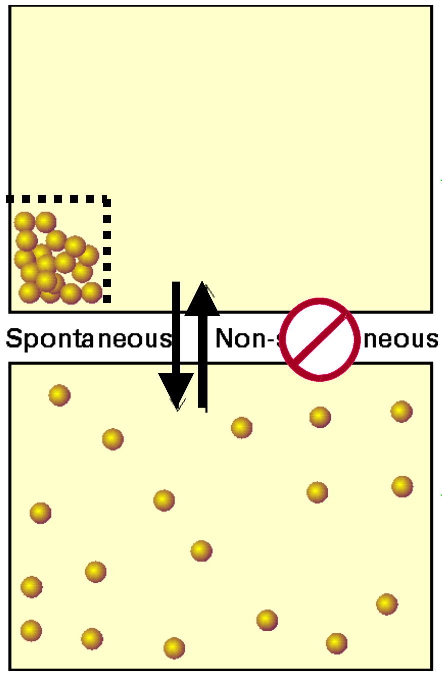
What about an isolated system? $\Rightarrow \Delta S_{Sys} \geq 0$!

A gas will not spontaneously compress



only 0.1 x volume

$W_2 = (0.10)^{18} = 10^{-18}$

1 x volume

# of molecules

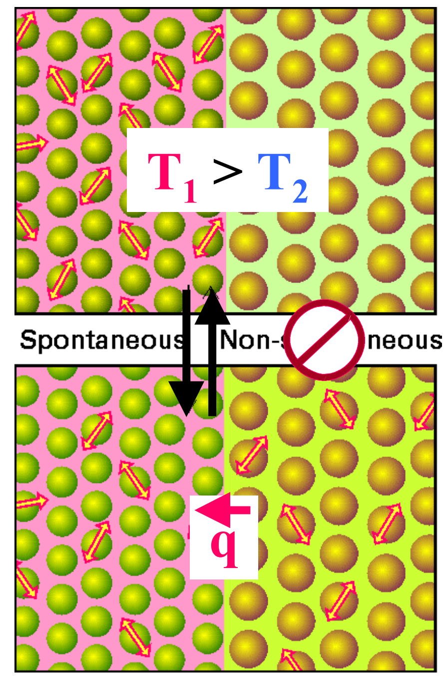
$W_1 = (1)^{18} = 1$

$\Delta S = S_2 - S_1 = k\,(\ln W_2 - \ln W_1)$
$= -39\ k$

in a truly macroscopic system $N \approx 10^{23}$

Matter and energy tend to become disordered

Heat will not spontaneously flow from a cooler to a warmer object



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

$\Delta S_2 = \frac{-q}{T_2}$

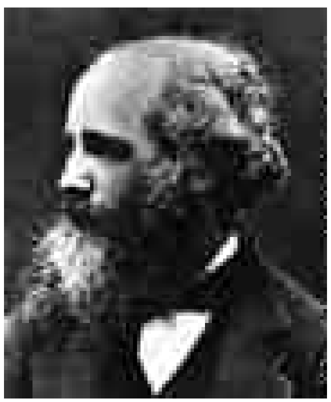
$$\Delta S_{Sys} = \Delta S_1 + \Delta S_2 = \frac{q}{T_1} + \frac{-q}{T_2} = q\left(\frac{T_2 - T_1}{T_1 T_2}\right) < 0$$

$\Delta S_{Sys} < 0$ would violate the 2nd law
$\Rightarrow$ it will not happen

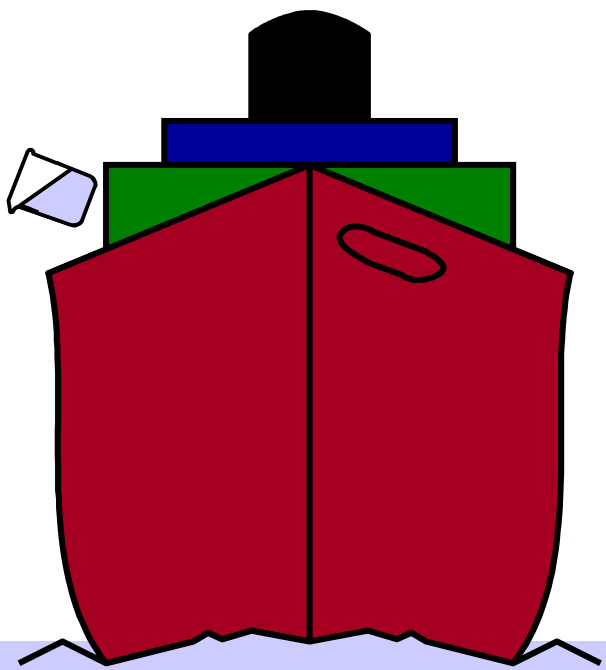
What other examples for the second law of thermodynamics are there in daily life?

