Chem 123 (section 201)
Lecture 6 (Jan. 16)

Announcement and reminder

- Clicker Quiz #2 is available and due Monday Jan. 19! Input of your answers will be done in class and requires the use of clicker

- Clicker Quiz #2 covers materials on the first law of thermodynamics, enthalpy, Hess’s law and reaction enthalpy

- New reading assignment is posted

Chapter 7 and Chapter 8

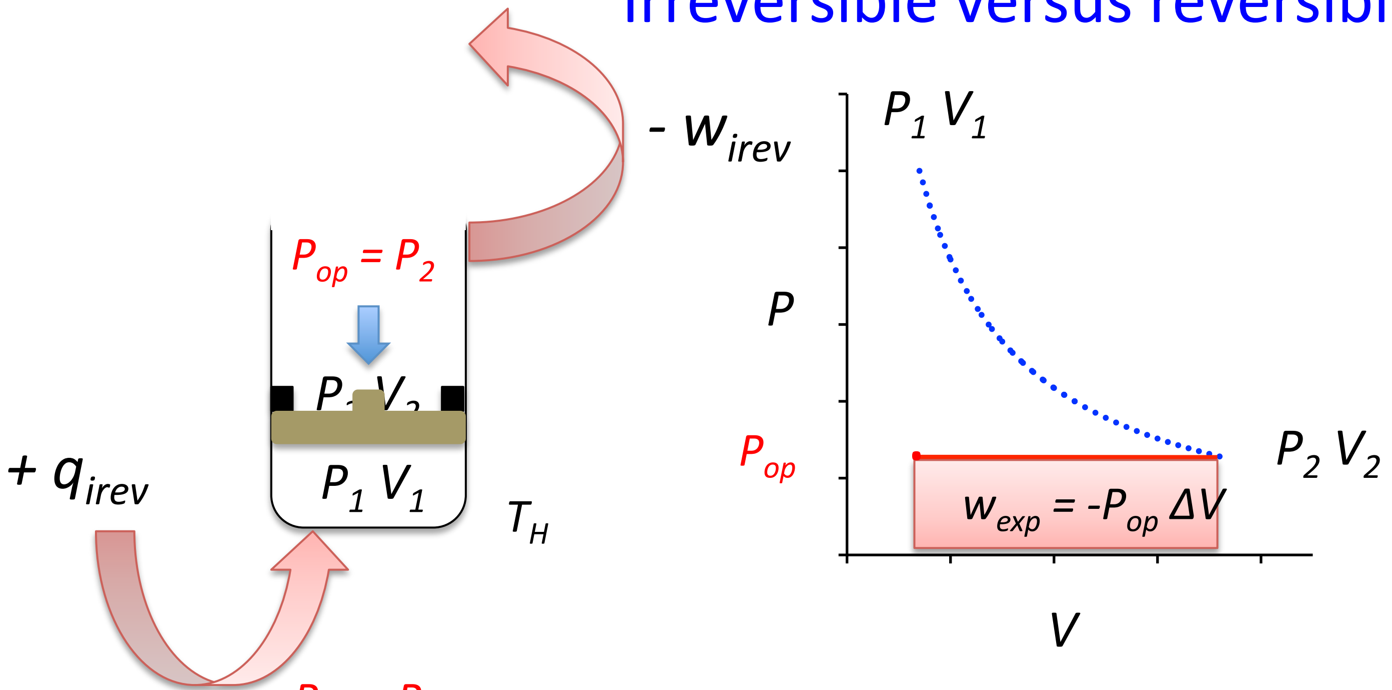
(p95-96, 116-120)

Learning Objectives

By the end of this section, successful learners will be able to:

- Define a reversible process.
- Define entropy and determine entropy qualitatively and quantitatively for a given reaction or process.
- Define standard molar entropy and the third law of thermodynamics,
- Understand the statistical description of entropy.

