

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, blunt/sharp writing instrument, and brain (your choice). 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:

$$\begin{aligned} |W_{\text{reversible}}| &= \left| \int_{V_1}^{V_2} P(N, V, T) dV \right| \\ &= \left| \int_{V_1}^{V_2} \frac{NRT}{V} dV \right| = \left| NRT \int_{V_1}^{V_2} \frac{dV}{V} \right| = \left| NRT \int_{V_1}^{V_2} d \ln V \right| \\ &= \left| (NRT) \ln \left(\frac{V_2}{V_1} \right) \right| \end{aligned}$$

1a. (1 Point). What are possible units for the quantity you analyzed in Part 1? Any units of **energy** (kJ/mol, kcal/mol, kcal, kJ, etc).

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

2b. (2 Points)
$$\left(\frac{\partial P(N, V, T)}{\partial V} \right)_T = \frac{-NRT}{(V - Nb)^2} + \frac{2N^2 a}{V^3}$$

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1 (2 Points). Match the choices on the right to the question on the left. Some blanks in the left column may require multiple selections from the column on the right.

1. Equilibrium states are transient, intermediates in a process, possessing no well-defined properties. True or False. <u> G </u>	a. two
2. Temperature and Pressure of a system are examples of <u> I </u> (intensive) <u> </u> properties.	b. process
3. The Ideal Gas Thermometer was an essential development in the definition of the <u> N </u> temperature scale	c. blue
4. For a pure fluid in a single-phase state, how many independently variable properties are necessary to fully describe the equilibrium state? <u> A </u> .	d. a material or fluid
5. $pV=NRT$ is a relation between state variables and is an example of a(n) <u> K </u> .	e. entropy increases
6? The universe is an open system. True/False? <u> G </u>	f. heat capacity
7. A <u> B </u> defines a change of a system from one equilibrium state to another.	g. False
8. <u> P </u> provides a rigorous formalism to connect an atomic view of matter to measurable macroscopic properties such as temperature, pressure, heat capacity, etc.	h. 1
9. Defining a temperature scale requires <u> D,Q,R,S </u> .	i. intensive
10. Water's boiling point temperature is independent of the external pressure; that is, it is an absolute constant. True/False? <u> G </u>	j. Maybe
	k. equation of state (EOS)
	l. zero
	m. True
	n. absolute
	o. a
	p. statistical thermodynamics
	q. property
	r. interpolation scheme
	s. reference points

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1 (5 Points) For a dilute gas the following data are measured. P is system pressure and V is volume.

One mole of dilute gas	t (Celsius)	PV (L-atm)
	0.00	24.35
	100.00	33.54

Assume that the ideal gas equation of state is valid and the relation between an absolute temperature scale and the temperature scale in degrees Celsius is $T=t(\text{Celsius}) + a$. Provide values of R and a based on the data and information given.

Solution:

$$R(t_1(\text{Celsius}) + a) = 24.35 \quad (1)$$

$$R(t_2(\text{Celsius}) + a) = 33.54 \quad (2)$$

$$t_1 = 0.00\text{Celsius} \rightarrow R = \frac{24.35}{a} \quad (3)$$

Thus, using Equation 2:

$$\left(\frac{(100)(24.35)}{a}\right) + 24.35 = 33.54 \rightarrow a = 264.96$$

Using Equation 3:

$$R = 0.0919 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot (\text{absolute T})}$$

2 (3 Points) In a mixture of gases described by the ideal gas equation of state, one finds N_{Ar} moles of Ar, N_{Ne} moles of Ne, N_{O_2} moles of O_2 , and N_{N_2} moles N_2 . The mixture is present at a temperature T and total pressure P. In terms of the variables given in this statement, what are the partial pressures for each component of the mixture?

For ideal gases, partial pressures are additive to give the total pressure which in this case is P. The weight of the contribution from each gas in the mixture is simply the mole fraction of that gas in the vapor. Thus, for a particular species, 'j':

$$p_j = y_j P_{\text{Total}} = y_j P = \left(\frac{N_j}{N_{\text{Total}}}\right) P$$

3 (Extra Credit 3 Points) How much work is done by a system undergoing a reversible expansion from V_1 to V_2 at constant temperature?

Since no EOS or other info was given or implied, we can choose any description we like. A very simple choice is the ideal gas EOS. So,

$$\begin{aligned} w_{\text{reversible}} &= -\int_{V_1}^{V_2} P dV = -\int_{V_1}^{V_2} \frac{NRT}{V} dV = -NRT \int_{V_1}^{V_2} d \ln V \\ &= NRT \ln\left(\frac{V_1}{V_2}\right) \end{aligned}$$

since the ratio in the natural log is less than 1, the work is negative, and the system does work on the

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1 (2 Points) Consider a process that occurs adiabatically and irreversibly, and takes a system from equilibrium state (P1,V1,T1) to equilibrium state (P2,V2,T2). *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 $-\eta_I(T)C_v(T) \equiv \left(\frac{\partial U}{\partial V}\right)_T$. You may leave your response in terms of $C_v(T)$, $\eta_I(T)$, and integral notation.

Solution:

We are asked for the internal energy change. This is:

$$\Delta U(T,V) = U(T_2,V_2) - U(T_1,V_1) = \int_{state1}^{state2} dU(T,V) = \int_{V_1}^{V_2} \left(\frac{\partial U}{\partial V}\right)_T dV + \int_{T_1}^{T_2} \left(\frac{\partial U}{\partial T}\right)_V dT$$

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

We stop here since we are not given any further information. The first integral can be evaluated either analytically (with a simple EOS) or numerically using appropriate methods (nowadays found in the latest state-of-the-art software packages such as Matlab).

