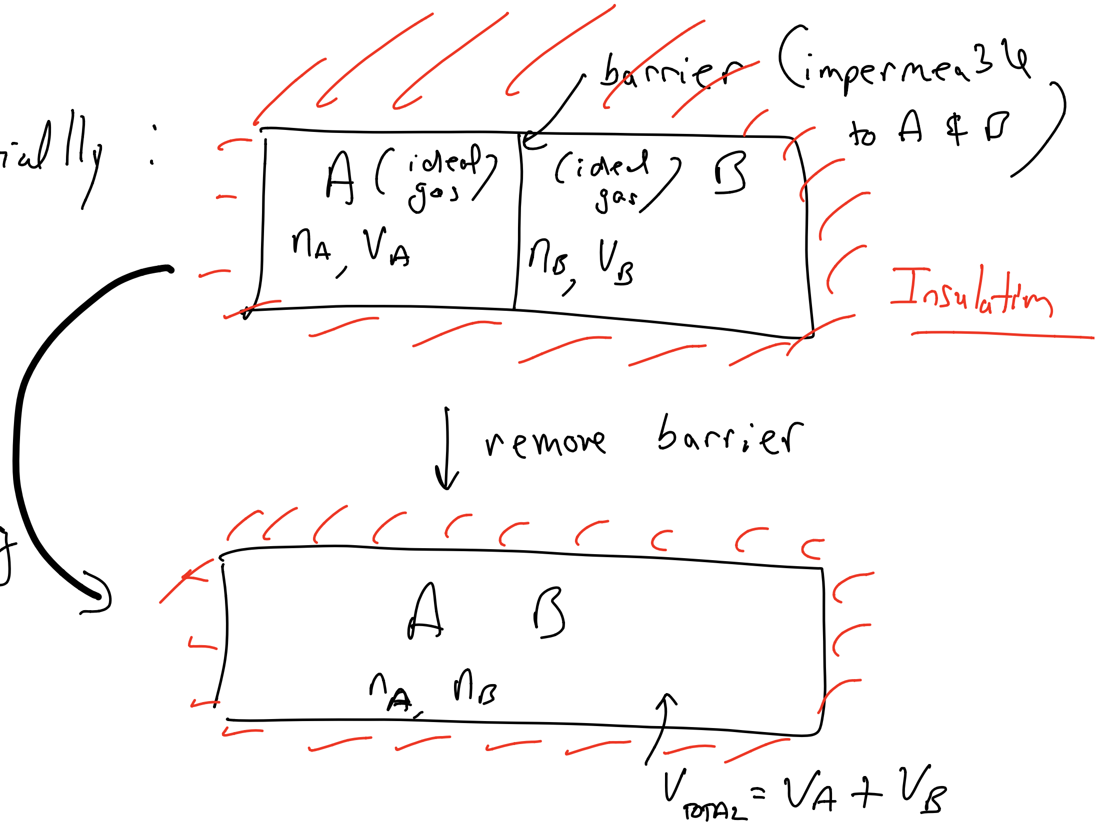
Question: what is ΔS for "mixing" of 2 ideal gases.

Final composition: x_A, x_B (y_A, y_B) — mole fractions

→ Isolated System ←

Initially:

? ΔS_{mixing}



Irreversible Process

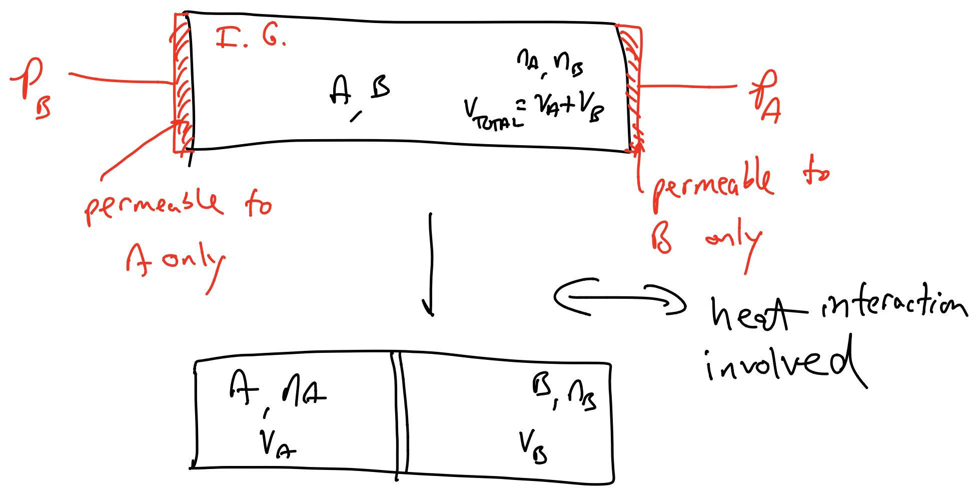
$$\Delta S_{mixing} > 0$$

1st "Law": $dU = \cancel{dQ}^{0} + \cancel{dW}^{0} = 0$

$$dS = \frac{đq_{rev}}{T}$$

Construct a Reversible Process

$\therefore đq \neq 0$ ← Isothermal, Reversible "Demixing"