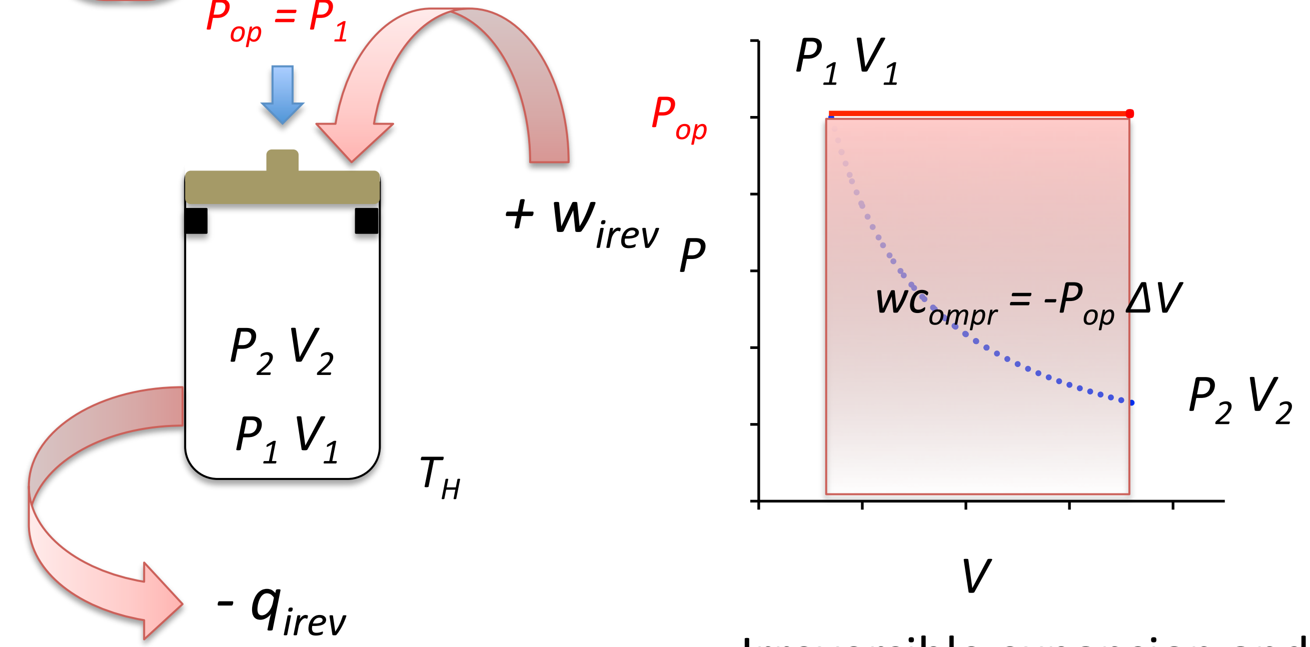
Irreversible versus reversible work



What is the work produced?

What is the sign of this work?

