E 3, 1a)

$$\Delta S = \int_i^f \frac{dq_{rev}}{T} = \frac{1}{T}\int_i^f dq \text{ (contant temp)} = \frac{q_{rev.}}{T}$$

a) $\Delta S = \frac{25.3 \times 10^3 \, J}{273.15 K} = 92 \, J/K$

b) $\Delta S = \frac{25 \times 10^3 \, J}{373.15 K} = 67 \, J/K$

E3, 7a) a) $\Delta_{vap} S = \frac{\Delta_{vap} H}{T_b} = \frac{29.4 \times 10^3 \, J/mol}{334.88 K} = 87.8 \, J/K \cdot mol$

b) Vaporization occurs reversibley: $\Delta S_{TOT} = 0$

$\Delta S_{surr} = {}^-87.8 \, J/K \cdot mol$

E 3.8a) a) $2CH_3CHO_{(g)} + O_{2\,(g)} \rightarrow 2CH_3COOH_{(l)}$ @ 298K

$$\Delta_r S^o = \sum_{products} \nu S_m^\theta - \sum_{Reactants} \nu S_m^\theta$$

Table 2.5 + 2.7:

$$\Delta_r S^o = 2S_m^\theta (CH_3CHOOH_{(l)}) - 2S_m^\theta (CH_3CHO_{g}) - S_m^\theta (O_2)$$

$$= 2 \cdot (159.8) - (2 \times 250.3) - 205.14) \, J K^{-1} mol^{-1}$$

$$= \boxed{{}^-386.1 \, J \cdot K^{-1} \cdot mol^{-1}}$$

b) $2AgCl_{(s)} + Br_{2\,(l)} \longrightarrow 2AgBr_{(s)} + Cl_2 \, (g)$

$$\Delta_r S_m^\theta = 2S_m^\theta (AgBr, s) + S_m^\theta (Cl_2, g) - 2S_m^\theta (AgCl, s) - S_m^\theta (Br_2, l)$$

$$= [2 \times 107.1 + 223.07 - 2 \times 96.2 - 152.23] \, J/K \cdot mol$$

$$= \boxed{92.6 \, J/K \cdot mol}$$

c) $Hg_{(l)} + Cl_{2\,(g)} \longrightarrow HgCl_{2}(s)$

$$\Delta_r S_m^\theta = S_m^\theta (HgCl_2, s) - S_m^\theta (Hg, l) - S_m^\theta (Cl_2, g)$$

$$= (146.0 - 76.02 - 223.07) \, J/K \cdot mol = \boxed{{}^-153.1 \, J/K \cdot mol}$$

P 3.4) Volume halved @ constant temperature; pressure doubles.

final $p_{B,f} = 2p_{B,i}$ initial

$p_{A,f} = 2p_{B,i} = 2p_{A,i}$

$$\frac{T_{A,f}}{T_{A,i}} = \frac{p_{A,f}V_{A,f}}{p_{A,i}V_{A,i}} = \frac{2p_{A,i} \cdot 3.00\,dm^3}{p_{A,i} \times 2.00\,dm^3} = 3.00$$ ∴ temp is tripled.

$T_{A,f} = 900k$

a) $$\Delta S_A = nC_{V,m} \ln\left(\frac{T_{A,f}}{T_{A,i}}\right) + nR\ln\left(\frac{V_{A,f}}{V_{A,i}}\right)$$

$$\Delta S_A = (2.0mol) \times (20\,J/K{\cdot}mol) \times \ln 3.00 + (2.0mol) \times (8.314\,J/K{\cdot}mol) \times \ln\left(\frac{3.00dm^3}{2.00dm^3}\right)$$
$$= \boxed{50.7\,J/K}$$

