

①

1. $S_m = 146.2 \text{ J/kmol} @ T = 298 \text{ K}$

$C_{v,m} = \frac{3}{2} R$

$S_m = ? @ 500 \text{ K} ?$

(assume 1 mol)

$$S_m(500 \text{ K}) = S_m(298 \text{ K}) + \int_{T_i}^{T_f} \frac{C_{v,m}}{T} dT$$

$$S_m(500 \text{ K}) = S_m(298 \text{ K}) + C_{v,m} \ln\left(\frac{T_f}{T_i}\right)$$

$$= 146.2 \text{ J/kmol} + \left(\frac{3}{2}\right) (8.314 \text{ J/kmol}) \ln\left(\frac{500 \text{ K}}{298 \text{ K}}\right)$$

$S_m(500 \text{ K}) = 153 \text{ J/kmol}$

2. $n = 3.0 \text{ mol}$

$C_{v,m} = \frac{3}{2} R, C_{p,m} = \frac{5}{2} R$

$T_i = 298 \text{ K}$

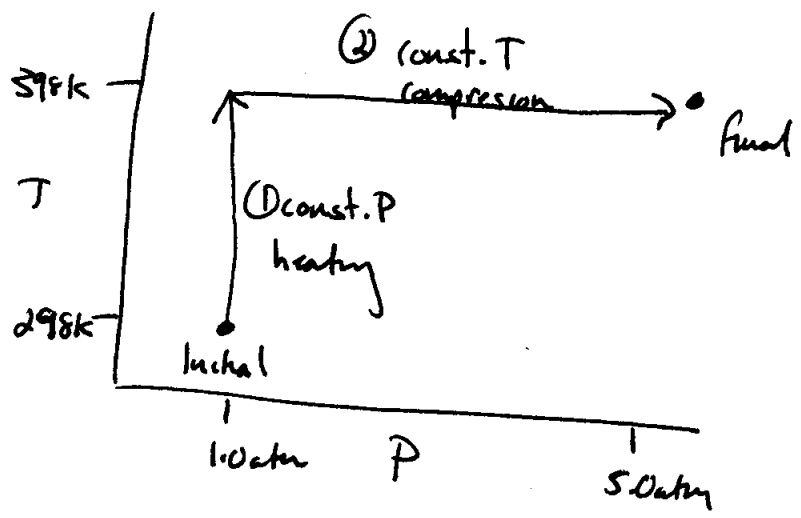
$P_i = 1.0 \text{ atm}$

$T_f = 398 \text{ K}$

$P_f = 5.0 \text{ atm}$

$\Delta S_{\text{sys}} = ?$

Break this up into two steps:



① $\Delta P = 0 \Rightarrow$ need $C_{p,m}$

$$\Delta S_{\text{①}} = n C_{p,m} \ln\left(\frac{T_f}{T_i}\right)$$

② $\Delta T = 0$

$$\Delta S_{\text{②}} = n R \ln\left(\frac{P_f}{P_i}\right)$$

(because $\frac{V_f}{V_i} = \frac{P_i}{P_f}$)

$$\Delta S_{\text{sys}} = \Delta S_{\text{①}} + \Delta S_{\text{②}} = n C_{p,m} \ln\left(\frac{T_f}{T_i}\right) + n R \ln\left(\frac{P_f}{P_i}\right)$$

$$= (3.0 \text{ mol}) \left(\frac{5}{2}\right) (8.314 \text{ J/kmol}) \ln\left(\frac{398 \text{ K}}{298 \text{ K}}\right) + (3.0 \text{ mol}) (8.314 \text{ J/kmol}) \ln\left(\frac{1.0 \text{ atm}}{5.0 \text{ atm}}\right)$$

$\Delta S_{\text{sys}} = 18.0 \text{ J/K} + -40.2 \text{ J/K} = -22.1 \text{ J/K}$