−

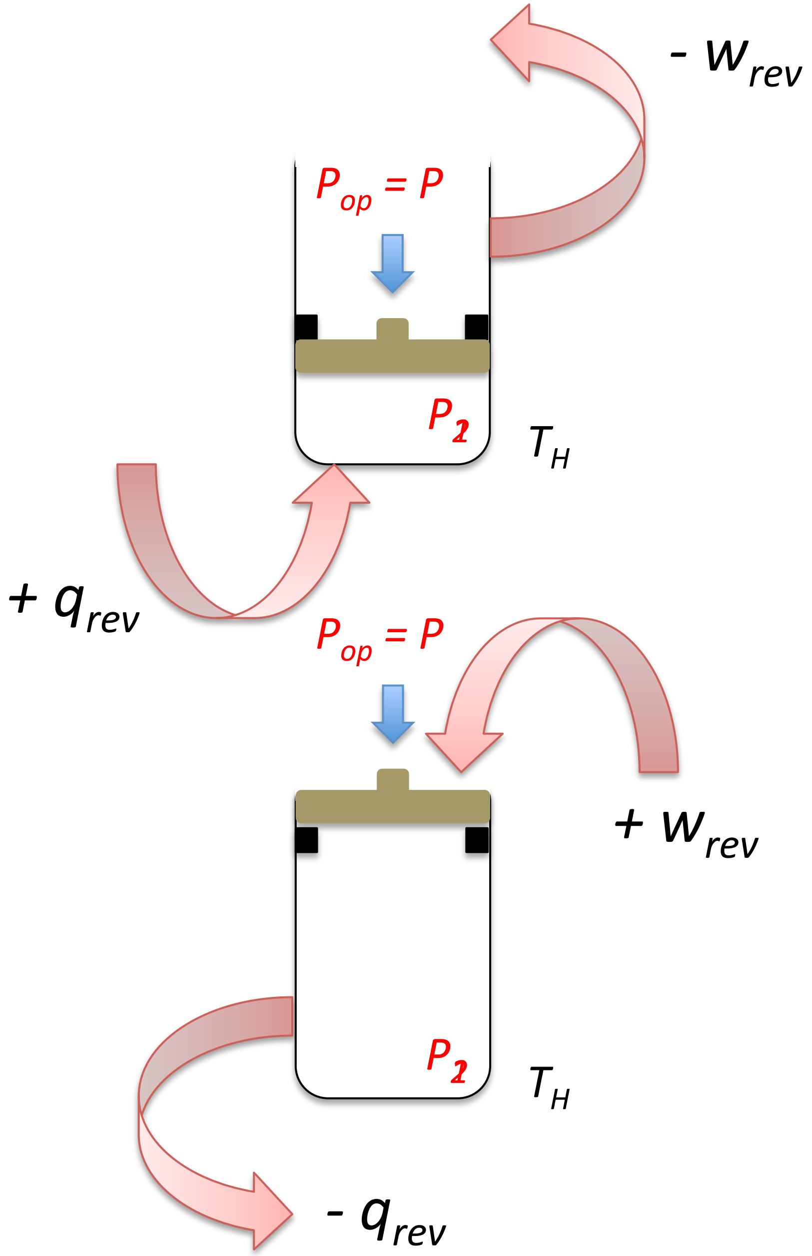


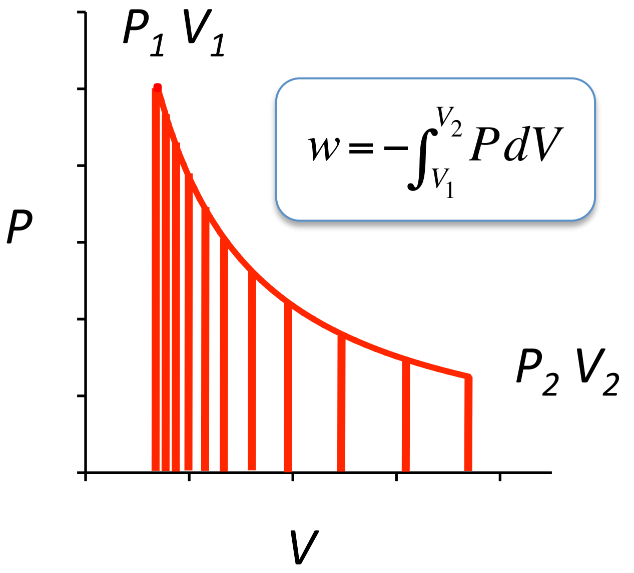
What is the work consumed?

What is the sign of this work?

+

Irreversible expansion and compression



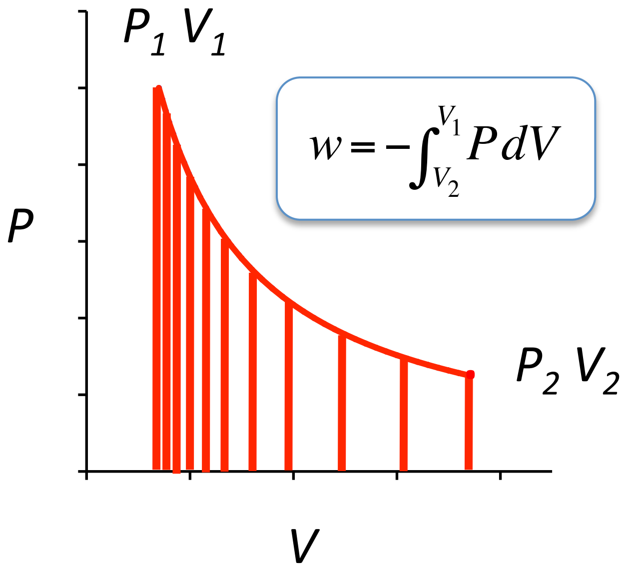


$$w = -\int_{V_1}^{V_2} P\,dV$$

What is the work produced?