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1. (3 Points). A fluid described by the ideal gas EOS is contained in a piston-cylinder assembly surrounded by non-vacuum environment. It undergoes an isothermal, adiabatic, reversible expansion from (P_1, V_1) to (P_2, V_2) . Derive the change in internal energy, ΔU .

Solution:

$$dU = dq + dw$$

$dq = 0$, Thus, $dU = dw$. However, for an ideal gas, if temperature is constant, we know that $dU = 0$ ($dU = C_V dT$). But since there was expansion against non-zero pressure, dw is not zero. This is inconsistent, and thus the process cannot be realized.

2. (5 Points) Consider one mole of an ideal monatomic gas initially at the state point $P = 2.0\text{bar}$ and $T = 273\text{K}$. The gas undergoes a reversible process taking it to a final state point where $P = 4.0\text{bar}$. The process is described by a path along which the following holds: $\frac{P}{V} = C$ where C is a constant (with appropriate units). Calculate ΔU , q , w for this process. The molar constant volume heat capacity (assume independent of temperature) to be

$$C_{V,molar} = 12.5 \frac{J}{mol \cdot K}$$

Solution:

Since $(P/V) = \text{constant}$, we have:

$$\frac{P_1}{V_1} = \frac{P_2}{V_2}, \text{ thus, } T_2 = \frac{P_2 V_2}{R} = \frac{P_2^2}{C R}$$

We can find the constant C as:

$$C = \frac{P_1^2}{T_1 R} = \frac{4.0 \text{ bar}^2}{(273\text{K})R}$$

Thus, T_2 is:

$$T_2 = \frac{P_2 V_2}{R} = \frac{P_2^2}{\left(\frac{4.0 \text{ bar}^2}{(273\text{K})R}\right)R} = \frac{16.0 \text{ bar}^2}{\left(\frac{4.0 \text{ bar}^2}{(273\text{K})R}\right)R} = 1092\text{K}$$

Because the constant volume specific heat is temperature independent, we can write:

$$\Delta U = \bar{C}_V (T_2 - T_1) = (1\text{mol})(12.5 \text{ J} \cdot \text{mole}^{-1} \cdot \text{K}^{-1})(1092\text{K} - 273\text{K}) = 10.2\text{kJ}$$

The work for this process, taken to be reversible **along the path described** is:

$$\begin{aligned}
 w &= -\int_{V_1}^{V_2} P dV = -\int_{V_1}^{V_2} CV dV = \frac{-C}{2}(V_2^2 - V_1^2) \\
 &= \frac{-C}{2C^2}(P_2^2 - P_1^2) = \frac{-1}{2C}(P_2^2 - P_1^2) = \frac{-(273K)(R)(12\text{bar}^2)}{(2)(4\text{bar}^2)} = \frac{-(273K)(0.083145\text{bar} \cdot \text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(12\text{bar}^2)}{(2)(4\text{bar}^2)} \\
 &= -3.4\text{kJ}
 \end{aligned}$$

The heat interaction for this process is:

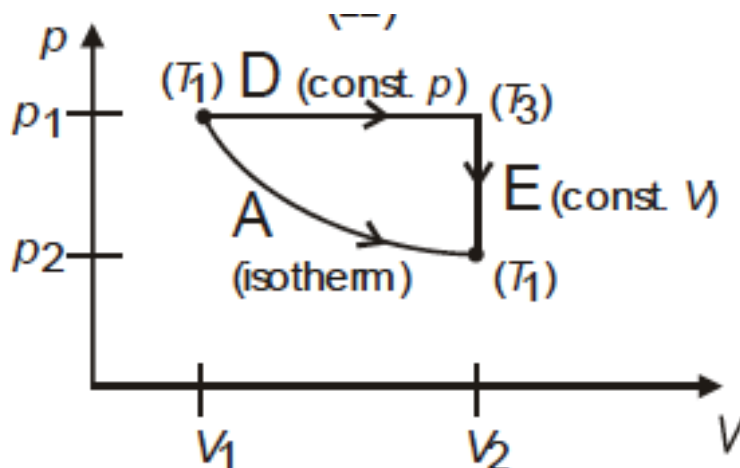
$$q = \Delta U - w = 13.6\text{kJ}$$

Extra Credit (2 Points). What is the change in enthalpy for the process described in Problem 2?

$$\begin{aligned}
 \Delta H &= \Delta U + nR\Delta T = 10.2\text{kJ} + (8.314\text{J/mol} \cdot \text{K})(819\text{K}) \\
 &= 17.0\text{kJ}
 \end{aligned}$$

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1. (3 Points) For the following cycle, evaluate q , w , ΔU and ΔH for **each step** of the cycle. The steps are A, D, and E.



Path A:

Isothermal. We can choose ideal gas EOS since none is specified:

$$dU = dq + dw$$

$$dw = -p_{ext}dV = -p(V,T)dV = -nRTd(\ln V)$$

$$w_A = -nRT_1 \ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta U = 0 = \Delta H$$

$$q = -w = nRT_1 \ln\left(\frac{V_2}{V_1}\right)$$

Path E:

$$dU = dq + dw$$

$$dw = 0$$

$$w = 0$$

$$\Delta U = C_V(T_1 - T_3)$$

$$\Delta H = C_P(T_1 - T_3)$$

$$q = \Delta U = C_V(T_1 - T_3) = -C_V(T_3 - T_1)$$

Path D:

$$dU = dq + dw$$

$$dw = -p_{\text{ext}}dV$$

$$w = -P_1(V_2 - V_1)$$

$$\Delta U = C_V(T_3 - T_1)$$

$$\Delta H = C_P(T_3 - T_1)$$

$$q = \Delta U - w = C_V(T_3 - T_1) + P_1(V_2 - V_1)$$

Note: all state function changes around the cycle sum to zero. q and w are not zero.

