

Module 8: Thermodynamics II, Lecture 2

2nd Law of Thermodynamics and Entropy Change



Learning Objective	Openstax 2e Chapter
2 nd Law of Thermodynamics	<u>16.3</u>
Entropy Change (ΔS)	<u>16.2</u> , <u>16.3</u>

Suggested Practice Problems

[Chapter 16 Exercises](#) – Questions: 3, 5, 15, 17, 19

Answers can be found in the [Chapter 16 Answer Key](#)

Entropy and the 2nd Law of Thermodynamics

Definition: Entropy is a measure of the disorder or randomness of a system. It is a measure of the ‘freedom’ of the system. The more microstates that are accessible in the system, the greater the entropy value.

Second Law of Thermodynamics:

- For a spontaneous process in a closed system, the entropy of the system increases ($\Delta S_{\text{sys}} > 0$).

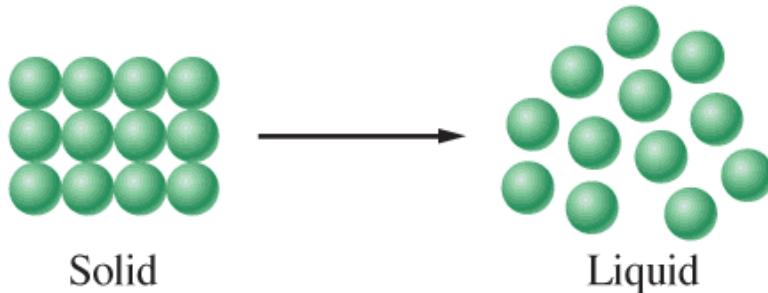
Or more generally

- For any spontaneous process, the entropy of the universe (system+surrounding) must increase. ($\Delta S_{\text{universe}} > 0$)

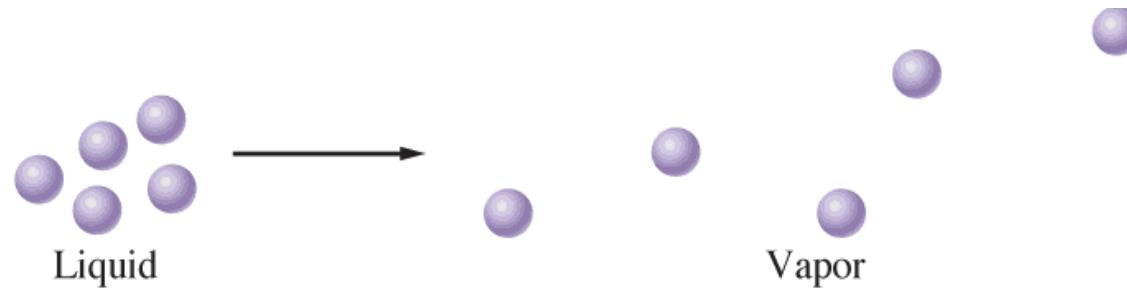
There are spontaneous processes where the entropy of the system decreases ($\Delta S_{\text{sys}} < 0$)

- Make sure to check if the system is closed or open.

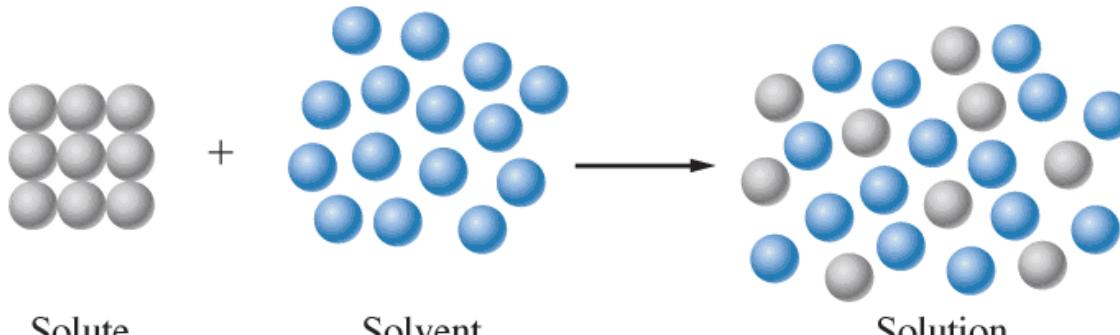
Entropy Change (ΔS): Qualitative Assessment



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



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



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

Entropy Change (ΔS): Qualitative Assessment

Four situations generally produce an increase in entropy:

- Liquids are formed from solids
- Gases are formed from either solids or liquids.
- The temperature of a substance increases.
- The number of molecules increases as a result of a chemical reaction.

