

Directions: Please answer each question to the best of your ability. Make sure your response is **legible, precise, includes relevant dimensional units (where appropriate), logically presented (include non-mathematical language if necessary to convey your intent clearly and transparently), and correct/accurate**. You are free to use your Equations Handbook, Calculator, and blunt/sharp writing instrument. If you have any doubt(s) about the meaning/intent of a question(s), please ask immediately so you do not wander off on an incorrect path!

1. (5 Points) Consider pressure, P , is a function of a system's volume, V , the system temperature, T , and amount of material (moles) present, N , as:

$$P(N, V, T) = \frac{NRT}{V}$$

Treat R as a constant. Evaluate the following integral related to the absolute value of the reversible work for a change in system volume from V_1 to V_2 when temperature is fixed for a closed system:

$$|W_{reversible}| = \left| \int_{V_1}^{V_2} P(N, V, T) dV \right|$$

Given:

$$P(N, V, T) = \frac{NRT}{V}$$

$R = \text{constant}$

$T = \text{constant (fixed)}$

$N = \text{constant (closed system)}$

$$\begin{aligned} \text{So: } |W_{rev}| &= \left| \int_{V_1}^{V_2} \frac{NRT}{V} dV \right| \quad \therefore |W_{rev}| = \left| NRT \ln \left(\frac{V_2}{V_1} \right) \right| \\ &= \left| NRT \int_{V_1}^{V_2} \left(\frac{1}{V} \right) dV \right| \\ &= \left| NRT \int_{V_1}^{V_2} \frac{dV}{V} \right| \end{aligned}$$

$$\boxed{|W_{rev}| = \left| NRT \ln \left(\frac{V_2}{V_1} \right) \right|}$$

note absolute value sign!

1a. (1 Point). What are possible units for the quantity you analyzed in Part 1? Give **specific** units, not just the type, i.e., not "time", or "distance", but units that are more precise and specific.

Joules or Joules/mole or (Newton-meter) or

2. Consider the following relation for pressure, $P(N, V, T)$: $P(N, V, T) = \frac{NRT}{V - Nb} - \frac{N^2 a}{V^2}$ with N , R , a , and b taken as constants for this problem.

Evaluate:

2a. (2 Points)

$$\left(\frac{\partial P(N, V, T)}{\partial T} \right)_V =$$

$$\boxed{\frac{NR}{V - Nb}}$$

2b. (2 Points)

$$\left(\frac{\partial P(N, V, T)}{\partial V} \right)_T = \frac{\partial}{\partial V} \left(NRT (V - Nb)^{-1} \right)_T - \frac{\partial}{\partial V} \left(N^2 a V^{-2} \right)_T$$

$$= NRT (-1) (V - Nb)^{-2} (1) + 2N^2 a V^{-3}$$

$$\boxed{= \frac{-NRT}{(V - Nb)^2} + \frac{2N^2 a}{V^3}}$$

1 (2 Points) The Debye model of solids is a useful theoretical model from which to extract the temperature dependence of specific heats at temperatures approaching absolute zero. The specific heat predicted by Debye's model depends on temperature in the following manner:

$$C = \frac{dU}{dT} = \frac{16\pi^5 k_B^4}{5 h^3 c_s^3} T^3$$

where h , c_s , k_B are constants, and T is absolute temperature. What is the limiting value of specific heat in the limit of $T \rightarrow 0$ Kelvin? (Note: for solids, constant pressure and constant volume heat capacities will be very similar numerically).

From given info: $\lim_{T \rightarrow 0} C_p = \lim_{T \rightarrow 0} C_v = \lim_{T \rightarrow 0} (dT^3) = 0$

$$\alpha = \left(\frac{16\pi^5 k_B^4}{5 h^3 c_s^3} \right)$$

2. (2 Points) Provide the correct answer from the right-hand column that completes the left-hand column.

1. Over a cyclic process, the total heat interaction between a system and surroundings will always be equal to zero. True or False? <u>False,</u>	a. Path-dependent
2. Work and heat are <u>A</u> functions.	b. What would
3. For an isolated system, heat interaction with surrounds = <u>0 (C is fine)</u>	c. Zero degrees
4. A reversible process occurs conditions of <u>equilibrium</u> in the system.	d. state
5. In considering the First "Law" of Thermodynamics, what important question might one ask: <u>g</u>	e. What would Justin Timberlake do?
	f. Is the world flat?
	g. How do we know the universe is isolated?

3A (4 Points) For a gas described by the Van der Waals Equation of State (EOS), what amount of work is done during a reversible, isothermal expansion of the gas from V_1 to V_2 ? Be careful and watch your sign convention. No numerical value is needed for this question, just the final equation one obtains in terms for the total work.

van der Waals EOS:

$$P = \frac{nRT}{(V-nb)} - \frac{an^2}{V^2}$$

$$dW = -P_{ext} dV$$

$$P_{ext} = P$$

$$T = \text{constant}$$

$$dW = - \left[\frac{nRT}{(V-nb)} - \frac{an^2}{V^2} \right] dV$$

$$W = - \int_{V_1}^{V_2} \left(\frac{nRT}{(V-nb)} - \frac{an^2}{V^2} \right) dV$$

$$W = -nRT \ln \left(\frac{V_2-nb}{V_1-nb} \right) + an^2 \left[\frac{1}{V_2} - \frac{1}{V_1} \right]$$

$$W = -nRT \ln \left(\frac{V_2-nb}{V_1-nb} \right) + an^2 \left[\frac{1}{V_1} - \frac{1}{V_2} \right]$$

3B. (2 Points) For a gas described by the Ideal Gas Equation of State (EOS), what amount of work is done during a reversible, isothermal expansion of the gas from V_1 to V_2 ? Be careful and watch your sign convention. No numerical value is needed for this question, just the final equation one obtains in terms for the total work.

