9. CO_2 FIRE EXTINGUISHER (8 points) — *Solution by Jaan Kalda.*

i) *(1.5 points)* At atmospheric pressure $p_{\rm atm} = 1.0 \times 10^5\,\mathrm{Pa}$, which is below the triple-point pressure $p_t = 5.18 \times 10^5\,\mathrm{Pa}$, no liquid CO_2 can exist. The exit stream is therefore either pure vapour, pure solid, or a solid–vapour mixture. Pure solid is impossible: a rigid (incompressible) solid cannot expand or accelerate through a converging–diverging nozzle. So the exit is either pure vapour, or a solid–vapour mixture; in the latter case the temperature must be the sublimation temperature at 1 atm, $T_{\rm sub} \approx 195\,\mathrm{K}$ ($\approx -78\,^\circ\mathrm{C}$).

Tracing the isentrope from the initial state to $p = 1$ bar on the T–s diagram (provided): for both scenarios (a) and (b), the trajectory crosses the saturation boundary into the two-phase region. Hence the stream is a solid–vapour mixture at $T \approx 195\,\mathrm{K}$ in both cases.

Grading.

- Recognising that liquid is impossible at $p_{\rm atm} < p_t$, so the stream is solid, vapour, or a mixture **0.5 pts**
- Excluding pure solid (cannot adiabatically expand through nozzle) **0.2 pts**
- If solid–vapour coexistence, identifying $T = T_{\rm sub}(1\,\mathrm{atm}) \approx 195\,\mathrm{K}$ ($\approx -78\,^\circ\mathrm{C}$), within $\pm 10\,\mathrm{K}$ **0.3 pts**
- Tracing the isentrope on the T–s diagram and concluding the stream is in the two-phase region for one scenario **0.3 pts**
- Two-phase for both scenarios **0.2 pts**

ii) *(3.5 points)* The expansion through the nozzle is reversible and adiabatic, so it is *isentropic*: the entropy per unit mass s is conserved between the inlet and the exit. On the T–s diagram, the trajectory is therefore vertical (constant s) until it crosses a phase boundary or a chosen isobar.

The exit pressure is $p_{\rm atm} = 1$ bar, well below the triple-point pressure $p_t = 5.18$ bar. From part (i), the exit state is in the two-phase (solid+vapour) region at $T_{\rm sub}(1\,\mathrm{bar}) \approx 195\,\mathrm{K}$ ($-78\,^\circ\mathrm{C}$).

Lever rule. In the two-phase region at fixed p, T, the total entropy per unit mass for a mixture with mass fraction x of solid (and $1-x$ vapour) is

$$s_{\rm end} = x\, s_{\rm sol} + (1-x)\, s_{\rm vap},$$

$$x = \frac{s_{\rm vap} - s_{\rm end}}{s_{\rm vap} - s_{\rm sol}},$$

where $s_{\rm sol}$ and $s_{\rm vap}$ are the entropies of pure solid and pure vapour at the boundaries of the two-phase region at $p = 1$ bar.

Reading entropies from the T–s diagram. At $p = 1$ bar (sublimation isobar at $T \approx -78\,^\circ\mathrm{C}$), the boundaries are

$$s_{\rm sol} \approx 400(50)\,\frac{\mathrm{J}}{\mathrm{kg}\cdot\mathrm{K}}, \qquad s_{\rm vap} \approx 3250(50)\,\frac{\mathrm{J}}{\mathrm{kg}\cdot\mathrm{K}}.$$

The initial entropies for the two scenarios are read at $T_0 = 298$ K ($25\,^\circ\mathrm{C}$) on the saturation dome:

- Scenario (a), saturated liquid at T_0: $s_a \approx 2100(50)\,\frac{\mathrm{J}}{\mathrm{kg}\cdot\mathrm{K}}$.
- Scenario (b), saturated vapour at T_0: $s_b \approx 2550(50)\,\frac{\mathrm{J}}{\mathrm{kg}\cdot\mathrm{K}}$.

Mass fractions. Applying the lever rule to each:

$$x_a = \frac{3250 - 2100}{3250 - 400} = \frac{1150}{2850} \approx 0.40,$$
$$x_b = \frac{3250 - 2550}{3250 - 400} = \frac{700}{2850} \approx 0.25.$$

So the liquid-fed extinguisher (a) produces a stream that is ∼40% dry ice (and 60% vapour) by mass, while the vapour-fed extinguisher (b) produces a stream that is only ∼25% dry ice. The liquid scenario yields about 1.6 times more solid CO_2 per unit mass discharged — which is why fire extinguishers are designed to draw liquid.

Grading.