Predicting the sign of ΔS of the following reactions:

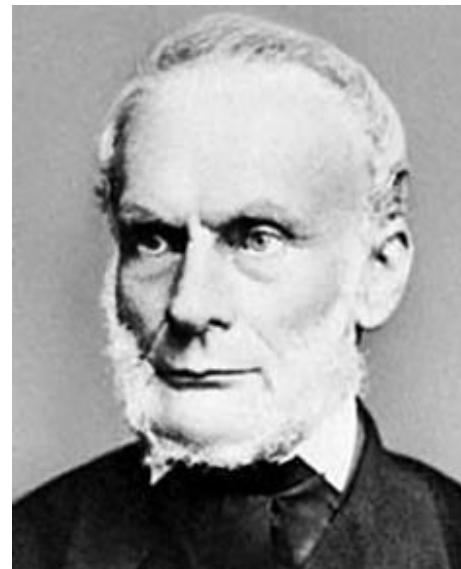


Entropy Change (ΔS)



Ludwig Boltzmann
1844 - 1906

Boltzmann's view of Entropy and
the 2nd Law of Thermodynamics
 $(\Delta S_{\text{universe}} \geq 0)$
is based on statistical mechanics
(probabilities)



Can we measure entropy?

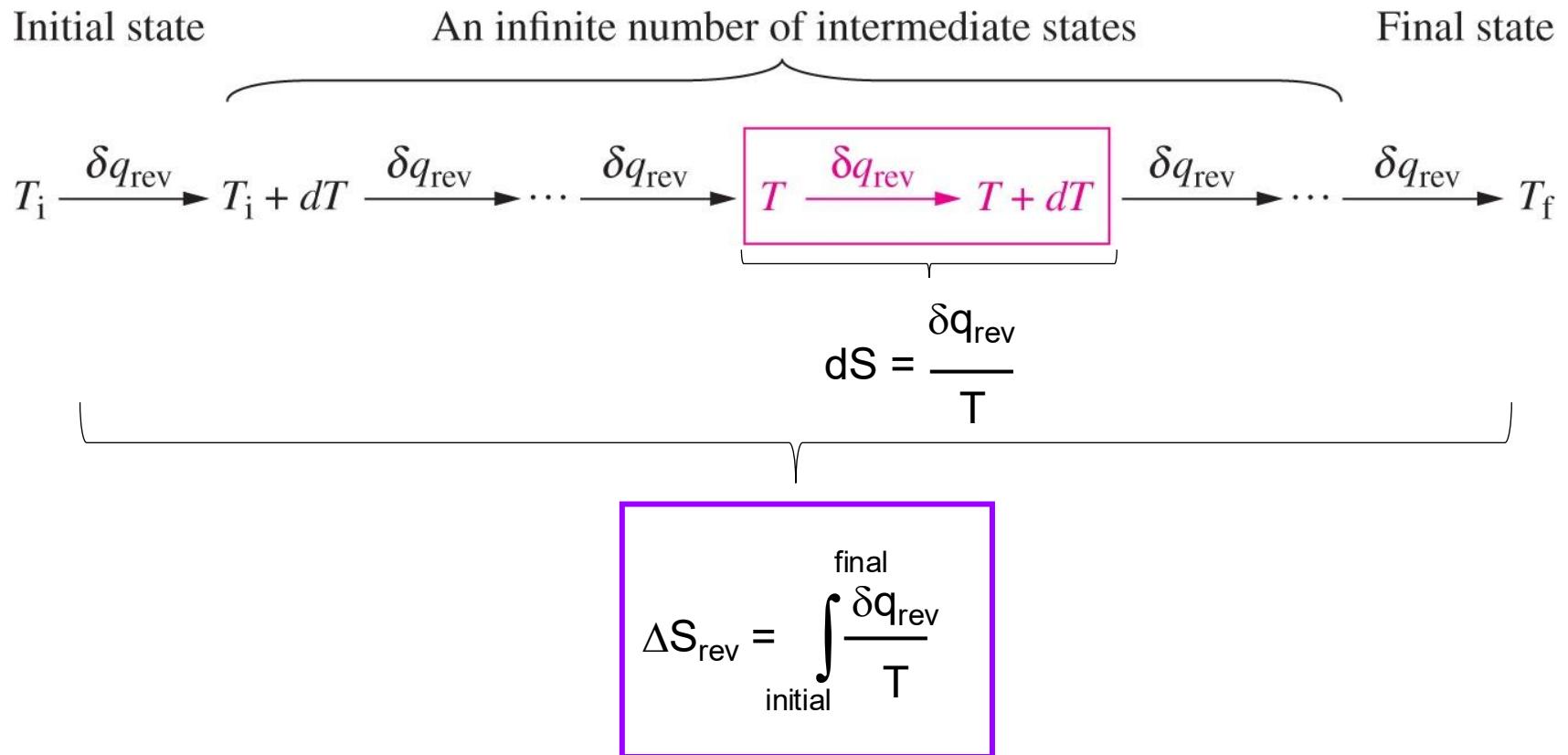
Let's look at Clausius's View for
Quantitative Calculation of Entropy Change

Rudolf Clausius
1822 - 1888

Entropy Change (ΔS): Quantitative Assessment

Entropy is related to heat transfer provided that the heat is transferred in a **reversible manner**.

Temperature can be changed from T_i to T_f in a **reversible** manner as a sum of infinite number of **infinitesimally small** reversible changes of temperature.



