Chemistry 304 - Midterm Solutions - 2016

PART I: (20 marks total)

Indicate whether each of the following statements 1–8 is true or false and on the line underneath write one sentence to justify your choice. There will be no penalties for incorrect answers. Each correct answer with accompanying explanation is worth 2.5 marks.

1. **For a constant-volume process in a closed system, $\Delta H = \Delta U$.**

   1) True 2) [✓ False]

   For constant V, $\Delta H = \Delta U + \Delta PV = \Delta U + V\Delta P$, so pressure changes will lead to enthalpy changes in this case.

2. **The volume of a fixed amount of pure gas is doubled using an isothermal process. The change in entropy of the gas is greater when the process is done irreversibly than when done reversibly.**

   1) True 2) [✓ False]

   Since the initial and final states of the gas are uniquely specified, they are the same whether the process is reversible or irreversible. Entropy is a state function, and since the initial and final states are fixed, ΔS will be the same regardless of the path.

3. **For every cyclic process, the final state of the surroundings is the same as the initial state of the surroundings.**

   1) True 2) [✓ False]

   The *system* returns to its initial state in a cyclic process but because such processes transfer heat and work to the surroundings, the final state of the surroundings after the cycle is not the same as it was initially.

4. **Because of the Boltzmann factor $e^{-\beta E}$, the most probable energy for a system is always its lowest energy.**

   1) True 2) [✓ False]

   The probability a system has a certain energy is $P(E_\ell) = \Omega(E_\ell)\exp(-\beta E_\ell)/Q$. While it is true that the *microstate* of lowest energy has the greatest probability due to the $\exp(-\beta E)$ term, the degeneracy factor changes this for the most probable energy. Since $\Omega(E_\ell)$ increases with energy, the most probable energy is rarely the lowest energy of the system.

5. **For the Berthelot equation of state, $P = \dfrac{RT}{V_m - c} - \dfrac{d}{TV_m^2}$, the parameter d gives a measure of the interactions among the particles in the system.** *Note:* $\alpha/\kappa = (\partial P/\partial T)_{V,n_i}$.

   1) [✓ True] 2) False

   Using the given equation of state, $(\partial U/\partial V)_{T,N} = T(\partial P/\partial T)_{V,N} - P = 2d/(TV_m^2)$. Since $(\partial U/\partial V)_{T,N}$ gives a measure of particle interactions (it is zero in the absence of interactions), and its value is directly proportional to d, d must give a measure of particle interactions.

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6. **A process produces more energy as work when done reversibly than when done irreversibly.**

   1) [✓ True] 2) False

   As shown in class, the Clausius Inequality (Second Law) can be used to show that $dw_{rev} \leq dw$. Here, the system is producing work so $w > 0$ so the inequality shows directly that reversible work will be larger than irreversible work for the same process.

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7. **In a closed system, any process that is both adiabatic and isochoric will not change the internal energy of the system.**

   1) True 2) [✓ False]

   At constant V, $dU = C_V dT + (\partial U/\partial V)_T dV = C_V dT$, so a change in temperature can still change the internal energy by performing non-PV work on the system (stirring an insulated container of water, for example).

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8. **If energy has flowed out of a system as a result of a reversible process, the entropy of the system has decreased.**

   1) True 2) [✓ False]

   This is only true if the energy flows out as heat. If the energy is due to reversible work only, no change in entropy of the system will occur.

PART II (8 marks total)

1. **Write and discuss the significance of the two fundamental postulates in equilibrium statistical mechanics.**

   One fundamental postulate is the Ergodic Hypothesis which states that given enough time, the system will visit all its microstates. This is significant because it implies ensemble averages will be the same as time averages, the former of which can be calculated in statistical mechanics with the latter representing reality.

   Another fundamental postulate states that an equilibrium system at constant N, V, and T has microstate probabilities that depend only upon the microstate energy. In other words, microstates with the same energy have the same probability. This is significant because it allows the probability distribution to be determined precisely, namely the Boltzmann distribution, and this is crucial for calculating ensemble averages.