$\Delta S_B = nR\ln\left(\frac{V_{B,f}}{V_{B,i}}\right)$ because constant temperature

$$= (2.00mol) \times (8.314\,J/K{\cdot}mol) \times \ln\left(\frac{1.00dm^3}{2.00dm^3}\right) = \boxed{-11.5\,J/K}$$

b) $\Delta A = U - TS$ Section B is isothermal; $\Delta U_B = 0$, $\Delta(TS) = T\Delta S$

$\Delta A = \Delta U - \Delta(TS)$

$$\Delta A_B = -T_B \Delta S_B = -(300k)(-11.5\,J/K) = \boxed{3.46 \times 10^3\,J}$$

For Section A, ΔU cannot be calculated, making ΔA indeterminate. We know U depends on temperature, so that $U(T)$ is increasing with temperature, & $\frac{\partial U}{\partial T} = C$ (heat capacity) $\frac{\partial U}{\partial T} > 0$, because $\Delta T > 0$ and $\Delta(TS) > 0$

c) $\Delta G = \Delta H - T\Delta S$

$\Delta H_B = 0$ (constant temp, perfect gas)

$\Delta G_B = -T_B \Delta S_B = -(300\,K)(11.5\,J/K) = \boxed{3.46 \times 10^3\,J}$

ΔG_A is indeterminate

d) $\Delta S_{Total\ sys.} = \Delta S_A + \Delta S_B = (50.7 - 11{,}5)\,J/K = \boxed{39.2\,J/K}$

Assuming reversible process: $\Delta S_{Tot\,(sys + surr)} = 0 = \Delta S_{sys} + \Delta S_{surr.}$

$\Delta S_{surroundings} = \boxed{-39{,}2\,J/K}$

P3.6) Path (a)

$w = -nRT \ln\left(\frac{V_f}{V_i}\right) = -nRT \ln\left(\frac{P_i}{P_f}\right)$

$= -(1{,}00\,mol) \times (8{,}314\,J/K\cdot mol) \times (300\,K) \times \ln\left(\frac{3.00\,atm}{1{,}00\,atm}\right) = -2{,}74 \times 10^3\,J$

$= \boxed{-2{,}74\,kJ}$

$\Delta H = \Delta U = 0$ for isothermal perfect gas

$q = \Delta U - w = 0 - (-2{,}74\,kJ) = \boxed{+2{,}74\,kJ}$

$\Delta S_{sys} = \frac{q_{rev}}{T}$ (isothermal) $= \frac{2.74 \times 10^3\,J}{300\,K} = \boxed{9{,}13\,J/K}$

$\Delta S_{Tot} = 0$ for a reversible process

$\Delta S_{surr} = \boxed{-9{,}13\,J/K}$

Path B

$$\text{Work} = -p_{ex}(V_f - V_i) = -p_{ex}\left(\frac{nRT}{p_f} - \frac{nRT}{p_i}\right) = -nRT\left(\frac{p_{ex}}{p_f} - \frac{p_{ex}}{p_i}\right)$$

$$= -(1.00\,mol)(8.314\,J/K)(300\,K)\left(\frac{1.00\,atm}{1.00\,atm} - \frac{1.00\,atm}{3.00\,atm}\right) = -1.66\times10^{3}\,J = \boxed{-1.66\,kJ}$$

$\Delta H = \Delta U = 0$ for isotherml perfect gas

$q = \Delta U - w = 0 - (-1.66\,kJ) = \boxed{+1.66\,kJ} \leftarrow$ q for [illegible]

$$\Delta S_{sys} = \frac{q_{rev}}{T} = \frac{2.74\times10^{3}\,J}{300\,K} = \boxed{9.13\,J/K}$$ used q from path a due to the fact it is reversible.

$$\Delta S_{sur} = \frac{q_{sur}}{T_{sur}} = \frac{-q}{T_{sur}} = \frac{-1.66\times10^{3}\,J}{300\,K} = \boxed{-5.53\,J/K}$$

$$\Delta S_{TOT} = \Delta S_{sys} + \Delta S_{sur} = (9.13 - 5.53)\,J/K = \boxed{3.60\,J/K}$$