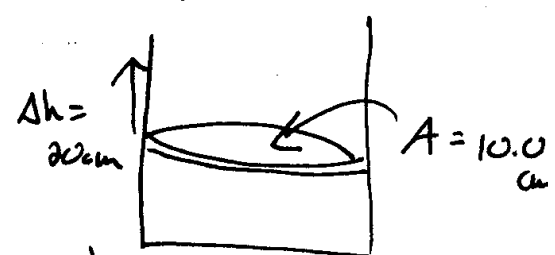


Continued: There are two competing processes here: increasing T , which will increase ΔS_{sys} , and increasing P , which will decrease ΔS_{sys} . In this case we have to plug in the #'s to see which wins, but the end result fits well w/ intuition. (That is to say, I would not expect this process to happen on its own.)

- 3. $n = 2.0 \text{ mol}$
- $T_c = 298 \text{ K}$
- $P_c = 1.0 \text{ atm}$
- $P_{ext} = 1.0 \text{ atm} = 1.01 \times 10^5 \text{ Pa}$
- $C_{v,m} = 28.8 \text{ J/kmol}$
- find $q, w, \Delta T, \Delta U, \Delta S$

adiabatic expansion $\Rightarrow q = 0$

$\Delta V = A \Delta h$



$\Delta V = (10 \text{ cm}^2)(20 \text{ cm}) = 200 \text{ cm}^3 \left(\frac{1 \text{ m}}{100 \text{ cm}}\right)^3 = 2.0 \times 10^{-4} \text{ m}^3$

$w = -P_{ext} \Delta V = -(1.01 \times 10^5 \text{ Pa})(2.0 \times 10^{-4} \text{ m}^3) = -20 \text{ Pa m}^3 = \boxed{-20 \text{ J} = w}$

$\Delta U = q + w = 0 + -20 \text{ J} = \boxed{-20 \text{ J} = \Delta U}$

$\Delta U = C_v \Delta T = n(C_{v,m} (T_f - T_c)) ; T_f = T_c + \frac{\Delta U}{n C_{v,m}} = 298 \text{ K} + \frac{-20 \text{ J}}{(2.0 \text{ mol})(28.8 \text{ J/kmol})}$

$T_f = 297.6 \text{ K}$

Break ΔS up into two steps: ① const. Volume cooling from $T_c \rightarrow T_f$
 ② isothermal expansion from $V_c \rightarrow V_f$

$\Delta S_{sys} = n(C_{v,m} \ln \frac{T_f}{T_c}) + nR \ln \frac{V_f}{V_c}$ →

Now need $V_i + V_f$: $V_L = \frac{nRT_L}{P_L} = \frac{(2.0 \text{ mol})(0.082 \frac{\text{L atm}}{\text{mol K}})(298 \text{ K})}{10 \text{ atm}} \left(\frac{1 \text{ dm}^3}{1 \text{ L}} \right) \left(\frac{1 \text{ m}}{10 \text{ dm}} \right)^3$

$$V_L = 4.89 \times 10^{-3} \text{ m}^3$$

$$V_f = V_L + \Delta V = 4.89 \times 10^{-3} \text{ m}^3 + 2.0 \times 10^{-4} \text{ m}^3$$

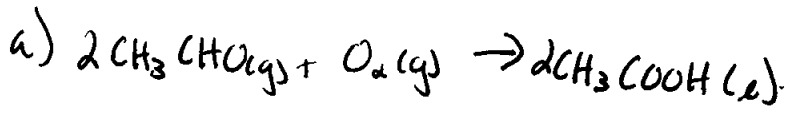
$$V_f = 5.09 \times 10^{-3} \text{ m}^3$$

plug everything into ΔS_{sys} :

$$\Delta S_{\text{sys}} = (2.0 \text{ mol})(28.8 \text{ J/kmol}) \ln \left(\frac{297.6 \text{ K}}{298 \text{ K}} \right) + (2.0 \text{ mol})(8.314 \text{ J/kmol}) \ln \left(\frac{5.09 \times 10^{-3} \text{ m}^3}{4.89 \times 10^{-3} \text{ m}^3} \right)$$

$$\Delta S_{\text{sys}} = 6.59 \text{ J/K}$$

4. $\Delta S_{\text{rxn}}^\circ = \sum_{\text{prod}} \nu S_{\text{m}}^\circ - \sum_{\text{react}} \nu S_{\text{m}}^\circ$



$$S_{\text{m}}^\circ (\text{CH}_3 \text{COOH}(\text{l})) = 159.8 \text{ J/kmol}$$

