Thermodynamics of Earth systems

Lecture 4:
Entropy, the Second Law of Thermodynamics

Material covered in Lecture 4

Conclusion of Part 1: Introduction

- Hydrostatic equation: application to ocean and hypothetical constant density atmosphere; solid earth
- Hypsometric equation (atmosphere)

Part 2: Framework

First Law of thermodynamics

- Basic concepts & processes
- Work; expansion work
- Heat: heat capacity, basics of heat transfer mechanisms
- First law: internal energy, enthalpy, specific heats, heat capacity.
- Applications of first law to ideal gases

Entropy and the 2nd law

- Entropy: reversible and irreversible processes; Boltzmann-Gibbs statistical picture of entropy; Clausius inequality
- Heat engines
- 2nd Law of thermodynamics

Heat engine

device which extracts work as thermal energy flows from a hot reservoir to a cold reservoir.

- external combustion engines

  (e.g. steam or Stirling engine)

- internal combustion engine

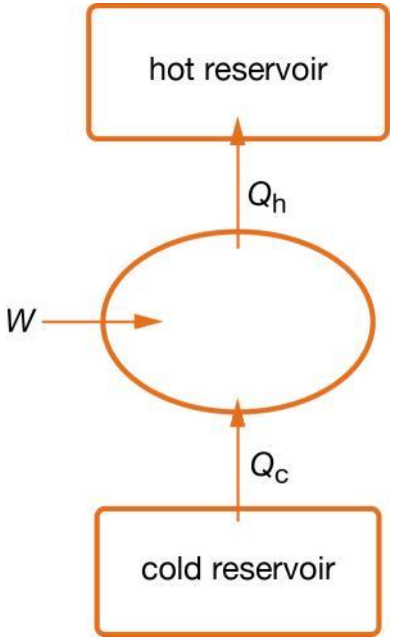
  (e.g. petrol or diesel engine, jet engine)

- refrigerators

- Clouds and weather systems

  (convective clouds, hurricanes)

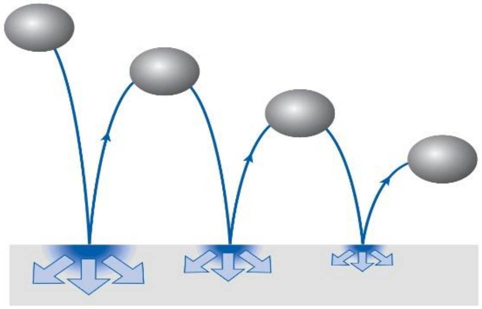
- Many other types

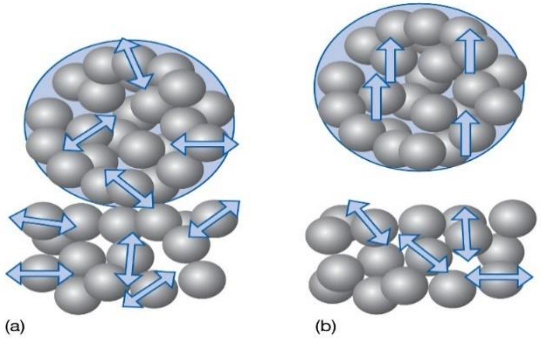


Spontaneity of processes

Some processes occurs **spontaneously** in the direction of change and need no work to occur.

- A gas expands to fill the available volume.
- A ball bouncing on the floor.
- A hot body cools to the temperature of its surroundings.
- A chemical reaction runs in one direction rather than another.





Internal energy (1st law) lets us see whether a change is *permissible*. But it cannot tell us about things being *spontaneous*. For that we need a property called entropy.

Spontaneity of processes

In general, product-favored reactions are exothermic.

