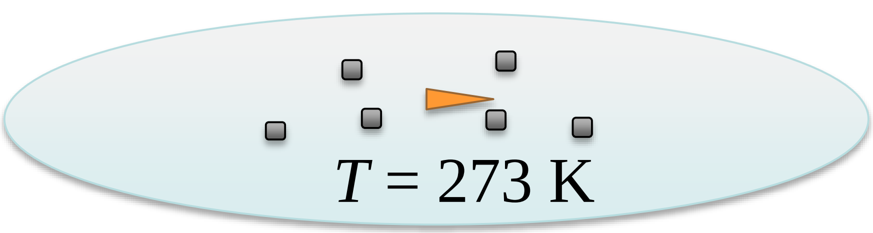


After

No temperature change in snowman or surroundings…

Now its daytime again and the puddle starts to melt…

$T = 275\ \text{K}$



$$\Delta S = Q/T$$
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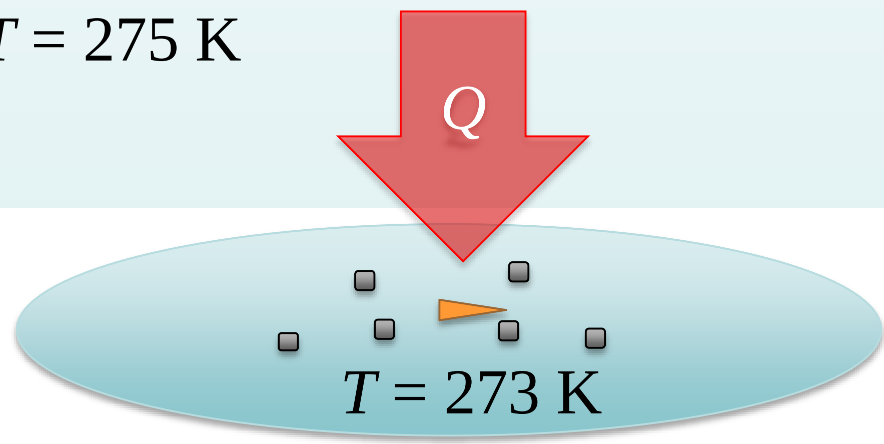
$$\Delta S_{\text{snowman}} = 122\ \text{kJ/K}$$

$$\Delta S = Q/T$$
$$\Delta S = (-33400\ \text{kJ})/275\ \text{K}$$
$$\Delta S_{\text{surroundings}} = -121\ \text{kJ/K}$$

$T = 275\ \text{K}$



Before

No temperature change in snowman or surroundings…

After

$$\Delta S = Q/T$$

$$\Delta S = (-33400 \text{ kJ})/273 \text{ K}$$

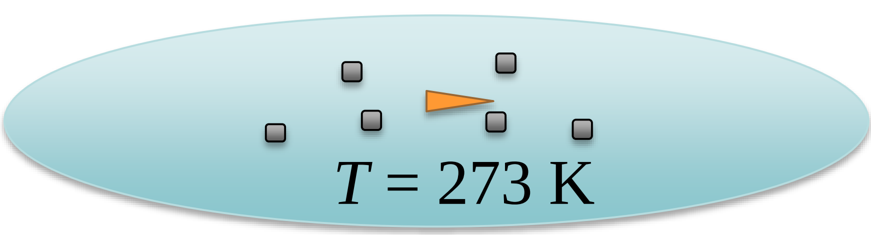
$$\Delta S_{\text{snowman}} = -122 \text{ kJ/K}$$

$$\Delta S = Q/T$$

$$\Delta S = (33400 \text{ kJ})/275 \text{ K}$$

$$\Delta S_{\text{surroundings}} = 121 \text{ kJ/K}$$

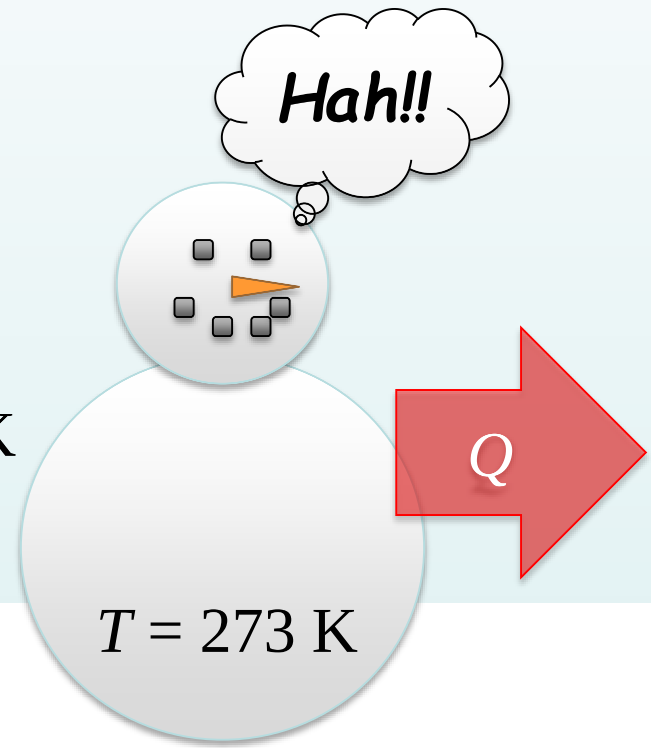
T = 275 K



Before

What?! I wasn't expecting that! Our guy spontaneously reformed – can he do that?!

T = 275 K



After

No temperature change in snowman or surroundings…

Our Story of the Snowman

- In each of the previous 4 pages water underwent a phase change at the freezing point.
- In each case energy is conserved – heat lost or gained by the water of the snowman is equal in amount to heat gained or lost by the environment.
- None of the actions depicted, including the spontaneous refreezing and reforming of the snowman, would violate the concept of conservation of energy.
- However the concept of entropy and the 2nd Law of Thermodynamics allows us to rule out the magical reformation of the snowman in precise terms…
- Look back at the events and consider the *total* change in entropy in each scenario – notice anything?