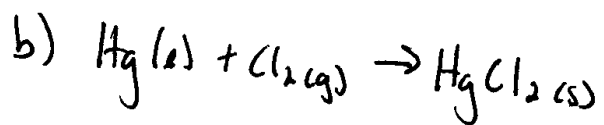
$$S_{\text{m}}^\circ (\text{CH}_3 \text{CHO}(\text{g})) = 250.3 \text{ J/kmol}$$

$$S_{\text{m}}^\circ (\text{O}_2(\text{g})) = 205.14 \text{ J/kmol}$$

$$\Delta S_{\text{rxn}}^\circ = 2(159.8 \text{ J/kmol}) - 2(250.3 \text{ J/kmol}) + 205.14 \text{ J/kmol}$$

$$\Delta S_{\text{rxn}}^\circ = -382.6 \text{ J/kmol}$$

(4)



$$S_m^\circ(\text{HgCl}_2) = 146.0 \text{ J/Kmol}$$

$$S_m^\circ(\text{Hg}) = 76.02 \text{ J/Kmol}$$

$$S_m^\circ(\text{Cl}_2(g)) = 223.07 \text{ J/Kmol}$$

$$\Delta S_{rxn} = S_m^\circ(\text{HgCl}_2) - S_m^\circ(\text{Hg}) - S_m^\circ(\text{Cl}_2)$$

$$= 146.0 \text{ J/Kmol} - 76.02 \text{ J/Kmol} - 223.07 \text{ J/Kmol}$$

$$\Delta S_{rxn} = -153.09 \text{ J/Kmol}$$

S. Cu: mass = 500g

$$FW(\text{Cu}) = 63.55 \text{ g/mol}$$

$$T_c = 293 \text{ K}$$

$$R = 1.00 \text{ k}\Omega$$

$$I = 1.00 \text{ A}$$

$$t = 15.0 \text{ sec}$$

$$C_p(\text{Cu}) = 24.4 \text{ J/Kmol}$$

$$n(\text{Cu}) = \frac{500 \text{ g}}{63.55 \text{ g/mol}} = 7.87 \text{ mols}$$

~~500g~~

Need T_f : $q = n C_{pm} \Delta T = n C_{pm} (T_f - T_c)$

$$T_f = T_c + \frac{q}{n C_{pm}}$$

$$q = I^2 R t \text{ (resistive heating)}$$

$$\Delta S = n C_{pm} \ln \left(\frac{T_c + \frac{I^2 R t}{n C_{pm}}}{T_c} \right)$$

$$\Delta S = (7.87 \text{ mols})(24.4 \text{ J/Kmol}) \ln \left(\frac{293 \text{ K} + \frac{(1.00 \text{ A})^2 (1000 \Omega) (15 \text{ s})}{(7.87 \text{ mols})(24.4 \text{ J/Kmol})}}{293 \text{ K}} \right)$$

$$\Delta S = 45.4 \text{ J/K}$$

→

alternate conditions: $T = 293\text{K}, \Delta T = 0$

$$\Delta S = n C_{pm} \ln \left(\frac{T_A}{T_L} \right) \rightarrow 0$$

$$\Delta S = 0$$

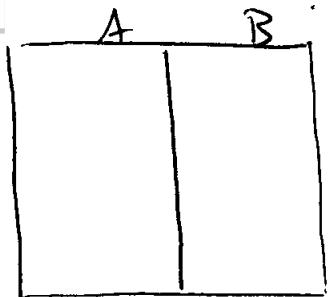
So what happens to the water?

$$\Delta S = \frac{q}{T} = \frac{I^2 R t}{T} = \frac{(1.00\text{A})(1000\Omega)(15\text{s})}{293\text{K}}$$

$$\Delta S = 51.2\text{J/K}$$

6.