I.G. EOS

$$PV = nRT$$

$$V_m = RT$$

$$dW = -P_{ext} dV$$

$$\text{reversible } \therefore P_{ext} = P$$

$$T = \text{constant}$$

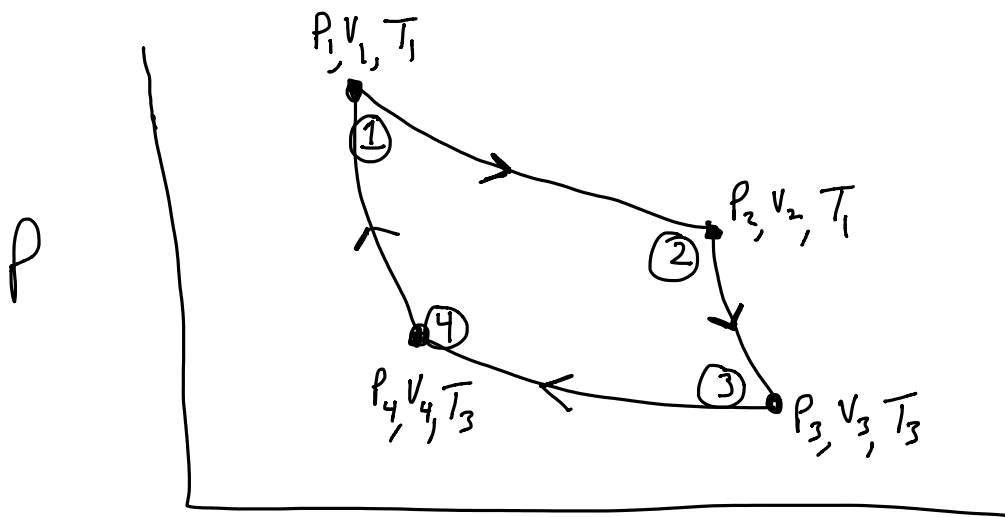
$$dW = - \left(\frac{nRT}{V} \right) dV$$

$$W = \int_{V_1}^{V_2} - \left(\frac{nRT}{V} \right) dV$$

$$W = -nRT \ln \left(\frac{V_2}{V_1} \right)$$

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1. (6 Points) Given below is the pressure-volume (P-V) diagram for a cyclical process involving an ideal gas. There are 4 stages of this cycle. The arrows indicate the direction of each stage of the cycle. All stages are reversible. Points 1, 2, 3, 4, as well as all intermediate points along the curves are equilibrium states. The stages from points 2 → 3 and points 4 → 1 are adiabatic. Obtain expressions for the heat and work interactions involved in each of the 4 stages: $Q_{12}, Q_{23}, Q_{34}, Q_{41}, W_{12}, W_{23}, W_{34}, W_{41}$.



This is a famous cycle, the Carnot Cycle.

Stage 1 → 2: $P_1, V_1, T_1 \rightarrow P_2, V_2, T_1$ ∴ Isothermal!

$$du^{ig}(T) = C_v(T) dT = C_v dT ; dT = 0 \quad \therefore \Delta U = 0$$

$$\therefore dq_{12} = -dw_{12} = +p_{\text{ext}} dV = +p dV = +nRT \frac{dV}{V}$$

reversible
I. G. EOS

So: $dq_{12} = -dw_{12} = +nRT_1 d(\ln V)$

$$q_{12} = -w_{12} = nRT_1 \int_{V_1}^{V_2} d(\ln V) = nRT_1 \ln\left(\frac{V_2}{V_1}\right)$$

Stage $2 \rightarrow 3$: $P_2, V_2, T_1 \rightarrow P_3, V_3, T_3$

Not Isothermal, but we are told it is Adiabatic.

$$\therefore \boxed{Q_{23} = 0} \text{ Adiabatic.}$$

$$dU = dW ; dU = C_v dT \text{ for ideal gas}$$

$$\boxed{\Delta U = W = \int_{T_1}^{T_3} C_v dT = C_v (T_3 - T_1)}$$

Stage $3 \rightarrow 4$: Isothermal $\rightarrow dU = 0$
for ideal gas

$$\therefore dQ_{34} = -dW_{34} = p dV$$

$$Q_{34} = -W_{34} = \int_{V_3}^{V_4} nRT_3 d(\ln V)$$

$$\boxed{Q_{34} = -W_{34} = nRT_3 \ln \left(\frac{V_4}{V_3} \right)}$$

Stage $4 \rightarrow 1$: Adiabatic $\rightarrow \boxed{Q_{41} = 0}$

$$dW_{41} = dU_{41} = C_v dT \Rightarrow \boxed{W_{41} = C_v (T_1 - T_3)}$$

2 (2 Points) Consider a process that occurs adiabatically and irreversibly, and takes a system from equilibrium state (P_1, V_1, T_1) to equilibrium state (P_2, V_2, T_2) . What is the internal energy change, ΔU , for this process? Recall that for state functions such as $f(x, y)$, the total differential of $f(x, y)$ can be written as

$$df(x, y) = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

Recall that $C_v(T) = \left(\frac{\partial U}{\partial T}\right)_v$ and one can consider $-\eta_J(T)C_v(T) = \left(\frac{\partial U}{\partial V}\right)_T$. You may leave your response in terms of $C_v(T)$, $\eta_J(T)$, and integral notation.

$$\begin{aligned} dU(T, V) &= \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \\ &= C_v(T) dT - \eta_J(T) C_v(T) dV \end{aligned}$$

$$\Delta U = \int_{T_1}^{T_2} C_v(T) dT - \int_{V_1}^{V_2} \eta_J(T) C_v(T) dV$$

3 (2 Points) Consider two processes involving an ideal gas. In one case, the system undergoes isothermal, reversible expansion from P_1, T_1, V_1 to P_2, T_1, V_2 . In the second, the system undergoes reversible, adiabatic expansion from P_1, T_1, V_1 , to P_2, T_2, V_2' . What can you say about the relationships between the pairs (P_1, P_2) , (T_1, T_2) , (V_1, V_2) , and (V_2, V_2') ? Incorporate inequality, equality notation in your discussion.

volumes: since in both cases we have expansion,
 $V_2 > V_1$, $V_2' > V_1$

For isothermal expansion of ideal gas:

$$\frac{P_2}{P_1} = \frac{nRT_2}{V_2} \cdot \frac{V_1}{nRT_1} = \frac{V_1}{V_2} < 1$$

$\therefore P_2 < P_1$

Let's Consider Temperatures

a) isothermal case (no ΔT)

b) adiabatic case: ($dq=0$)

$$dU = dq + dw$$

$$dU = C_v dT \quad (\text{I.G.})$$

$$C_v dT = dw$$

For gas expansion, $dw < 0$ (gas does work according to our sign convention)

$$\therefore C_v dT < 0$$

$$\therefore \int C_v dT < \int 0 < 0$$

$$C_v (T_2 - T_1) < 0$$

$$T_2 < T_1$$

To compare V_2 and V_2^I , we use the fact that both final pressures, for IsoT and adiabatic processes, are the same:

I.G.
EOS

$$P_2^{\text{isot}} = P_2^{\text{adiabatic}}$$
$$\frac{nRT_1}{V_2} = \frac{nRT_2}{V_2'}$$

$$\therefore \frac{V_2'}{V_2} = \frac{T_2}{T_1}$$

but, we found above $T_2 < T_1$,

So.

