

Practice Final Solutions

QUESTION 1 (25 points)

TRUE or FALSE (if false, provide the correct answer/explain why it is false. If true, just write TRUE, you do not need to justify)

1. For a one component system: $\mu = \left(\frac{\partial H}{\partial n} \right)_{S,P}$

True

2. At the triple point $\mu_{solid} = \mu_{gas}$

True

3. Consider an ideal gas that is thermally isolated from the surroundings, and undergoes a free expansion to twice its initial volume. The temperature of the gas will increase.

False $q=0$ & $w=0 \Rightarrow \Delta U=0$
for free expansion
 $\Delta U=0 \Rightarrow \Delta T=0$ for ideal gas

4. ΔH_{mix} of two ideal gases is always positive.

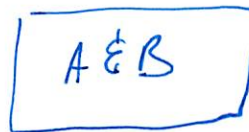
False $\Delta H_{mix} = 0$ for two ideal gases

Since $\Delta H=0$ for free expansion of each gas into the larger box

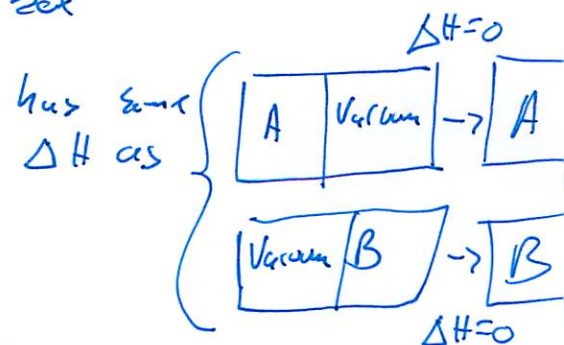
i.e.



→



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5. For the isothermal reversible expansion of an ideal gas, ΔG is greater than ΔF .

False

$$\Delta G = \Delta A + \Delta(PV) \quad ; \quad \Delta(PV) = \Delta(nRT) = 0$$

$$\text{So } \Delta G = \Delta A$$

6. For an monoatomic ideal gas, $\left(\frac{\partial C_v}{\partial V}\right)_T$ is always positive.

False

$$C_v = \frac{3}{2} nR \quad \frac{\partial C_v}{\partial V}_T = 0$$

7. In a paramagnet system, negative temperatures are hotter than positive temperatures.

True

8. A paramagnetic sample in a magnetic field (B) is prepared so that 40% of the magnetic dipoles (μ) are in states which are anti-aligned with the direction of the magnetic. The temperature is positive.

True

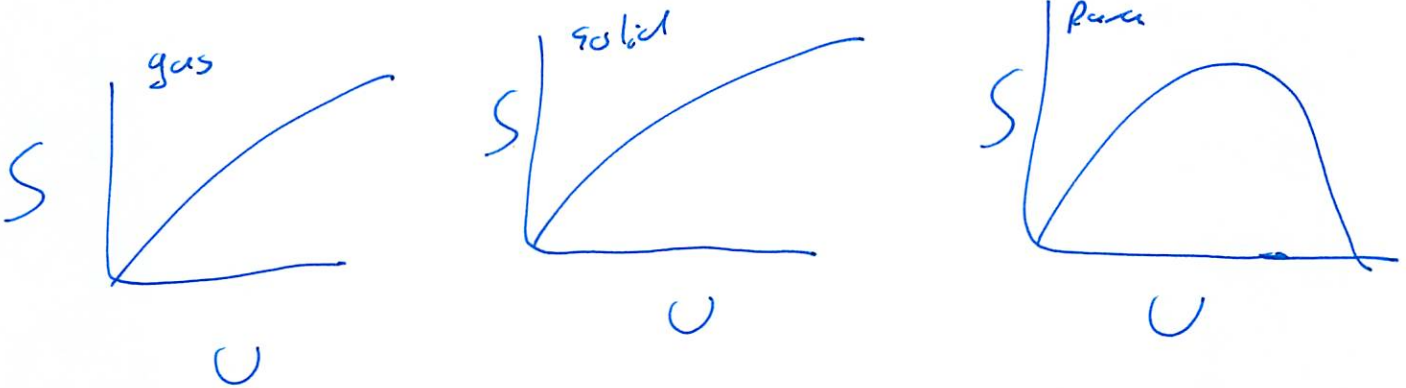
9. The slope of the solid-liquid boundary line in the P-T phase diagrams is always positive.