3.28) $\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$

a) perfect gas: $pV = nRT$; $\frac{\partial V}{\partial T} = \frac{nR}{p}$

$$\left(\frac{\partial H}{\partial p}\right)_T = \cancel{-\frac{nRT}{p}}^{V} + V = \boxed{0}$$

b) Van der Waals eqn: $p = \frac{nRT}{V-nb} - \frac{an^2}{V^2}$

cannot solve for V, solve for $\underline{T}$

$$T = \frac{p(V-nb)}{nR} + \frac{na(V-nb)}{RV^2} \; ; \; \left(\frac{\partial H}{\partial P}\right)_T = V - \frac{T}{\left(\frac{\partial T}{\partial V}\right)_P}$$ (reciprocal)

$$\left(\frac{\partial T}{\partial V}\right)_P = \frac{p}{nR} + \frac{na}{RV^2} - \frac{2na(V-nb)}{RV^3}$$

$$\left(\frac{\partial H}{\partial P}\right)_T = \frac{-T}{\frac{P}{nR} + \frac{na}{RV^2} - \frac{2na(V-nb)}{RV^3}} + V$$

algebraic manipulation gives

$$\left(\frac{\partial H}{\partial P}\right)_T = \frac{nb - \left(\frac{2na}{RT}\right)\lambda^2}{1 - \left(\frac{2na}{RTV}\right)\lambda^2} \quad \text{where } \lambda = 1 - \frac{nb}{V}$$

approximately ideal gas

$$\frac{b}{V_m} \ll 1, \ \lambda \approx 1 \ ; \quad \frac{2na}{RTV} \approx \frac{2na}{RT} \cdot \frac{P}{nRT} = \frac{2pa}{R^2T^2}$$

$$\left(\frac{\partial H}{\partial P}\right)_T \approx \frac{nb - \left(\frac{2na}{RT}\right)}{1 - \left(\frac{2pa}{R^2T^2}\right)} \ ; \text{ plugging in we get:}$$

$$\left(\frac{\partial H}{\partial P}\right)_T \approx \boxed{-8.3\ \text{J/atm}} \ \text{ or } \ \Delta H = -8.3\ \text{J/atm} \cdot 1\,\text{atm} \approx \boxed{-8\ \text{J}}$$

1) $C_{p_1} = 1000\ J/K$ $\quad$ $C_{p_2} = 500\ J/K$

$T_{I_1} = 10°C = 283K$ $\quad$ $T_{I_2} = 40°C = 313K$

$\Delta H = C_p \Delta T$

amount of heat from one block = amount of heat gained by the other.

$\Delta H_1 + \Delta H_2 = 0$

$\Delta H_1 = {}^-\Delta H_2$

$\Delta H_2 = 500\ J/K\ (T_f - 313K)$

$\Delta H_1 = 1000\ J/K\ (T_f - 283K)$

$500J/K \cdot T_f - (313 \cdot 500\ J) + 1000\ J/K \cdot T_f - (1000 \cdot 283)J = 0$

$T_f = \dfrac{439500\ J \cdot K}{1500\ J} = \boxed{293K}$

$\Delta H(\text{block } 1) = 10{,}000\ J$

$\Delta H(\text{block } 2) = {}^-10{,}000\ J$

$\Delta S_{\text{block 1}}\ \Delta S = S(t_f) - S(t_i) = \dfrac{dq}{T} = \displaystyle\int_{T_i}^{T_f} \dfrac{C_p\, dT}{T} = C_p \ln(T_f/T_i)$

$\Delta S(\text{block } 1) = S(t_f) - S(t_i) = C_p \ln\left(\frac{298K}{283K}\right) = \boxed{34.73\ J/K}$

$\Delta S(\text{block } 2) = C_p \ln\left(\frac{293}{313}\right) = \boxed{-33.02\ J/K}$

