20.110J / 2.772J / 5.601J
Thermodynamics of Biomolecular Systems
Instructors: Linda G. Griffith, Kimberly Hamad-Schifferli, Moungi G. Bawendi, Robert W. Field

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Entropy, Reversible and Irreversible Processes and Disorder

Examples of spontaneous processes
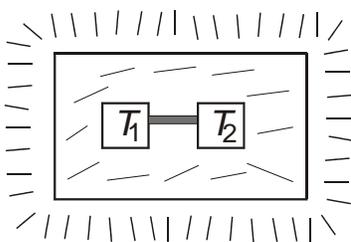
Connect two metal blocks thermally in an isolated system   ($\Delta U = 0$)

Initially $T_1 \neq T_2$

$$dS = dS_1 + dS_2 = \frac{đq_1}{T_1} - \frac{đq_2}{T_2} = đq_1 \frac{(T_2 - T_1)}{T_1 T_2} \qquad (đq_1 = -đq_2)$$

$dS > 0$ for spontaneous process

$$\Rightarrow \quad \text{if} \quad T_2 > T_1 \quad \Rightarrow \quad đq_1 > 0 \quad \left.\begin{array}{l} \\ \\ \end{array}\right\} \text{in both cases heat flows}$$
$$T_2 < T_1 \quad \Rightarrow \quad đq_1 < 0 \quad \quad \text{from hot to cold as expected}$$
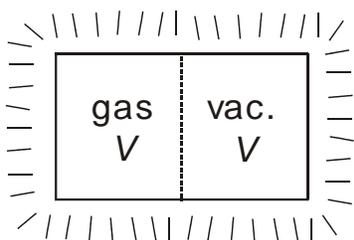
Joule expansion with an <u>ideal</u> gas

$$\text{1 mol gas } (V, T) \stackrel{adiabatic}{=} \text{1 mol gas } (2V, T)$$
$$\Delta U = 0 \qquad q = 0 \qquad w = 0$$

Need a reversible path to compute ΔS from q! Close the cycle and go back to the initial state reversibly and isothermally

$$\Delta S = -\Delta S_{backwards}$$

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$$q_{rev} \neq 0$$

$$1 \text{ mol gas } (2V, T) = 1 \text{ mol gas } (V, T)$$

$$\Delta S_{backwards} = \int \frac{\text{d}q_{rev}}{T} = -\int \frac{\text{d}w}{T} = \int_{2V}^{V} \frac{RdV}{V} = R\ln\frac{1}{2}$$

$$\therefore \quad \boxed{\Delta S = R\ln 2 > 0} \qquad \text{spontaneous}$$

IMPORTANT!! To calculate ΔS for the *irreversible* process, we needed to find a <u>reversible</u> path so we could determine

$$\text{d}q_{rev} \quad \text{and} \quad \int \frac{\text{d}q_{rev}}{T}.$$

- Mixing of ideal gases at constant T and p
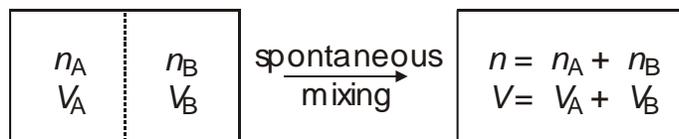
$$n_A \text{ A } (g, V_A, T) + n_B \text{ A } (g, V_B, T) = n (A + B) (g, V, T)$$

To calculate ΔS_{mix}, we need to find a reversible path between the two states.

piston permeable to A only   piston permeable to B only   back to initial state
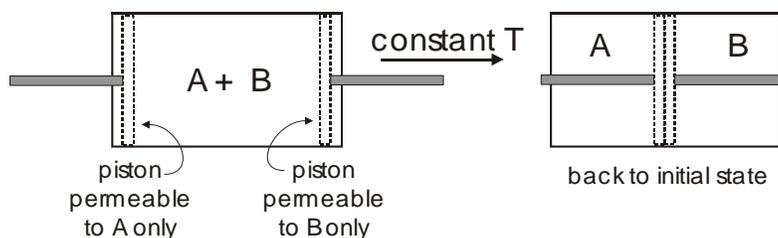
$$\Delta S_{demix} = -\Delta S_{mix} \qquad \text{function of state}$$

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For demixing process

$$\Rightarrow \quad \Delta U = 0 \quad \Rightarrow \quad q_{rev} = -w_{rev} = p_A dV_A + p_B dV_B$$

work of compression of each gas

$$\therefore \quad \Delta S_{demix} = \int \frac{dq_{rev}}{T} = \int_V^{V_A} \frac{p_A dV_A}{T} + \int_V^{V_B} \frac{p_B dV_B}{T} = n_A R \ln \frac{V_A}{V} + n_B R \ln \frac{V_B}{V}$$

Put in terms of mole fractions $\quad X_A = \frac{n_A}{n} \quad X_B = \frac{n_B}{n}$

Ideal gas $\quad \Rightarrow \quad X_A = \frac{V_A}{V} \quad X_B = \frac{V_B}{V}$

$$\therefore \quad \Delta S_{demix} = nR[X_A \ln X_A + X_B \ln X_B]$$

$$\Rightarrow \quad \boxed{\Delta S_{mix} = -nR[X_A \ln X_A + X_B \ln X_B]}$$

Since $X_A, X_B < 1 \quad \Rightarrow \quad \boxed{\Delta S_{mix} > 0}$ mixing is always spontaneous

The mixed state is more "disordered" or "random" than the demixed state.

$$S_{mixed} > S_{demixed}$$

This is a <u>general</u> result:

Entropy is a measure of the disorder of a system

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∴   For an <u>isolated</u> system (or the universe)

$\Delta S > 0$ Spontaneous, increased randomness
$\Delta S = 0$ Reversible, no change in disorder
$\Delta S < 0$ Impossible, order cannot "happen" in isolation

> There is an inexorable drive for the universe to go to a maximally disordered state.