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1 (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.

Solution:

The two processes, one adiabatic and the other isothermal, both start at the same conditions, P_1, T_1 , and V_1 . Both end up at the same pressure, P_2 via expansion. We have seen in class and reading that for ideal gas isothermal expansion, pressure drops. Thus, $P_2 < P_1$. Also, for the isothermal case, since the gas expands, $V_2 > V_1$.

Now we have to consider the temperatures T_2 and T_1 . For the isothermal case, there is no change in temperature. For the adiabatic case, we seek recourse to First 'Law':

$$dU = dq + dw = dw$$

$$dU = C_V dT \text{ for ideal gas}$$

Thus

$$C_V dT = dw$$

however, gas expands; thus, $dw < 0$

Thus, $dT < 0$

$$\int dT = \Delta T < 0$$

$$T_2 - T_1 < 0$$

$$T_2 < T_1$$

Now, to consider the final volumes for the adiabatic versus isothermal cases. Since the final pressure in the two cases are equal, we have an easy way to carry out the analysis:

$$P_2^{isoT} = P_2^{adiabatic}$$

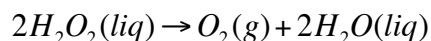
$$\frac{nRT_1}{V_2} = \frac{nRT_2}{V_2'}$$

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

Thus, $V_2' < V_2$

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1 (3 Points). For the reaction performed in class,



Estimate the reaction enthalpy at $P=1\text{bar}$ and $T=298.15\text{K}$.

Possibly Useful Information

Compound	Phase	Formula	$\Delta H_f(1\text{ bar}, 298.15\text{K})\text{ kJ/mol}$
Hydrogen	Gas	H_2	0
Water	Gas	H_2O	-241.818
Water	Liquid	H_2O	-285.8
Hydrogen Peroxide	Liquid	H_2O_2	-187.8
Phosphoric Acid	Liquid	H_3PO_4	-1288
Hydrogen Cyanide	Gas	HCN	+130.5
Hydrogen bromide	Liquid	HBr	-36.3

$$\begin{aligned} \Delta H_{rxn}(T = 298.15, P = 1\text{bar}) &= \sum_i \nu_i \Delta H_{f,i}^0 \\ &= (1)(\Delta H_{f,O_2}^0) + (2)(\Delta H_{f,water}^0) + (-2)(\Delta H_{f,H_2O_2}^0) \\ &= (1)(0) + (2\text{moles})\left(-285.8 \frac{\text{kJ}}{\text{mol}}\right) + (-2\text{moles})\left(-187.8 \frac{\text{kJ}}{\text{mole}}\right) \\ &= (2)\left(-285.8 \frac{\text{kJ}}{\text{mol}} + 187.8 \frac{\text{kJ}}{\text{mol}}\right) = -196\text{kJ} \end{aligned}$$

This is consistent with the observation that heat is released (with the emergent scary 'nuclear' plume we saw as the water began to boil).

2. (2 Points). If an ice cube of mass 'm' is quickly placed in 'n' moles of water at 298K, the entire system then immediately isolated in a well-insulated, rigid container, derive an equation for the final temperature that the water would reach at equilibrium. **Explicitly state** any assumptions you (need to) make in order to arrive at your final response.

Solution:

Consider as the system the water and ice, all taken together just inside the walls of the container (rigid). The container walls are well-insulated, so no heat flow occurs. Since the walls are rigid, no work is done by or to this system. Thus, considering the water and ice as a total system, first 'law' analysis says that $dU=0$. Now, consider the fact that U is an extensive state function. This means that the total U (and hence dU) is a sum of the U (dU) of the individual components of the system. Thus:

$$dU_{Total} = 0 = dU_{ice} + dU_{water}$$

Thus, we have:

$$\begin{aligned} dU_{ice} &= -dU_{water} \\ dq_{ice} + dw_{ice} &= -dq_{water} - dw_{water} \end{aligned}$$

Assumption: (PV) changes associated with the melting and heating / cooling processes involved here are small and negligible. Thus, no work will be considered.

$$dq_{ice} = -dq_{water}$$

Also, we will concern ourselves with the heat interactions between water and ice, which means that the heat from the water is transferred to the ice. Since the (PV) changes are assumed negligible, we will consider this constant volume process equivalent to a constant pressure process in terms of how we treat the internal energy / enthalpy.

Since the ice melts at 273K, and then there is heating of that amount of water, the heat involved for the ice block is the sum of the enthalpy involved with melting and then the heat required to increase its temperature. For the water, we only consider the heat lost in order to decrease its temperature.

$$dq_{ice} = -dq_{water}$$

$$dH_{ice \rightarrow water}(T = 273K) + \left(\frac{m_{ice}}{(MW)_{water}} \right) C_{p,molar,ice}(T) dT = -n_{water} C_{p,molar,water}(T) dT$$

Integrating:

$$\Delta H_{ice \rightarrow water}(T = 273.15K) + \left(\frac{m_{ice}}{(MW)_{water}} \right) C_{p,molar,ice}(T) \int_{273.15}^T dT' = -n_{water} C_{p,molar,water}(T) \int_{298}^T dT'$$

$$\Delta H_{ice \rightarrow water}(T = 273.15K) + \left(\frac{m_{ice}}{(MW)_{water}} \right) C_{p,molar,ice}(T)(T - 273.15) = -n_{water} C_{p,molar,water}(T)(T - 298)$$

where we **assume specific heats are independent of temperature.**

Now, we solve for T, which is the final temperature of water at thermal equilibrium.

