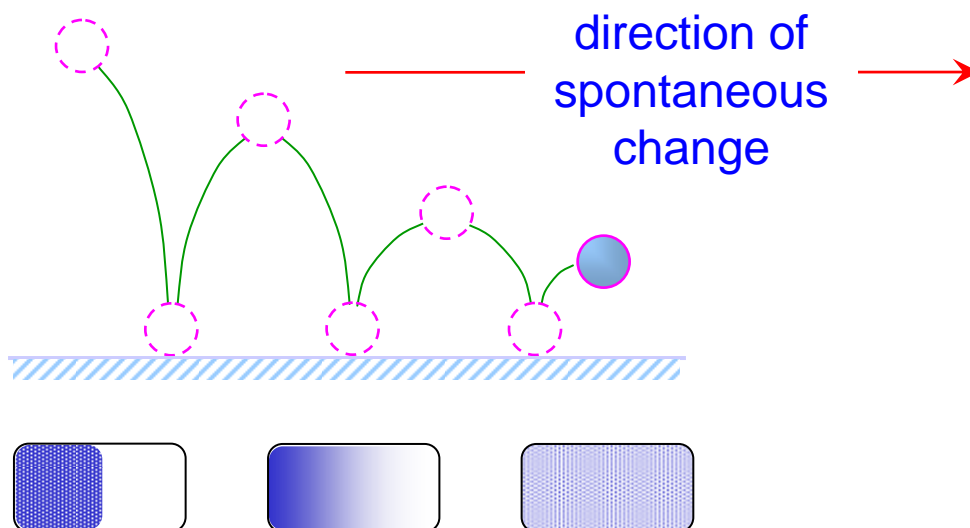


Spontaneous Change

Who needs entropy, anyway?



The direction of spontaneous change is that which

- leads to chaotic dispersal of the total energy
- moves from a state of low intrinsic probability towards one of greater probability.

Work is needed to reverse a spontaneous process.

We need a quantity – **entropy** – to describe energy dispersal, i.e. the probability of a state.

Spontaneous processes are irreversible.

They “generate” entropy

Reversible processes do not generate entropy – **but they may transfer it from one part of the universe to another.**

Entropy 1

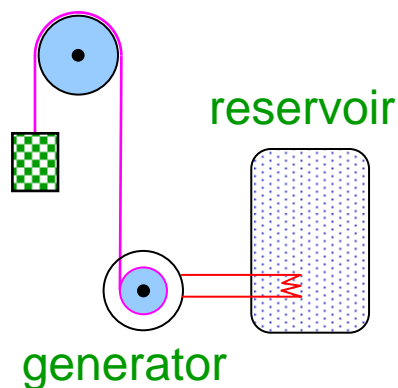
- ❖ Entropy is a state variable (property) which determines if a state is accessible from another by a spontaneous change.
- ❖ Entropy is a measure of chaotic dispersal of energy.
- ❖ The natural tendency of spontaneous change is towards states of higher entropy.
- ❖ There are both thermodynamic (how much heat is produced?) and statistical definitions (how probable is a state?). They both become equivalent when statistics is applied to a large number of molecules.

Consider a falling weight which drives a generator and thus results in heat q being added to the reservoir (the surroundings).

Define a system variable S

$$dS(\text{surr}) = -\delta q / T$$

Use stored energy to restore the weight to its original height. The reservoir gives up δq_{rev} to the system, and there is no overall change in the universe.



$$dS(\text{sys}) = -dS(\text{surr}) = \frac{\delta q_{\text{rev}}}{T}$$

Entropy 2

In general, $dS(\text{sys}) + dS(\text{surr}) \geq 0$
 $dS(\text{sys}) \geq -dS(\text{surr})$

Equality for reversible processes only

or, for the system, $dS \geq \frac{\delta q}{T}$ Clausius inequality

For an isolated system, $q = 0$ hence $\Delta S \geq 0$

Isothermal Processes $\Delta S = q_{\text{rev}} / T$

e.g. $\Delta S(\text{fusion}) = \frac{\Delta H_{\text{fus}}}{T_m}$ $\Delta S(\text{vap}) = \frac{\Delta H_{\text{vap}}}{T_b}$

Trouton's Rule: $\Delta S(\text{vap}) \approx 85 \text{ J K}^{-1} \text{ mol}^{-1}$

Can be used to estimate ΔH_{vap} if T_b is known. Not good for associated liquids.