E.g. thermite reaction

$Fe_2O_3(s) + 2\ Al(s)$

$\rightarrow 2\ Fe(s) + Al_2O_3(s)$

$\Delta H = -848\ kJ$

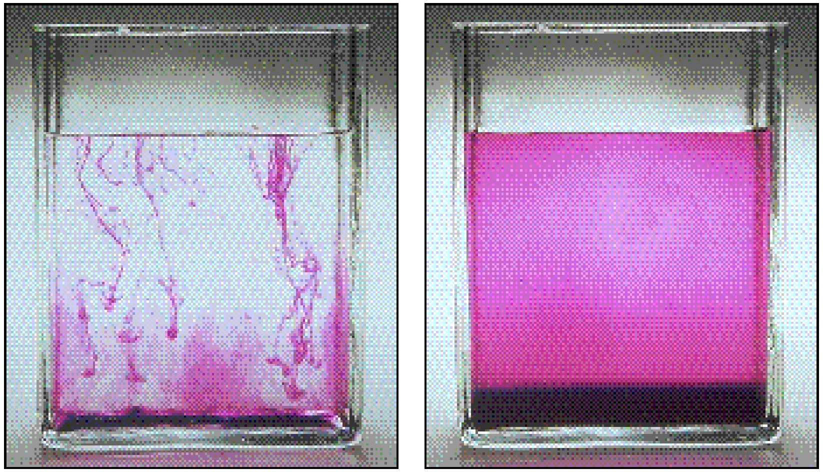
Spontaneity of processes

But many <u>spontaneous</u> reactions or processes are endothermic . . .

$$NH_4NO_3(s) + \text{heat} \rightarrow NH_4^+(aq) + NO_3^-(aq)$$

$$\Delta H_{sol} = +25.7 \text{ kJ/mol}$$

or have $\Delta H = 0$ . . .



Internal energy (1st law) lets us see whether a change is *permissible*. But it cannot tell us about things being *spontaneous*. For that we need a property called entropy.

Entropy of a system, S

S is a measure of the disorder of its matter and energy.

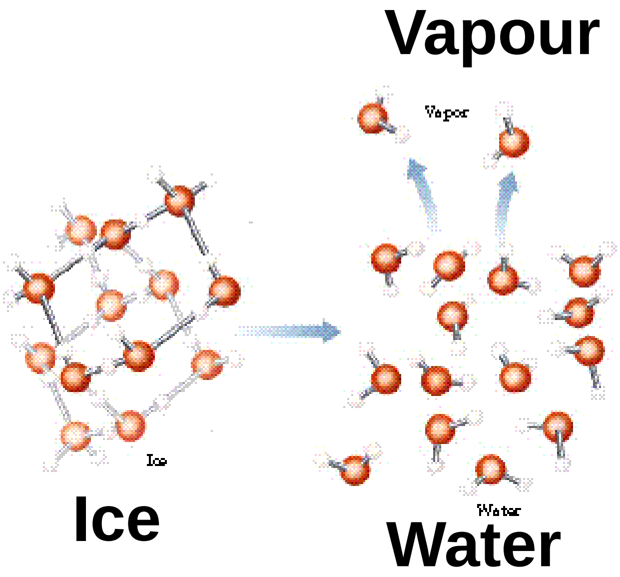
A gas has high entropy, crystal has low entropy.

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

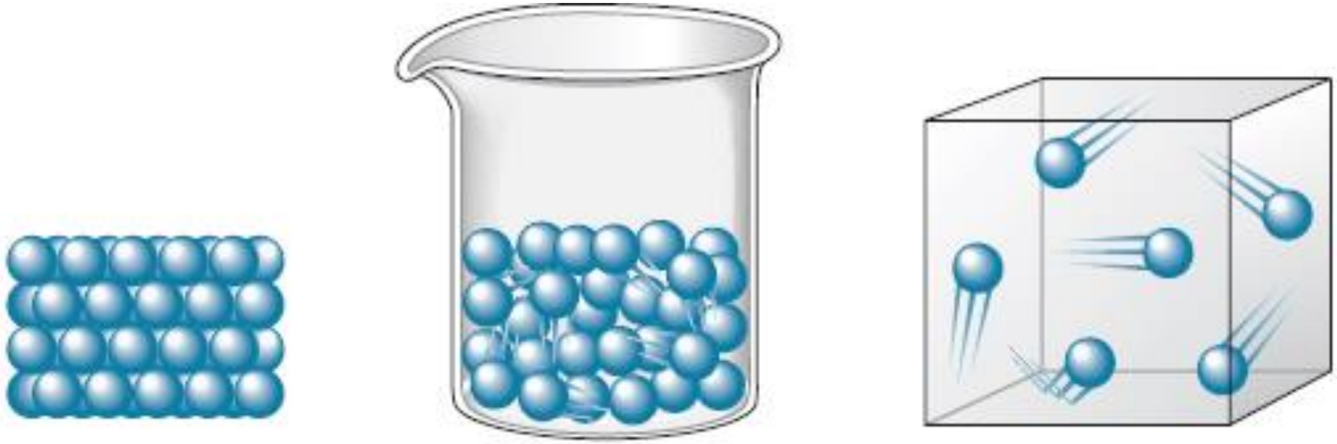
Entropy is the thermodynamic property that emerges from heat, just like pressure emerges from work (see lecture notes).