$$\Delta H_{ice \rightarrow water}(T = 273.15K) + \left(\frac{m_{ice}}{(MW)_{water}} \right) C_{p,molar,ice}(T - 273.15K) = -n_{water} C_{p,molar,water}(T - 298K)$$

$$T = \frac{\left(\frac{m_{ice}}{(MW)_{water}} \right) C_{p,molar,ice}(273.15K) + n_{water} C_{p,molar,water}(298K) - \Delta H_{ice \rightarrow water}(T = 273.15K)}{\left(\frac{m_{ice}}{(MW)_{water}} \right) C_{p,molar,ice} + n_{water} C_{p,molar,water}}$$

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1 (10 Points) A certain calorimeter absorbs 24 J/°C. If 50.0 g of 52.7°C water is mixed with the calorimeter's original 50.0 g of 22.3°C water, what will be the final temperature of the mixture?

Solutions:

$$dU = dU_{\text{water}} + dU_{\text{calorimeter}} = 0$$

$$0 = dq_{\text{water}} + dw_{\text{water}} + dq_{\text{cal}} + dw_{\text{cal}}$$

$$0 = dq_{\text{water}} + dq_{\text{cal}}$$

$$0 = m_{\text{water}} C_{\text{water}} dT + C_{\text{cal}} dT = m_{\text{hotwater}} C_{\text{water}} dT + m_{\text{coldwater}} C_{\text{water}} dT + C_{\text{cal}} dT$$

$$-C_{\text{cal}} dT = m_{\text{hotwater}} C_{\text{water}} dT + m_{\text{coldwater}} C_{\text{water}} dT$$

$$-C_{\text{cal}} \Delta T = m_{\text{hotwater}} C_{\text{water}} \Delta T + m_{\text{coldwater}} C_{\text{water}} \Delta T$$

$$-C_{\text{cal}} (T - 22.3\text{C}) = (50.0\text{g}) \left(4.19 \frac{\text{J}}{\text{g} \cdot \text{C}}\right) (T - 52.7\text{C}) + (50.0\text{g}) \left(4.19 \frac{\text{J}}{\text{g} \cdot \text{C}}\right) (T - 22.3\text{C})$$

$$\left(-24 \frac{\text{J}}{\text{C}}\right) (T - 22.3\text{C}) = (50.0\text{g}) \left(4.19 \frac{\text{J}}{\text{g} \cdot \text{C}}\right) (T - 52.7\text{C}) + (50.0\text{g}) \left(4.19 \frac{\text{J}}{\text{g} \cdot \text{C}}\right) (T - 22.3\text{C})$$

$$T = 37\text{C}$$

Bonus (5 Points)

What is the entropy change for the Joule expansion of one mole of an ideal gas from initial conditions (P_1, T_1, V_1) to final conditions ($P_2, T_1, V_2=2V_1$)?

Solution:

Since the expansion is irreversible, adiabatic and does no work (expanding against vacuum as per the definition of Joule free expansion), we must devise a reversible path between the two states. Since this is an ideal gas, and the change is isothermal, we can propose a reversible isothermal expansion

From First 'Law':

$$dU = 0 = dq_{\text{rev}} + dw_{\text{rev}}$$

$$dq_{\text{rev}} = -dw_{\text{rev}} = nRT_1 d(\ln V)$$

The entropy change would then be:

$$dS = \frac{dq_{\text{rev}}}{T} = nR d(\ln V)$$

$$\Delta S = \int_{V_1}^{V_2} nR d(\ln V) = nR \ln\left(\frac{V_2}{V_1}\right) = nR \ln(2) > 0$$

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1 (1 Points) Consider the following function:

$$f(x, y) = \frac{kx}{(y-j)} - \frac{z}{y^2}$$

where k , z , and j are constants, and f , x , and y can be considered state variables for this problem. Determine the following partial derivative:

$$\left(\frac{\partial y}{\partial x}\right)_f = ?$$

Solution: We use the cyclic 'rule' and the inverse 'rule' for functions of state variables and exactly differentiable functions:

$$\left(\frac{\partial y}{\partial x}\right)_f = \frac{-\left(\frac{\partial y}{\partial f}\right)_x}{\left(\frac{\partial x}{\partial f}\right)_y} = \frac{-\left(\frac{\partial f}{\partial x}\right)_y}{\left(\frac{\partial f}{\partial y}\right)_x} = \frac{-\left(\frac{k}{(y-j)}\right)}{\left(\frac{-kx}{(y-j)^2}\right) + \frac{2z}{y^3}}$$

2 (1 Points) For a fluid described by the ideal gas equation of state, show that the following relation holds: $\left(\frac{\partial H}{\partial P}\right)_T = 0$. Remember that $H(T, P(T, V)) = U + PV$ where P is pressure, T is temperature, and V is volume.

$$H(T, P(T, V)) = U + PV$$

$$dH = dU + d(PV)$$

$$\begin{aligned} \left(\frac{\partial H}{\partial P}\right)_T &= \left(\frac{\partial U}{\partial P}\right)_T + \left(\frac{\partial(PV)}{\partial P}\right)_T = 0 + P\left(\frac{\partial V}{\partial P}\right)_T + V\left(\frac{\partial P}{\partial P}\right)_T = P\left(\frac{\partial V}{\partial P}\right)_T + V(1) = P\left(\frac{\partial V}{\partial P}\right)_T + V \\ &= P\left(\frac{-nRT}{P^2}\right) + V = \left(\frac{-nRT}{P}\right) + \left(\frac{nRT}{P}\right) = 0 \end{aligned}$$

