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5.60 Thermodynamics & Kinetics
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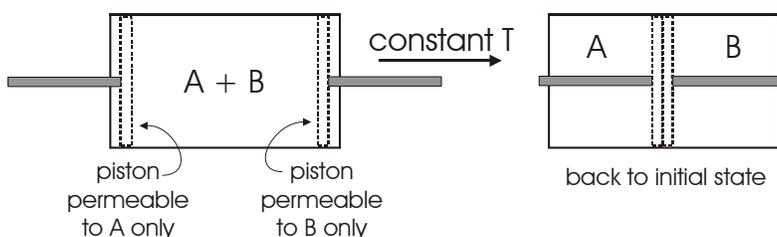
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Entropy and Disorder

- Mixing of ideal gases at constant T and p



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



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

For demixing process

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

work of compression of each gas

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

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

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

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

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

Since $X_A, X_B < 1 \Rightarrow \boxed{\Delta S_{mix} > 0}$ 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 ΔS calculations

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

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



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

(b) Heating (or cooling) at constant V

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

$$\Delta S = \int \frac{\mathrm{d}q_{\text{rev}}}{T} = \int_{T_1}^{T_2} \frac{C_V dT}{T} \quad \begin{array}{l} \text{if } C_V \text{ is} \\ T\text{-independent} \end{array} = C_V \ln \frac{T_2}{T_1}$$

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

(c) Reversible phase change at constant T and p

e.g. $\text{H}_2\text{O}(\ell, 100^\circ\text{C}, 1 \text{ bar}) = \text{H}_2\text{O}(\text{g}, 100^\circ\text{C}, 1 \text{ bar})$

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

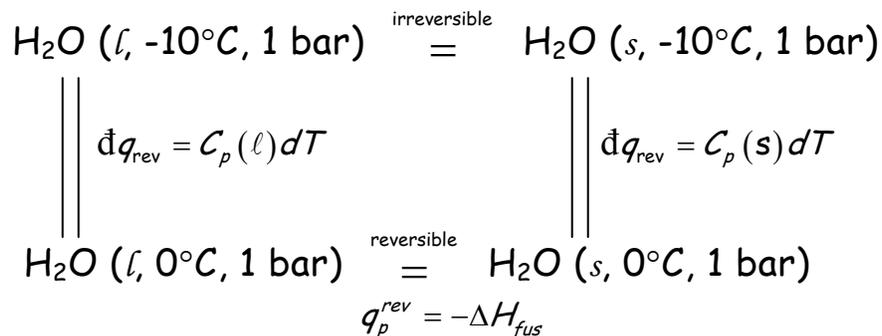
$$\Delta S_{\text{vap}}(100^\circ\text{C}) = \frac{q_p^{\text{vap}}}{T_b} = \frac{\Delta H^{\text{vap}}}{T_b} \quad (T_b = \text{boiling Temp at 1 bar})$$

(d) Irreversible phase change at constant T and p

e.g. $\text{H}_2\text{O}(\ell, -10^\circ\text{C}, 1 \text{ bar}) = \text{H}_2\text{O}(s, -10^\circ\text{C}, 1 \text{ bar})$

This is spontaneous and irreversible.

\therefore We need to find a reversible path between the two states to calculate ΔS .



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

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

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