2. **In the injection moulding process, plastic is injected at constant temperature into a mould at pressures of about $25\,\mathrm{MPa}$ to form a plastic part, after which the mould opens and the part is removed at atmospheric pressure $(1\,\mathrm{bar})$. If $\alpha = 200 \times 10^{-6}\,\mathrm{K}^{-1}$ and $\kappa = 5.0 \times 10^{-10}\,\mathrm{Pa}^{-1}$ for the plastic, by what percentage will the part's volume expand when it is released from the mould?**

   This process is isothermal and closed, so the general equation of state gives $dV = -\kappa V dP$ which upon rearranging and integrating gives

$$
\begin{aligned}
\frac{dV}{V} &= -\kappa dP \\
\int_{V_1}^{V_2} \frac{dV}{V} &= -\int_{P_1}^{P_2} \kappa dP \\
\ln\left(\frac{V_2}{V_1}\right) &= -\kappa(P_2 - P_1) \\
\frac{V_2}{V_1} &= e^{-\kappa(P_2 - P_1)} \\
&= e^{-5.0\times10^{-10}\,\mathrm{Pa}^{-1}\times(10^5\,\mathrm{Pa} - 25\times10^6\,\mathrm{Pa})} \\
&= 1.0125\ ,
\end{aligned}
$$

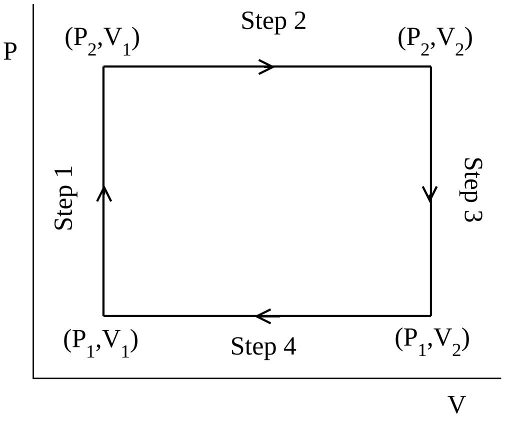
   where κ has been taken as constant in the integral, and $P_2 = 1\,\mathrm{bar} = 10^5\,\mathrm{Pa}$. The volume of the part is 1.0125 times larger than it was in mould, so its volume has expanded by about 1.3%.

PART III (11 marks total)

1\. a) **A heat engine uses an ideal gas in the four step thermodynamic cycle pictured in the graph to the right. The efficiency is given by**

$$\eta = \frac{|w|}{q_{in}} \ ,$$

where w is the total work done in the cycle, and q_{in} is the total heat transferred into the cycle. If $V_2 = 10V_1$, $P_2 = 5P_1$, and $C_{V,m}/R = 3.0$ for the gas (assumed constant), calculate the efficiency.



Steps 1 and 3 are isochoric so the $P - V$ work is zero for them. Steps 2 and 4 are isobaric, so for them $dw = -P_{ext}dV = -PdV$ and integrating gives $w = -P\Delta V$. Applying this general formula to each of these steps gives

$$\begin{aligned} w_2 &= -P_2(V_2 - V_1) = -5P_1(10V_1 - V_1) = -45P_1V_1 \ , \\ w_4 &= -P_1(V_1 - V_2) = -P_1(V_1 - 10V_1) = 9P_1V_1 \ , \\ w &= w_2 + w_4 = -45P_1V_1 + 9P_1V_1 = -36P_1V_1 \ , \end{aligned}$$

where the relationships $P_2 = 5P_1$ and $V_2 = 10V_1$ have been used. All the Steps in the cycle involve heat exchange. In Step 1, the pressure increases at constant volume so the temperature of the gas must be increasing, that is heat flows into the system in Step 1. In Step 2, the volume increases at constant pressure so again the temperature of the gas must be increasing, meaning heat also flows into the system in Step 2. In contrast, in Steps 3 and 4 the pressure or volume is decreasing, signaling a decrease in temperature and hence a loss of heat from the system. In other words, $q_{in} = q_1 + q_2$. These processes are isochoric or isobaric so the basic definitions of heat capacity can be used, namely

$$\begin{aligned} q_1 &= C_V(T_2 - T_1) = C_V\left(\frac{P_2V_1}{nR} - \frac{P_1V_1}{nR}\right) = \frac{C_V}{nR}(P_2 - P_1)V_1 = 3(5P_1 - P_1)V_1 = 12P_1V_1 \ , \\ q_2 &= C_P(T_3 - T_2) \\ &= (C_V + nR)\left(\frac{P_2V_2}{nR} - \frac{P_2V_1}{nR}\right) = \left(\frac{C_V}{nR} + 1\right)(V_2 - V_1)P_2 = 4(10V_1 - V_1)5P_1 = 180P_1V_1 \ , \\ q_{in} &= q_1 + q_2 = 12P_1V_1 + 180P_1V_1 = 192P_1V_1 \ , \end{aligned}$$

where the relationships $P_2 = 5P_1$, $V_2 = 10V_1$, and $C_V/nR = C_{V,m}/R = 3$ have been used, as well the relation between C_V and C_P for an ideal gas. Putting all this information together gives