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, blunt/sharp writing instrument, and brain (your choice). 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 (4 Points) Imagine that you have two **indistinguishable** \$100 bills, and you want to place them in the following two boxes; the boxes can be considered isolated from the rest of the universe. The box on the left (A) has 2 spaces (each space can only hold one bill), the box on the right (B) 4 spaces (size of spaces is irrelevant for this discussion; it only matters that they are the same in both boxes). The location of the space is important and unique (i.e. the left space is not the same as the right space in Box A). In how many different ways can you put the two bills in each box? The bills do not influence one another (i.e., one bill does not exert any external force on the other \$100 bill).



Solution:

The brute force way would be to try various combinations of placing **indistinguishable** items (in this case \$100 bills) in the spaces shown in the diagram. For the left box, since we have two bills, there is only 1 way to put those two indistinguishable objects in two spaces. For the case of 4 spaces, the following combinations are possible (remember the bills are indistinguishable):

SPACE 1	SPACE 2	SPACE 3	SPACE 4
bill1	bill2		
bill1		bill2	
bill1			bill2
	bill1	bill2	
	bill1		bill2
		bill1	bill2

From combinatorics, this is a problem of finding how many ways one can put 2 indistinguishable objects in 4 bins. Or, having 4 slots, how many ways are there to realize 2 filled and 2 unfilled slots. This is given by the following expression:

$$W = \frac{4!}{2!2!} = \frac{(N_{\text{total slots}})!}{(N_{\text{filled}})! (N_{\text{unfilled}})!} = 6$$

2 (4 Points) The molar condensation enthalpy of pure ethanol at 78.3 Celsius and P=1bar is -38.56 kJ/mol. Single specie, two-phase equilibrium satisfies the requirements for reversible transition. What is the molar vaporization entropy change for ethanol?

For this problem, the entropy change for vaporization is the reversible for the phase change (i.e., the enthalpy of vaporization) divided by the temperature of the transition:

$$\Delta S_{\text{vap}} = \int_{\text{liq}}^{\text{vap}} \frac{dq_{\text{rev}}}{T} = \frac{1}{T} \int dq_{\text{rev}} = \frac{1}{T} \int_{\text{liq}}^{\text{vap}} dq_p = \frac{1}{T} \int_{\text{liq}}^{\text{vap}} dH_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_{\text{vap}}}$$

Using the values given:

$$\Delta S_{\text{vap}} = \frac{38.56 \text{ kJ} / \text{mol}}{(78.3 + 273.15) \text{ K}} = 0.11 \frac{\text{kJ}}{\text{mol} \cdot \text{K}} > 0$$

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, blunt/sharp writing instrument, and brain (your choice). 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 (0.5 Point) What is the entropy change for 'n' moles of Ne gas being isothermally and reversibly expanded from (T,V1) to (T,V2) where V2>V1. **Explicitly** state any assumption(s) you make. Show all steps in a systematic and logical, stepwise manner.

Solution:

Since this is a reversible process, the calculation of entropy is straightforward. Isothermal change for Ne treated as an ideal gas (our assumption) means that internal energy change is zero. Thus, dq=-dw. We just need the reversible work expression to obtain reversible heat exchange.

$$\begin{aligned}\Delta S &= \int \frac{dq_{rev}}{T} = \int \frac{-dw_{rev}}{T} = \int \frac{pdV}{T} = \int \frac{nRTdV}{TV} = \int \frac{nRdV}{V} = \int_{V_1}^{V_2} nRd(\ln V) \\ &= nR \ln\left(\frac{V_2}{V_1}\right)\end{aligned}$$

Since $V_2 > V_1$, this will be positive entropy change (>0).

2. (0.5 Point) Since this is a reversible process, if your answer to question #1 is greater than zero (positive sign for any specific expansion), why is it not equal to zero? If your answer to question #1 is equal to zero, why is it not greater than zero?

This is not equal to zero because the system is NOT ISOLATED. It undergoes an isothermal change, thus requiring interaction with its surroundings, with the surroundings offering energy as heat. Thus, the overall entropy change that includes the change in the surroundings is zero.

$$\Delta S_{Total} = \Delta S_{system} + \Delta S_{surroundings} \geq 0$$

In this case the equality would hold.

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, blunt/sharp writing instrument, and brain (your choice). 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 (9 Points) One mole of a van der Waals gas at 25.0 Celsius is expanded isothermally and reversibly from an initial volume of 0.010 m^3 to a final volume of 0.095 m^3 . For the van der Waals gas, the following relation holds: $\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V_m^2}$ where we use molar volume. Taking $a=0.556 \text{ Pa m}^6 \text{ mol}^{-2}$ and $b=64.0 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ calculate q , w , and ΔS .