$$\frac{V_2'}{V_2} = \frac{T_2}{T_1} < 1$$

$$V_2' < V_2$$

So, to summarize:

$$P_2 < P_1, \quad V_2 > V_1, \quad T_2 < T_1, \quad V_2' < V_2$$

Quiz 4 Solutions

1. Given: Joule Coefficient is defined by following thermodynamic relation:

$$\eta_{\text{Joule}}(T) = \left(\frac{\partial T}{\partial v} \right)_u = \frac{1}{C_v(T)} \left[p - T \left(\frac{\partial p}{\partial T} \right)_v \right] \quad (1)$$

constant internal energy *constant volume*

a. For Ideal Gas: $pV = nRT$

$$\therefore p = \frac{nRT}{V}$$

Use this in equation (1)!

$$\begin{aligned} \eta_{\text{Joule}}^{\text{Ideal Gas}}(T) &= \frac{1}{C_v^{\text{I.G.}}(T)} \left[\frac{nRT}{V} - T \left(\frac{\partial \left(\frac{nRT}{V} \right)}{\partial T} \right)_v \right] \\ &= \frac{1}{C_v^{\text{I.G.}}(T)} \left[\frac{nRT}{V} - T \left(\frac{nR}{V} \right) \right] \\ &= \frac{1}{C_v^{\text{I.G.}}(T)} \left[\frac{nRT}{V} - \frac{nRT}{V} \right] = \underline{\underline{0}} \end{aligned}$$

Since $\eta_{\text{Joule}}^{\text{Ideal Gas}}(T) = 0$, we can see

$$\begin{aligned} dU^{\text{I.G.}} &= \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \\ &= C_v^{\text{I.G.}} dT - C_v^{\text{I.G.}} \underbrace{\eta_{\text{Joule}}^{\text{I.G.}}(T)}_{=0 \text{ (as shown above)}} dV \end{aligned}$$

$$\therefore dU^{\text{I.G.}} = C_v^{\text{I.G.}} dT$$

Since $C_v^{\text{I.G.}}(T)$ can be a function of T in most general case, this problem shows that $U^{\text{I.G.}}$ is a function of T only.

The only question remaining now is how do we get to the equation initially given to us

$$\eta_{\text{Joule}}(T) = \frac{1}{C_v(T)} \left[p - T \left(\frac{\partial p}{\partial T} \right)_V \right] ?$$

We will see this later in the course.

b). $\eta_{\text{Joule}}(T)$ for Van der Waals fluid (EOS)

For Van der Waals fluid:

$$p = \frac{nRT}{v-nb} - \frac{an^2}{v^2}$$

So: $\left(\frac{\partial p}{\partial T}\right)_v = \frac{nR}{v-nb}$

$$\eta_{\text{Joule}}^{\text{VdW}}(T) = \frac{1}{C_v(T)} \left[\frac{nRT}{v-nb} - \frac{an^2}{v^2} - \frac{nRT}{v-nb} \right]$$

$$\eta_{\text{Joule}}^{\text{VdW}}(T) = \frac{1}{C_v(T)} \left[-\frac{an^2}{v^2} \right]$$

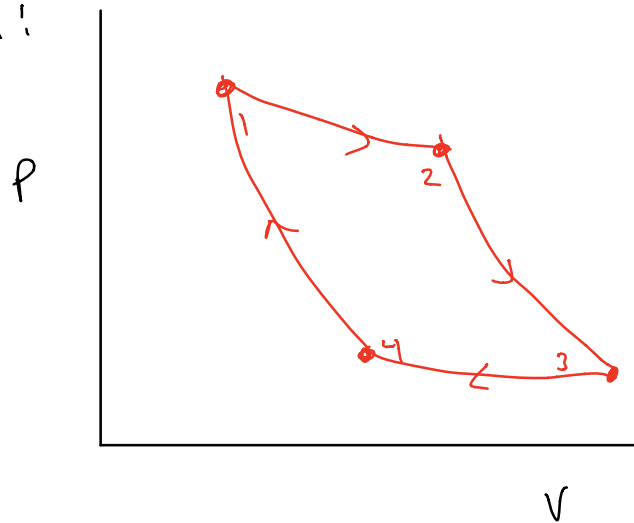
$\eta_{\text{Joule}}(T)$ is not 0 for non-ideal gas of fluid.

η_{Joule} is also a function of n and V
↑ moles ↑ total volume

So: U for non-ideal fluids is not a function of T only.

2. This problem addresses enthalpy change around a Carnot cycle.

Recall:



Enthalpy Change over the cycle is the sum of enthalpy changes for each leg of the cycle.

$$\Delta H_{\text{cycle}} = \Delta H_{12} + \Delta H_{23} + \Delta H_{34} + \Delta H_{41}$$

H is a state function:

$$\therefore \Delta H_{\text{cycle}} = 0$$

$$\text{So: } \underbrace{\Delta H_{12} + \Delta H_{23} + \Delta H_{34} + \Delta H_{41}}_{= \Delta H_{123}} = 0$$

So:

$$\begin{aligned}\Delta H_{123} &= -\Delta H_{34} - \Delta H_{41} \\ &= -[\Delta H_{34} + \Delta H_{41}] \\ &= -[\Delta H_{341}]\end{aligned}$$

$$\therefore \Delta H_{341} = -\Delta H_{123}$$

Due to fact that $\Delta H_{\text{cycle}} = 0$

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1. (5 Points) Boiling of water at normal conditions ($P=1\text{atm}$, $T=100\text{C}$) is accompanied by a change in water (the system) entropy. For 1 mole of water, compute the change in entropy as it totally boils under conditions stated. Remember that vaporization, because it involves a change (transformation from liquid to vapor) under conditions of equilibrium, is a reversible process. Data in Table 6.1 of Equations Handbook will be of use. Use correct math and words (the latter as needed) to come up with your answer. If you assume anything, state your assumption. Make sure every detail of your logic is clear.

$$P = 1\text{atm}; T = 373.15\text{ K (normal boiling point)}$$

Boiling is reversible since we have equilibrium

$$dS = \frac{dq_{rev}}{T} \Rightarrow \Delta S = \int \frac{dq_{rev}}{T} = \frac{1}{T_{vap}} \int dq_{rev} = \frac{n \Delta H_{vap}}{T_{vap}}$$

$$n = 1\text{ mole} \quad \Delta H_{vap} = 9.71558\text{ kcal/mole}$$

$$\Delta S = \frac{(1\text{ mole}) (9.71558\text{ kcal/mole})}{373.15\text{ K}} = 0.026 \frac{\text{Kcal}}{\text{K}} = 0.109 \frac{\text{KJ}}{\text{K}}$$

2 (5 Points) We discovered in class discussion that entropy is related to probabilities of 'microstates' in which we can find a system (i.e., each configuration of particle arrangements in a box is a 'microstate'). We arrived at one

(of several) very insightful equations to compute entropy: $S = -k_B \sum_{i=1}^{\text{total \# of states}} p_i \ln(p_i)$. Recall, p_i is the probability

of finding the system in 'microstate' i , and the summation runs over all of the possible 'microstates' available to the system. Consider a very simple system that can only be found in one of two states, 1 and 2. Thus, if we were to perform an experiment to 'look' at the system and find what state it is in, we could only have one of two outcomes (the system can be in one of the two possible states when we look at it with our 'instrument'). If the probability of state 1 is p_1 and the probability of state 2 is p_2 (remember, $p_2 = 1 - p_1$ since the sum of all probabilities **must** add to 1), what **numerical values** of p_1 and p_2 will **maximize** entropy of this system? Use correct math and words (the latter as needed) to come up with your answer. If you assume anything, state your assumption. Make sure every detail of your logic is clear.