1st "Law":

$$dU = đq_{rev} + đW_{rev}$$

b.c. IsoT & I. G. $dU = 0$

for I. G. $dU = C_v(T)\, dT$ $(dT = 0)$

$$đq_{rev} = -đW_{rev}$$

$$đq_{rev} = -\left[đW^A_{rev} + đW^B_{rev}\right]$$

$$đq_{rev} = -\left[-P_A dV_A - P_B dV_B\right]$$

$$đq_{rev} = \frac{n_A RT}{V_A} dV_A + \frac{n_B RT}{V_B} dV_B$$

$$đq_{rev} = n_A RT\, d(\ln V_A) + n_B RT\, d(\ln V_B)$$

$$dS_{demix} = \frac{dq_{rev}}{T} = \frac{n_A RT\, d(\ln V_A) + n_B RT\, d(\ln V_B)}{T}$$

$$dS_{demix} = n_A R\, d(\ln V_A) + n_B R\, d(\ln V_B)$$

$$\Delta S_{demix} = \int dS_{demix} = n_A R \int_{V_{TOTAL}}^{V_A} d(\ln V_A) + n_B R \int_{V_{TOTAL}}^{V_B} d(\ln V_B)$$

$$\Delta S_{demix} = n_A R \ln\left(\frac{V_A}{V_{TOTAL}}\right) + n_B R \ln\left(\frac{V_B}{V_{TOTAL}}\right)$$

V_A = volume occupied by gas A initially in mixing process

V_B = - - - - - B - - - - -

$V_{TOTAL} = V_A + V_B$

$$\Delta S_{mix} = -\left[n_A R \ln\left(\frac{V_A}{V_{TOTAL}}\right) + n_B R \ln\left(\frac{V_B}{V_{TOTAL}}\right)\right]$$

$$\Delta S_{mixing} > 0$$

$X_A, X_B \leftarrow$

I.G. $P_{TOTAL} V_{TOTAL} = nRT$

n: total moles $n = n_A + n_B$

$P_A + P_B = P_{TOTAL}$

$X_A P_{TOTAL} + X_B P_{TOTAL} = P_{TOTAL} \Rightarrow P_{TOTAL}\underbrace{(X_A + X_B)}_{1} = P_{TOTAL}$

$$\rightarrow (X_A P_{TOTAL} + X_B P_{TOTAL}) V_{TOTAL} = nRT$$

$$P_{TOTAL} (X_A V_{TOTAL} + X_B V_{TOTAL}) = nRT$$

Define: $V_A = X_A V_{TOTAL}$

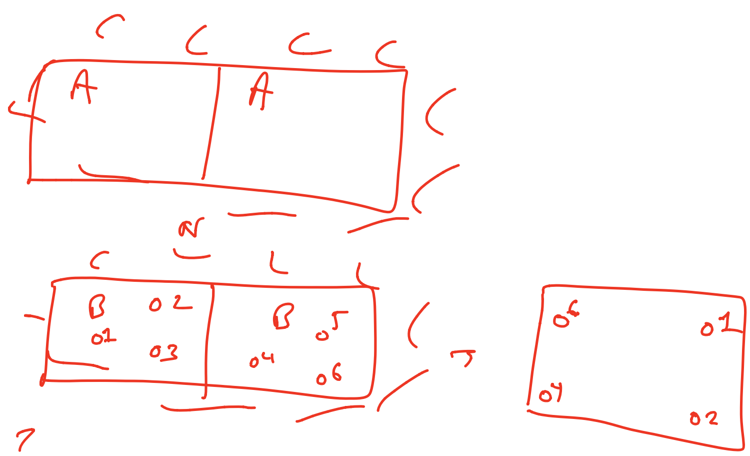
$V_B = X_B V_{TOTAL}$

$$\frac{V_A}{V_{TOTAL}} = X_A \; ; \qquad \frac{V_B}{V_{TOTAL}} = X_B$$

$$\Delta S_{mix} = -\left[n_A R \ln(X_A) + n_B R \ln(X_B) \right]$$

$$= -\left[n X_A R \ln(X_A) + n X_B R \ln(X_B) \right]$$

$$\Delta S^{I.G.}_{mix} = -nR \left[X_A \ln(X_A) + X_B \ln(X_B) \right]$$



$\Delta S_{mix} = ?$

$X_A = 1$

$N!$ $\quad \therefore \ln(X_A) = \ln(1) = 0$