Solution:

For this process, we can evaluate the change in internal energy, U , as:

$$\begin{aligned}\Delta U &= \int_{0.01 \text{ m}^3 \text{ mol}^{-1}}^{0.095 \text{ m}^3 \text{ mol}^{-1}} \left(\frac{\partial U}{\partial V}\right)_T dV_m = \int_{0.01 \text{ m}^3 \text{ mol}^{-1}}^{0.095 \text{ m}^3 \text{ mol}^{-1}} \frac{a}{V_m^2} dV_m = \frac{-a}{V_m} \Bigg|_{0.01 \text{ m}^3 \text{ mol}^{-1}}^{0.095 \text{ m}^3 \text{ mol}^{-1}} \\ &= a \left(\frac{1}{0.01 \text{ m}^3 \text{ mol}^{-1}} - \frac{1}{0.095 \text{ m}^3 \text{ mol}^{-1}} \right) = a (89.47368 \text{ m}^{-3} \text{ mol}^1) \\ &= (0.556 \text{ Pa m}^6 \text{ mol}^{-2}) (89.47368 \text{ m}^{-3} \text{ mol}^1) \\ &= 49.75 \text{ Pa m}^3 \text{ mol}^{-1}\end{aligned}$$

Since this is isothermal and reversible, we can compute the work for a VDW fluid:

$$\begin{aligned}
dw_{rev} &= -pdV_m \\
&= -\left(\frac{RT}{V_m - b} - \frac{a}{V_m^2}\right)dV_m \\
w_{rev} &= \int_{0.01\text{m}^3\text{mol}^{-1}}^{0.095\text{m}^3\text{mol}^{-1}} -\left(\frac{RT}{V_m - b} - \frac{a}{V_m^2}\right)dV_m \\
&= -RT \ln\left(\frac{0.095\text{m}^3\text{mol}^{-1} - b}{0.01\text{m}^3\text{mol}^{-1} - b}\right) - \frac{a}{V_m} \Bigg|_{0.01\text{m}^3\text{mol}^{-1}}^{0.095\text{m}^3\text{mol}^{-1}} \\
&= -RT \ln\left(\frac{0.095\text{m}^3\text{mol}^{-1} - b}{0.01\text{m}^3\text{mol}^{-1} - b}\right) + \left(\frac{a}{0.01\text{m}^3\text{mol}^{-1}} - \frac{a}{0.095\text{m}^3\text{mol}^{-1}}\right) \\
&= -RT \ln\left(\frac{0.095\text{m}^3\text{mol}^{-1} - 64.0 \times 10^{-6}\text{m}^3\text{mol}^{-1}}{0.01\text{m}^3\text{mol}^{-1} - 64.0 \times 10^{-6}\text{m}^3\text{mol}^{-1}}\right) + \left(\frac{0.556\text{Pa m}^6\text{mol}^{-2}}{0.01\text{m}^3\text{mol}^{-1}} - \frac{0.556\text{Pa m}^6\text{mol}^{-2}}{0.095\text{m}^3\text{mol}^{-1}}\right) \\
&= -R(298.15\text{K}) \ln\left(\frac{0.095\text{m}^3\text{mol}^{-1} - 64.0 \times 10^{-6}\text{m}^3\text{mol}^{-1}}{0.01\text{m}^3\text{mol}^{-1} - 64.0 \times 10^{-6}\text{m}^3\text{mol}^{-1}}\right) + 49.75\text{Pa m}^3\text{mol}^{-1} \\
&= -R(298.15\text{K})(2.25704) + 49.75\text{Pa m}^3\text{mol}^{-1} \\
&= -(8.314\text{Pa m}^3\text{mol}^{-1}\text{K}^{-1})(298.15\text{K})(2.25704) + 49.75\text{Pa m}^3\text{mol}^{-1} \\
&= -5545.4\text{Pa m}^3\text{mol}^{-1}
\end{aligned}$$

The heat for this process, reversible, is the difference between the change in internal energy and the work done. This allows us to calculate the entropy (via a reversible heat exchange):

$$\begin{aligned}
dS &= \int \frac{dq_{rev}}{T} = \frac{1}{T} \int dq_{rev} = \frac{q_{rev}}{T} \\
&= \frac{\Delta U - w_{rev}}{T} = \frac{49.75\text{Pa m}^3\text{mol}^{-1} - (-5545.4\text{Pa m}^3\text{mol}^{-1})}{298.15\text{K}} = \frac{5595.10\text{Pa m}^3\text{mol}^{-1}}{298.15\text{K}} = 18.8\text{Pa m}^3\text{mol}^{-1}\text{K}^{-1}
\end{aligned}$$

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, blunt/sharp writing instrument, and brain (your choice). 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!

1a. (0.5 Point) Consider a simple model of a generalized polymer (you can think of it as a synthetic polymer, a protein/peptide, etc.) as a collection of coarse-grained beads attached by rigid bonds and angles, and having only 2 accessible torsion states (i.e., a cis and a trans conformation for each torsion angle). For this generalized polymer model, with a length of 100 beads, what would be an estimate of the entropy using the given information and based on your understanding of the microscopic origin of entropy? Consider the case where all angles are equally probable and there are no external constraints or forces/potentials to bias any particular torsion toward or away from a particular value of the angle (torsion state). Recall $S = k_B \ln(W)$.

Solution:

For a chain of bead length 'N', with 'N' even number, there are N-3 torsions. Since each torsion has only two states that are equally accessible, the total number of ways/conformations/microstates that the unconstrained polymer chain can exist in is $2^{N-3} = 2^{100-3} = 2^{97}$. Thus, the entropy is $S = k_B \ln(2^{97}) = 97 k_B \ln(2)$.

1b. (0.5 Point) What is your estimate of entropy when the latter half of the polymer (the last 45 torsions) binds (via non-covalent interactions such as hydrogen bonds) to a surface, with these 45 torsions taking on a single trans conformation, and the remaining torsion angles being free to access all available torsion states?

Here we only have 97 - 45 torsions that are free. Thus, $S = 52 k_B \ln(2)$

Extra Credit (2 Points)

2. The final grade you earn in this course is based on a curve, True or False? _____ False _____

3. At this point in the course, if you were to self-analyze your performance in **and demonstration of learning and understanding the required material and concepts of this important area of science, applying generally that understanding to an array of problems, and critically thinking and using fundamental knowledge and skills you learned in the past two years as a college student**, with performance being taken as a letter 'grade', what 'grade' would you have earned so far?

