

HW5 key

1. a) irreversible $\Rightarrow \Delta S_{TOT} > 0$
 adiabatic $\Rightarrow \Delta S_{surr} = 0$
 $\therefore \Delta S_{sys} > 0$

b) reversible $\Rightarrow \Delta S_{TOT} = 0$
 adiabatic $\Rightarrow \Delta S_{surr} = 0$
 $\therefore \Delta S_{sys} = 0$

c) irreversible $\Rightarrow \Delta S_{TOT} > 0$
 expansion $\Rightarrow V_f > V_i$
 $\therefore \Delta S_{sys} > 0$ (no information about ΔS_{surr})

d) reversible $\Rightarrow \Delta S_{TOT} = 0$
 expansion $\Rightarrow V_f > V_i$
 $\therefore \Delta S_{sys} > 0$ (and $\Delta S_{surr} = -\Delta S_{sys}$)

2. Step 1: $P_1, V_1, T_1 \rightarrow P_2, V_1, T_4$ constant volume, reversible

$$dU = dq + dw \rightarrow 0$$

$$dU = dq_{rev,1} = C_v dT$$

$$\Delta S_1 = \int_{T_1}^{T_4} \frac{C_v dT}{T}; \quad q_{rev,1} = \int_{T_1}^{T_4} C_v dT$$

Step 2: P_2, V_1, T_4 constant P , reversible $\rightarrow P_2, V_2, T_1$

$$dq_{rev,2} = dU - dw = C_v dT + P dV$$

$$q_{rev,2} = \int_{T_4}^{T_1} C_v dT + \int_{V_1}^{V_2} P_2 dV$$

$$\Delta S_2 = \frac{q_{rev,2}}{T} = \int_{T_4}^{T_1} \frac{C_v dT}{T} + \int_{V_1}^{V_2} \frac{P_2}{T} dV; \quad \frac{P_2}{T} = \frac{nR}{V}$$

$$\Delta S_2 = \int_{T_4}^{T_1} \frac{C_v dT}{T} + \int_{V_1}^{V_2} \frac{nR dV}{V}$$

Step 1 + Step 2: $q_{rev} = \int_{T_1}^{T_4} C_v dT + \int_{T_4}^{T_1} C_v dT + \int_{V_1}^{V_2} P_2 dV = P_2 \Delta V$

$$\Delta S = \int_{T_1}^{T_4} \frac{C_v dT}{T} + \int_{T_4}^{T_1} \frac{C_v dT}{T} + \int_{V_1}^{V_2} \frac{nR}{V} dV = nR \ln\left(\frac{V_2}{V_1}\right)$$

Path B+C (from M+S sec. 20-3): $q_{rev} = \int_{T_3}^{T_1} C_v dT = C_v \Delta T$ path function

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

state function

$$3. \quad \Delta S_{\text{vap}} = \frac{n \Delta H_{\text{vap}}}{T_{\text{vap}}} = \frac{(2.0 \text{ mol})(40.65 \text{ kJ/mol})}{373.15 \text{ K}}$$

$$\Delta S_{\text{vap}} = 217.9 \text{ J/K}$$

$\Delta S_{\text{vap}} > 0$ because the system is becoming more disordered as it goes from a liquid to a gas.