Entropy Change (ΔS): Quantitative Assessment

$$\Delta S_{\text{rev}} = \int_{\text{initial}}^{\text{final}} \frac{\delta q_{\text{rev}}}{T}$$

At constant T

At constant P

Phase change
(e.g., melting of ice)

Temperature change
(e.g., heating water)

$$\Delta S = \int_{\text{initial}}^{\text{final}} \frac{\delta q_{\text{rev}}}{T} = \frac{1}{T} \int \delta q_{\text{rev}}$$

Temperature is
constant at T

$$\Delta S = \frac{1}{T} q_{\text{rev}}$$

$$\begin{aligned}\Delta S &= \int_{\text{initial}}^{\text{final}} \frac{\delta q_{\text{rev}}}{T} = \int_{T_i}^{T_f} \frac{C_p dT}{T} = C_p \int_{T_i}^{T_f} \frac{dT}{T} \\ &= C_p \ln \frac{T_f}{T_i}\end{aligned}$$

C_p = Molar heat capacity at
constant pressure, constant over
small temperature range

Entropy Change (ΔS): Quantitative Assessment

EXAMPLE 13-4 Calculating the Entropy Change for Heating Ice Under Constant Pressure

Calculate the entropy change for the following constant pressure process.



The molar heat capacities of ice and water are, respectively, $C_{p,\text{m}} = 37.12 \text{ J mol}^{-1} \text{ K}^{-1}$ and $C_{p,\text{m}} = 75.3 \text{ J mol}^{-1} \text{ K}^{-1}$. The enthalpy of fusion for ice is $\Delta_{\text{fus}}H^\circ = 6.01 \text{ kJ mol}^{-1}$ at 0°C .

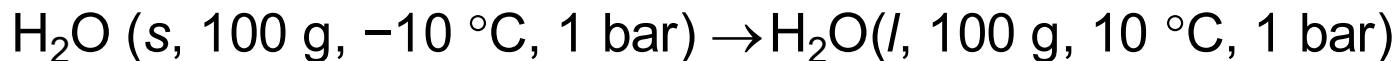
Entropy Change (ΔS): Quantitative Assessment

EXAMPLE 13-4 Calculating the Entropy Change for Heating Ice Under Constant Pressure

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$$C_{p,m, (\text{ice})} = 37.12 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$C_{p,m, (\text{water})} = 75.3 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta H_{\text{fus}}^\circ = 6.01 \text{ kJ mol}^{-1} \text{ at } 0^\circ\text{C}$$

$$-10^\circ\text{C} \rightarrow 10^\circ\text{C}$$

$$\Delta_rS = ?$$



$$\Delta S_2$$



$$\Delta_rS = \Delta S_1 + \Delta S_2 + \Delta S_3$$

Entropy Change (ΔS): Quantitative Assessment

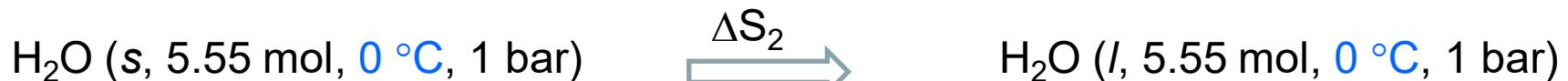
$$n_{(\text{water})} = 100 \text{ g}/18.02 \text{ g mol}^{-1} = \mathbf{5.55 \text{ mol}}$$



T change: 263 K to 273 K

$$\begin{aligned}\Delta S_1 &= n \cdot C_{p,m(\text{ice})} \ln \frac{T_f}{T_i} \\ &= 5.55 \text{ mol} \times 37.12 \text{ J mol}^{-1} \text{ K}^{-1} \ln (273 \text{ K}/263 \text{ K})\end{aligned}$$

$$\Delta S_1 = \mathbf{7.69 \text{ J K}^{-1}}$$



$$\Delta S_2 = \frac{1}{T} q_{rev} = \frac{1}{T_{melting}} n \times \Delta H_{fus}^0$$

$$\Delta S_2 = \frac{1}{273 \text{ K}} (5.55 \text{ mol} \times 6010 \frac{\text{J}}{\text{mol}}) = \mathbf{122 \text{ J K}^{-1}}$$

Entropy Change (ΔS): Quantitative Assessment

$$n_{(\text{water})} = 5.55 \text{ mol} \quad \Delta S_1 = 7.69 \text{ J K}^{-1} \quad \Delta S_2 = 122 \text{ J K}^{-1}$$



T: 273 K to 283 K

$$\begin{aligned}\Delta S_3 &= n \cdot C_{p,m(\text{water})} \ln \frac{T_f}{T_i} \\ &= 5.55 \text{ mol} \times 75.3 \text{ J mol}^{-1} \text{ K}^{-1} \ln (283 \text{ K}/273 \text{ K}) = \mathbf{15.0 \text{ J K}^{-1}}\end{aligned}$$

$$\begin{aligned}\Delta S_r &= \Delta S_1 + \Delta S_2 + \Delta S_3 \\ &= (7.69 + 122 + 15.0) \text{ J K}^{-1} = \mathbf{145 \text{ J K}^{-1}}\end{aligned}$$