Lecture 18: Entropy Calculations

Isothermal, Isochoric, and Isobaric Entropy Changes

Constant Temperature Entropy

Constant Temperature ΔS

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

Used for phase change, isothermal

For a phase change (assume reversible):

$$q = \pm n\Delta H$$

Phase Change ΔS

$$\Delta S = \pm\frac{n\Delta H}{T}$$

For isothermal reversible:

$$\Delta U = 0 \implies q = -w = +nRT\ln\left(\frac{V_2}{V_1}\right)$$

Isothermal ΔS

$$\Delta S = nR\ln\left(\frac{V_2}{V_1}\right)$$

Changing V, constant T

Isochoric Entropy

Starting from 3rd Law:

$$dS = \frac{dq_{\text{rev}}}{T}$$

Using Isochoric and First Law:

$$dU = dq + dw = dq - \cancel{PdV}$$
$$dU = dq = n\overline{C_v}\,dT$$

Substitute:

$$dS = \frac{n\overline{C_v}\,dT}{T}$$

Isochoric Entropy

Integrate the state function:

$$\begin{aligned}\Delta S &= \int_{T_1}^{T_2} dS \\ &= \int_{T_1}^{T_2} \frac{n\overline{C_v}\,dT}{T} \\ &= n\overline{C_v}\ln\frac{T_2}{T_1}\end{aligned}$$

Isochoric ΔS

$$\Delta S = n\overline{C_v}\ln\frac{T_2}{T_1}$$

Changing T, constant V

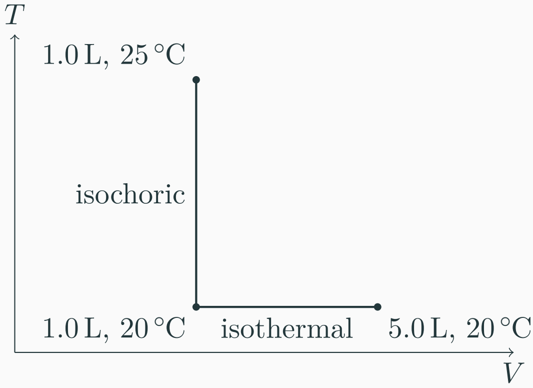
T must be in K

$$T_2 > T_1 \implies \Delta S > 0$$

$$T_2 < T_1 \implies \Delta S < 0$$

Example: Isothermal Isochoric 2 Step Process

1 mol of a monoatomic ideal gas is reversibly compressed from 5 L to 1 L, causing the temperature to rise from 20 °C to 25 °C. Calculate ΔS associated with this.



Isothermal step:

$$\Delta S = nR\ln\frac{V_2}{V_1}$$

$$= (1\,\mathrm{mol})(8.314\,\tfrac{\mathrm{J}}{\mathrm{mol}\cdot\mathrm{K}})\ln\frac{1}{5} = -13.4\,\tfrac{\mathrm{J}}{\mathrm{K}}$$

Isochoric step:

$$\Delta S = n\overline{C_v}\ln\frac{T_2}{T_1}$$

$$= (1\,\mathrm{mol})\left(\frac{3}{2}\times 8.314\,\tfrac{\mathrm{J}}{\mathrm{mol}\cdot\mathrm{K}}\right)\ln\frac{298}{293} = 0.22\,\tfrac{\mathrm{J}}{\mathrm{K}}$$

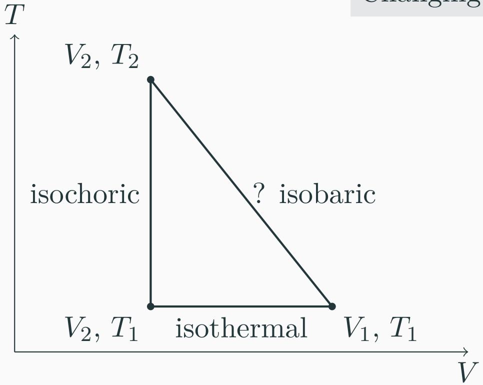
$$\Delta S_{\mathrm{tot}} = -13.1\,\tfrac{\mathrm{J}}{\mathrm{K}}$$