4. CO vs. CO₂

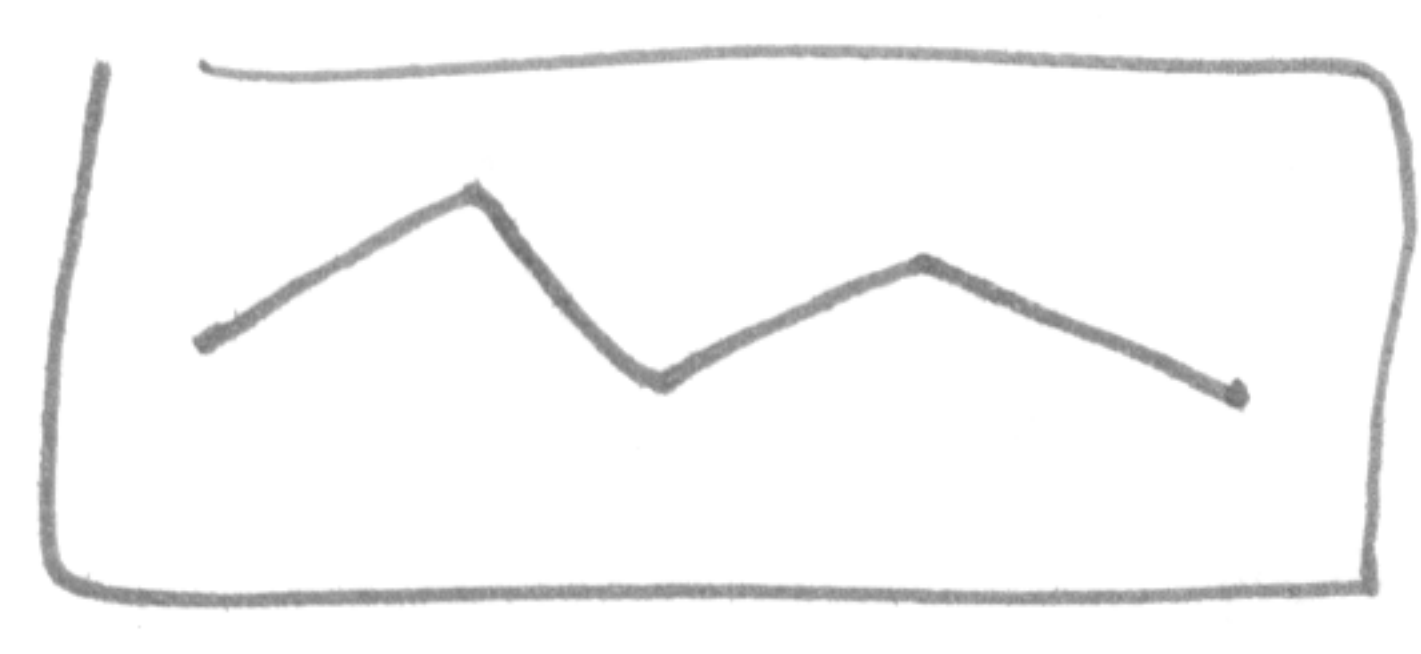
more atoms \Rightarrow more disorder



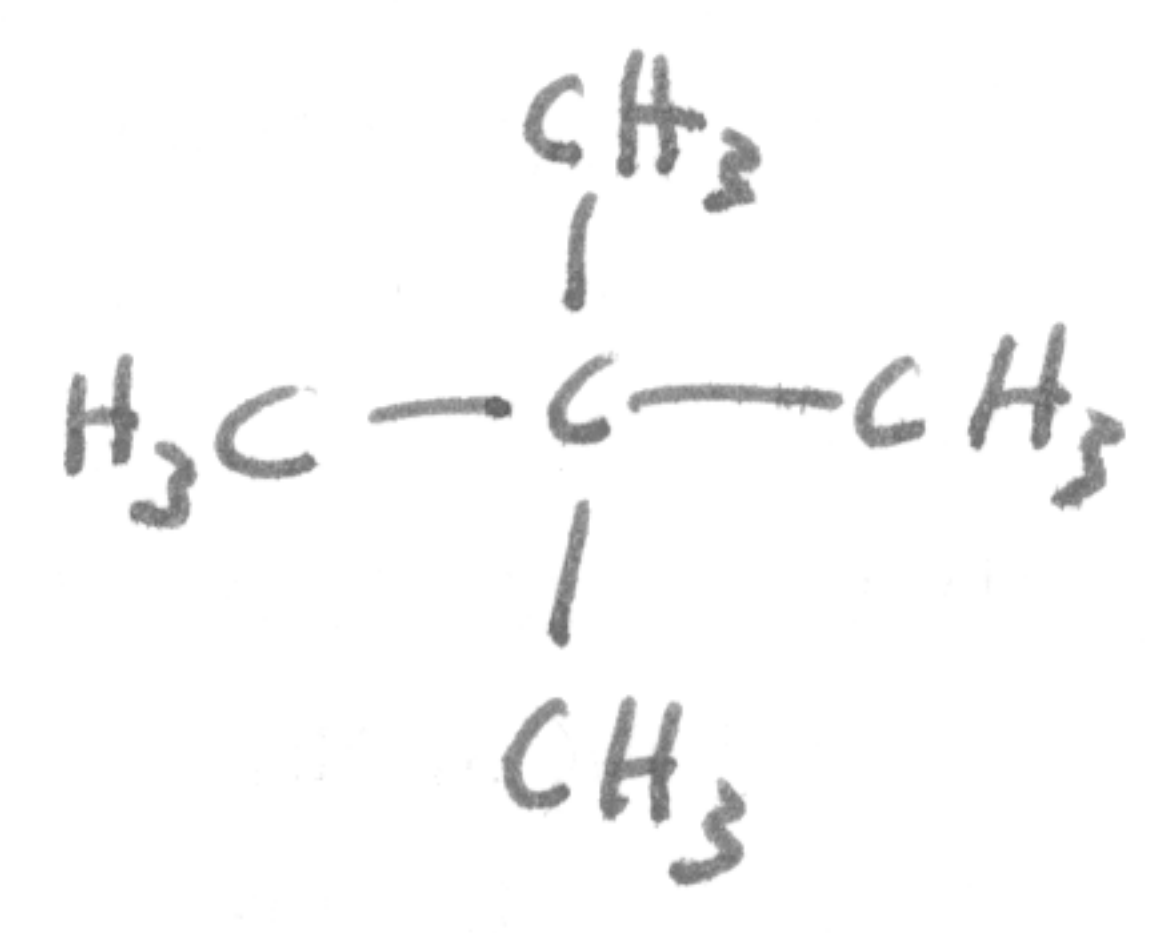
vs.