What is the sign of this work?

−



$$w = -\int_{V_2}^{V_1} P\,dV$$

What is the work consumed?

What is the sign of this work?

+

Reversible expansion and compression

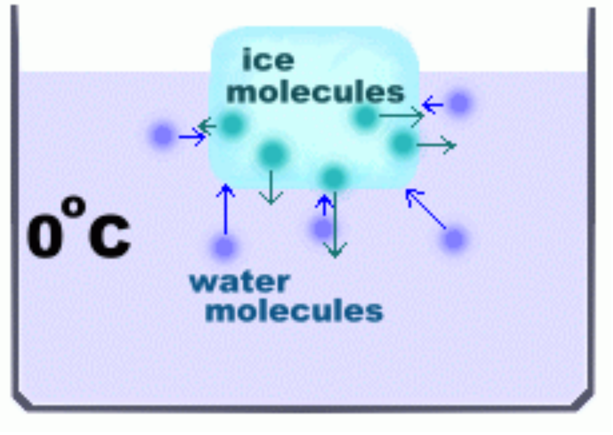
Note:

- Reversible processes do the most work to the surroundings
- Irreversible processes result in the loss of usable work (as heat)

In real life…

- Reversible processes are very very difficult to achieve since they require an infinite number of steps.

- Most processes around us are irreversible, leading to the loss of usable work.



Reversible processes

Ice melting at 1 atm 0 °C
(water freezing)

Water boiling at 1 atm and 100 °C

Thermodynamic definition of Entropy

a) For every system a ***state function*** exists called **Entropy *S***.

$$\boxed{\Delta S = S_2 - S_1 = \frac{q_{rev}}{T}}$$

Entropy: $[S]=[\mathrm{J/K}]$ **(Extensive property)**
Molar entropy: $S_m = S/n$; $[S_m] = [\mathrm{J} / (\mathrm{K \cdot mol})]$

Entropy is a measure of disorder

A change in entropy can be calculated by the energy transferred as heat in a **reversible process** divided by the temperature at which the reversible process occurred.

The Second Law of Thermodynamics

a) For reversible processes holds:

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$$

b) For spontaneous processes holds:

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$

$$\Delta S_{total} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \geq 0$$

For an isolated system (the system does not exchange energy with the surroundings)

$$\Delta S_{total} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = \Delta S_{\text{system}}$$

a) For reversible processes holds:

$$\Delta S_{\text{system}} = 0$$

b) For spontaneous processes holds:

$$\Delta S_{\text{system}} > 0$$

$$\Delta S_{\text{system}} \geq 0$$

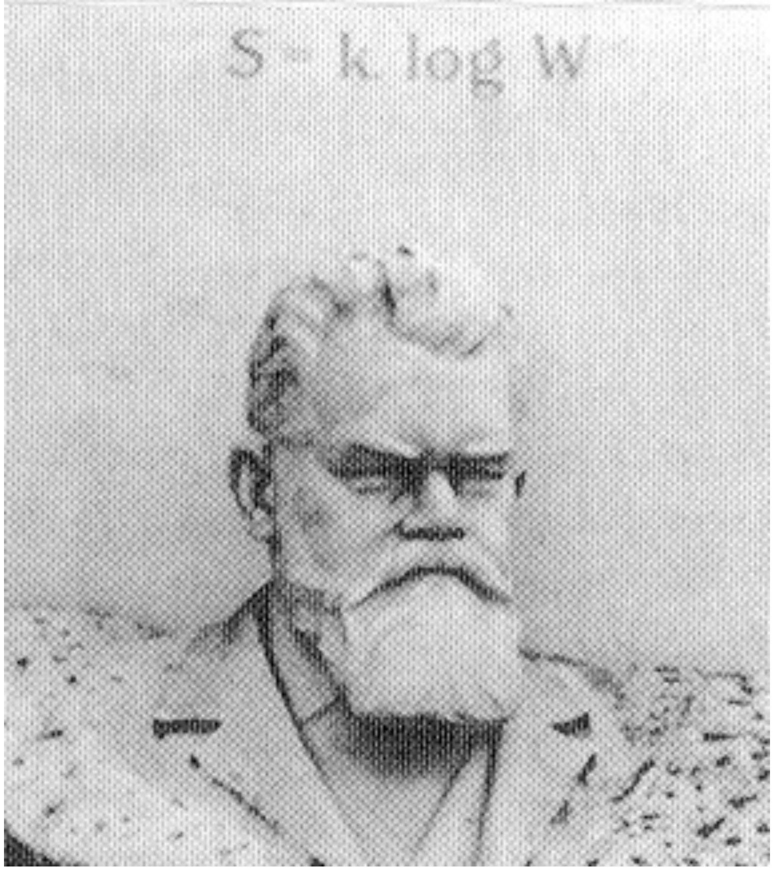
“Entropy is a measure of disorder (numbers of ways to realize a macroscopic state)” -------- related to probability

Low entropy means: “little disorder” “more order” (low probability)

High entropy means: “great disorder” (high probability)