Given: 2 equilibrium states possible for a system. probabilities are p_1 & p_2 ($p_2 = 1 - p_1$)

$$S = -k_B [p_1 \ln(p_1) + p_2 \ln(p_2)]$$

$$S = -k_B [p_1 \ln(p_1) + (1-p_1) \ln(1-p_1)]$$

maximize S means $\boxed{\frac{dS}{dp_1} = 0}$; $\boxed{\frac{d^2S}{dp_1^2} < 0}$

Take 1st derivative of S:

$$\frac{dS}{dp_1} = -k_B \left[\ln(p_1) + \frac{p_1}{p_1} - \ln(1-p_1) - \frac{(1-p_1)}{(1-p_1)} \right]$$

$$= -k_B \left[\ln(p_1) + 1 - \ln(1-p_1) - 1 \right]$$

$$\frac{dS}{dp_1} = 0 = -k_B \left[\ln(p_1) - \ln(1-p_1) \right]$$

$$\text{So: } \ln(p_1) - \ln(1-p_1) = 0$$

$$\ln(p_1) = \ln(1-p_1)$$

$$p_1 = 1-p_1$$

$$2p_1 = 1$$

$$\boxed{p_1 = \frac{1}{2}}$$

$$p_2 = 1-p_1 = 1-\frac{1}{2}$$

$$\boxed{p_2 = \frac{1}{2}}$$

To really check for a maximum we need to check 2nd derivative.

$$\left. \frac{d^2 S}{d p_1^2} \right|_{p_1 = \frac{1}{2}}$$

2nd derivative evaluated at value of p_1

where $\frac{dS}{dp_1} = 0$

$$\begin{aligned} \frac{d^2 S}{d p_1^2} &= \frac{d}{d p_1} \left\{ -k_B \left[\ln(p_1) - \ln(1-p_1) \right] \right\} \\ &= -k_B \left[\frac{1}{p_1} + \frac{1}{1-p_1} \right] \end{aligned}$$

Evaluate $\frac{d^2 S}{d p_1^2}$ at $p_1 = \frac{1}{2}$

$$\left. \frac{d^2 S}{d p_1^2} \right|_{p_1 = \frac{1}{2}} = -k_B [2 + 2] = -4k_B < \underline{\underline{0}}$$

\therefore Indeed $p_1 = p_2 = \frac{1}{2}$ is maximum

1. Helium gas in a well-insulated, solid container is initially confined to a volume of 10 L. The constraint holding the gas in the volume is removed, allowing the gas to expand against a vacuum to a final volume of 20 L.

Assume
Ideal
Gas

Since this system is isolated (solid container $\rightarrow dV=0$; well-insulated $\rightarrow dT=0$) we need to devise a reversible path to compute $\Delta S = \int dS = \int \frac{dq_{rev}}{T}$. we choose isothermal compression.

A. What is the associated entropy change for this process?

For IsoT compression: $dq_{rev} = -dw_{rev} = pdv = nRT d(\ln v)$
 $\frac{dq_{rev}}{T} = nR d(\ln v) \Rightarrow \Delta S = \int \frac{dq_{rev}}{T} = \int nR d(\ln v) = nR \ln \left(\frac{v_2}{v_1}\right)$

$$\Delta S = nR \ln \left(\frac{10L}{20L}\right) = nR \ln \left(\frac{1}{2}\right); \text{ so, for expansion } \Delta S = nR \ln (2)$$

B. Is this a spontaneous, or irreversible process? Please provide an explanation for your answer.

This is spontaneous process because $\Delta S > 0$ and the system is isolated.

$$(dS)_{u,v} > 0 \text{ for isolated system.}$$

2. Consider a universe where we can make up a container whose volume can be partitioned into 9 containers (or voxels, "volume elements"). If we have 7 indistinguishable particles of type A and 4 indistinguishable particles of type B, what is the entropy of the mixed system? How does this compare to the case where we only have 2 indistinguishable particles of type B?

Case 1: $N = 9$ containers; 7 A particles; 4 B particles
 \hookrightarrow can fit total of 11 particles in 9 containers. (undefined scenario)

Case 2: $N = 9$ containers; 7 A particles; 2 B particles

$$S = k_B \ln \Omega = k_B \ln \left(\frac{9!}{7! 2!}\right) = k_B \ln (36)$$

$$= (1.38 \times 10^{-23} \text{ J/K}) \ln (36) = 4.94 \times 10^{-23} \frac{\text{J}}{\text{K}}$$

Can't really make a comparison because the first case is undefined. However what if we had 7 A particles, 1 B particle?

$$W = \frac{9!}{7! 1! 1!} = \frac{9 \times 8 \times 7!}{7!} = 72$$

So, S for $B=1$ particle is larger than S for $B=2$ particles

If we thought of the system as a solution, it seems that S can increase as we go to the limit of infinite dilution.

In fact, this effect is a hidden driving "force" behind the osmotic effect!

1. (10 Points) One mole of H₂O (liquid) is super-cooled to -2.25 Celsius at 1 bar pressure. The equilibrium freezing temperature at this pressure is 0.0 Celsius. The transformation H₂O (liquid) → H₂O (solid) is suddenly observed to occur. Show that the transformation (i.e., freezing) is spontaneous at this state point. Consider the surroundings to be at constant temperature of -2.25 Celsius. The following information may be useful:

$$C_p(\text{H}_2\text{O, liquid}) = 75.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$C_p(\text{H}_2\text{O, solid}) = 37.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta H_{\text{fusion}} = 6.008 \text{ kJ mol}^{-1} \text{ at } 0.0 \text{ Celsius}$$

$$T = -2.25 \text{ }^\circ\text{C} = 270.9 \text{ K}; \text{ normal freezing point} = 273.15 \text{ K (at } 1 \text{ bar} = P)$$