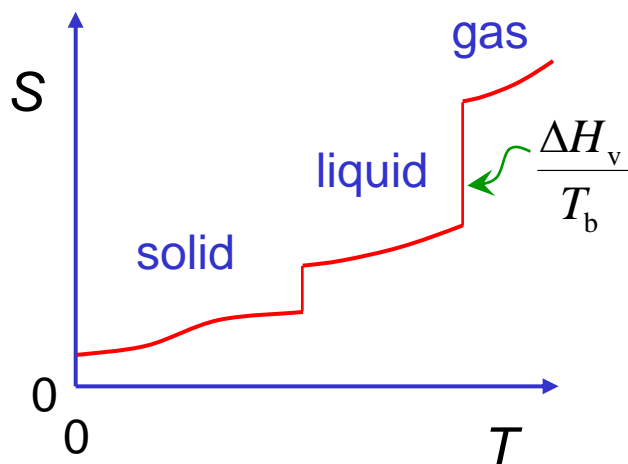
Temperature Variation $\delta q_{\text{rev}} = CdT$

$$(\Delta S)_V = \int_{T_1}^{T_2} \frac{C_V}{T} dT$$

and $(\Delta S)_P = \int_{T_1}^{T_2} \frac{C_P}{T} dT$

Absolute Entropy

$$S(T) = S(0) + \int_0^T \frac{C_P}{T} dT$$

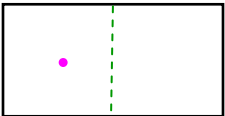
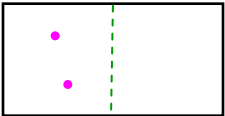
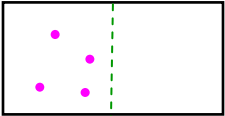
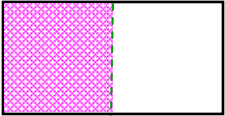


Entropy 3

Entropy depends on Probability.

Consider the number of ways Ω of arranging n molecules between two sides (A and B) of a container.

The probability P_A that all molecules are on side A depends on the ratio of Ω_A to the total number of arrangements.

A	B			
		$\Omega_A = 1$	$\Omega_{\text{tot}} = 2$	$P_A = \frac{1}{2}$
		$\Omega_A = 1$	$\Omega_{\text{tot}} = 4$	$P_A = \frac{1}{4}$
		$\Omega_A = 1$	$\Omega_{\text{tot}} = 16$	$P_A = \frac{1}{16}$
		$\Omega_A = 1$	$\Omega_{\text{tot}} = 2^n$	$P_A = 2^{-n}$

State A becomes less and less probable as n increases. Conversely, the probability of the less ordered, roughly evenly distributed states, increases.

Since entropy is a measure of disorder, it follows that S depends on Ω .

Boltzmann equation $S = k \ln \Omega$

Since $P(x \text{ AND } y) = P_x \cdot P_y$, $\ln P_{x+y} = \ln P_x + \ln P_y$

The Second Law of Thermodynamics

- “An isothermal cyclic process in which there is a net conversion of heat into work is impossible.”
- “No process is possible in which the sole result is the absorption of heat from a reservoir and its conversion into work.” It is possible to convert all work into heat!
- “It is impossible for heat to be transformed from a body at a lower temperature to one at a higher temperature unless work is done.”
- “The entropy of an isolated system increases during any natural process.” The universe is an isolated system.
 $\Delta S(\text{sys}) < 0$ is allowed provided $\Delta S(\text{sys}) + \Delta S(\text{surr}) > 0$
- “All reversible Carnot cycles operating between the same two temperatures have the same thermodynamic efficiency.”
- “There is a state function called entropy S that can be calculated from $dS = \delta q_{\text{rev}}/T$. The change in entropy in any process is given by $dS \geq \delta q/T$, where the inequality refers to a spontaneous (irreversible) process.”

The 1st Law uses U to identify permissible changes of state.

The 2nd Law uses S to identify natural changes among the permissible ones.

The Third Law of Thermodynamics

- “If the entropy of every element in its stable state at $T = 0$ is taken as zero, every substance has a positive entropy which at $T = 0$ may become zero, and does become zero for all perfect crystalline substances, including compounds.”

Nernst Heat Theorem “The entropy change accompanying transformation between condensed phases in equilibrium, including chemical reactions, approaches zero as $T \rightarrow 0$.”

$$\lim_{T \rightarrow 0} \Delta S = 0$$

Practical consequence: Set $S(0) = 0$ for elements by convention. Apply Nernst to determine $S(0)$ for all else.

- “It is impossible to reach absolute zero in a finite number of steps.”

The **1st Law** says U cannot be created or destroyed.

The **2nd Law** says S cannot decrease.

The **3rd Law** says zero Kelvin cannot be reached.

The Clausius Inequality

Given $dS = \frac{\delta q_{\text{rev}}}{T}$ and $\delta w_{\text{rev}} = -PdV$

Substitute into the 1st Law:

$$dU = TdS - PdV$$

Fundamental Equation
of Thermodynamics

All exact differentials, so path independent.