Statistical Thermodynamics Interpretation of Entropy

$$S = k_B \ln W$$

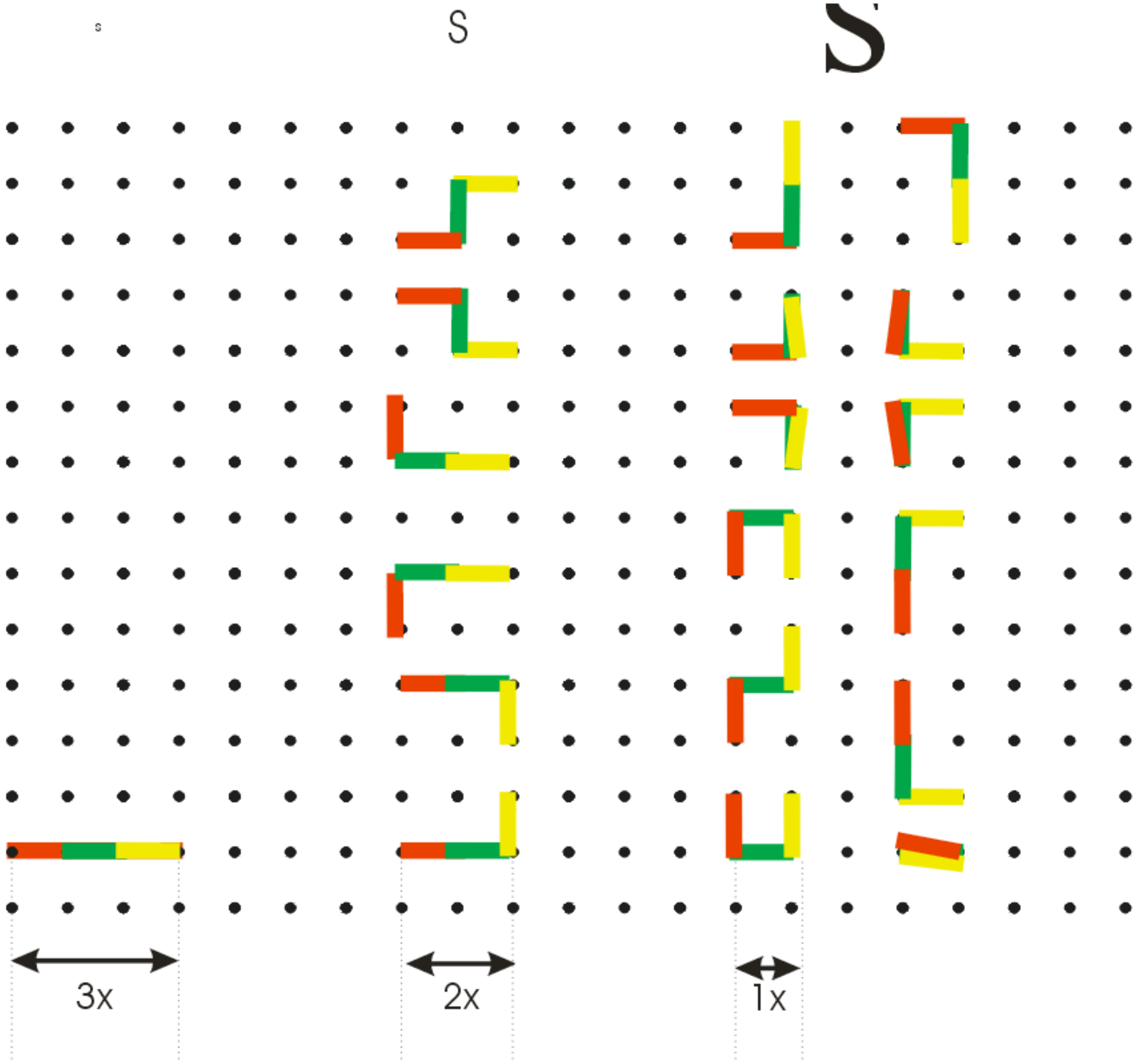


W is the number of microscopic states available to the system for a macroscopic state of given internal energy

k_B is the Boltzmann constant, 1.38×10^{-23} J K^{-1}

Hand	State	Number of Hands that Lead to This State
	Royal flush	4
	“Nothing”	1,302,540

Statistical Mechanics Interpretation of Entropy



$$S = k_B \ln W$$

Austrian physicist who established the relationship between entropy and the statistical analysis of molecular motions

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For an isolated system (the system does not exchange energy with the surroundings)

$$\Delta S_{total} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = \Delta S_{\text{system}}$$

a) For reversible processes holds:

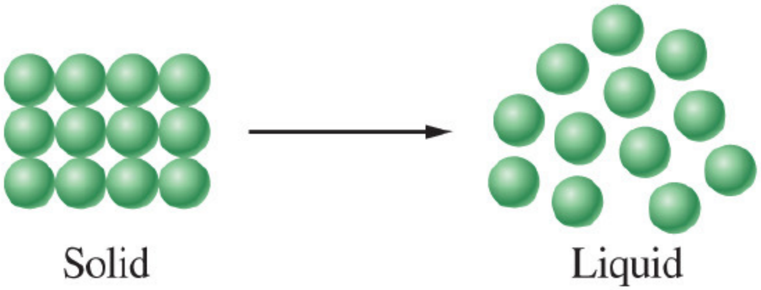
$$\Delta S_{\text{system}} = 0$$

b) For irreversible (spontaneous) processes holds:

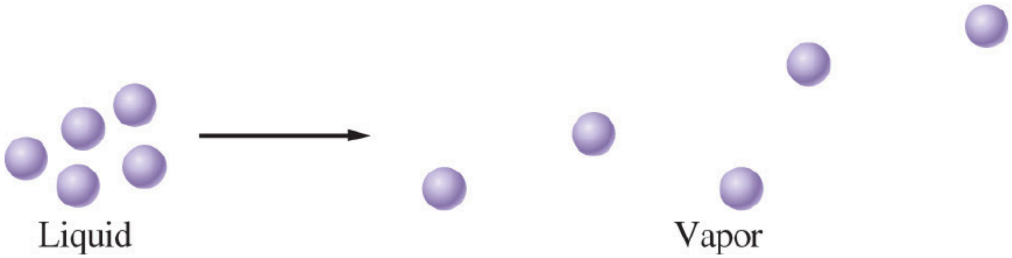
$$\Delta S_{\text{system}} > 0$$

$$\Delta S_{\text{system}} \geq 0$$

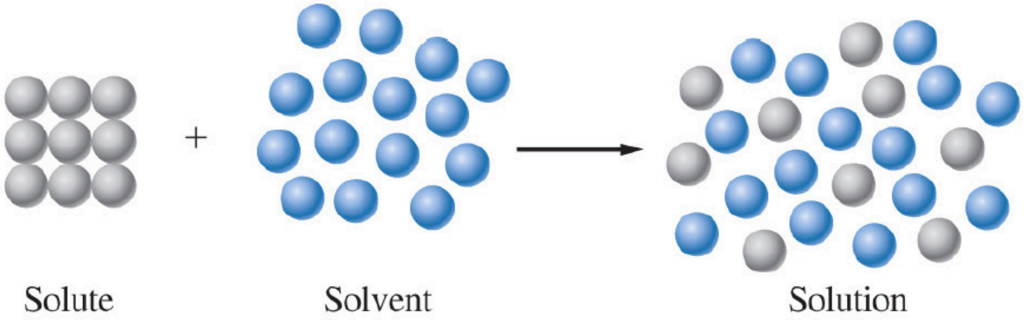
Qualitative entropy change



(a) Melting: $S_{liquid} > S_{solid}$



(b) Vaporization: $S_{vapor} > S_{liquid}$



(c) Dissolving: $S_{soln} > (S_{solvent} + S_{solute})$

1. Increasing number of moles of high entropy species
2. Increasing temperature of a substance
3. Increasing molecular size/complexity

Clicker question 1

Predict whether ΔS is positive or negative for the following process:

$2\ Cl_2O_7\ (g) \rightarrow 2\ Cl_2\ (g) + 7\ O_2\ (g)$

A) Negative
B) Positive
C) Unchanged
D) Not enough information to determine

Clicker question 2

Arrange the following molecules in terms of increasing entropy:
$He(g)$, $H_2O(g)$, $H_2O(l)$, $CaO(s)$

A) $CaO(s) < He < H_2O(g) < H_2O(l)$
B) $CaO(s) < He < H_2O(l) < H_2O(g)$
C) $CaO(s) < H_2O(l) < He < H_2O(g)$
D) $CaO(s) < H_2O(l) < H_2O(g) < He$