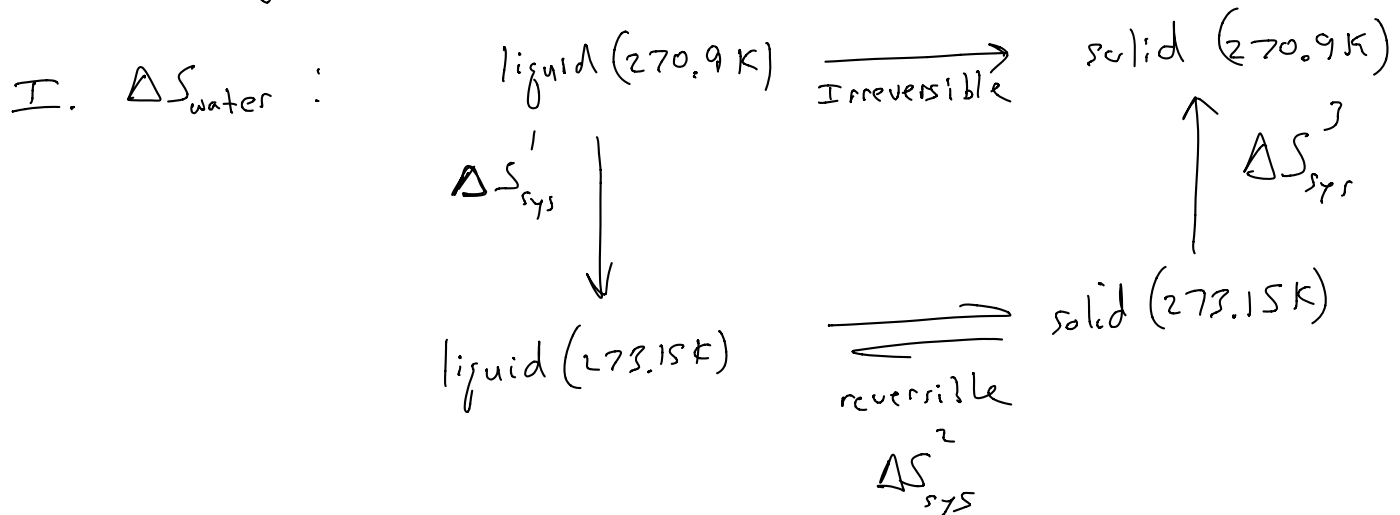
Supercooled water freezes Irreversibly at $T = -2.25 \text{ }^\circ\text{C}$

Since Irreversible, overall process has $\Delta S_{\text{TOTAL}} = \Delta S_{\text{universe}} > 0$

$$\Delta S_{\text{TOTAL}} = \Delta S_{\text{universe}} = (\Delta S_{\text{system}} + \Delta S_{\text{surroundings}}) > 0$$

System = water (liquid + solid)

surroundings = everything not water
(All at $P = 1 \text{ bar}$)



$$\text{So, } \Delta S_{\text{system}} = \Delta S_{\text{sys}}^1 + \Delta S_{\text{sys}}^2 + \Delta S_{\text{sys}}^3$$

Recall! $du = Tds - pdv$ (combined 1st and 2nd "Laws", closed system)

$$ds = \frac{du + pdv}{T}$$

At constant pressure, $ds = \frac{d(u+pv)}{T}$

$$ds = \frac{1}{T} dH$$

but, $dH = dq_p = C_p dT = n\bar{C}_p dT$
(at constant pressure)

So: $ds = \frac{1}{T} C_p dT = \frac{1}{T} n\bar{C}_p dT = n\bar{C}_p d(\ln T)$

Thus: $\Delta S_{sys}^1 = \int_{270.9K}^{273.15K} n\bar{C}_p^L d(\ln T) = n\bar{C}_p^L \ln \left(\frac{273.15K}{270.9K} \right)$

$$\Delta S_{sys}^1 = (1 \text{ mole}) (75.3 \frac{J}{\text{mol}\cdot K}) \ln \left(\frac{273.15K}{270.9K} \right)$$

$$\Delta S_{sys}^3 = \int_{273.15K}^{270.9K} n\bar{C}_p^{\text{solid}} d(\ln T) = n\bar{C}_p^{\text{solid}} \ln \left(\frac{270.9K}{273.15K} \right)$$

$$\Delta S_{sys}^2 = \frac{1}{T_f} \int dq_{rev}^{L \rightarrow \text{solid}} = \frac{1}{T_f} (-\Delta H_f) = \frac{-\Delta H_f}{T_f} = \frac{-n\Delta H_f}{T_f}$$

$$\Delta S_{sys}^2 = \frac{-(1 \text{ mole}) (6.008 \frac{kJ}{\text{mol}})}{273.15K}$$

$$\Delta S_{sys} = \Delta S_{sys}^1 + \Delta S_{sys}^2 + \Delta S_{sys}^3 = -21.7 \text{ J/K}$$

This is entropy of H₂O freezing; negative as expected.

Now, consider $\Delta S_{\text{surroundings}}$

Since surroundings are conceptualized as being of sufficient vastness, they are always at equilibrium. Any process the surroundings undergoes while gaining/losing heat is reversible.

$$\text{So, } \Delta S_{\text{surroundings}} = \frac{n \Delta \bar{H}^{\text{lig-solid}}(270.9 \text{ K})}{T_{270.9 \text{ K}}}$$

However, we need $\Delta \bar{H}^{\text{lig-solid}}$ at 270.9 K; we are given $\Delta \bar{H}^{\text{lig-solid}}$ at 273.15 K. How to get $\Delta H(T_2)$ given $\Delta H(T_1)$? We studied this for "chemical reactions". This approach applies for any transformation or process.



$$\Delta \bar{H}_{\text{rxn}}(270.9 \text{ K}) = n \Delta \bar{H}^{\text{liq-solid}}(273.15 \text{ K}) + \int_{273.15}^{270.9} \Delta \bar{C}_p \, dT$$

$$= n \Delta \bar{H}^{\text{liq-solid}}(273.15 \text{ K}) + \int_{273.15 \text{ K}}^{270.9 \text{ K}} \left[(1 \text{ mole}) (\bar{C}_p^{\text{solid}}) - (1 \text{ mole}) (\bar{C}_p^{\text{liquid}}) \right] dT$$

$$= n \Delta \bar{H}^{\text{liq-solid}}(273.15 \text{ K}) + \int_{273.15 \text{ K}}^{270.9 \text{ K}} \left[(1 \text{ mole}) \left\{ 37.7 \frac{\text{J}}{\text{mol} \cdot \text{K}} - 75.15 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right\} \right] dT$$

$$= n \Delta \bar{H}^{\text{liq-solid}}(273.15 \text{ K}) + \left(-35.45 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) (1 \text{ mole}) (-2.25 \text{ K})$$

$$= (1 \text{ mole}) \left(6008 \frac{\text{J}}{\text{mol}} \right) + \left(35.45 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) (1 \text{ mole}) (2.25 \text{ K})$$

$$= -5928 \text{ J} \quad \leftarrow \text{This is the heat lost by water (system) upon freezing.}$$

So, heat is gained by surroundings

$$Q_{\text{surroundings}} = +5928 \text{ J}$$

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T} = \frac{5928 \text{ J}}{270.9 \text{ K}} = 21.9 \frac{\text{J}}{\text{K}}$$

So!

$$\Delta S_{\text{TOTAL}} = \Delta S_{\text{universe}} = 21.9 \frac{\text{J}}{\text{K}} - 21.7 \frac{\text{J}}{\text{K}}$$

$$\Delta S_{\text{TOTAL}} = 0.2 \frac{\text{J}}{\text{K}} > 0$$

This demonstrates that the process is indeed irreversible.