<u>Microscopic understanding: Boltzmann Equation of Entropy:</u>

$$S = k \ln \Omega$$

Where k is Boltzmann's constant ($k = R/N_A$).
And Ω is the number of equally probable microscopic arrangements for the system.

This can also be used to calculate ΔS

In the case of the Joule expansion of an ideal gas in volume V expanding to a volume 2V (as on the first page of these notes): if we divide the initial volume V into m small cubes, each with volume v, so that mv=V, the number of ways of placing the N molecules of ideal gas into these small cubes initially is m^N. After the expansion the number of ways of placing the n molecules of ideal gas into the now 2m small cubes is $(2m)^N$.

The number of probably microscopic arrangements initially is:
$\Omega \propto (m)^N$, or $\Omega = C(m)^N$ (C is a constant)

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After the expansion it is:

$\Omega \propto (2m)^N$, or $\Omega = C(2m)^N$

So using Boltzmann's equation to calculate ΔS for the expansion:

$$\Delta S = k \ln\left[(2m)^N\right] - k \ln\left[m^N\right] = kN \ln 2 = R \ln 2$$

As we had found above!

More examples of ΔS calculations

In all cases, we must find a reversible path to calculate $\int \frac{đq_{rev}}{T}$

(a)   Mixing of ideal gases at constant T and p

n_A A (g, V_A, T) + n_B A (g, V_B, T) = n (A + B) (g, $V = V_A + V_B$, T)
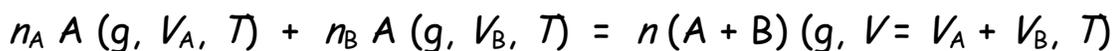
$$\Delta S_{mix} = -nR[X_A \ln X_A + X_B \ln X_B]$$

(b) Heating (or cooling) at constant V

$$A (T_1, V) = A (T_2, V)$$

$$\Delta S = \int \frac{đq_{rev}}{T} = \int_{T_1}^{T_2} \frac{C_V dT}{T} \underset{\substack{T\text{-independent}}}{\overset{\text{if } C_V \text{ is}}{=}} C_V \ln \frac{T_2}{T_1}$$

$$[\text{Note } \Delta S > 0 \text{ if } T_2 > T_1]$$

(c)   Reversible phase change at constant T and p
e.g. H_2O (l, 100°C, 1 bar) = H_2O (g, 100°C, 1 bar)

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$$q_p = \Delta H_{vap}$$

$$\Delta S_{vap}(100°C) = \frac{q_p^{vap}}{T_b} = \frac{\Delta H^{vap}}{T_b} \qquad (T_b = \text{boiling Temp at 1 bar})$$

(d)   <u>Irreversible</u> phase change at constant T and p

e.g. H_2O (ℓ, -10°C, 1 bar) = H_2O (s, -10°C, 1 bar)

This is <u>spontaneous</u> and <u>irreversible</u>.

∴   We need to find a <u>reversible path</u> between the two states to calculate ΔS.

H_2O (ℓ, -10°C, 1 bar) $\overset{\text{irreversible}}{=}$ H_2O (s, -10°C, 1 bar)

$$đq_{rev} = C_p(\ell)dT \qquad\qquad đq_{rev} = C_p(s)dT$$

H_2O (ℓ, 0°C, 1 bar) $\overset{\text{reversible}}{=}$ H_2O (s, 0°C, 1 bar)

$$q_p^{rev} = -\Delta H_{fus}$$

Note: ΔH_{fus} is for the process going from the solid state to the liquid state, the opposite of what we have above, same for ΔS_{fus}.

$$\Delta S = \Delta S_{heating} - \Delta S_{fus} + \Delta S_{cooling}$$
$$= \int_{T_1}^{T_{fus}} \frac{C_p(\ell)dT}{T} + \frac{-\Delta H_{fus}}{T_{fus}} + \int_{T_{fus}}^{T_1} \frac{C_p(s)dT}{T}$$

∴ $$\boxed{\Delta S = \frac{-\Delta H_{fus}}{T} + \int_{T_1}^{T_{fus}} \left[C_p(\ell) - C_p(s) \right] \frac{dT}{T}}$$

$$\Delta S = \frac{-\Delta H_{fus}}{T} + \left[C_p(\ell) - C_p(s) \right] \ln \frac{T_{fus}}{T_1} \qquad \text{if } C_p \text{ values are } T\text{-independent}$$