2nd Law of Thermodynamics

The total entropy of an isolated system can never decrease. The total entropy of any system plus that of its environment increases as a result of any natural process.

$$\Delta S_{\mathrm{univ}} = \Delta S_{\mathrm{sys}} + \Delta S_{\mathrm{env}} > 0$$

where: The three changes are that of the universe, the system, and its environment.

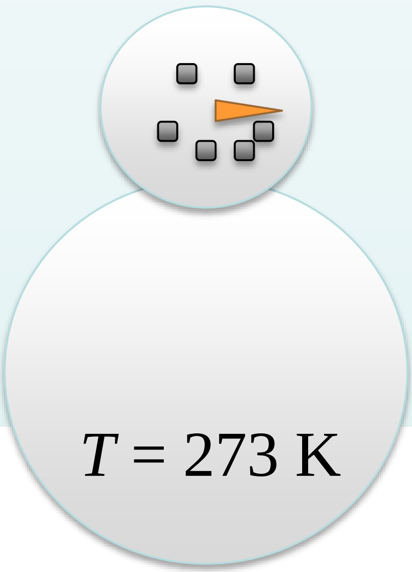
$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{env}$$

$$\Delta S_{univ} = 122 - 121$$

$$\boxed{\Delta S_{univ} = 1\ \text{kJ/K}}$$

The entropy of the universe increases…

$T = 275$ K



Before

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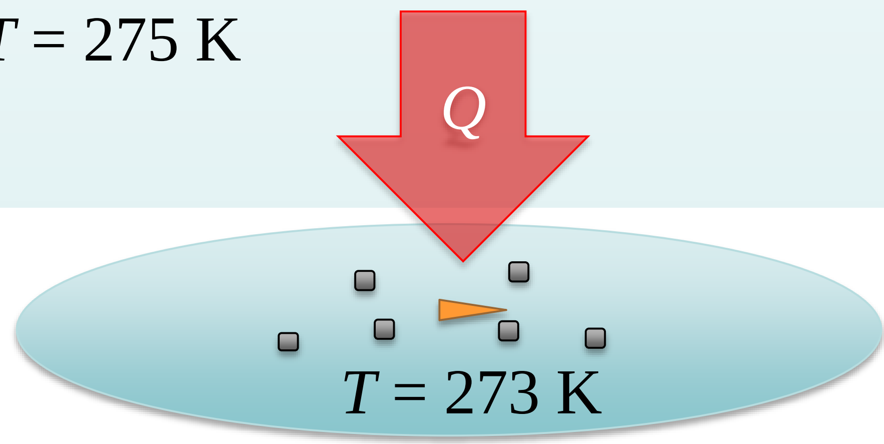
$$\Delta S_{surroundings} = -121\ \text{kJ/K}$$

$T = 275$ K



After

No temperature change in snowman or surroundings…

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{env}$$

$$\Delta S_{univ} = -122 + 123$$

$$\boxed{\Delta S_{univ} = 1 \text{ kJ/K}}$$

The entropy of the universe increases…

$$\Delta S = Q/T$$

$$\Delta S = (-33400 \text{ kJ})/273 \text{ K}$$

$$\Delta S_{remains} = -122 \text{ kJ/K}$$

$$\Delta S = Q/T$$

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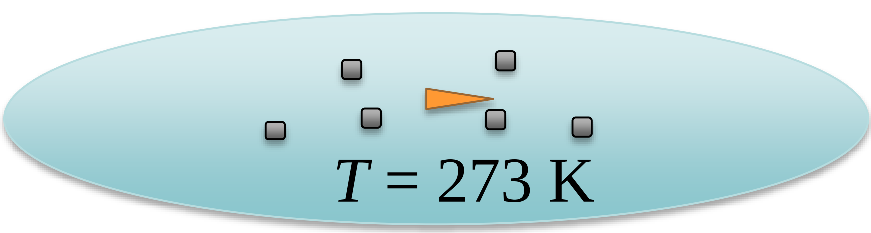
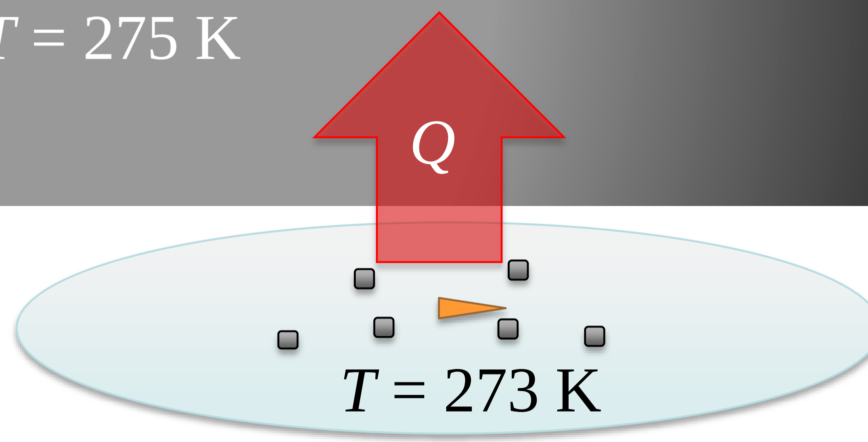
$T = 271$ K