2. (Bonus **5 Points**) Under anaerobic conditions, glucose is broken down in muscle tissue to form lactic acid according to the reaction:

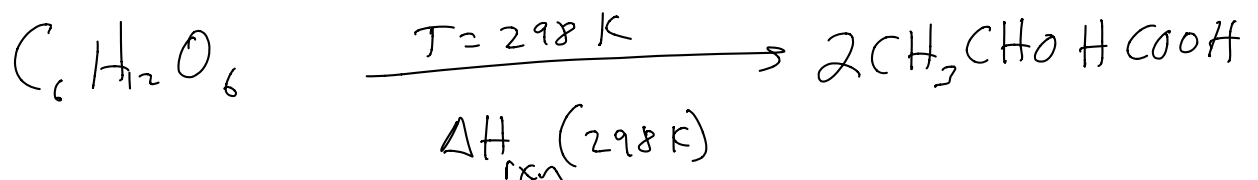
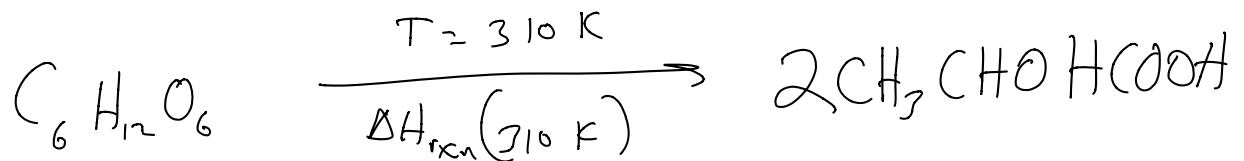


Thermochemical data for 298K are as follow:

	$\Delta H_f^\circ (kJ mol^{-1})$	$C_{p,molar}^\circ (JK^{-1} mol^{-1})$	$S_{molar}^\circ (JK^{-1} mol^{-1})$
$C_6H_{12}O_6$	-1273.1	219.2	209.2
$CH_3CHOHCOOH$	-673.6	127.6	192.1

Calculate ΔS for the system (taken to be the reaction components), the surroundings, and the universe at $T=310K$. State any assumptions you invoke in your solution.

This problem is similar to question 1. It requires similar types of calculations. First, let's write the chemical rxn.



First let's find ΔS_{rxn} and ΔH_{rxn} at 298K using the given information since that info applies to 298K and $P=1bar$.

$$\Delta H_{\text{rxn}}^{\circ} = \sum_{i=1}^{\text{species}} \nu_i \Delta H_{f,i}^{\circ} = 2 \Delta H_{f,\text{CH}_3\text{CHOHCOOH}}^{\circ} - (1) \Delta H_{f,\text{C}_6\text{H}_{12}\text{O}_6}^{\circ}$$

$$= (2) \left(-673.6 \frac{\text{kJ}}{\text{mol}} \right) - (1) \left(1273.1 \frac{\text{kJ}}{\text{mol}} \right) = \boxed{-740.2 \frac{\text{kJ}}{\text{mol}}}$$

$$\Delta S_{\text{rxn}}^{\circ} = \sum_{i=1}^{\text{species}} \nu_i \Delta S_{f,i}^{\circ} = 2 \Delta S_{f,\text{CH}_3\text{CHOHCOOH}}^{\circ} - (1) \Delta S_{f,\text{C}_6\text{H}_{12}\text{O}_6}^{\circ}$$

$$= (2) \left(192.1 \frac{\text{J}}{\text{K}\cdot\text{mol}} \right) - (1) \left(209.2 \frac{\text{J}}{\text{K}\cdot\text{mol}} \right)$$

$$= \boxed{175.0 \frac{\text{J}}{\text{K}\cdot\text{mol}}}$$

Now, we consider the changes in ΔH_{rxn} and ΔS_{rxn} due to temperature change from 298K to 310K.

$$\Delta H_{\text{rxn}}(310\text{K}) = \Delta H_{\text{rxn}}(298\text{K}) + \int_{298\text{K}}^{310\text{K}} \Delta \bar{C}_p dT$$

$$= \Delta H_{\text{rxn}}(298\text{K}) + \int_{298\text{K}}^{310\text{K}} \left[2 \bar{C}_{p,\text{CH}_3\text{CHOHCOOH}} - \bar{C}_{p,\text{C}_6\text{H}_{12}\text{O}_6} \right] dT$$

$$= \Delta H_{\text{rxn}}(298\text{K}) + \int_{298\text{K}}^{310\text{K}} \left[(2) \left(127.6 \frac{\text{J}}{\text{K}\cdot\text{mol}} \right) - (1) \left(219.2 \frac{\text{J}}{\text{K}\cdot\text{mol}} \right) \right] dT$$

Assume heat capacities are constant over this temperature range.

$$\Delta H_{\text{rxn}}(310\text{K}) = -740.2 \frac{\text{kJ}}{\text{mol}} + (0.036 \frac{\text{kJ}}{\text{K}\cdot\text{mol}})(12\text{K}) = \boxed{-737 \frac{\text{kJ}}{\text{mol}}}$$

Now we address entropy change at 310 K.

$$\Delta S_{\text{rxn}}(310\text{K}) = \Delta S_{\text{rxn}}(298\text{K}) + \int_{298\text{K}}^{310\text{K}} \Delta \bar{C}_p d(\ln T)$$

$$= 175 \frac{\text{J}}{\text{K}\cdot\text{mol}} + \int_{298\text{K}}^{310\text{K}} \left[\nu_{\text{C}_2\text{H}_3\text{CO}_2\text{H}} \bar{C}_{p,\text{C}_2\text{H}_3\text{CO}_2\text{H}} - \nu_{\text{C}_6\text{H}_{12}\text{O}_6} \bar{C}_{p,\text{C}_6\text{H}_{12}\text{O}_6} \right] d(\ln T)$$

$$= 175.0 \frac{\text{J}}{\text{K}\cdot\text{mol}} + \left(360 \frac{\text{J}}{\text{K}\cdot\text{mol}} \right) \ln \left(\frac{310\text{K}}{298\text{K}} \right) = 176.4 \frac{\text{J}}{\text{mol}\cdot\text{K}}$$

$$\Delta S_{\text{rxn}}(310\text{K}) = \Delta S_{\text{system}}(310\text{K})$$

Now, we compute $\Delta S_{\text{surr}}(310\text{K})$, which is straightforward.

