1. a) 1 mol $C_V = 5/2\,R$

$$w = \int -P_{ext}\,dV \underset{\text{rev}}{=} -\int P\,dV \underset{P\text{ cte}}{=} -P\,\Delta V_{2\to3}$$

$$P_3 = \frac{nRT_3}{V_3} = \frac{1 \times 0.08314 \times 393.75}{5.87} = 5.58 \text{ bar}$$

$120.6°C = 393.75\ K$

$-52.8°C = 220.35 K$

$30.2°C = 303.35 K$

$94.6°C = 367.75 K$

$P_3 = P_2 = 5.58$ bar

$$V_2 = \frac{nRT_2}{P_2} = \frac{1 \times 0.08314 \times 303.35}{5.58} = 4.52 \text{ dm}^3$$

$$w_{2\to3} = -5.58 \times 10^5 \times (5.87 - 4.52) \times 10^{-3}$$
$$= -752\ J$$

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b) V cte $dw = 0$ $\quad \Delta U = Q + w$

$\Delta U = Q$

$$\Delta U = \int n C_V\,dT = 1 \times 2.5 \times 8.314 \times (T_4 - T_3)$$
$$= 1 \times 2.5 \times 8.314 \times (220.35 - 393.75) = -3604\ J$$

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c) $P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$

$C_p = C_v + R = 5/2\,R + R = 7/2\,R$

$\gamma = C_p / C_v = 1.4$

$P_2 V_2^{\gamma} = P_2 \left(\frac{mRT_2}{P_2} \right)^{1.4} =$

$= P_2 \times P_2^{-1.4} \times (mRT_2)^{1.4} =$

$= 5.58^{-0.4} \times (1 \times 0.08314 \times 303.35)^{1.4} =$

$= 46.121$

$46.121 = P_1 V_1^{\gamma} = P_1 \times \left(\frac{mRT_1}{P_1} \right)^{\gamma} =$

$= P_1^{-0.4} \times (1 \times 0.08314 \times 367.75)^{1.4}$

$P_1 = 10.94$ bar

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d) $\Delta S_t \overset{\text{new}}{=} 0 = \Delta S + \Delta S_{viz}$

$\Delta S_{4 \to 5} = \int n \frac{C_v}{T} dT + mR \ln \frac{V_+}{V_i}$

$\Delta U_{4 \to 5} = \int n C_v dT = 1 \times 2.5 \times 8.314 \times$

$\times (T_5 - T_4) = 208$ J

$T_4 = 220.35\ K$

$208 = 1 \times 2.5 \times 8.314 \times (T_5 - 220.35)$

$T_5 = 230.36\ K$

$V_4 = V_3 = 5.87\ dm^3$

$V_5 = \frac{nRT_5}{P_5} = \frac{1 \times 0.08314 \times 230.36}{1.26} =$

$= 15.20\ dm^3$

$\Delta S_{4 \to 5} = 1 \times 2.5 \times 8.314 \ln \frac{230.36}{220.35} +$

$+ 1 \times 8.314 \times \ln \frac{15.20}{5.87} =$

$= 0.92 + 7.91 = 8.8\ JK^{-1}$

$\Delta S_{uk} = -8.8\ JK^{-1}$

2.a) P ctte $\Delta U = ?$ (1)

$H = U + PV$ $\quad \Delta H = \Delta U + P\Delta V$

P ctte

$\Delta U = \Delta H - P\Delta V$

P ctte

$138.9°C = 412.05\ K$

$\Delta H = \int n C_p dT$ (p ctte.)

$- n \Delta H_{vap}$.

$\Delta H = 1 \times 36 \times (100 - 138.9) + 1 \times (-40700)$

$+ 1 \times 75 \times (0 - 100) + 1 \times (-6010) = -55610\ J$

$\Delta V = V_{m,sol} - V_{m,gaz}$

$V_{m,sol} = \frac{1}{0.92} \times 18 = 19.56\ cm^3\ mol^{-1}$

$V_{m,gaz} = \frac{nRT}{P} = \frac{1 \times 0.08314 \times 412.05}{1.01}$

$= 33.92\ dm^3$

$\Delta U = -55610 - 1.01 \times 10^5 \times (19.56 \times 10^{-6} - 33.92 \times 10^{-3})$

$= -55610 + 3424 = -52186\ J$

b) $\Delta A = ?$ $\qquad A = U - TS$

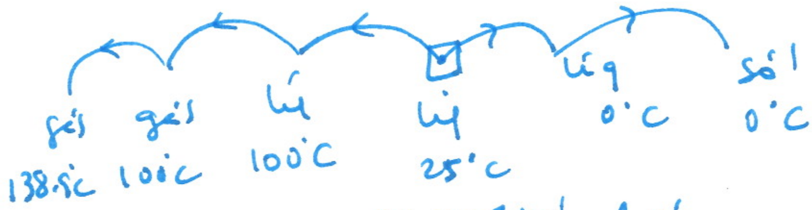
$$\Delta A = \Delta U - \Delta(TS) =$$
$$= \Delta U - (T_f S_f - T_i S_i)$$

$\Delta U = -52186\ J$

$T_f = 0°C \qquad T_i = 138.9°C$

$S_f = S_{ref} + \Delta S_{ref-f}$

$S_i = S_{ref} + \Delta S_{ref-i}$



$\Delta S \leftarrow \int n \frac{C_p}{T} dT \qquad$ (P cte)

$\quad \nwarrow \frac{\Delta H_{trans}}{T_{trans}}$

$$S_f = 69.95 + 1 \times 75 \times \ln \frac{273.15}{298.15} + \frac{(-6010)}{273.15}$$

$$= 69.95 - 6.57 - 22.00 = 41.38\ J K^{-1} mol^{-1}$$

$$S_i = 69.95 + 1 \times 75 \times \ln \frac{373.15}{298.15} + \frac{40700}{373.15} +$$

$$+ 1 \times 36 \times \ln \frac{412.05}{373.15} =$$

$$= 69.95 + 16.83 + 109.07 + 3.57 = 199.42\ J K^{-1} mol^{-1}$$

$$\Delta A = -52186 - (273.15 \times 41.38 -$$

$$- 412.05 \times 199.42) =$$

$$= -52186 + 70868 = 18682 \text{ J}$$