more flexible, rotational + vibrational freedom



vs.



the same as above

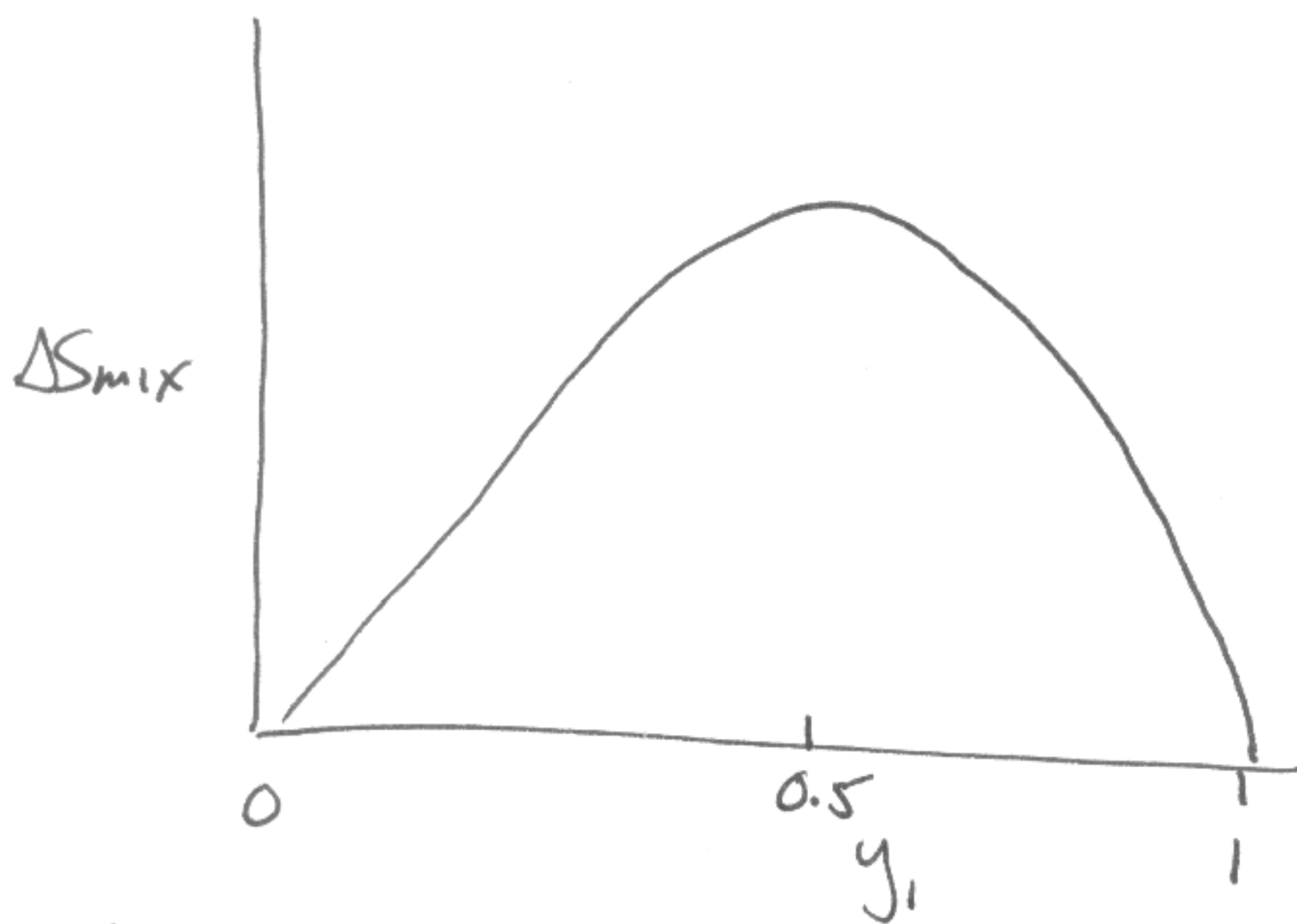
- 5. a) $\text{S}_{(s)} + \text{O}_{2(g)} \rightarrow \text{SO}_{2(g)}$ 1 mole of gas on both sides \rightarrow neutral
- b) $\text{H}_2(g) + \text{O}_2(g) \rightarrow \text{H}_2\text{O}_{(l)}$ net loss of 2 moles of gas \rightarrow bad
- c) $\text{CO}_{2(g)} + 3\text{H}_2(g) \rightarrow \text{CH}_4(g) + \text{H}_2\text{O}_{(l)}$ net loss of 3 moles of gas \rightarrow worse
- d) $\text{C}_{(s)} + \text{H}_2\text{O}_{(g)} \rightarrow \text{CO}_{(g)} + \text{H}_2(g)$ net gain of 1 mole of gas \rightarrow good