$$\Delta S_{\text{surr}}(310\text{K}) = \frac{\Delta H_{\text{surr}}(310\text{K})}{T_{310\text{K}}} = \frac{+77.7 \frac{\text{kJ}}{\text{mol}}}{310\text{K}}$$

$$\Delta S_{\text{surr}}(310\text{K}) = -238 \frac{\text{J}}{\text{K}\cdot\text{mol}}$$

$$\Delta S_{\text{TOTAL}}(310\text{K}) = \Delta S_{\text{system}}(310\text{K}) + \Delta S_{\text{surr}}(310\text{K})$$

$$= 176.4 \frac{\text{J}}{\text{mol}\cdot\text{K}} + 238 \frac{\text{J}}{\text{mol}\cdot\text{K}}$$

$$\Delta S_{\text{TOTAL}}(310\text{K}) = 414 \frac{\text{J}}{\text{mol}\cdot\text{K}}$$

1 (7 Points). Consider the reversible reaction:



Pages 145-146
of Assigned
Reading

A. Use the following data to determine the equilibrium constant at 25 Celsius.

Substance	CaCO ₃ (solid)	CaO(solid)	CO ₂ (gas)
μ_i^0 (kJ/mol)	-1128.8	-604.0	-394.36
$\Delta H_{\text{formation,molar}}^0$ (kJ/mol)	-1206.9	-635.09	-393.51

Solution:

Assumptions: solids are not volatile and gases are ideal. Enthalpies of formation have little temperature dependence (though this will be a big assumption).

For this problem, we know the relation between the equilibrium constant and the standard state free energy change:

$$\Delta G^0(T) = -RT \ln K_{eq}(T)$$

The Standard free energy change is given by the standard state chemical potentials:

$$\begin{aligned} \Delta G^0(T) &= \sum_{i=1,3} \nu_i \mu_i = (1)\mu_{\text{CO}_2}^0 + (1)\mu_{\text{CaO}}^0 + (-1)\mu_{\text{CaCO}_3}^0 \\ &= \mu_{\text{CO}_2}^0 + \mu_{\text{CaO}}^0 - \mu_{\text{CaCO}_3}^0 \\ &= -394.36 \frac{\text{kJ}}{\text{mol}} - 604.0 \frac{\text{kJ}}{\text{mol}} + 1128.8 \frac{\text{kJ}}{\text{mol}} \\ &= 130.44 \frac{\text{kJ}}{\text{mol}} \end{aligned}$$

← Egn 6.58
in Text

Thus,

$$\Delta G^0(T) = -RT \ln K_{eq}(T)$$

$$\begin{aligned} K_{eq}(T) &= e^{\frac{-\Delta G^0(T)}{RT}} = e^{\frac{-130.44 \frac{\text{kJ}}{\text{mol}}}{(0.008314 \text{ kJ/mol-K})(298.15 \text{ K})}} \\ &= e^{-52.6} = 1.43 \times 10^{-23} \approx 0! \end{aligned}$$

There is essentially nothing in the gas phase at 298.15K

B What is the equilibrium pressure of CO₂? State any assumptions you make.

The equilibrium constant is more specifically written as:

$$K_{eq}(T) = \frac{p_{CO_2}}{p_{CO_2}^o} = \frac{p_{CO_2}}{1bar} = 1.43 \times 10^{-23}$$

$$p_{CO_2} = (1.43 \times 10^{-23})(1bar) = 1.43 \times 10^{-23} bar \approx 0!$$

2 (3 Points) Using your knowledge of the various thermodynamic potentials we have discussed in class and you have read about in your assigned readings, provide a derivation of a relationship between the Helmholtz Free Energy, A, and state variables T, V, n, P for a van der Waals fluid. Show all work, make sure all mathematical manipulations are correct. Assume constant temperature.

We know the total differential of the Helmholtz Free Energy:

$$dA(T, V) = -pdV - SdT$$

\circledast $dT = 0$ (constant T) $dA(T, V) = dA(V; T) = -pdV$
 ↳ indicates T is held constant while V allowed to vary

We are told the EOS is van der Waals. So:

$$p = \frac{nRT}{v-nb} - \frac{an^2}{v^2} \quad (\text{vdW EOS})$$

$$dA(v;T) = - \left[\frac{nRT}{v-nb} - \frac{an^2}{v^2} \right] dv$$

To obtain $A(v;T)$ as a function of v
at a particular T , integrate

$$A(v;T) = \int \left[-\frac{nRT}{v-nb} + \frac{an^2}{v^2} \right] dv$$

$$A(v;T) = -nRT \ln(v-nb) - \frac{an^2}{v} + C$$

constant
of integration

1. (4 Points) An ideal solution of 5.0 moles of benzene and 3.25 moles of toluene is placed in a piston and cylinder assembly. At 298K, the vapor pressure of the pure substances are $P^{\text{sat}}(\text{benzene})=96.4 \text{ Torr}$ and $P^{\text{sat}}(\text{toluene})=28.9 \text{ Torr}$.

A. The system is initially at pressure of 760 Torr (temperature = 298K). The pressure is reduced. At what pressure does the vapor phase first appear?

B. What is the composition of the vapor phase at the point discussed in part A?

Solution:

$$P_{\text{total}} = x_{\text{benzene}} P_{\text{benzene}}^{\text{saturation}} + x_{\text{toluene}} P_{\text{toluene}}^{\text{saturation}}$$

A. = $(0.606)(96.4\text{Torr}) + (0.394)(28.9\text{Torr})$
= 69.8Torr

Thus, need to reduce to 69.8 Torr to form first bubble of vapor.

B. Use Raoult's relation:

$$y_{\text{benzene}} P_{\text{Total}} = x_{\text{benzene}} P_{\text{benzene}}^{\text{saturation}}$$
$$y_{\text{benzene}} = \frac{x_{\text{benzene}} P_{\text{benzene}}^{\text{saturation}}}{P_{\text{Total}}}$$
$$= \frac{(0.606)(96.4\text{Torr})}{(69.8\text{Torr})}$$
$$= 0.837$$

2. (4 Points) **A).** Using the following data, estimate the vaporization enthalpy of ethanol. State any approximations you use. **B).** Compare your result to the heat of vaporization at the normal boiling point of ethanol. Data in Table 6.1 of your Handbook may be helpful.