$T = 275$ K





Before

No temperature change in snowman or surroundings…

After

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{env}$$

$$\Delta S_{univ} = 122 - 121$$

$$\boxed{\Delta S_{univ} = 1 \text{ kJ/K}}$$

The entropy of the universe increases…

$$\Delta S = Q/T$$

$$\Delta S = (33400 \text{ kJ})/273 \text{ K}$$

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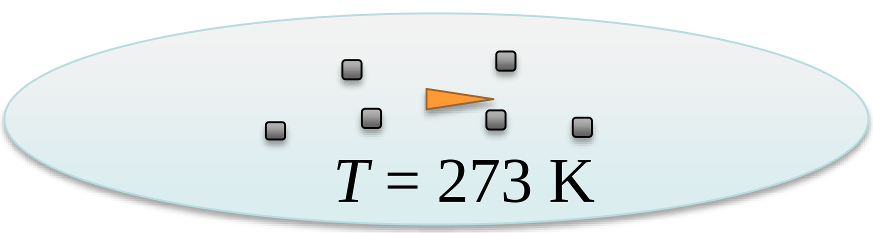
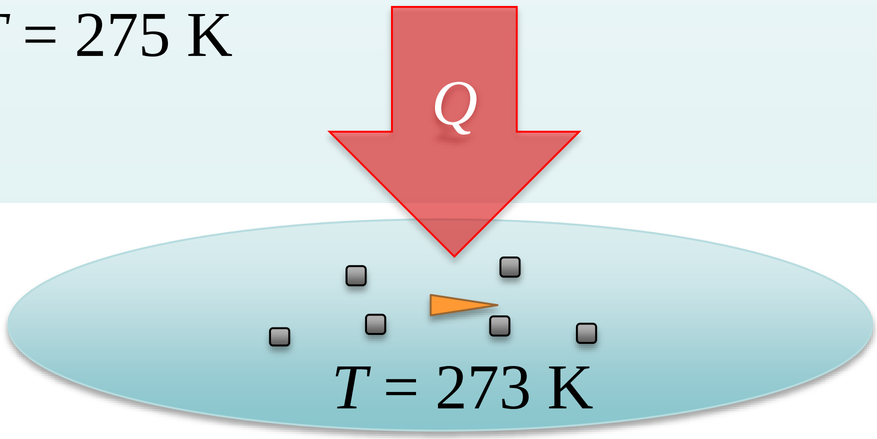
$T = 275$ K



Before

$T = 275$ K



After

No temperature change in snowman or surroundings…

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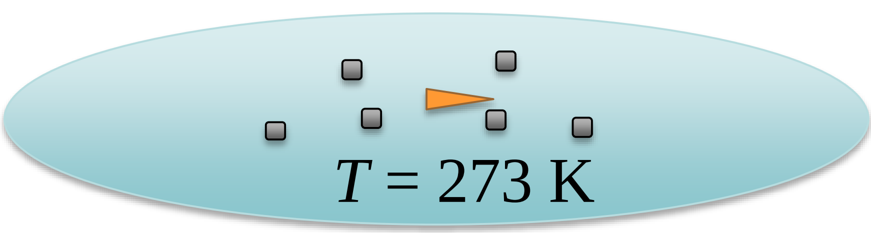
$$\Delta S_{surroundings} = 121\ \text{kJ/K}$$

$T = 275$ K



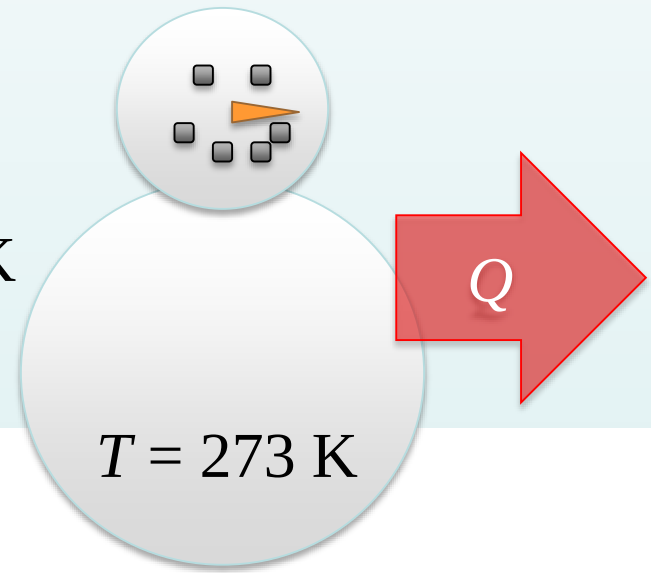
$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{env}$$

$$\Delta S_{univ} = -122 + 121$$

$$\boxed{\Delta S_{univ} = -1\ \text{kJ/K}}$$

The entropy of the universe decreases?!

$T = 275$ K



Before

No temperature change in snowman or surroundings…

After

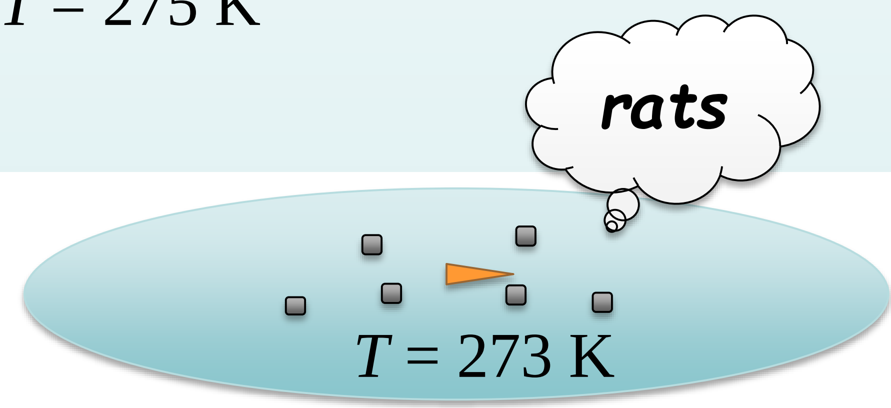
The snowman refreezing and reforming when environment is warm would violate the 2nd Law of Thermodynamics!

Sorry dude, can't do that! You gotta stay melted here!