Isobaric Entropy

Isobaric ΔS

$$\Delta S = n\overline{C_p}\ln\frac{T_2}{T_1} = n\overline{C_p}\ln\frac{V_2}{V_1}$$

Changing T, changing V



$$\Delta S_{\text{tot}} = nR\ln\frac{V_2}{V_1} + n\overline{C_v}\ln\frac{T_2}{T_1}$$

Isobaric: $V \propto T$, so $V_2/V_1 = T_2/T_1$:

$$\begin{aligned} &= nR\ln\frac{T_2}{T_1} + n\overline{C_v}\ln\frac{T_2}{T_1} \\ &= n\ln\frac{T_2}{T_1}\left(\overline{C_V} + R\right) \\ &= n\overline{C_p}\ln\frac{T_2}{T_1} = n\overline{C_p}\ln\frac{V_2}{V_1} \end{aligned}$$

Entropy formulas

Phase Change ΔS

$$\Delta S = \pm\frac{n\Delta H}{T}$$

Isothermal ΔS

$$\Delta S = nR\ln\left(\frac{V_2}{V_1}\right)$$

Changing V, constant T

Isochoric ΔS

$$\Delta S = n\overline{C_v}\ln\frac{T_2}{T_1}$$

Changing T, constant V

Isobaric ΔS

$$\Delta S = n\overline{C_p}\ln\frac{T_2}{T_1} = n\overline{C_p}\ln\frac{V_2}{V_1}$$

Changing T, changing V

Spontaneous and ΔS

$\Delta S_{\text{sys}} > 0$ is not spontaneous, $\Delta S_{\text{universe}} > 0$ means spontaneous

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

Surroundings are massive, can assume isothermal and absorb heat from the system

ΔS_{surr}

$$\Delta S_{\text{surr}} = -\frac{\Delta H}{T}$$

We've been calculating ΔS_{sys}
Example: Freezing of water

$$H_2O\,(l) \longrightarrow H_2O\,(s)$$

$$\Delta S_{\text{sys}} < 0 \qquad \Delta S_{\text{surr}} > 0$$

Can be spontaneous depending on the temperature!

Total Entropy and Spontaneity

$$\frac{1}{2}\,\mathrm{H_2(g)} + \frac{1}{2}\,\mathrm{F_2(g)} \longrightarrow \mathrm{HF\,(g)}$$

	S_m° $\left(\frac{\mathrm{J}}{\mathrm{K\cdot mol}}\right)$	ΔH_f° $\left(\frac{\mathrm{kJ}}{\mathrm{mol}}\right)$
$H_2(g)$	130.68	0.0
$F_2(g)$	202.78	0.0
HF (g)	173.78	-271.1

$$\begin{aligned}\Delta S_{\text{universe}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}}\\ &= \sum nS_m^\circ(\text{prod}) - \sum nS_m^\circ(\text{react}) - \frac{\Delta H}{T}\\ &= 7.05\,\tfrac{\mathrm{J}}{\mathrm{K}} - \frac{-271.1\,\mathrm{kJ}}{298\,\mathrm{K}}\left(\frac{1000\,\mathrm{J}}{1\,\mathrm{kJ}}\right)\\ &= 917\,\tfrac{\mathrm{J}}{\mathrm{K}}\end{aligned}$$

Spontaneity Criteria

- Spontaneous: $\Delta S_{\text{universe}} > 0$ (product favored)
- Equilibrium: $\Delta S_{\text{universe}} = 0$ (equally favored)
- Non-spontaneous: $\Delta S_{\text{universe}} < 0$ (reactant favored)

$\Delta S_{\text{universe}}$ leads to Gibbs Free Energy

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

Use definition of ΔS_{surr}:

$$\begin{aligned} \Delta S_{\text{universe}} &= \Delta S_{\text{sys}} - \frac{\Delta H}{T} \\ -T\Delta S_{\text{universe}} &= \Delta H - T\Delta S_{\text{sys}} \end{aligned}$$

Define $\Delta G = -T\Delta S_{\text{universe}}$:

$$\Delta G \equiv \Delta H - T\Delta S_{\text{sys}}$$