False, it is negative for H_2O

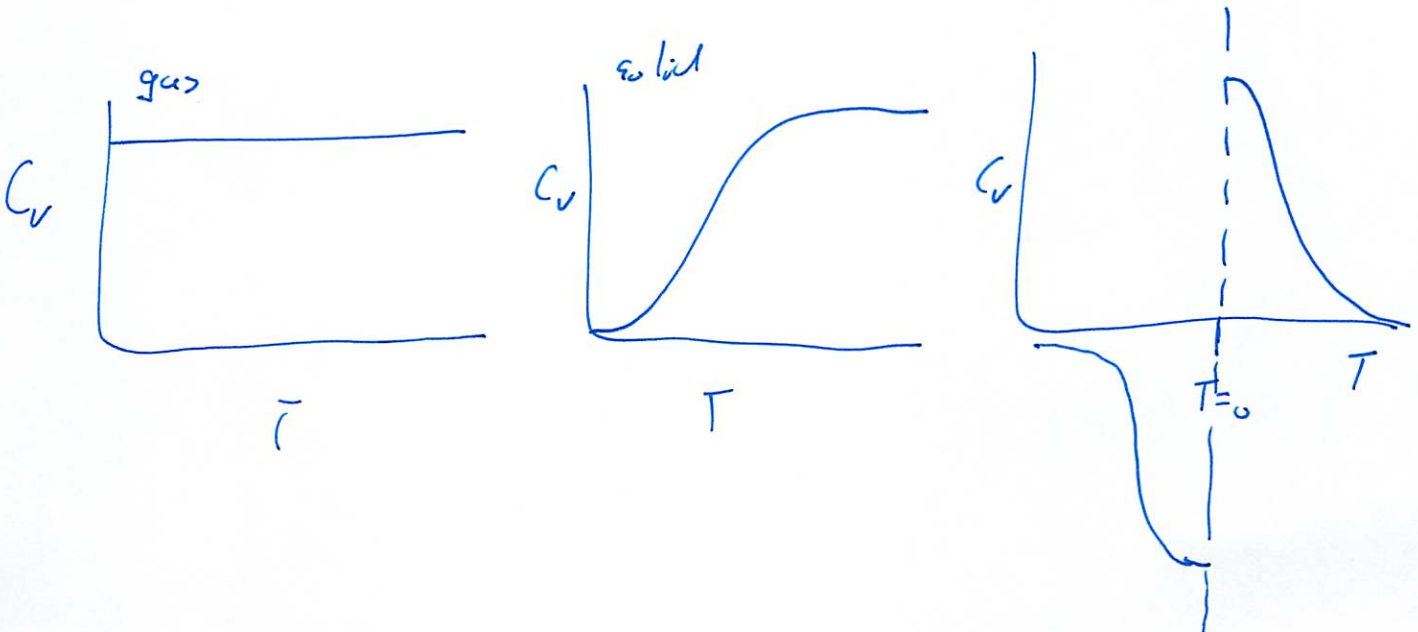
Question 2: (25 points) Short Questions (There are 7 independent parts)

Part 1: We considered three model systems in this class: an ideal gas, an Einstein solid and a paramagnet. For each of these systems, draw **qualitatively**:

a) a plot of S versus U



b) a plot of C_v versus T



Part 2: If an isolated Einstein solid is in thermodynamic equilibrium and has $N_A = 300$ oscillators in one subsystem and $N_B = 200$ oscillators in the other subsystem, and if the entire solid has 100 units of energy, what is the most likely amount of energy to be observed in system B?

Since energy is extensive, we expect the most likely (equilibrium) distribution to be the one where ^{i.e.} highest S

$$\frac{U_A}{N_A} = \frac{U_B}{N_B} \Rightarrow U_A = 60, \boxed{U_B = 40}$$

Part 3: The entropy $S = S(N, U, A)$ of an ideal two-dimensional monoatomic gas consisting of N atoms, energy U , and area A is given by the following version of the Sackur-Tetrode equation:

$$S = Nk_B \left[2 + \ln \left(\left(\frac{2\pi m}{h^2} \right) \frac{A U}{N N} \right) \right]$$

Here π is the two dimensional pressure (force per length as opposed to force per area). Derive an expression for the pressure π of this two-dimensional gas (simplify your expression as much as possible).

$$dU = T dS - \pi dA + \mu dN$$

$$dS = \frac{1}{T} dU + \frac{\pi}{T} dA - \frac{\mu}{T} dN$$

$$\frac{\pi}{T} = \left. \frac{\partial S}{\partial A} \right|_{U, N} = \frac{Nk_B}{A}$$

$$\boxed{\pi = \frac{Nk_B T}{A}}$$

Part 4: The vapor pressure P of solid ammonia in mm of Hg, in the vicinity of its triple point, is given by $\ln P_s = 23.03 - 3754/T$ and that of liquid ammonia by is given by $\ln P_l = 19.49 - 3063/T$. What are the latent heats of sublimation, vaporization and melting at or near the triple point?