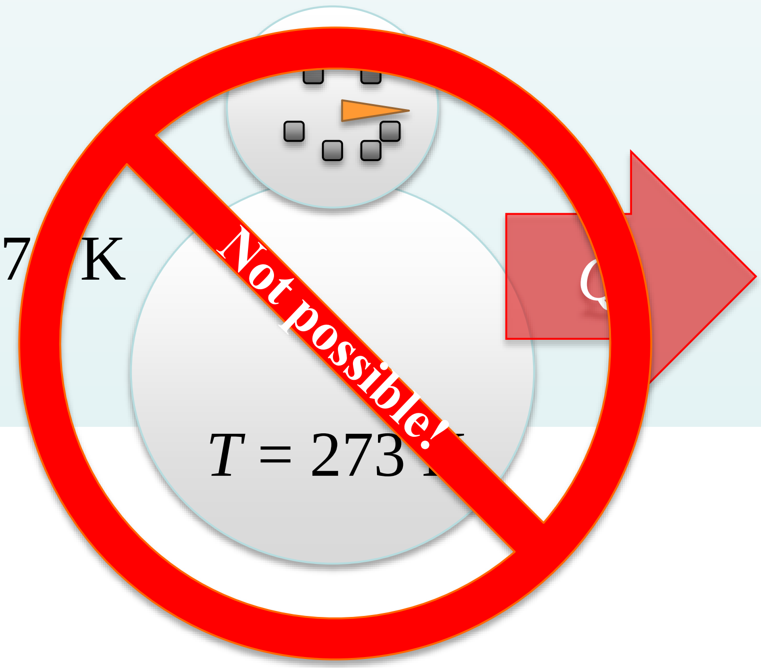
$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{env}$$
$$\Delta S_{univ} = -122 + 121$$
$$\Delta S_{univ} = -1 \text{ kJ/K}$$

The entropy of the universe decreases?!

T = 275 K



T = 27 K



Before

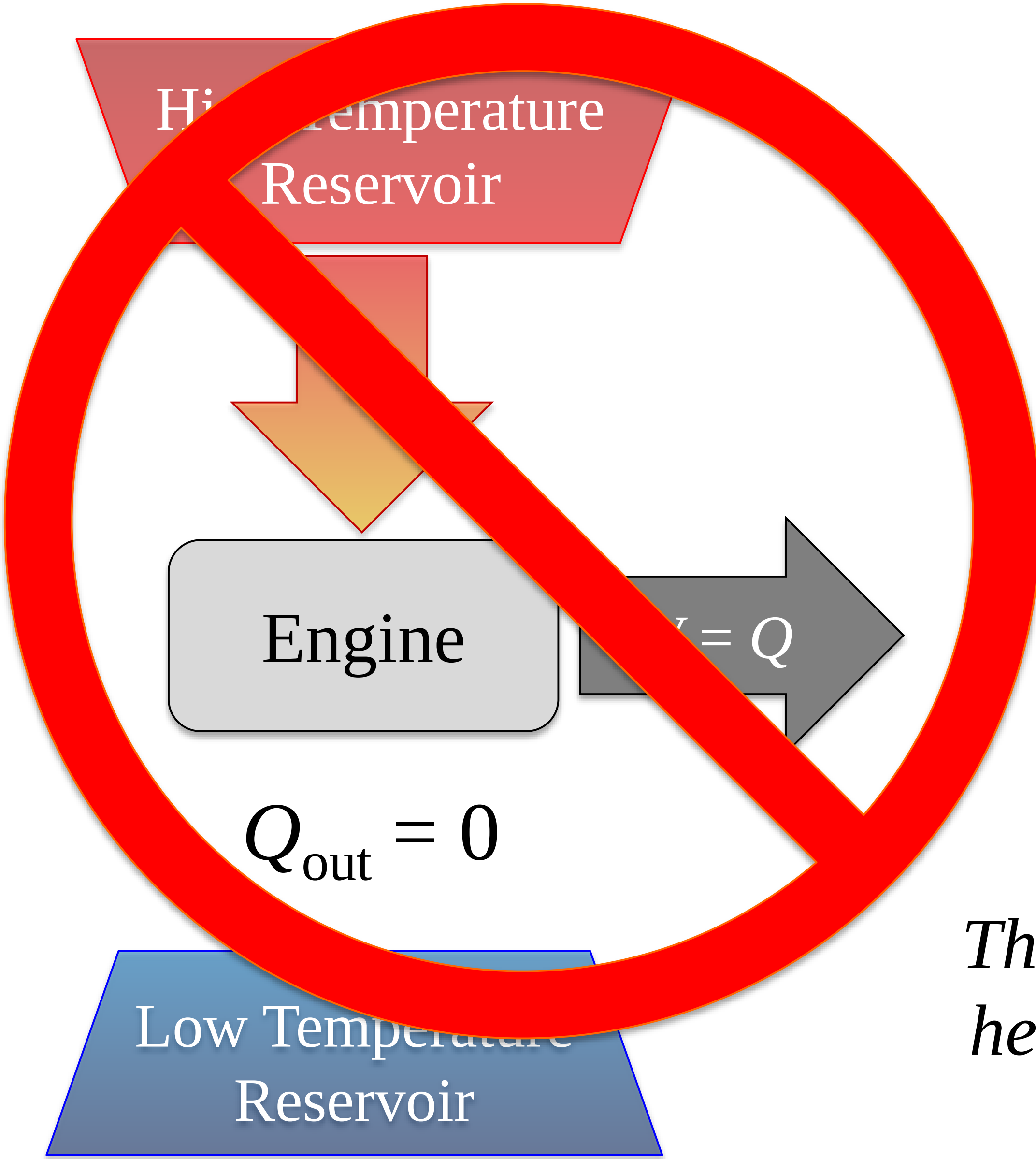
After

No temperature change in snowman or surroundings…

2^{nd} Law Alternate Versions

- Heat always flows from higher to lower temperature; it never flows spontaneously from lower to higher temperature. (Clausius statement.)
- No device is possible whose sole effect is to transform a given amount of heat completely into work. *i.e.* No heat engine can ever achieve 100% efficiency. (Kelvin-Planck statement)
- Natural processes tend to move toward a state of greater disorder and randomness.
- The direction of time in which entropy increases is called "the future" – reversing events such that entropy decreases is not possible.