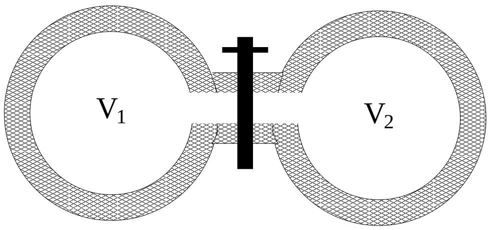
$$\eta = \frac{|w|}{q_{in}} = \frac{36P_1V_1}{192P_1V_1} = \frac{3}{16} = 0.1875 \ .$$

b) **If the engine were to operate between hot and cold baths each maintained at constant temperature, would its efficiency be greater than, less than, or equal to a Carnot engine operating between the same temperature baths? Please justify your response.**

No heat engine can be more efficient than the Carnot engine. The cycle in part a) would have this same efficiency if it could be performed reversibly. Now, if the cycle in part a) operates between a hot bath (presumably hotter than T_3, the highest temperature in the cycle after Step 2) and a cold bath (presumably colder than T_1, the coldest temperature in the cycle after Step 4), heat flows into the cycle in Steps 1 and 2 in isochoric and isobaric processes. These processes each involve changing the system temperature, meaning heat transfers from the hot bath across a finite temperature difference. From calculations we showed in class, heat transfer across a finite temperature difference is always an irreversible process. The same issue occurs during Steps 3 and 4 where the cooling part of the cycle is again done across a finite temperature difference, and is thus irreversible. Since the heat engine in part a) cannot be operated reversibly with constant temperature baths, its efficiency must be less than that for a Carnot engine operating between the same temperature baths.

PART IV (6 marks total)

As shown in the diagram to the right (not drawn to scale), an apparatus to determine the Joule coefficient consists of two insulated chambers. The first has volume $V_1 = 5\,\mathrm{L}$ and the second $V_2 = 10\,\mathrm{L}$. 4 moles of dimethyl ether at $300\,\mathrm{K}$ are placed in the first chamber and the second chamber is evacuated. When the stopper is turned, the gas expands to fill both chambers. Treating the dimethyl ether as a van der Waals gas with $C_{V,m} = 57.26\,\mathrm{J\,K^{-1}\,mol^{-1}}$, $a = 8.073\,\mathrm{L^2\,atm\,mol^{-2}}$, and $b = 0.07246\,\mathrm{L\,mol^{-1}}$, calculate ΔS, in $\mathrm{J\,K^{-1}}$, for this process.



An incorrect solution for this problem is given below. Circle all the methodological errors in the solution that is, errors caused by incorrect assumptions, the inappropriate use of equations, or the incorrect use of data in equations, for example. Please do not use your calculator to confirm the numerical operations given below because they are all numerically correct. For each circled quantity, write one sentence explaining why it is an error.

Solution Begins Here

The process is irreversible so it is necessary to construct a reversible path to calculate ΔS.

Since the process is $\boxed{\textbf{isothermal (a)}}$**,** $\Delta U = 0$**, and we need to find a reversible process from** (P_1, V_1, T) **to** (P_2, V_2, T)**, where** $T = 300\,\mathrm{K}$ **and using the van der Waals equation gives**

$$P_1 = \frac{4 \times \boxed{\textbf{8.3145 (b)}} \times 300}{5 - 4 \times 0.07246} - \frac{4^2 \times 8.073}{5^2} = 2113\,\mathrm{atm}\ .$$