Clausius-Clapeyron: $\frac{dP}{dT} = \frac{\Delta \bar{S}}{\Delta \bar{V}} = \frac{\Delta \bar{H}}{T \Delta \bar{V}} = \frac{\Delta \bar{H}}{T(RT/P)} \Rightarrow \frac{d \ln P}{dT} = \frac{\Delta \bar{H}}{RT^2}$

$\Delta \bar{G} = 0$ at coexist
 $\Delta \bar{V} = RT/P$ for condensed to gas

$$\Delta \bar{H}_{\text{sub}} = RT^2 \left(\frac{3754}{T^2} \right) = 8.314 \frac{\text{J}}{\text{K mol}} \times 3754 \text{ K} = \boxed{31.2 \text{ kJ/mol} = \Delta \bar{H}_{\text{sub}}}$$

$$\Delta \bar{H}_{\text{vap}} = RT^2 \left(\frac{3063}{T^2} \right) = 8.314 \frac{\text{J}}{\text{K mol}} \times 3063 = \boxed{25.5 \text{ kJ/mol} = \Delta \bar{H}_{\text{vap}}}$$

$$\Delta \bar{H}_{\text{melt}} = \Delta \bar{H}_{\text{sub}} - \Delta \bar{H}_{\text{vap}} = \bar{H}_g - \bar{H}_s - \bar{H}_g + \bar{H}_l = \bar{H}_l - \bar{H}_s \quad (\bar{H} \text{ is a state function})$$

$$\boxed{\Delta \bar{H}_{\text{melt}} = 5.7 \text{ kJ/mol}}$$

Part 5: The energy of a photon gas is given by $U = \alpha VT^4$ and the entropy by $S(U, V) = \alpha U^{3/4} V^{1/4}$ where α is a constant. Find an expression for the **Gibbs Free Energy** G in terms of α , T and V .

$$A = U - TS$$

$$= \alpha VT^4 - T \left[\alpha (\alpha VT^4)^{3/4} V^{1/4} \right]$$

$$= \alpha VT^4 - \alpha^{7/4} T^4 V = V(\alpha T^4 - \alpha^{7/4} T^4)$$

$$P = - \frac{\partial A}{\partial V} = \alpha^{7/4} T^4 - \alpha T^4 = - \frac{A}{V}$$

$$G = A + PV = A - \frac{A}{V} V = \boxed{0}$$

This odd result means that the chemical potential of photons is zero. This is true for "particles" that are not conserved.

Part 6: Use the appropriate Maxwell relation to show that: $\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V$

$$\begin{aligned}\frac{\partial H}{\partial P}\bigg|_T &= \frac{\partial H}{\partial P}\bigg|_S + \frac{\partial H}{\partial S}\bigg|_P \frac{\partial S}{\partial P}\bigg|_T \\ &= V + T \frac{\partial S}{\partial P}\bigg|_T \quad \text{Maxwell} \quad \frac{\partial S}{\partial P}\bigg|_T = -\frac{\partial V}{\partial T}\bigg|_P \\ &= V - T \frac{\partial V}{\partial T}\bigg|_P\end{aligned}$$

Part 7: Consider one mole of a Van der Waals gas, with equation:

$$P = \frac{RT}{(V-b)} - \frac{a}{V^2}$$

Consider ^{a reversible} adiabatic expansion from a volume V_1 to a volume V_2 . Find an expression for the final temperature T_2 in terms of the initial temperature T_1 , volume and other constants. You can consider C_v to be a constant.