$c < b < a < d$ - increasing ΔS_{rxn}

$$6. \Delta S_{\text{mix}} = nR (-y_1 \ln y_1 - y_2 \ln y_2)$$

$$y_1 = \frac{n_1}{n}; \quad y_2 = \frac{n_2}{n}$$

(4)



ΔS_{mix} has a maximum at $y_1 = y_2 = 0.5$. The system is most disordered when there are equal amounts of both gases.

$$7. n_{\text{Au}} = 0.051 \text{ mols}$$

$$n_{\text{Ag}} = 0.093 \text{ mols}$$

Thermal equilibrium w/ no heat transfer to surroundings $\Rightarrow q_{\text{Au}} + q_{\text{Ag}} = 0$

$$q_{\text{Au}} = -q_{\text{Ag}}$$

i.e. all heat lost by Au is gained by Ag

$$n_{\text{Au}} c_{p,\text{Au}} (T_f - T_{i,\text{Au}}) + n_{\text{Ag}} c_{p,\text{Ag}} (T_f - T_{i,\text{Ag}}) = 0$$

$$\text{Rearrange: } T_f = \frac{n_{\text{Au}} c_{p,\text{Au}} T_{i,\text{Au}} + n_{\text{Ag}} c_{p,\text{Ag}} T_{i,\text{Ag}}}{n_{\text{Au}} c_{p,\text{Au}} + n_{\text{Ag}} c_{p,\text{Ag}}}; \quad \boxed{T_f = 512.5 \text{ K}}$$

$$\Delta S_{\text{sys}} = \Delta S_{\text{Au}} + \Delta S_{\text{Ag}} = n_{\text{Au}} c_{p,\text{Au}} \ln \left(\frac{T_f}{T_{i,\text{Au}}} \right) + n_{\text{Ag}} c_{p,\text{Ag}} \ln \left(\frac{T_f}{T_{i,\text{Ag}}} \right)$$

$$\Delta S_{\text{sys}} = 0.54 \text{ J/K}$$

$$\Delta S_{\text{surr}} = 0 \quad (\text{because adiabatic})$$

$$\Delta S_{\text{TOT}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0.54 \text{ J/K}$$