We then have

$$\Delta S = \frac{q_{rev}}{T} = \frac{\boxed{\Delta U\ \textbf{(c)}} - w}{T} = -\frac{w}{T}\ ,$$

in which $\boxed{\Delta U = 0\ \textbf{(c)}}$ **from above has been used. The work is given by**

$$w = -\boxed{\textbf{P (d)}}\Delta V = -2113 \times (\boxed{\textbf{10 (e)}} - 5) = -10,565\ \boxed{\textbf{J, (f)}}$$

which when substituted into the equation above for ΔS **yields**

$$\Delta S = \frac{10,565}{300} = 35.22\,\mathrm{J\,K^{-1}}\ .$$

As expected, $\Delta S > 0$ **because the process is spontaneous.**

(a) Because the chambers are insulated ($q = 0$) and the second chamber is evacuated ($P_{ext} = 0 = w$), the First Law gives $\Delta U = q + w = 0$ so the process does conserve internal energy. However, for a van der Waals gas $0 = dU = C_V dT + (n^2 a/V^2)dV$ and since $dV \neq 0$ in the expansion, it must be the case that $dT = -(n^2 a/V^2 C_V)dV$ so that $dT \neq 0$. Since $dV > 0$ this equation shows that $dT < 0$, that is the temperature of the gas decreases as a result of the expansion, so the process is not isothermal. The expansion must overcome the attractive interactions among the particles, since the average distance between particles increases after the expansion. Since the internal energy is constant, this expansion energy must come from the kinetic energy of the particles, resulting in a lower temperature.

(b) This value of R has the wrong units compared with the other quantities and instead should be $0.082057\,\mathrm{L\,atm\,mol^{-1}\,K^{-1}}$.

(c) It is true that $\Delta U = 0$ for the expansion but when calculating the entropy we have constructed a reversible path, along which $\Delta U \neq 0$. Specifically, if one takes the isothermal premise of the solution as valid,

$$dS = \frac{dU - dw}{T} = \frac{C_V dT + (n^2 a/V^2)dV + PdV}{T} = \frac{nR}{V - nb}dV\ .$$

(d) Even given the isothermal premise, the expansion is into an evacuated chamber so $P_{ext} = 0$, and $w = 0$. Using a constant pressure, let alone the initial pressure of the gas, is not justified.

(e) Even given the equation, the final volume of the gas is $15\,\mathrm{L}$ not $10\,\mathrm{L}$ since the gas occupies both chambers at the end of the expansion.

(f) There is a unit conversion mistake here. The units should be $\mathrm{L\,atm}$ not J.

PART V (10 marks total)

Sperm whales can dive to great depths (over 2000 m), and have special rib cages that collapse under the large pressures at these depths. At sea level, a sperm whale with lungs of volume $1000\,\mathrm{L}$ inhales $40\,\mathrm{mol}$ of air. As it dives, the pressure increases until at feeding depth, the volume of the lungs is only $5\,\mathrm{L}$. The body temperature of a sperm whale is constant at $38\,^\circ\mathrm{C}$.

Treating the air as a van der Waals gas with $C_{V,m} = 20.8\,\mathrm{J\,K^{-1}\,mol^{-1}}$, $a = 1.37\,\mathrm{L^2\,atm\,mol^{-2}}$, and $b = 0.037\,\mathrm{L\,mol^{-1}}$, calculate ΔA, in kJ, for the air in the lungs as a result of the diving process. *Note: for a van der Waals gas, $(\partial U/\partial V)_T = n^2a/V^2$.*

The pressure builds up slowly as the whale dives so the compression can be treated as a reversible process. Actually, in this case since the initial and final states of the air are given, and only state functions are being calculated, the result will be independent of the way the process was performed. In any case, we need a reversible process to calculate the change in entropy so let's use a reversible process to solve the problem. The process is an isothermal, reversible compression of a van der Waals gas.

Since $A = U - TS$, we have $dA = dU - TdS$ when T is constant. Now $TdS = dq_{rev}$ and $dU = dq_{rev} + dw_{rev}$. Combining these gives

$$dA = dq_{rev} + dw_{rev} - dq_{rev} = dw_{rev} = -PdV\ .$$

This result could also be obtained from the general thermodynamic equation on the formula sheet, $dA = -SdT - PdV = -PdV$, since $dT = 0$. In either case, integration gives