“The second law of thermodynamics has as much truth as saying that, if you poured a glass of water into the ocean, it would not be possible to get the same glass of water back again”

James Clerk Maxwell (1831-1879)



Kinetic theory of gases (Maxwell-Boltzmann distribution of velocities) ⇒ heat = thermal motion of particles; Also: theories of electricity and magnetism



The variation of entropy with temperature

$$dS_{Sys} = \frac{dq_{rev}}{T}$$

small change

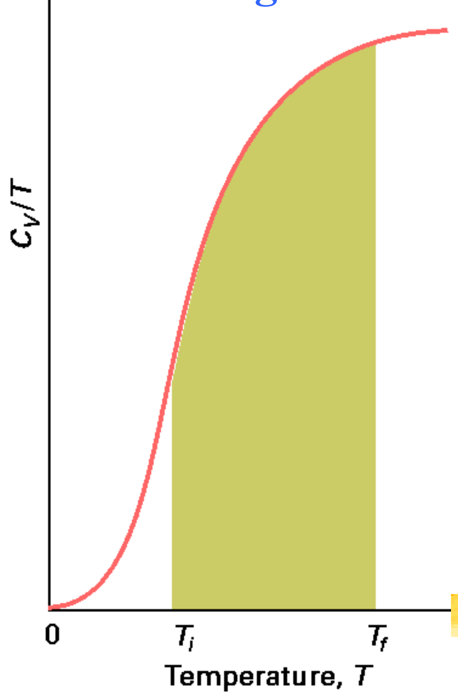
@ constant volume: $dq_v = C_v\, dT$

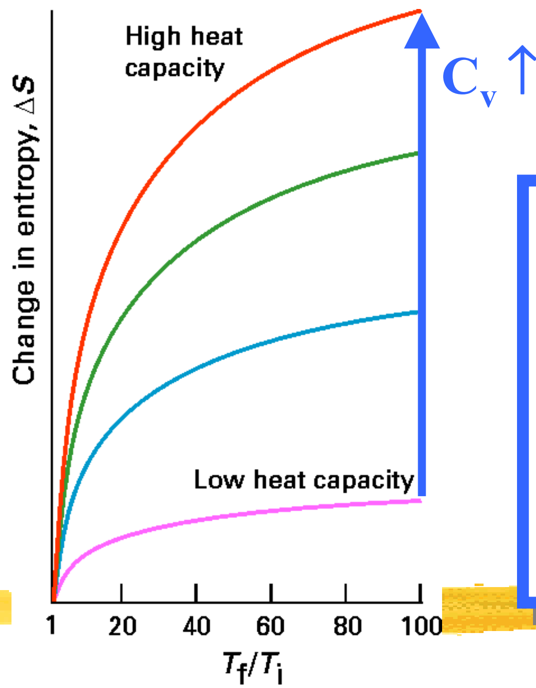
$$\Rightarrow \quad dS_{Sys} = \frac{C_v dT}{T} \qquad \Rightarrow \Delta S_{Sys} = \int_{T_i}^{T_f} \frac{C_v dT}{T} = C_v \int_{T_i}^{T_f} \frac{dT}{T} = C_v \ln\left(\frac{T_f}{T_i}\right)$$