Spontaneous processes are those for which the disorder (entropy) tends to increase – this is what the second law is all about.

Entropy and Phase State



	S^o (J/K•mol)
H_2O(gas)	188.8
H_2O(liq)	69.9
H_2O (s)	47.9



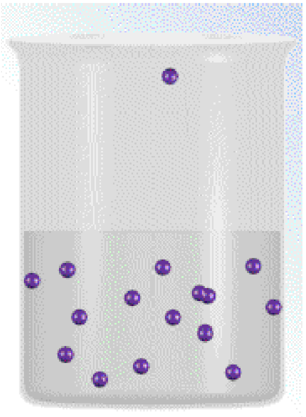
S (gases) > S (liquids) > S (solids)

Entropy Change in a Phase Change

For a phase change,

$$\Delta S = q/T$$

where q = heat transferred in phase change



$$\mathbf{H_2O\ (liq)} \rightarrow \mathbf{H_2O(g)}$$

For vaporization of water:

$$\Delta H = q = +40{,}700\ \text{J/mol}$$

$$\boxed{\Delta S = \frac{q}{T} = \frac{40{,}700\ \text{J/mol}}{373.15\ \text{K}} = +109\ \text{J/K} \bullet \text{mol}}$$

Entropy: Temperature and complexity

Increase in molecular complexity generally leads to increase in S.

	S^o (J/K•mol)
CH_4	248.2
C_2H_6	336.1
C_3H_8	419.4

The entropy of a substance increases with temperature.

Higher T means :
- **more randomness**
- **larger S**

- Entropy changes in the surrounding primarily determined by heat flow
- Magnitude of entropy is dependent on the temperature
- The lower the temperature, the higher the impact to the surroundings of the transfer of energy

Second Law of Thermodynamics

- "In any spontaneous process there is always an increase in the entropy of the universe"
- "The entropy of the universe is increasing"
- For a given change to be spontaneous, $\Delta S_{\text{universe}}$ must be positive

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

Application: Calculating ΔS(universe)

$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(liq)$

$\Delta S^o_{system} = -326.9\ J/K$

$$\Delta S^o_{surroundings} = \frac{q_{surroundings}}{T} = \frac{-\Delta H^o_{system}}{T}$$

Can calculate that $\Delta H^o_{rxn} = \Delta H^o_{system} = -571.7\ kJ$

$$\Delta S^o_{surroundings} = \frac{-(-571.7\,kJ)(1000\,J/kJ)}{298.15\,K}$$

$$\Delta S^o_{surroundings} = +1917\ J/K$$

Calculating ΔS(universe)

$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(liq)$

ΔS^o_{system} = -326.9 J/K (less matter dispersal)

$\Delta S^o_{surroundings}$ = +1917 J/K (more energy dispersal)

$\Delta S^o_{universe}$ = +1590 J/K

The entropy of the universe increases so the reaction is spontaneous.

Second law: other forms

Can be stated various ways:

(Kelvin): ‘No cyclic process is possible in which heat is taken from a hot source and converted completely into work.’ (e.g. engine)

(Clausius): ‘Heat cannot pass from a body at low temperature to one at higher temperature without work being done.’ (e.g. refrigerator)