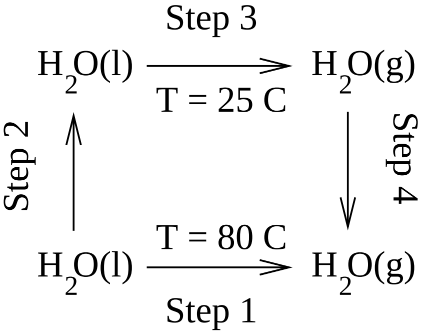
$$\begin{aligned}
\Delta A &= -\int_{V_1}^{V_2} PdV \\
&= -\int_{V_1}^{V_2} \left(\frac{nRT}{V-nb} - \frac{n^2a}{V^2}\right) dV \\
&= -nRT\int_{V_1}^{V_2} \frac{dV}{V-nb} + n^2a\int_{V_1}^{V_2} \frac{dV}{V^2} \\
&= -nRT\ln\left(\frac{V_2-nb}{V_1-nb}\right) + n^2a\left(\frac{1}{V_1} - \frac{1}{V_2}\right) \\
&= -40\,\mathrm{mol} \times 8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}} \times (38+273.15)\,\mathrm{K} \times \ln\left(\frac{5\,\mathrm{L} - 40\,\mathrm{mol}\times 0.037\,\mathrm{L\,mol^{-1}}}{1000\,\mathrm{L} - 40\times 0.037\,\mathrm{L\,mol^{-1}}}\right) \\
&\quad + (40\,\mathrm{mol})^2 \times 1.37\,\mathrm{L^2\,atm\,mol^{-2}} \times \left(\frac{1}{1000\,\mathrm{L}} - \frac{1}{5\,\mathrm{L}}\right) \\
&= 584,448\,\mathrm{J} - 436.21\,\mathrm{L\,atm} \\
&= 584.4 - 44.2\,\mathrm{kJ} \\
&= 540.2\,\mathrm{kJ}\ .
\end{aligned}$$

PART VI (15 marks total)

a) **Calculate $\Delta S_{universe}$, in $\mathrm{J\,K^{-1}}$, for the isothermal and isobaric vapourization of $2\,\mathrm{mol}$ of liquid water at $80\,^\circ\mathrm{C}$ and $1\,\mathrm{bar}$, given the thermodynamic data below and treating heat capacities as constant.**

$\Delta_f H^\circ(liquid\ water, 25\,^\circ\mathrm{C}) = -285.83\,\mathrm{kJ\,mol^{-1}}$; $\Delta_f H^\circ(water\ vapour, 25\,^\circ\mathrm{C}) = -241.82\,\mathrm{kJ\,mol^{-1}}$; $S^\circ(liquid\ water, 25\,^\circ\mathrm{C}) = 69.91\,\mathrm{J\,K^{-1}\,mol^{-1}}$; $S^\circ(water\ vapour, 25\,^\circ\mathrm{C}) = 188.72\,\mathrm{J\,K^{-1}\,mol^{-1}}$; $C_{P,m}(liquid\ water) = 75.3\,\mathrm{J\,K^{-1}\,mol^{-1}}$; $C_{P,m}(water\ vapour) = 37.5\,\mathrm{J\,K^{-1}\,mol^{-1}}$.

To calculate $\Delta S_{universe}$ we need to find the change in entropy for each of the system and surroundings. For the latter, we need to know the heat exchange with and the temperature of the surroundings. Since the vapourization is done under constant temperature and pressure, $T_{surr} = 80\,^\circ\mathrm{C}$ and $q_{surr} = -q = -\Delta H$ since $q = \Delta H$ when pressure is constant. Ultimately we need to find ΔS and ΔH for the vapourization at $80\,^\circ\mathrm{C}$ using the supplied information. The thermodynamic cycle to the right provides this. We desire ΔS and ΔH for Step 1. Using the supplied information, ΔS and ΔH for Step 3 are



$$\begin{aligned}
\Delta S_3 &= n[S^\circ(water\ vapour, 25\,^\circ\mathrm{C}) - S^\circ(liquid\ water, 25\,^\circ\mathrm{C})] \\
&= 2\,\mathrm{mol} \times [188.72 - 69.91]\,\mathrm{J\,K^{-1}\,mol^{-1}} = 237.62\,\mathrm{J\,K^{-1}} \\
\Delta H_3 &= n[\Delta_f H^\circ(water\ vapour, 25\,^\circ\mathrm{C}) - \Delta_f H^\circ(liquid\ water, 25\,^\circ\mathrm{C})] \\
&= 2\,\mathrm{mol} \times [-241.82 - (-285.83)]\,\mathrm{kJ\,mol^{-1}} = 88.02\,\mathrm{kJ}
\end{aligned}$$