But $dU = \delta q + \delta w = \delta q - P_{\text{ex}} dV$

In general,
i.e. any path

$$TdS - PdV = \delta q - P_{\text{ex}} dV$$

$$\Rightarrow dS = \frac{\delta q}{T} + \frac{(P - P_{\text{ex}})}{T} dV$$

If $P > P_{\text{ex}}$, $dV > 0$; if $P < P_{\text{ex}}$, $dV < 0$

$$\therefore (P - P_{\text{ex}})dV \geq 0$$

Clausius Inequality

$$dS \geq \frac{\delta q}{T}$$

Equal for
reversible
change

Even more generally,

$$dS_{\text{univ}} = \left(\frac{T - T_{\text{surr}}}{T} \right) dS_{\text{surr}} + \frac{(P - P_{\text{surr}})}{T} dV$$

Conditions for: thermal equilibrium mechanical equilibrium

The Fundamental Equation of Thermodynamics

Combine $dU = \delta q - PdV$ with $dS = \frac{\delta q_{\text{rev}}}{T}$

\Rightarrow $dU = TdS - PdV$

or $dS = \left(\frac{1}{T}\right)dU + \left(\frac{P}{T}\right)dV$

Reversible change but true for all paths since dV exact

This fundamental equation generates many more relationships.

Example 1: Comparison with $dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$

\Rightarrow $\left(\frac{\partial U}{\partial S}\right)_V = T$ and $\left(\frac{\partial U}{\partial V}\right)_S = -P$

Example 2: Consider that dU is exact and cross differentiate.

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

a Maxwell relation

Example 3: $\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial T}{\partial V}\right)_S \left(\frac{\partial S}{\partial T}\right)_V$

cyclic rule

$$= \left(\frac{\partial P}{\partial S}\right)_V \left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial P}{\partial T}\right)_V$$

and again!

$$= -\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P / \left(\frac{\partial P}{\partial V}\right)_T$$

$$= \alpha / \kappa$$

How Entropy Depends on T and V

$$dS = \left(\frac{1}{T}\right) dU + \left(\frac{P}{T}\right) dV$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$\Rightarrow dS = \frac{C_V}{T} dT + \frac{1}{T} \left[P + \left(\frac{\partial U}{\partial V}\right)_T \right] dV$$

Compare with $dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$$

$$\Delta S_V = \int \frac{C_V}{T} dT$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T} \left[P + \left(\frac{\partial U}{\partial V}\right)_T \right]$$

0 for ideal gases

$$\begin{aligned} \Delta S_T &= \int \frac{P}{T} dV = nR \int \frac{1}{V} dV \\ &= nR \ln(V_2 / V_1) \end{aligned}$$

For any substance,

$$dS = \frac{C_V}{T} dT + \frac{\alpha}{\kappa} dV$$

For ideal gases,

$$\Delta S = C_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

assuming C_V is T independent

How Entropy Depends on T and P

$$dS = \left(\frac{1}{T}\right)dU + \left(\frac{P}{T}\right)dV$$

First problem: replace dU ; second problem: replace dV .

Use $dU = dH - PdV - VdP$ and both are solved!

$$dS = \left(\frac{1}{T}\right)dH - \left(\frac{V}{T}\right)dP$$

But $dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$

$$\Rightarrow dS = \frac{C_P}{T} dT + \frac{1}{T} \left[\left(\frac{\partial H}{\partial P}\right)_T - V \right] dP$$

Compare with $dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

$$\Delta S_P = \int \frac{C_P}{T} dT$$

$$\left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T} \left[\left(\frac{\partial H}{\partial P}\right)_T - V \right]$$

0 for ideal gases

$$\Delta S_T = - \int \frac{V}{T} dP = -nR \int \frac{1}{P} dP$$

$$\Delta S_T = -nR \ln(P_2 / P_1) = nR \ln(V_2 / V_1)$$

Entropy Changes in Spontaneous Processes

Entropy is a state function, so

$$\Delta S(\text{sys}) = S_2 - S_1 \quad \text{independent of path}$$

This can be used to calculate ΔS for an irreversible process.

