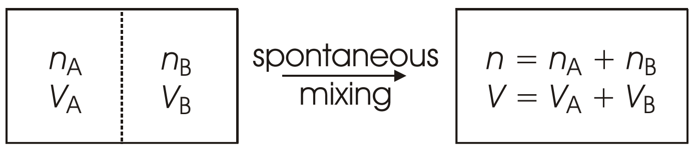
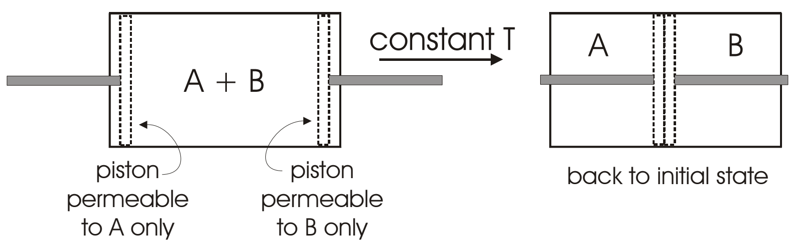
# Entropy and Disorder

- Mixing of ideal gases at constant $T$ and $p$

$$n_A\,A(g,V_A,T) + n_B\,A(g,V_B,T) = n\,(A+B)(g,V,T)$$




To calculate $\Delta S_{mix}$ , we need to find a reversible path between the two states.




$$\Delta S_{demix} = -\Delta S_{mix} \qquad \text{function of state}$$

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

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

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

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 general result $\Rightarrow$
Entropy is a measure of the disorder of a system

$\therefore$ For an isolated 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.

Examples of $\Delta S$ 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 $V$

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

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

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

(c) Reversible phase change at constant $T$ and $p$

e.g. $H_2O$ ($\ell$, 100°C, 1 bar) = $H_2O$ (g, 100°C, 1 bar)

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

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

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

e.g. $H_2O$ ($\ell$, -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 $\Delta S$.

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

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

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

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

$$\Delta S = \Delta S_{heating} + \Delta S_{fus} + \Delta S_{cooling}$$

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

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

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