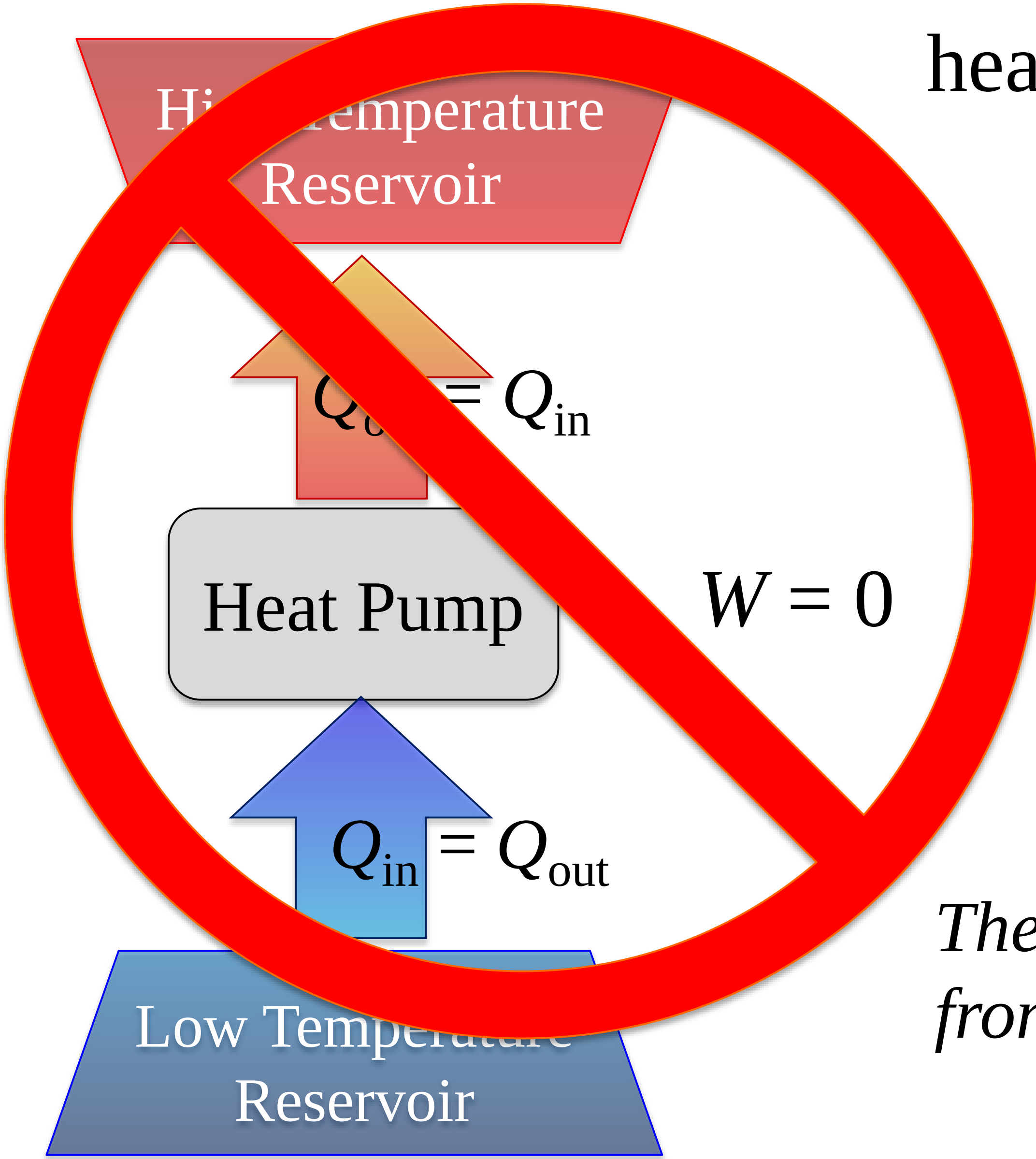
Magic Engine!



Not possible!

There is no way to convert heat into useful work with 100 % efficiency!