❖ Consider isothermal expansion of a gas from V_1 to V_2 :

$$\Delta S(\text{sys}) = nR \ln(V_2/V_1) \quad \text{reversible and irreversible cases}$$

For the reversible case $\Delta S(\text{surr}) = -\Delta S(\text{sys})$

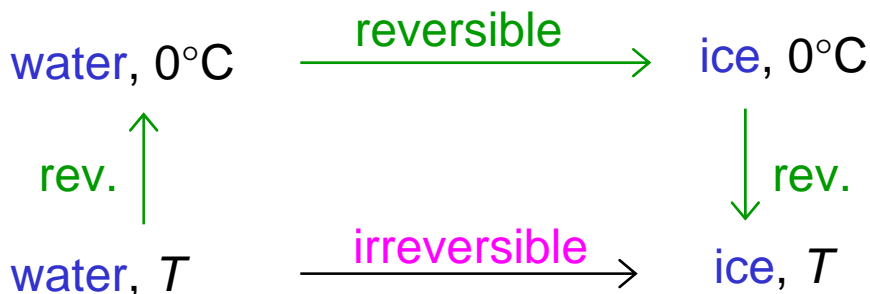
For the irreversible case $\Delta S(\text{surr}) > -\Delta S(\text{sys})$

$$\Delta S(\text{surr}) = -\frac{q}{T} = \frac{w}{T}$$

e.g. for free expansion, $w = 0$

$$\Rightarrow \Delta S(\text{surr}) = 0, \quad \Delta S(\text{univ}) = \Delta S(\text{sys}) > 0$$

❖ Consider freezing of supercooled water at $T < 273 \text{ K}$

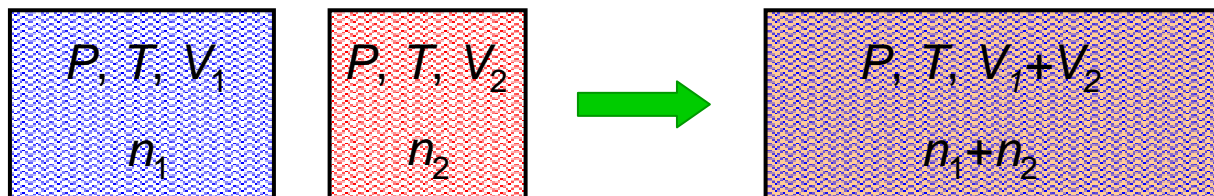


$$\Delta S(\text{sys}) = C_P(\text{l}) \ln\left(\frac{273}{T}\right) + \frac{(-\Delta H_{\text{fus}}^\circ)}{273} + C_P(\text{s}) \ln\left(\frac{T}{273}\right)$$

$$\Delta S(\text{surr}) = \frac{\Delta H_{\text{fus}}(T)}{T} = \frac{1}{T} \left\{ \Delta H_{\text{fus}}(273) + [C_P(\text{l}) - C_P(\text{s})](T - 273) \right\}$$

Entropy of Mixing

❖ Consider the mixing of two ideal gases :



$$\Delta S_1 = -n_1 R \ln \frac{V_1}{V_1 + V_2} = -n_1 R \ln \frac{n_1}{n_1 + n_2} = -n_1 R \ln \chi_1$$

$$\Delta S_2 = -n_2 R \ln \frac{V_2}{V_1 + V_2} = -n_2 R \ln \frac{n_2}{n_1 + n_2} = -n_2 R \ln \chi_2$$

$$\Delta S_{\text{mix}} = -n_1 R \ln \chi_1 - n_2 R \ln \chi_2 = -(n_1 + n_2) R (\chi_1 \ln \chi_1 + \chi_2 \ln \chi_2)$$

In general

$$\Delta S_{\text{mix}} = -n_{\text{tot}} R \sum_i \chi_i \ln \chi_i$$

This expression applies to the arrangement of objects (molecules) just as well as fluids (gases and liquids).

For example, arrange N identical atoms in N sites in a crystal:

$$\Omega = N! / N! = 1 \quad S = k \ln \Omega = 0$$

Compare with the arrangement of two types of atom, A and B.

$$\Omega = \frac{N!}{N_A! N_B!} \quad \Delta S = k (\ln N! - \ln N_A! - \ln N_B!)$$

Application of Stirling's approximation $\ln(z!) = z \ln z - z$

leads to $\Delta S_{\text{config}} = -kN (\chi_A \ln \chi_A + \chi_B \ln \chi_B)$

Using Entropy to Achieve Low T

$$\Delta S_P = \int \frac{C_P}{T} dT \approx C_P \ln(T_2/T_1) \quad \text{if } C_P \text{ is } \approx \text{constant}$$

To achieve lower temperatures, S must be reduced.

Choose some property X that varies with S , i.e. $S = f(X, T)$.

This could be the pressure of a gas or, for example, the magnetic moment of a paramagnetic salt (whose energy varies with magnetic field).

1. Alter X isothermally. Entropy changes. $\Delta S_T \approx \left(\frac{\partial S}{\partial X} \right)_T \Delta X, \quad q = T \Delta S$
2. Restore X by a reversible adiabatic process. $q = 0, \quad \Delta S = 0$
3. Repeat cycle.