- Recognising that "reversible adiabatic" means isentropic ($s = \text{const}$), so the end-point is found by tracing vertically downward on the T–s diagram **0.6 pts**
- Deriving the lever rule for mass fraction x in the two-phase region: $x = (s_{\text{vap}} - s_{\text{end}})/(s_{\text{vap}} - s_{\text{sol}})$ **0.7 pts**
- Reading the initial entropy s_a from the saturated-liquid line at $T_0 = 298$ K (scenario a) **0.5 pts**
- Reading the initial entropy s_b from the saturated-vapour line at T_0 (scenario b) **0.5 pts**
- Reading s_{sol} at the 1-bar solid boundary **0.3 pts**
- Reading s_{vap} at the 1-bar vapour boundary **0.3 pts**
- Computing $x_a \approx 0.40 \pm 0.05$ for scenario (a) **0.3 pts**
- Computing $x_b \approx 0.25 \pm 0.05$ for scenario (b) **0.3 pts**

iii) *(3 points)* Consider an infinitesimal isentropic (reversible adiabatic) expansion of the saturated vapour from $(T, p_{\text{sat}}(T))$. Two trajectories meet at this point: the saturation curve $p_{\text{sat}}(T)$, and the adiabat (constant entropy). The expansion follows the adiabat. If the adiabat falls *below* the saturation curve in T–p space (i.e., the vapour cools more slowly than the saturation temperature drops with pressure), then a finite fraction of the vapour condenses into droplets. Otherwise the expansion remains in the pure-vapour region.

Saturation slope (Clausius–Clapeyron). The saturated vapour above a liquid has number density n_{vap} in thermal equilibrium with the liquid. By the Boltzmann distribution, the probability of a molecule occupying the vapour state (energy ℓ per molecule above the liquid) versus the liquid state is

$$\frac{n_{\text{vap}}}{n_{\text{liq}}} \propto \exp\!\left(-\frac{\ell}{k_B T}\right).$$

Treating n_{liq} as T-independent and using $p_{\text{sat}} = n_{\text{vap}} k_B T \approx (\text{const}) \cdot T \cdot \exp(-\ell/k_B T)$, the dominant temperature dependence is exponential. Per unit mass, $\ell/k_B = L/R_s$ where R_s is the specific gas constant of the vapour. Differentiating $\ln p_{\text{sat}}$:

$$\frac{1}{p_{\text{sat}}}\frac{\mathrm{d}p_{\text{sat}}}{\mathrm{d}T} = \frac{L}{R_s T^2}.$$

Equivalently,

$$\left.\frac{\mathrm{d}T}{\mathrm{d}p}\right|_{\text{sat}} = \frac{R_s T^2}{pL}.$$

Adiabat slope. For the ideal-gas adiabat $T p^{(1-\gamma)/\gamma} = \text{const}$, with $R_s = c_p - c_v$ and $\gamma = c_p/c_v$:

$$\left.\frac{\mathrm{d}T}{\mathrm{d}p}\right|_{\text{adiab}} = \frac{R_s T}{c_p p}.$$

Condensation condition. The vapour condenses on expansion iff the adiabat cools less than the saturation curve, i.e. $\left.\frac{\mathrm{d}T}{\mathrm{d}p}\right|_{\text{adiab}} < \left.\frac{\mathrm{d}T}{\mathrm{d}p}\right|_{\text{sat}}$:

$$\frac{R_s T}{c_p p} < \frac{R_s T^2}{pL},$$

$$\boxed{L > c_p T}.$$

Numerical check (water at $T = 373$ K). $L = 2260\,\frac{\text{kJ}}{\text{kg}}$, $c_p = 2.0\,\frac{\text{kJ}}{\text{kg·K}}$:

$$\frac{L}{c_p T} = \frac{2260}{2.0 \cdot 373} \approx 3.0 > 1.$$

So water vapour does condense on isentropic expansion. This is precisely why steam from a kettle appears as a visible white plume of fine droplets, rather than as invisible pure water vapour.

iv) *(? points)* Consider an infinitesimal isentropic (reversible adiabatic) expansion of the saturated vapour from $(T, p_{\text{sat}}(T))$. Two trajectories meet at this point: the saturation curve $p_{\text{sat}}(T)$, and the adiabat (constant entropy). The expansion follows the adiabat. If the adiabat falls *below* the saturation curve in T–p space (i.e., the vapour cools more slowly than the saturation temperature drops with pressure), then a finite fraction of the vapour condenses into droplets. Otherwise the expansion remains in the pure-vapour region.

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So water vapour does condense on isentropic expansion. This is precisely why steam from a kettle appears as a visible white plume of fine droplets, rather than as invisible pure water vapour.

Grading.

- Setting up the comparison: condensation occurs iff the adiabat lies below the saturation curve in T–p space **0.5 pts**
- Deriving the saturation slope via Boltzmann: $n_{\text{vap}}/n_{\text{liq}} \propto \exp(-\ell/k_B T)$ (those who know and use the Clausius–Clapeyron equation do not need to derive it) **0.6 pts**
- Obtaining the Clausius–Clapeyron form $\frac{\mathrm{d}p_{\text{sat}}}{\mathrm{d}T} = pL/(R_s T^2)$ **0.6 pts**
- Adiabat slope $\frac{\mathrm{d}T}{\mathrm{d}p} = R_s T/(c_p p)$ from ideal-gas adiabatic relation **0.4 pts**
- Comparing slopes to obtain the condition $L > c_p T$ **0.6 pts**
- Numerical check for water giving $L/(c_p T) \approx 3 > 1$, hence condensation **0.3 pts**