Magic
heat pump, refrigerator

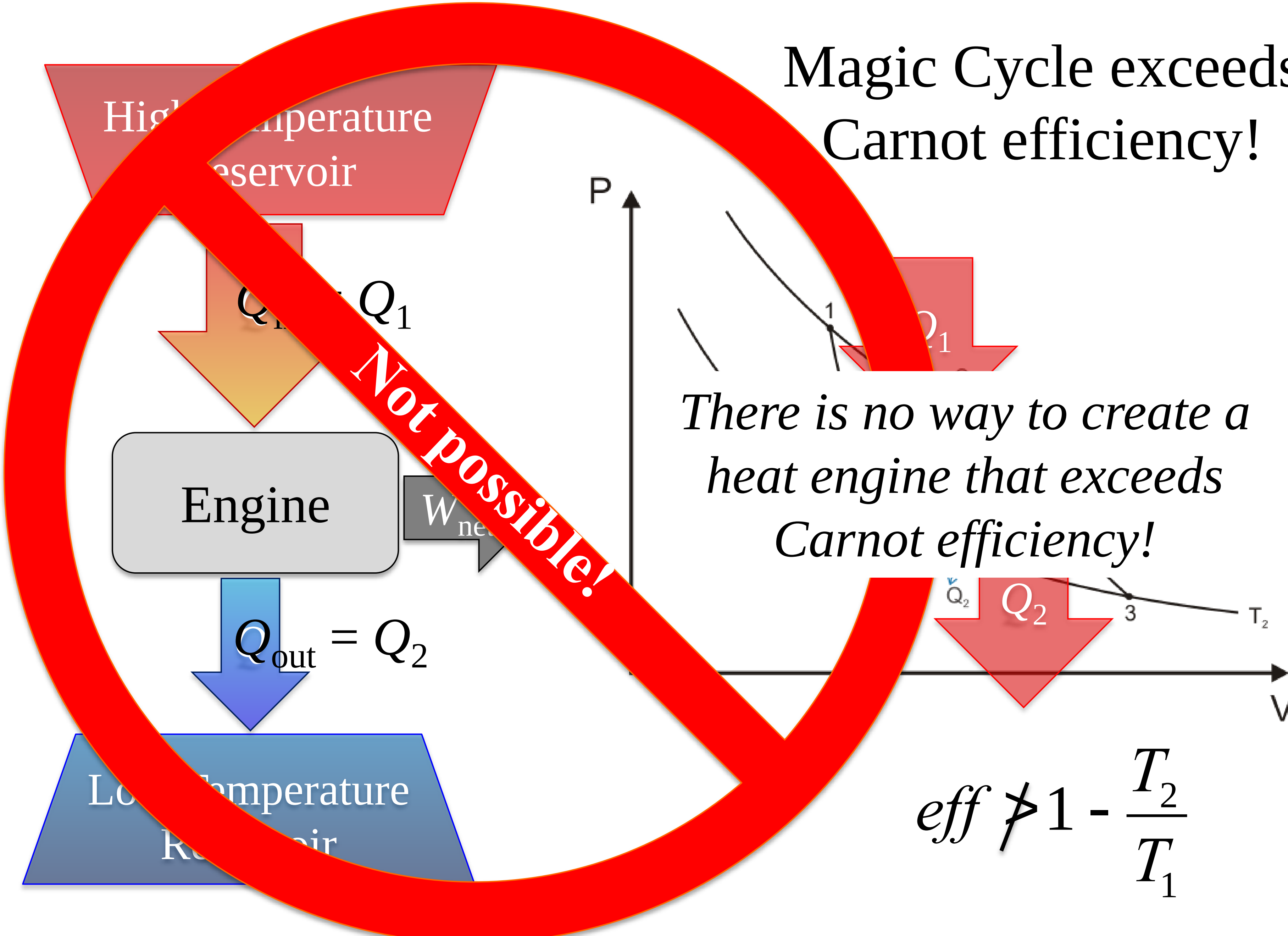


Not possible!

There is no way transfer heat from low to high temperature with no work done.

image credit: Keta, Wikipedia

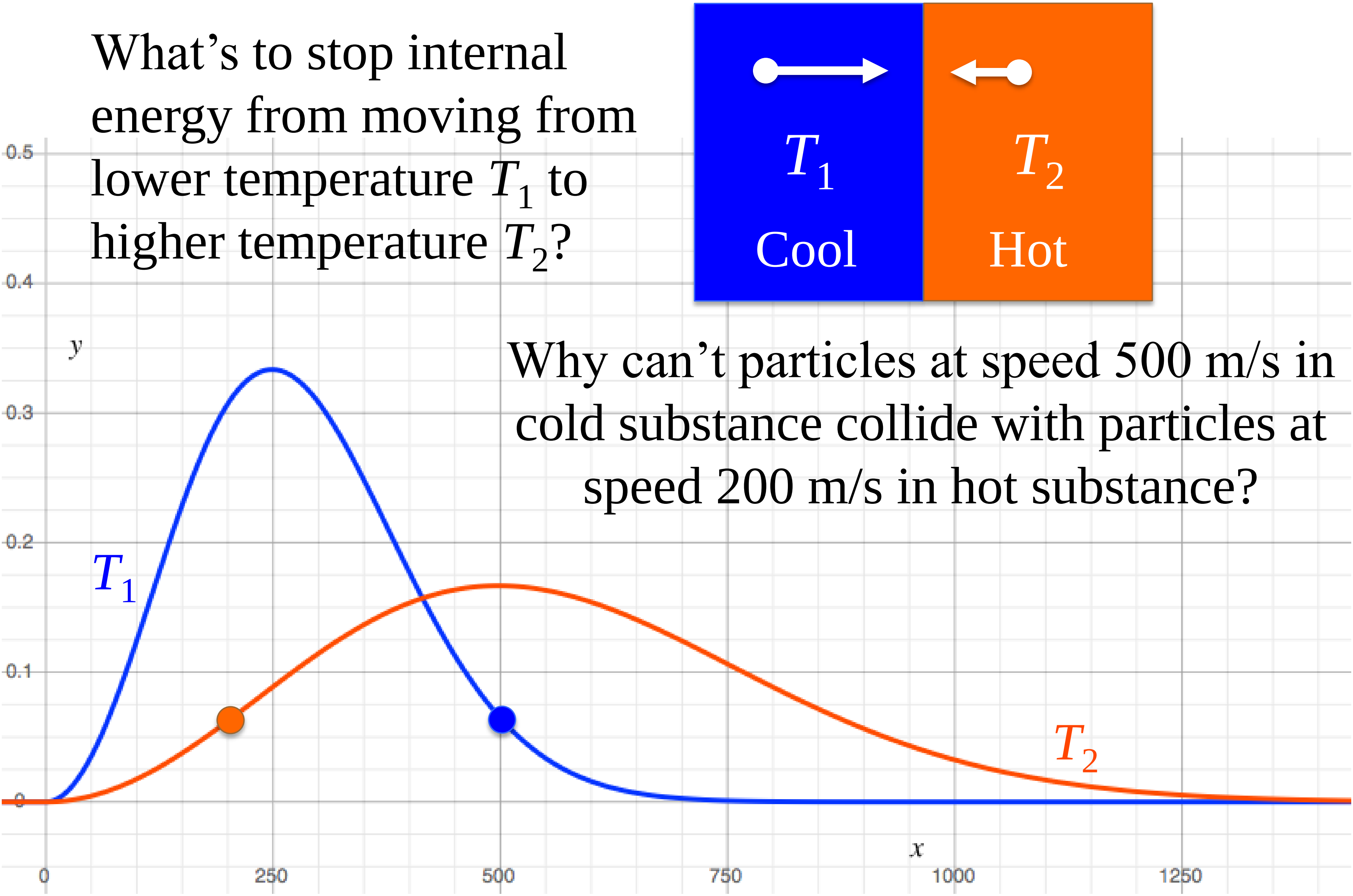
Magic Cycle exceeds Carnot efficiency!