$$\begin{aligned}dS &= \frac{C_v}{T} dT + \frac{\partial S}{\partial V}\bigg|_T dV \\ \text{reversible } q=0 \quad \hookrightarrow \quad 0 &= \frac{C_v}{T} dT + \frac{\partial P}{\partial T}\bigg|_V dV \quad \text{Maxwell}\end{aligned}$$

$$\int C_v \frac{dT}{T} = - \int \frac{R}{(V-b)} dV$$

$$C_v \ln\left(\frac{T_2}{T_1}\right) = R \ln\left(\frac{V_1-b}{V_2-b}\right)$$

$$T_2 = T_1 \exp\left[\frac{R}{C_v}\right] \left\{ \frac{(V_1-b)}{(V_2-b)} \right\}$$

Question 3: (15 points)

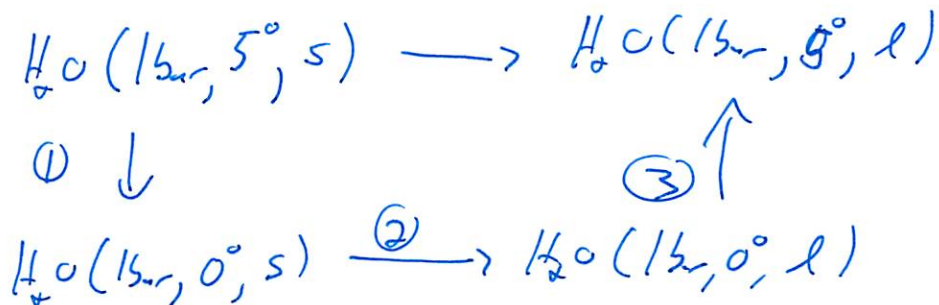
Calculate ΔS for the melting of 1 mol of H_2O (ice) at $5^\circ C$ and 1 bar (ie, solid to liquid transition). The molar heat capacity for liquid water is:

$$\overline{C}_{p,l} = 75 + 0.01T^2 \quad \text{in } JK^{-1}mol^{-1}$$

The molar heat capacity for ice is:

$$\overline{C}_{p,s} = 37.3 \quad \text{in } JK^{-1}mol^{-1}$$

The molar heat of melting at $0^\circ C$ and 1 bar is: 6.008 kJ/mol



$$\Delta S = \Delta S_{\textcircled{1}} + \Delta S_{\textcircled{2}} + \Delta S_{\textcircled{3}}$$

$$\Delta S_1 = \int_{273}^{278} \frac{\overline{C}_{p,s}}{T} dT = 37.3 \frac{J}{K} \ln\left(\frac{273}{278}\right)$$

$$\Delta S_2 = \frac{\Delta H_m}{273} = \frac{6008 \text{ J}}{273 \text{ K}}$$

$$\begin{aligned} \Delta S_3 &= \int_{273}^{278} \frac{\overline{C}_{p,l}}{T} dT = 75 \ln\left(\frac{278}{273}\right) \frac{J}{K} + \frac{0.01}{2} [278^2 - 273^2] \frac{J}{K} \\ &= 36.4 \frac{J}{K} \end{aligned}$$

Question 4: (20 points) There are 2 parts to this question

Consider 1 mol of a real gas obeying the following equation of state:

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{T\bar{V}^2}$$

with $a = 0.556 \text{ Pa m}^6 \text{ mol}^{-2} \text{ K}$
and $b = 64 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$

Part a) Consider the reversible isothermal change in state at 300K from an initial volume of 10 L to a final state of volume 20L. Calculate ΔS_{sys}

$$\begin{aligned} dS &= \left. \frac{\partial P}{\partial T} \right|_V dV \quad \leftarrow (\text{see prob. 2.7 with } dT=0) \\ \Delta S &= \int_{\bar{V}_1}^{\bar{V}_2} d\bar{V} \left[\frac{R}{(\bar{V} - b)} + \frac{a}{T^2 \bar{V}^2} \right] \\ &= R \ln \left(\frac{\bar{V}_2 - b}{\bar{V}_1 - b} \right) + \frac{a}{T^2} \left[\frac{1}{\bar{V}_1} - \frac{1}{\bar{V}_2} \right] \\ &= 5.78 \text{ J/K} \end{aligned}$$

Part b) Consider the same change in state, but carried out irreversibly against an external pressure equal to the final pressure in part a. The surroundings are kept constant at $T_{\text{surr}} = 300\text{K}$. Calculate ΔS_{tot} .