P (mm Hg)	40	100	400	760	1520	3800	7600	15200	30400	45600
T °C	19.0	34.9	63.5	78.4	97.5	126.0	151.8	183.0	218.0	242.0

Table data obtained from CRC Handbook of Chemistry and Physics 44th ed.

Solution:

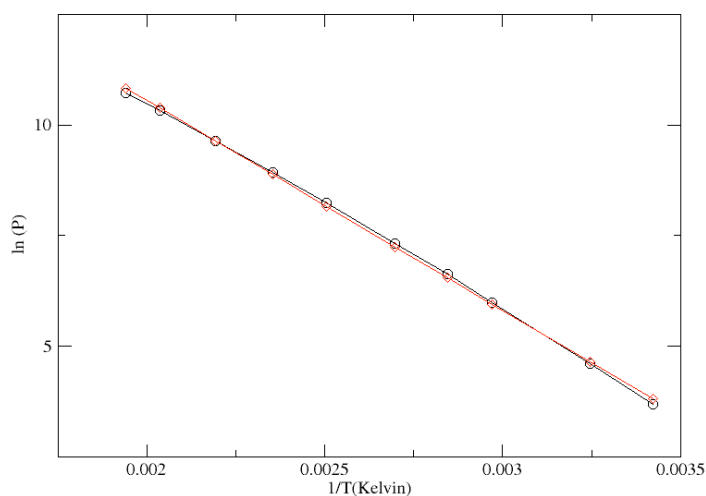
Using the Clausius-Clapeyron equation with the assumption that the vapor is ideal gas and the vaporization enthalpy is constant over the temperature range given in the data set:

$$d(\ln P) = \frac{\Delta H_v}{R} \frac{dT}{T^2}$$

$$\ln P + C_1 = -\frac{\Delta H_v}{RT} + C_2$$

$$\ln P = -\left(\frac{\Delta H_v}{R}\right) \frac{1}{T} + b$$

Thus, plot $\ln(P)$ versus $(1/T)$. The slope multiplied by $-R$ is the vaporization enthalpy (red diamonds are the fit to the experimental data shown as black circles)



Number of observations	= 10
Mean of independent variable	= 0.00262101
Mean of dependent variable	= 7.610287
Standard dev. of ind. variable	= 0.0005038954
Standard dev. of dep. variable	= 2.389071
Correlation coefficient	= -0.9994531

Regression coefficient (SLOPE) = -4738.612
 Standard error of coefficient = 55.42907
 t - value for coefficient = -85.48964
 Regression constant (INTERCEPT) = 20.03024
 Standard error of constant = 0.1476768
 t - value for constant = 135.6357

Analysis of variance

Source	d.f	Sum of squares	Mean Square	F
Regression	1	51.31278	51.31278	7308.478
Residual	8	0.05616795	0.007020994	
Total	9	51.36895		

$$y = 20.03 - 4738.6 * x$$

$$\Delta H_{\text{vap}} = -4738.6 * -8.314 \text{ J / (mol K)} = 39.4 \text{ kJ/mol}$$

This value is in remarkably good agreement with the experimentally measured value of 38.56 kJ/mol quoted in your book. Considering uncertainties in the experimental data and regression, these numbers are quite close.

3. (2 Points). Using the following form of the Clausius-Clapeyron Equation:

$$\left(\frac{dP}{dT}\right)_{\text{coexistence}} = \frac{\Delta\bar{S}}{\Delta\bar{V}}$$

explain why the slope of the solid-liquid equilibrium line (on a P-T phase diagram) is negative for water and positive for most all other fluids.

Solution:

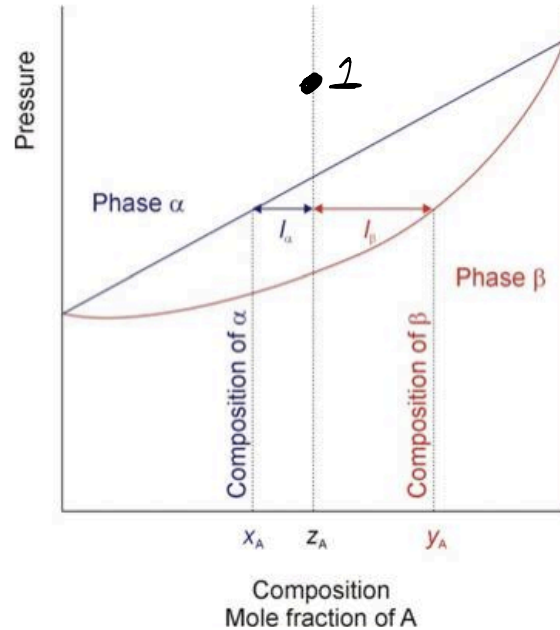
For solid to liquid transition, the change in molar entropy is positive for all fluids. So the numerator is positive in all cases. For water, since the density of ice is lower than that of liquid water (icebergs float), the molar volume of ice is higher (inverse of density) than that of liquid water. Thus, in the case of water, the denominator is negative, thus leading to negative slope. In the case of most other fluids, the denominator is positive, as the numerator is, thus giving positive slope.

$$\left(\frac{dP}{dT}\right)_{\text{coexistence}}^{\text{ice-water}} = \frac{\Delta\bar{S}_{\text{ice-water}}}{\Delta\bar{V}_{\text{ice-water}}} = \frac{+}{-} = \textit{negative}$$

$$\left(\frac{dP}{dT}\right)_{\text{coexistence}}^{\text{solid-liquid, general}} = \frac{\Delta\bar{S}_{\text{solid-liquid}}}{\Delta\bar{V}_{\text{solid-liquid}}} = \frac{+}{+} = \textit{positive}$$

Problem 1 (10 Points)

Consider a binary mixture of two substances A and B that exists as separate phases α and β .



In terms of any relevant variables from those shown in the graph, what is the ratio of moles of phase alpha to moles of phase beta (or the inverse, either one is fine).

Solution:

apply mole balance on species A

At point 1 shown in graph: $n_A = z_A n^{\text{TOTAL}} = z_A n^\alpha$

At point in question: $n_A = x_A n^\alpha + y_A n^\beta$

Conservation of moles of A:

$$z_A [n^\alpha + n^\beta] = x_A n^\alpha + y_A n^\beta$$

$$(Z_A - X_A) n^\alpha = (Y_A - Z_A) n^\beta$$

$$\frac{n^\alpha}{n^\beta} = \frac{Y_A - Z_A}{Z_A - X_A} = \frac{l_\beta}{l_\alpha}$$

lever "Rule"