There is no way to create a heat engine that exceeds Carnot efficiency!

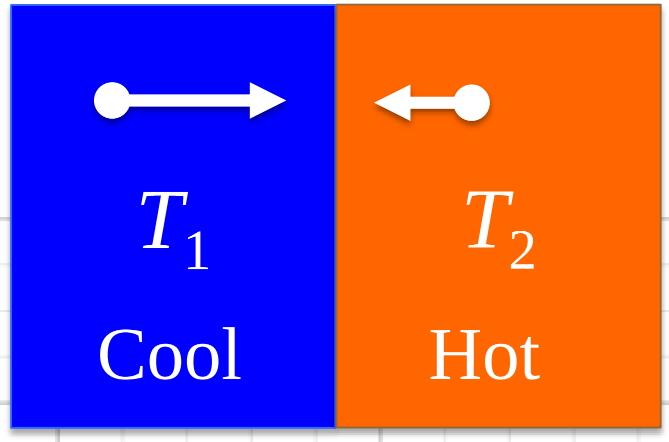
$$eff \ngtr 1 - \frac{T_2}{T_1}$$

image credit: Keta, Wikipedia



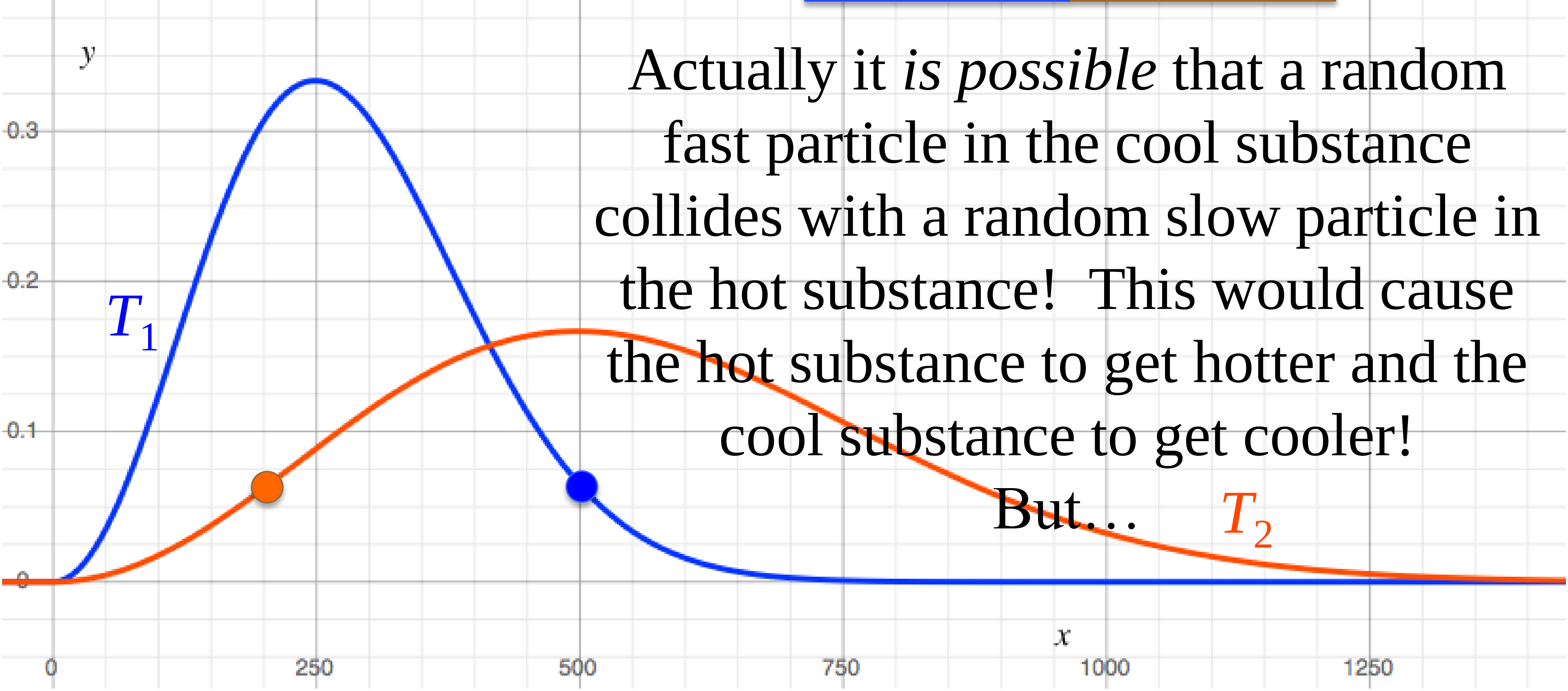
What's to stop internal energy from moving from lower temperature T_1 to higher temperature T_2?
T_1
Cool
T_2
Hot
Why can't particles at speed 500 m/s in cold substance collide with particles at speed 200 m/s in hot substance?
0.5
0.4
0.3
0.2
0.1
0
y
T_1
T_2
x
0
250
500
750
1000
1250
© Matthew W. Milligan

What's to stop internal energy from moving from lower temperature T_1 to higher temperature T_2?