4. What compelling reasons can you give for having earned the grade you stated in Question 3, above?

5. What final 'grade' do you project you will earn at the end of the course? _____

6. What compelling reason(s) can you give for projecting the grade you will earn at the end of the course?

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, blunt/sharp writing instrument, and brain (your choice). 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. (4.5 Points) Using the combined First and Second 'Law' expression (Fundamental Equation of thermodynamics), determine the entropy change associated with the isothermal, irreversible expansion of one mole of an ideal gas from volume $V=10 \text{ m}^3$ to $V=30 \text{ m}^3$. The gas is enclosed in a rigid well-insulated container.

Solution:

The combined First and Second 'Law' expression is :

$$dU = TdS - pdV$$

We can rearrange, isolate dS, use the ideal gas EOS, and find the change in entropy for this process.

$$dU = TdS - pdV$$

$$dS = \frac{dU}{T} + \frac{p}{T}dV$$

$$\Delta S = 0 + nR \int_{10 \text{ m}^3}^{30 \text{ m}^3} d(\ln V)$$

$$= nR \ln(3) = (1)R \ln(3) = R \ln(3)$$

2 (4.5 Points) Starting with the expression for the total differential of enthalpy (remembering that this form suggests the inherent variables for enthalpy), use an appropriate Maxwell Relation to prove that for an ideal gas:

$$\left(\frac{\partial H}{\partial P}\right)_T = 0$$

Solution:

As discussed in class, this is a problem solved by using chain rule and an appropriate Maxwell Relation.

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial H}{\partial S}\right)_P \left(\frac{\partial S}{\partial P}\right)_T + \left(\frac{\partial H}{\partial P}\right)_S \left(\frac{\partial P}{\partial P}\right)_T = T \left(\frac{\partial S}{\partial P}\right)_T + V(1) = T \left(\frac{\partial S}{\partial P}\right)_T + V$$

The appropriate Maxwell Relation comes from the total differential relation for the Gibbs Free Energy:

$$dG = VdP - SdT$$

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

Thus, we obtain:

$$\left(\frac{\partial H}{\partial P}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_P + V = -\frac{nRT}{P} + \frac{nRT}{P} = 0$$

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, blunt/sharp writing instrument, and brain (your choice). 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 (2 Points) Using appropriate and correct mathematical relationships, derive an expression for the following partial derivative. Pay close attention to correct mathematical conventions.

$$\left(\frac{\partial A}{\partial P}\right)_T = ?$$

Solution:

$$\begin{aligned} \left(\frac{\partial A(T,V)}{\partial P}\right)_T &= \left(\frac{\partial A(T,V)}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_T + \left(\frac{\partial A(T,V)}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T \\ &= -P \left(\frac{\partial V}{\partial P}\right)_T \end{aligned}$$

2. (8 Points) For the reversible, endothermic reaction:



starting with n_o moles of chlorine gas, determine an expression for the equilibrium constant in terms of total system pressure, the ratio $\alpha = (\text{moles of chlorine gas at equilibrium})/n_o$, and any other relevant system parameters.

	Cl_2	Cl
Initial	n_o	0
Equilibrium	$n_o - x$	$2x$
Equilibrium mole fraction	$(n_o - x)/(n_o + x)$	$2x/(n_o + x)$

$$K_{eq} = \frac{4p_{total}x^2}{(n_o + x)(n_o - x)}$$

We are given that:

$$\alpha \equiv \frac{n_o - x}{n_o}$$

$$\therefore x = n_o(1 - \alpha)$$

So

$$\begin{aligned} K_{eq} &= \frac{4p_{total}(n_o(1 - \alpha))^2}{(n_o + n_o(1 - \alpha))(n_o - n_o(1 - \alpha))} \\ &= 4p_{total}(n_o(1 - \alpha))^2 \end{aligned}$$

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, blunt/sharp writing instrument, and brain (your choice). 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 (10 Points). Consider the reversible reaction:



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

Substance	CaCO ₃ (solid)	CaO(solid)	CO ₂ (gas)
μ° (kJ/mol)	-1128.8	-604.0	-394.36
$\Delta H^\circ_{\text{formation,molar}}$ (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:

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

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

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

Thus,

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

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

There is essentially nothing in the gas phase at 298.15K

B. What is the equilibrium vapor pressure of the system?

The equilibrium constant is more specifically written as:

$$K_{eq}(T) = \frac{P_{CO_2}}{P_{CO_2}^0} = \frac{P_{CO_2}}{1bar} = 1.43 \times 10^{-23} \\ P_{CO_2} = (1.43 \times 10^{-23})(1bar) = 1.43 \times 10^{-23} bar \approx 0!$$

C. Estimate the equilibrium vapor pressure at 1100 Kelvin.

$$\frac{d(\ln K_{eq}(T))}{dT} = \frac{d\left(\frac{-\Delta G^0}{RT}\right)}{dT} = \frac{\Delta H^0(T)}{RT^2} \\ \ln K_{eq}(T_2) = \ln K_{eq}(T_1) + \frac{\Delta H^0(T)}{R} \left(\frac{T_2 - T_1}{T_2 T_1} \right)$$