$\Delta S_{TOT} = 34.73J/K - 33.02J/K = \boxed{1.71J/K}$

2) Step 1

$$\Delta S_{sys} = -nR\ln\left(\frac{P_f}{P_i}\right) + C_p \ln\left(\frac{T_f}{T_i}\right); \quad C_v = 3Rn \quad C_p = 5Rn$$

$$\Delta S_{sys} = -(2\,mol)(8.314\,J/K\cdot mol)\ln\left(\frac{10\,bar}{1\,bar}\right) + (2\,mol)(5)(8.314\,J/K\cdot mol)\ln\left(\frac{500\,K}{300\,K}\right)$$

$$= -38.29\,J/K + 42.47\,J/K = \boxed{4.18\,J/K}$$

Step 2

$$\Delta S_{surr} = \frac{-q}{T}$$

$$q = \Delta U - w$$

$$\Delta U = C_v \Delta T$$

$$= (1.5R)(2\,moles)(500\,K - 300\,K)$$

$$= 4{,}988\,J$$

$$w = -P_{ext}\Delta V = -P_f(V_f - V_i) = -P_f\left(\frac{nRT}{P_f} - \frac{nRT_i}{P_i}\right)$$

$$= nRT_f - \frac{nRT_iP_f}{P_i} = (2\,moles)(8.314\,J/K\cdot mol)(500\,K) - (2\,moles)(8.314\,J/K\cdot mol)(300\,K)\left(\frac{10\,bar}{1\,bar}\right)$$

$$w = 8314\,J - 49884\,J = -41570\,J$$

$$\Delta S_{surr} = -\left(\frac{-41570\,J}{500\,K}\right) = \boxed{83.14\,J/K}$$

$$\Delta S_{TOT} = 4.18\,J/K + 83.14\,J/K = \boxed{87.32\,J/K}$$

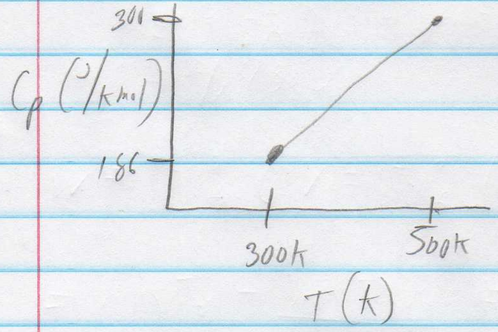
3) $An(s, 298) \xrightarrow{\Delta S_1} An(s, 340) \xrightarrow{\Delta S_2} An(v, 340) \xrightarrow{\Delta S_3} An(v, 500)$

$\underset{298\to 340}{\Delta S_1} = \int_{T_i}^{T_f} \frac{C_p}{T} dT$, Cp is constant

$\Delta S_1 = C_p \ln\left(\frac{T_f}{T_i}\right) = (210\ J/K\,mol) \ln\left(\frac{340}{298}\right) = \boxed{27.7\ J/K\,mol}$

$\Delta S_2 = \frac{\Delta_f H}{T} = \frac{125\ kJ/mol}{340\ K} = \frac{125 \times 10^3\ J/mol}{340\ K} = \boxed{367.6\ J/K\cdot mol}$

$\Delta S_3 = \int_{T_i}^{T_f} \frac{C_{p,vap}^{vap}}{T} dT$ Cp is a function of temperature, find change in Cp



$\text{slope} = \frac{\Delta Y}{\Delta X} = \frac{\Delta C_p}{\Delta T} = \frac{(300 - 186)\ J/K\cdot mol}{(500 - 300)\ K} = 0.57\ J/K^2\cdot mol$

$\Delta S_3 = \int_{T_i}^{T_f} \frac{\text{slope}\ T}{T} dT = (0.57\ J/K^2\,mol)(T_f - T_i) = (0.57\ J/K^2\cdot mol)(500 - 340)\ K$