The Third Law of Thermodynamics

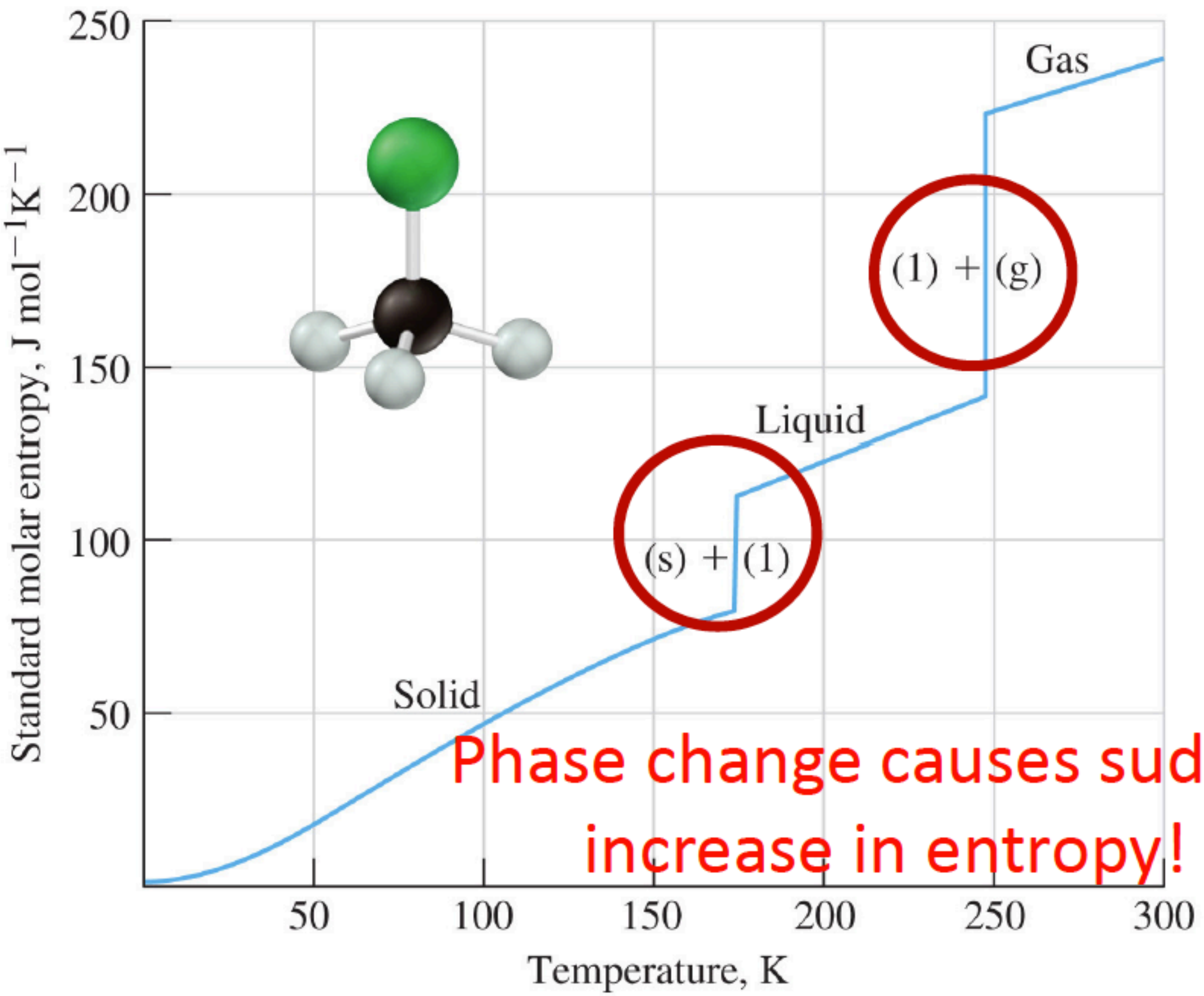
At 0 K all perfect crystals in equilibrium have the same entropy. It is defined as zero

$$S(0\mathrm{K}) = 0$$

“Absolute entropy scale”: tabulated are the standard molar entropies

$$\overline{S}^0$$

At temperatures higher than zero, more different microscopic arrangements become available to the molecules for the same macroscopic state, thus the entropy will be greater than zero.



Phase change causes sudden increase in entropy!

standard molar entropies S°

S° Entropy of one mole of substance under standard state conditions. Units: J K^{-1} mol^{-1}

By default, 298 K

the standard molar entropies are tabulated

$$\boxed{\Delta S^\circ = \sum_{i(products)} \upsilon_i \Delta S^\circ_{298,i} - \sum_{j(react.)} \upsilon_j \Delta S^\circ_{298,j}}$$

ν = Stoichiometric coefficient

S^o = Standard molar entropy

Example

Third Law standard entropies for reactants and products in the combustion of methanol

Example	S°_{298} (J mol^{-1} K^{-1})
$CH_3OH_{(l)}$	126.3
$O_2(g)$	205.1
$CO_{2(g)}$	213.6
$H_2O_{(g)}$	188.7

Find ΔS^0_{298} for the reaction:

$$2CH_3OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 4H_2O_{(g)}$$

$$\boxed{\Delta S^\circ = \sum_{i(products)} \upsilon_i \Delta S^\circ{}_{298,i} - \sum_{j(react.)} \upsilon_j \Delta S^\circ{}_{298,j}}$$

$$\Delta S^\circ = \left[4S^\circ_{H_2O_{(g)}} + 2S^\circ_{CO_{2(g)}} - 2S^\circ_{CH_3OH_{(l)}} - 3S^\circ_{O_{2(g)}}\right] = 314.1 \text{ J K}^{-1}$$