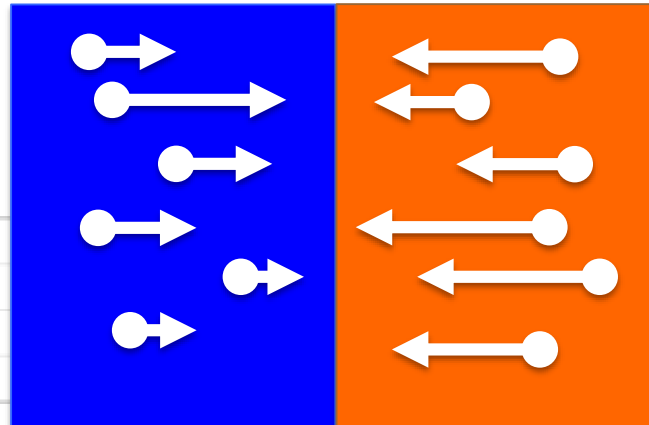
Actually it *is possible* that a random fast particle in the cool substance collides with a random slow particle in the hot substance! This would cause the hot substance to get hotter and the cool substance to get cooler!

But…

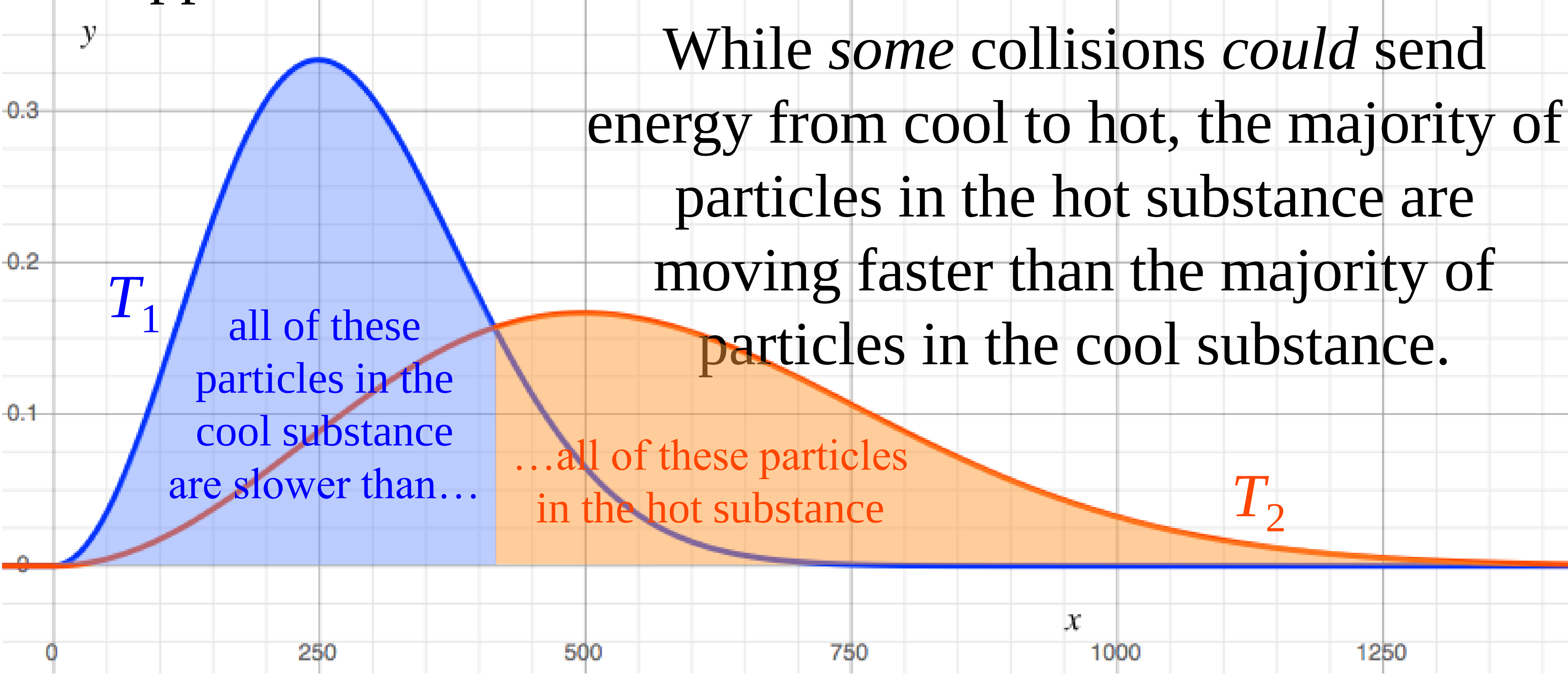


2nd Law Viewed in Terms of Statistics:

It is a statistical certainty that collisions transferring energy from hot to cold will far outnumber collisions doing the opposite!



While *some* collisions *could* send energy from cool to hot, the majority of particles in the hot substance are moving faster than the majority of particles in the cool substance.



Fate of the Universe (?!)

- There is lots of stuff in the universe – some at high temperature, some at low temperature. Over time, heat will flow…? The hot stuff will…? The cold stuff will…?
- For work to be done there must be a temperature differential. When materials are at the same temperature there is thermal equilibrium. If *everything* were at the same temperature then…?
- By the laws of thermodynamics, given enough passage of time (a lot), the fate of the universe is…

Fate of the Universe (?!)

- There is lots of stuff in the universe – some at high temperature, some at low temperature. But over time the hot stuff cools and the cool stuff heats until everything in the universe is at the same temperature.
- For work to be done there must be a temperature differential. Once everything in the universe is the same temperature no work can be done and nothing happens anywhere in the universe.
- By the laws of thermodynamics, given enough passage of time (a lot), the fate is "heat death" – the universe becomes a static, randomized, collection of matter that is all at the same temperature – energy is all around, but none is "available" and so nothing occurs.

Quality of Energy

- Energy is always conserved in one form or another.
- However, the laws of thermodynamics allow us to conclude the availability of energy to use for some practical purpose is dependent on temperature differences.
- As temperatures tend to level out it can be said that the "availability" of energy is decreasing.
- The increase of entropy means that energy is "degraded" as the order of the universe decreases and energy is dissipated into more average and uniform and random forms.