Initial:



$$n_A = n_B = 2.0\text{mols}$$

$$T_A = T_B = 300\text{K}$$

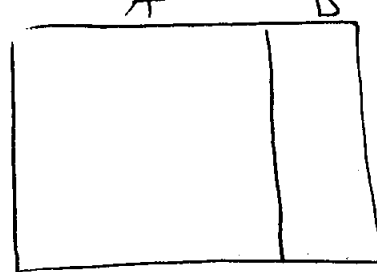
$$V_A = V_B = 2.0\text{L}$$

$$C_{v,m} = 20\text{J/Kmol}$$

$$\Delta H_B = 0$$

(because $\Delta T_B = 0$)

final



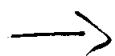
$$n_A = n_B = 2.0\text{mol}$$

$$V_A = 3.0\text{L}$$

$$V_B = 1.0\text{L}$$

$$T_B = 300\text{K}$$

$$T_A = ?$$



(6)

To determine ΔH_A we need to know ΔT_A

$$\Delta T_B = 0 \Rightarrow P_{BL} V_{BL} = P_{BF} V_{BF} \quad V_{BF} = \frac{V_{BL}}{2}$$

$$P_{BL} \frac{V_{BL}}{2} = P_{BF} \frac{V_{BL}}{2}$$

$$P_{BF} = 2P_{BL} = P_{Af} = 2P_A$$

(because the boundary has stopped moving because the pressure on both sides is equal)

$$\frac{T_{Af}}{T_{Al}} = \frac{P_{Af} V_{Af}}{P_{Al} V_{Al}} = \frac{2P_{Al} V_{Af}}{P_{Al} V_{Al}} = \frac{2V_{Af}}{V_{Al}} = \frac{2(3.0K)}{1.0K} = 3$$

$$\underline{T_{Af} = 3T_{Al} = (3)(300K) = 900K}$$

$$\Delta H_A = n(p_m \Delta T) = (2.0 \text{ mole}) (20 \text{ J/kmol} + 8.314 \text{ J/kmol}) (900 - 300 \text{ K})$$

$$\boxed{\Delta H_A = 34 \text{ KJ}}$$

↖
(remember $C_p = C_v + R$)

* This problem is actually just an ideal gas problem in disguise. It is challenging only because you need to manipulate $PV = nRT$ creatively to get all of the information that you need.

7. a) adiabatic $\Rightarrow q = 0$, $\Delta S_{\text{sys}} = \frac{q_{\text{sys}}}{T} = 0$

b) $\Delta T = 0$ expansion
 $\Rightarrow V_f > V_i$ $\Delta S_{\text{sys}} = nR \ln\left(\frac{V_f}{V_i}\right) > 0$

c) $\Delta P = 0$ cooling
 $T_f < T_i$ $\Delta S_{\text{sys}} = C_v \ln\left(\frac{T_f}{T_i}\right) = C_p \ln\left(\frac{T_f}{T_i}\right) < 0$

d) $\Delta P = 0$ vaporation $\Delta S_{\text{sys}} = \frac{\Delta H_{\text{vap}}}{T_{\text{vap}}} > 0; (\Delta H_{\text{vap}} > 0)$

8. $\Delta S_{\text{vap}} = \frac{n \Delta H_{\text{vap}}}{T_{\text{vap}}} = \frac{(2.0 \text{ mol})(40.65 \text{ kJ/mol})}{373 \text{ K}} = 218 \text{ J/K} = \Delta S_{\text{vap}}$

$\Delta S_{\text{vap}} > 0$ because the system is becoming more disordered (i.e. has more microstates) as it moves from liquid to gas.