To calculate ΔS and ΔH for Steps 2 and 4, we use the heat capacities, recognizing that these Steps are reversible, isobaric heating and cooling processes, so $dH = dq = nC_{P,m}dT$ and $dS = dq_{rev}/T = nC_{P,m}dT/T$. Treating the heat capacities are constant then gives

$$\begin{aligned}
\Delta S_2 &= nC_{P,m}(liquid\ water)\ln\left(\frac{T_2}{T_1}\right) = 2\,\mathrm{mol} \times 75.3\,\mathrm{J\,K^{-1}\,mol^{-1}} \times \ln\left(\frac{(25+273.15)\,\mathrm{K}}{(80+273.15)\,\mathrm{K}}\right) = -25.496\,\mathrm{J\,K^{-1}} \\
\Delta S_4 &= nC_{P,m}(water\ vapour)\ln\left(\frac{T_2}{T_1}\right) = 2\,\mathrm{mol} \times 37.5\,\mathrm{J\,K^{-1}\,mol^{-1}} \times \ln\left(\frac{(80+273.15)\,\mathrm{K}}{(25+273.15)\,\mathrm{K}}\right) = 12.697\,\mathrm{J\,K^{-1}} \\
\Delta H_2 &= nC_{P,m}(liquid\ water)(T_2 - T_1) = 2\,\mathrm{mol} \times 75.3\,\mathrm{J\,K^{-1}\,mol^{-1}} \times (25 - 80)\,\mathrm{K} = -8283\,\mathrm{J} \\
\Delta H_4 &= nC_{P,m}(water\ vapour)(T_2 - T_1) = 2\,\mathrm{mol} \times 37.5\,\mathrm{J\,K^{-1}\,mol^{-1}} \times (80 - 25)\,\mathrm{K} = 4125\,\mathrm{J}
\end{aligned}$$

These could also be done in a single step using the value of $\Delta C_{P,m}$, the difference in heat capacities between the vapour and liquid water states. Putting all the pieces together gives

$$\begin{aligned}
\Delta S_1 &= \Delta S_2 + \Delta S_3 + \Delta S_4 = -25.496 + 237.62 + 12.697\,\mathrm{J\,K^{-1}} = 224.82\,\mathrm{J\,K^{-1}} \\
\Delta H_1 &= \Delta H_2 + \Delta H_3 + \Delta H_4 = -8.283 + 88.02 + 4.125\,\mathrm{kJ} = 83.862\,\mathrm{kJ} \\
\Delta S_{universe} &= \Delta S_1 - \frac{\Delta H_1}{T} = 224.82\,\mathrm{J\,K^{-1}} - \frac{83.862\,\mathrm{kJ}}{(80+273.15)\,\mathrm{K}} = -12.65\,\mathrm{J\,K^{-1}}
\end{aligned}$$

b) **Would the process in part a) occur in reality? Please justify your response.**

According to the Second Law, $\Delta S_{universe} \geq 0$. Since the calculated $\Delta S_{universe}$ is negative, the process in part a) cannot occur in reality. In other words, it is not possible to vapourize water at $80\,^{\circ}\mathrm{C}$ at constant temperature and a pressure of $1\,\mathrm{bar}$. This is consistent with reality since water must reach $100\,^{\circ}\mathrm{C}$ in order to vapourize at a pressure of $1\,\mathrm{bar}$. The reverse process though, water vapour condensing to liquid water at $80\,^{\circ}\mathrm{C}$ has a positive value of $\Delta S_{universe}$ so the reverse process is possible and is also irreversible, again because it does not occur at the normal boiling point of $100\,^{\circ}\mathrm{C}$.

Note that $\Delta S_{universe}$ for Step 3 is also negative, indicating that the reverse process is possible and irreversible. This means one **cannot** use the relation $\Delta S_3 = \Delta H_3/T$. In fact, you can see that $\Delta H_3/T = 88.02\,\mathrm{kJ}/298.15\,\mathrm{K} = 295.2\,\mathrm{J\,K^{-1}} \neq \Delta S_3$. Recall that the relation $\Delta S = \Delta H/T$ is obtained for an isobaric process by assigning $dq_{rev} = dH$, that is it requires a **reversible** process in order to use the heat calculated from dH. A phase transition occurring at its normal transition temperature is indeed a reversible process, and happens at constant temperature and pressure. So, for such phase transitions, it is appropriate to use $\Delta S = \Delta H/T$. However, if a phase transition occurs at a temperature different from the normal transition temperature, the process will be irreversible, and the relation cannot be used. This is the case for the processes in this problem. This can be a subtle point but it is good to be aware of it.