Now we need to find the standard state enthalpy of reaction, which is just determined from the enthalpies of formation given in the table:

$$\Delta H^0 = \bar{H}_{formation, CaO} + \bar{H}_{formation, CO_2} - \bar{H}_{formation, CO_3} \\ = (-635.09 - 393.51 + 1206.9) \frac{kJ}{mol} \\ = 178.3 \frac{kJ}{mol}$$

We can now estimate the new equilibrium constant:

$$\ln K_{eq}(T_2) = -52.6 + \frac{178.3 \frac{kJ}{mol}}{0.008314 \frac{kJ}{mol-K}} \left(\frac{1100K - 298.15K}{(1100K)(298.15K)} \right) \\ = -0.17$$

The vapor pressure is:

$$K_{eq}(T) = \frac{p_{CO_2}}{p_{CO_2}^o} = \frac{p_{CO_2}}{1bar}$$

$$\ln K_{eq}(T) = \ln\left(\frac{p_{CO_2}}{1bar}\right) = -0.17$$

$$\ln p_{CO_2} - \ln(1) = -0.17$$

$$\ln p_{CO_2} = -0.17$$

$$p_{CO_2} = 0.84bar$$

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, blunt/sharp writing instrument, and brain (your choice). 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!

Solution:

For the triple point, we set the equations for the pressure equal since P and T for all phases at the triple are EQUAL.

This gives us:

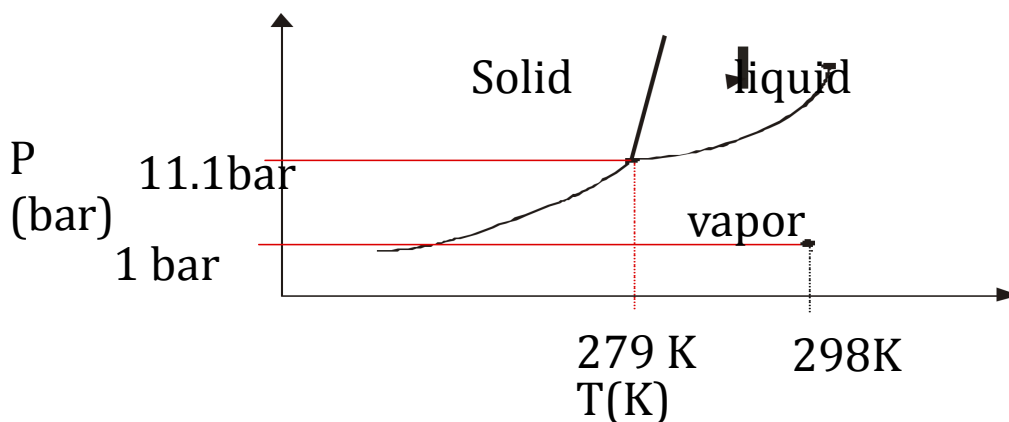
$$\ln(p_s^{vap}) = \ln(p_l^{vap})$$

$$\frac{-3010K}{T} + 13.2 = \frac{-3820K}{T} + 16.1$$

$$T_{tp} = 279K$$

$$p_{tp} = 11.1bar$$

To determine if the material is a solid, liquid, or gas at (298K, 1bar), we construct a generic phase diagram for a pure fluid (T,P) and since we are not told that this is a 'strange' material, we have:



Thus, it is a GAS at 298K and 1 bar

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, blunt/sharp writing instrument, and brain (your choice). 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 (1 Point) A new molecule has been synthesized and its phase diagram is being determined. Near the triple point, experiments show that the vapor pressure (in units of bar) over the liquid and solid are given by, respectively:

$$\ln(p_l^{vap}(T)) = \frac{-3,010K}{T} + 13.2$$
$$\ln(p_s^{vap}(T)) = \frac{-3,820K}{T} + 16.1$$

Estimate the enthalpy of sublimation.

Solution:

We can apply Clausius-Clapeyron Equation, assuming ideal vapor phase:

$$\frac{d \ln(p_s^{sat})}{dT} = \frac{3820K}{T^2} = \frac{\Delta \bar{H}_{subl}}{RT^2}$$
$$\Delta \bar{H}_{subl} = R(3820K) = (8.314J / K - mol)(3820K)$$
$$= 31760J / mol = 31.76kJ / mol$$

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, blunt/sharp writing instrument, and brain (your choice). 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. (9 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 $P^{\text{sat}}(\text{benzene})=96.4$ Torr and $P^{\text{sat}}(\text{toluene})=28.9$ 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?

Solution:

To have vapor and liquid in equilibrium at this composition of liquid, we have:

$$\begin{aligned} P_{\text{total}} &= x_{\text{benzene}} P_{\text{benzene}}^{\text{sat}} + x_{\text{toluene}} P_{\text{toluene}}^{\text{sat}} \\ &= \left(\frac{5 \text{ moles}}{8.25 \text{ moles}} \right) 96.4 \text{ torr} + \left(\frac{3.25 \text{ moles}}{8.25 \text{ moles}} \right) 28.9 \text{ torr} \\ &= (0.606)(96.4 \text{ torr}) + (0.394)(28.9 \text{ torr}) \\ &= 69.8 \text{ torr} \end{aligned}$$

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

Solution: initially there is no vapor phase, so we are only dealing with the composition after the liquid-vapor split.

$$\begin{aligned} y_{\text{benzene}} P_{\text{total}} &= x_{\text{benzene}} P_{\text{benzene}}^{\text{sat}} \\ y_{\text{benzene}} &= \frac{x_{\text{benzene}} P_{\text{benzene}}^{\text{sat}}}{P_{\text{total}}} \\ &= \frac{(0.606)(96.4 \text{ torr})}{69.8 \text{ torr}} \\ &= 0.837 \end{aligned}$$