$= \boxed{91.2\ J/K\cdot mol}$

$S_{\text{absolute}}\ S(500K) = S^0 + S^1 + S^2 + S^3$

$= 208\ J/K\cdot mol + 367.6\ J/K\,mol + 91.2\ J/K\,mol = \boxed{667\ J/K\,mol}$

4) Step 1 $A \rightarrow B$

isothermal, therefore $\Delta S = \frac{q}{T} = \frac{10.37\ \text{kJ}}{300\ \text{K}} = \boxed{34.57\ \text{J/K}}$

Step 2

For an ideal gas, $\Delta S = 0$ for a reversible adiabatic process.

$\Delta S_{TOT} = \Delta S_{sys} + \Delta S_{surr} = 40\ \text{J/K}$ $\Delta S_{sys}(B-C)$

$\Delta S_{sys} = \Delta S(A \rightarrow B) + \Delta S(B-C)$

$40\ \text{J/K} = 34.57\ \text{J/K} + \Delta S_{surr}$

$\boxed{\Delta S_{surr} = 5.43\ \text{J/K}}$

5)

$$3H_2(g) + N_2(g) \rightarrow 2NH_3 \quad @\,500K$$

$$\Delta_r S^\ominus = \underset{prod}{\sum} \nu S_m^\ominus - \underset{react}{\sum} \nu S_m^\ominus$$

$$S(500k) = S(298\ k) + \int_{T_i}^{T_f} \frac{C_p\, dT}{T}$$

$$S_{H_2}\, 500K = S_{m\,H_2}(298K) + C_{p_m\,H_2}(500 - 298\,K)$$

$$\frac{130.68\ J}{K \cdot mole} + \frac{28.82\ J}{K \cdot mole} \ln(202\ K) = \frac{283.7\ J}{mole \cdot K}$$

$$S_{N_2}\, 500k = \frac{191.61\ J}{K \cdot mole} + \frac{29.13\ J}{K \cdot mole} \ln(202\,K) = \frac{346.2\ J}{mole \cdot K}$$

$$S_{NH_3}\, 500K = \frac{192.45\ J}{K \cdot mole} + \frac{35.06\ J}{K \cdot mole} \ln(202\,K) = \frac{378.6\ J}{mole \cdot K}$$

$$\Delta_r S = 2(S_{NH_3} @500K) - 3(S_{H_2} @500K) - S_{N_2} @500K$$

$$\Delta_r S^\circ = 2\left(\frac{378.6\ J}{mole \cdot K}\right) - 3\left(\frac{283.7\ J}{mole \cdot K}\right) - \left(\frac{346.2\ J}{mole \cdot K}\right) = \boxed{\frac{-440.1\ J}{mole \cdot K} = \Delta_r S^\circ}$$

$$\Delta_r H^\circ = \underset{prod}{\sum} \nu H^\circ - \underset{react}{\sum} \nu H^\circ$$

$$\Delta_r H^\circ = 2\, H_{NH_3} @500k - \cancelto{0}{3\, H_{H_2} @500k} - \cancelto{0}{H_{N_2} @500k}$$

$$\Delta_r H^\circ = 2(-39.0\ kJ/mole)$$

$$\boxed{\Delta_r H^\circ = -78.1\ kJ/mole}$$

$$H_{NH_3}(500k) = H_{NH_3}(298k) + \int_{T_1}^{T_2} C_p\, dT \qquad \Delta H_{NH_3}\, 500k =$$

-46 kJ … 35.06 J

$$G = H - TS$$

$$G = \frac{-78.1\,kJ}{mole} - (500\,K)\left(\frac{-440.1\,\cancel{J}}{mole}\right)\left(\frac{1\,kJ}{1000\,\cancel{J}}\right)$$

$$\boxed{\Delta_r G^\circ = 142.0\,\frac{kJ}{mole}}$$