ΔS_{system} same as part a

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T_{\text{surr}}} = -\frac{q_{\text{sys}}}{T_{\text{surr}}}$$

$$q_{\text{sys}} = \Delta U_{\text{sys}} - w$$

$$dU = \left. \frac{\partial U}{\partial T} \right|_V dT + \left. \frac{\partial U}{\partial V} \right|_T dV$$

Clairaut's theorem

$$= -P + T \left. \frac{\partial S}{\partial V} \right|_T$$

$$= -P + T \left. \frac{\partial P}{\partial T} \right|_V$$

Maxwell

$$\Delta U = \int dV \left[-P + T \left. \frac{\partial P}{\partial T} \right|_V \right]$$

$$= \int dV \left(\frac{2a}{T V^2} \right) = \frac{2a}{T} \left(\frac{1}{V_2} - \frac{1}{V_1} \right)$$

$$w = -P_{\text{ext}} \Delta V$$

$$q_{\text{sys}} = 1250 \text{ J} \quad \Delta S_{\text{surr}} = \frac{-1250 \text{ J}}{300 \text{ K}} = -4.16 \text{ J/K}$$

$$\Delta S_{\text{tot}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 1.6 \text{ J/K}$$

$\Delta S_{\text{tot}} > 0$ spontaneous

Question 5 (15 points):

Adsorption is the process of particles sticking to the surface of a solid (rather than getting absorbed inside of it). To model adsorption, consider a surface that consists of $M \gg 1$ discrete sites; each site has two possible states: vacant (with energy $\epsilon = 0$), or bound to a single atom (with energy ϵ_0). The system is held at constant temperature T . If $N \gg 1$ atoms are bound (with $M \gg N$), find expressions for the following parameters of the system of adsorbed atoms. (Take care to express each parameter in terms of the requested variables, and make simplifying approximations where appropriate).

(a) The energy, $U(N, \epsilon_0)$.

$$U = N\epsilon_0$$

(b) The multiplicity, $\Omega(M, N)$.

$$\Omega = \frac{M!}{N!(M-N)!}$$

c) The entropy, $S(M, N)$.

$$\begin{aligned} S &= k_B \ln \Omega \\ &= [M \ln M - N \ln N - (M-N) \ln (M-N)] k_B \\ &= k_B \left\{ M \ln \left(\frac{M}{M-N} \right) + N \ln \left(\frac{M-N}{N} \right) \right\} \end{aligned}$$

d) The Helmholtz free energy, $F(M, N, T, \epsilon_0)$.

$$\begin{aligned} A &= U - TS \\ &= N\epsilon_0 - k_B T \left\{ M \ln \left(\frac{M}{M-N} \right) + N \ln \left(\frac{M-N}{N} \right) \right\} \end{aligned}$$

f) Now, the system of adsorbed atoms is placed in thermal and diffusive contact with an ideal gas of the same type of atoms. In equilibrium, find the number of adsorbed atoms N as a function of the pressure P of the ideal gas (and other constants of the problem). Note that the chemical potential of an ideal gas is $\varepsilon = k_B T \ln\left(\frac{N}{\alpha V}\right)$ where α is a constant.

$$\mu_{ads} = \mu_{gas} \quad \text{at equilibrium}$$

$$\begin{aligned} \mu_{ads} &= \left. \frac{\partial A}{\partial N} \right|_{T,V} = \varepsilon_0 - k_B T \left\{ -\ln N - 1 + \ln(M-N) + 1 \right\} \\ &= \varepsilon_0 + k_B T \left[\ln N - \ln(M-N) \right] \end{aligned}$$

$$\begin{aligned} \text{So, } \varepsilon_0 - k_B T \ln\left(\frac{M}{N} - 1\right) &= k_B T \ln\left(\frac{\mu_{gas}}{\alpha V}\right) \quad \leftarrow \mu_{gas} \\ &= k_B T \ln\left(\frac{P}{\alpha k_B T}\right) \end{aligned}$$

$$\varepsilon_0 / k_B T = \ln\left(\frac{P}{\alpha k_B T} \left[\frac{M}{N} - 1\right]\right)$$

$$e^{\varepsilon_0 / k_B T} = \frac{P}{\alpha k_B T} \left[\frac{M}{N} - 1\right]$$

$$N = \frac{M}{1 + \frac{\alpha k_B T}{P} e^{\varepsilon_0 / k_B T}}$$

BONUS QUESTION

Consider a three-state paramagnetic material with N atoms. $N_{\uparrow}$ have spin up, $N_{\downarrow}$ have spin down and N_0 have spin component 0. Find an expression for the multiplicity.

$$\Omega = \frac{N!}{N_{\uparrow}! N_{\downarrow}! N_0!}$$