≈ constant heat capacity

$T_f > T_i \Rightarrow S \uparrow$

ΔS = integral under C_v/T

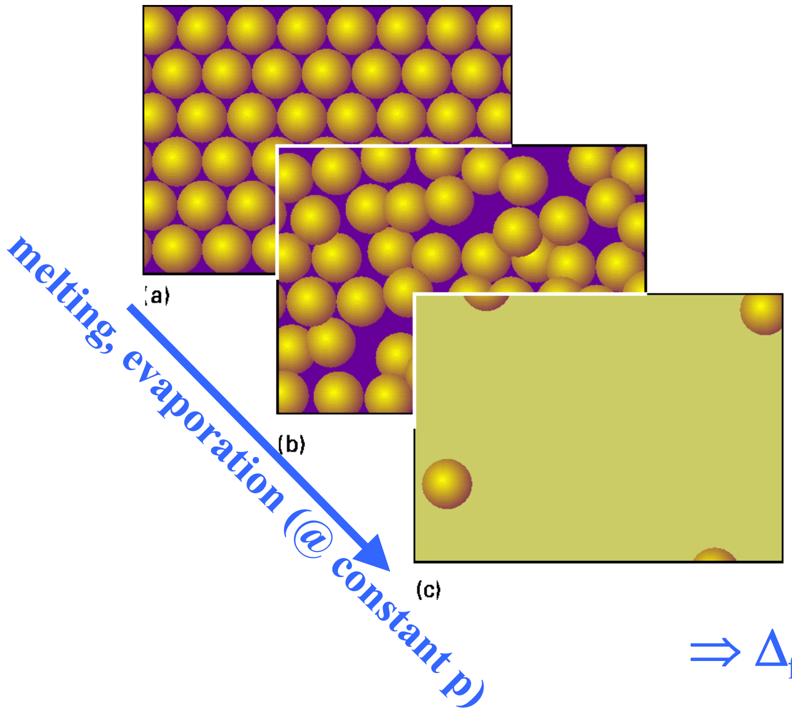




@ constant pressure: $dq_p = C_p\, dT$

$$\Delta S_{Sys} = C_p \ln\left(\frac{T_f}{T_i}\right)$$

Fusion and boiling entropies



Melting is in equilibrium at T_{fus}:
$q_{rev} = \Delta_{fus}H$

$$\Rightarrow \quad \Delta_{fus}S = \frac{\Delta_{fus}H}{T_{fus}}$$

entropy of fusion (per mole)

For ice: $\Delta_{fus}H = 6.01\ \text{kJ mol}^{-1}$ (1 bar, 0°C)

$\Rightarrow \Delta_{fus}S = (6.01\ \text{kJ mol}^{-1})/273.15\ \text{K} = +\ 22\ \text{J mol}^{-1}\ \text{K}^{-1}$

Trouton's rule: $\Delta_{vap}H/T \approx 85\ \text{J mol}^{-1}\ \text{K}^{-1}$

Table 4.1 *Entropies of vaporization at 1 atm and the normal boiling point*

	$\Delta_{vap}S/(\text{J K}^{-1}\ \text{mol}^{-1})$
Bromine, Br_2	88.6
Benzene, C_6H_6	87.2
Carbon tetrachloride, CCl_4	85.9
Cyclohexane, C_6H_{12}	85.1
Hydrogen sulfide, H_2S	87.9
Ammonia, NH_3	97.4
Water, H_2O	109.1
Mercury	94.2

$$\Delta_{vap}S = \frac{\Delta_{vap}H}{T_{vap}}$$

entropy of vaporization (per mole)

For water: $\Delta_{vap}H = 40.7\ \text{kJ mol}^{-1}$ (1 bar, 100°C)

$\Rightarrow \Delta_{vap}S = (40.7\ \text{kJ mol}^{-1})/373.15\ \text{K} = +\ 109\ \text{J mol}^{-1}\ \text{K}^{-1}$

When will a chemical reaction occur spontaneously?

Endothermic, exothermic and energy neutral processes all may occur spontaneously

$\Rightarrow \Delta H_{Sys}$ and ΔU_{Sys} do not control spontaneity!

Second Law: $\Delta S_{Universe} = \Delta S_{System} + \Delta S_{Surroundings} \geq 0$

A reaction is spontaneous if $\Delta S_{Univ} > 0$

In a chemical reaction: $\Delta S_{Sys} = \Delta_r S$

Heat absorbed or released from system (typically @ constant p)

$$\Delta S_{Surr} = -\frac{q_{Sys}}{T} = -\frac{\Delta_r H}{T}$$

$$\Delta S_{Univ} = \Delta_r S - \frac{\Delta_r H}{T} \geq 0$$

A reaction is spontaneous if and only if:

$$\Delta_r S > \frac{\Delta_r H}{T}$$

Enthalpy	Entropy	Exothermic?	Spontaneous?
$\Delta_r H > 0$	$\Delta_r S < 0$	Endothermic *"heat required"*	NO $\Delta S_{Univ} < 0$
$\Delta_r H < 0$	$\Delta_r S > 0$	Exothermic *"heat released"*	YES $\Delta S_{Univ} > 0$
$\Delta_r H > 0$	$\Delta_r S > 0$	Endothermic *"heat required"*	IF $\Delta_r S > \frac{\Delta_r H}{T}$ *Entropy Driven*
$\Delta_r H < 0$	$\Delta_r S < 0$	Exothermic *"heat released"*	IF $\frac{-\Delta_r H}{T} > -\Delta_r S$ *Enthalpy Driven*

Energy must be conserved

First Law

But ...

$$\Delta S_{Univ} = \Delta_r S - \frac{\Delta_r H}{T} \geq 0$$

Entropy Rules!

Second Law

Sample problem:

A typical resting person generates about 100 W in heat. Estimate the entropy they generate in the surroundings in the course of a day at 20^{o}C!