

1. (5 Points). Place the letter of the correct answer, found in the column on the right, in the line provided in the left column.

1. Equilibrium state variables and functions depend on the path a system takes to achieve the equilibrium. (T or F) _____ False _____	A. Equation of State
2. Work is a state function. (T or F) _____ False _____	B. zero
3. An adiabatic boundary prevents heat interactions between a system and its surroundings. (T or F) _____ True _____	C. Fluid
4. A physical model that relates state variables in order to describe a material is an example of a(n) _____ A _____	D. low density
5. Elements needed for defining a temperature scale include: _____ C _____, _____ G _____, _____ J _____, and _____ N _____.	E. high temperature
6. The change in a state variable (or function) associated with a system that undergoes a cyclic process is _____ B _____.	F. 100 feet below sea level
7. The ideal gas equation of state is a suitable approximation for real gases under what condition(s)? _____ D, L _____, E _____	G. Physical property that varies with temperature
8. Thermodynamics directly tells us information about the kinetics (timescales) needed to observe changes. (T or F) _____ False _____	H. static
9. As defined in this course, the amount of pressure-volume work is related to _____ O _____ on a pressure-volume graph.	I. equilibrium
10. Processes in which a system is constantly at equilibrium are referred to as _____ Q _____.	J. Interpolation scheme
	K. steady-state
	L. low pressure
	M. true
	N. reference points
	O. area under curve
	P. False
	Q. reversible

2. (5 Points) Derive the expression for the work needed to expand an ideal gas isothermally from volume V_1 to volume V_2 using a reversible process. Show all work in as detailed a manner as possible.

$$dw = -p_{ext}dV = -pdV$$

$$= -\frac{nRT}{V}dV = -nRTd(\ln V)$$

$$w = \int_{V_1}^{V_2} -nRTd(\ln V) = -nRT \ln\left(\frac{V_2}{V_1}\right) = nRT \ln\left(\frac{V_1}{V_2}\right)$$

1. (5 Points) Consider an isothermal, reversible expansion of an ideal gas from volume V_1 to volume V_2 .

A. What is the change in the internal energy of the gas during this process?

For ideal gas, we showed in class that internal energy is only a function of temperature; thus, for isothermal process, $\Delta U = 0$

B. What amount of heat is exchanged with the environment, and what is the direction of the exchange?

Applying the First law:

$$\Delta U = q + w = 0$$

$$q = -w$$

Thus, once we find the amount of work for this process, we know that the heat is equal in magnitude to that. Also, since the gas expands, the heat must be **added** to the system in order to maintain constant temperature.

C. What amount of work is associated with this process, and what is the direction of the exchange of work with the environment?

Work is done by the system on the surroundings. The amount of work is:

$$dw = -p_{ext}dV = -pdV = -\frac{nRT}{V}dV = -nRTd(\ln V)$$
$$w = \int_{V_1}^{V_2} -nRTd(\ln V) = -nRT \ln\left(\frac{V_2}{V_1}\right) = nRT \ln\left(\frac{V_1}{V_2}\right)$$
$$w < 0$$

2. (5 Points) For a reversible, adiabatic expansion of an ideal gas of constant volume heat capacity $C_V = \frac{3}{2}R$ from volume V_1 to volume V_2 , what is the final temperature? (Provide an expression via appropriate derivation).

This is an adiabatic process; thus no heat is exchanged ($q=0$). To find the final temperature, we perform our first law analysis:

$$dU = d'w$$

$$nC_V dT = -pdV = -nRT \frac{dV}{V} = -nRT d(\ln V)$$

$$nC_V d(\ln T) = -nR d(\ln V)$$

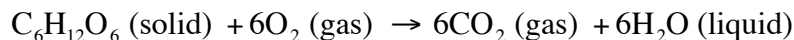
Integrating:

$$C_V d(\ln T) = -R d(\ln V)$$

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

$$T_2 = T_1 \left(\frac{V_2}{V_1}\right)^{\frac{-R}{C_V}}$$

1. **(3 Points)** The heat (enthalpy) of reaction at constant pressure (1 bar) and 298.15K is -2826.7 kJ for the combustion of one mole of fructose:



What is the standard enthalpy of formation of fructose at 298.15K?

$$\Delta H_{rxn}^{\circ} = -2826.7 \text{ kJ} = \sum_{i=\text{reactants, products}} \nu_i \Delta \bar{H}_{\text{formation}, i}^{\circ} = (6 \text{ mol}) \Delta \bar{H}_{\text{formation}, \text{CO}_2}^{\circ} + (6 \text{ mol}) \Delta \bar{H}_{\text{formation}, \text{H}_2\text{O}}^{\circ} - (1 \text{ mol}) \Delta \bar{H}_{\text{formation}, \text{C}_6\text{H}_{12}\text{O}_6}^{\circ} - (6 \text{ mol}) \Delta \bar{H}_{\text{formation}, \text{O}_2}^{\circ}$$

$$(1 \text{ mol}) \Delta \bar{H}_{\text{formation}, \text{C}_6\text{H}_{12}\text{O}_6}^{\circ} = 2826.7 \text{ kJ} + (6 \text{ mol}) \Delta \bar{H}_{\text{formation}, \text{CO}_2}^{\circ} + (6 \text{ mol}) \Delta \bar{H}_{\text{formation}, \text{H}_2\text{O}}^{\circ} - (6 \text{ mol}) \Delta \bar{H}_{\text{formation}, \text{O}_2}^{\circ}$$

$$(1 \text{ mol}) \Delta \bar{H}_{\text{formation}, \text{C}_6\text{H}_{12}\text{O}_6}^{\circ} = 2826.7 \text{ kJ} + (6 \text{ mol}) \Delta \bar{H}_{\text{formation}, \text{CO}_2}^{\circ} + (6 \text{ mol}) \Delta \bar{H}_{\text{formation}, \text{H}_2\text{O}}^{\circ} - (6 \text{ mol})(0 \text{ kJ/mol})$$

$$(1 \text{ mol}) \Delta \bar{H}_{\text{formation}, \text{C}_6\text{H}_{12}\text{O}_6}^{\circ} = 2826.7 \text{ kJ} + (6 \text{ mol})(-393.5 \text{ kJ/mol}) + (6 \text{ mol})(-285.8 \text{ kJ/mol})$$

$$\Delta \bar{H}_{\text{formation}, \text{C}_6\text{H}_{12}\text{O}_6}^{\circ} = -1249.1 \text{ kJ/mol}$$

2. **(2 Points)** For a gas that is described by the Van der Waals equation of state:

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

the Joule-Thomson coefficient in the limit of zero pressure is determined to be:

$$\mu_{J-T} = \frac{1}{C_p} \left(\frac{2a}{RT} - b \right)$$

In this limit, what expression for the inversion temperature does one obtain?

$$\mu_{J-T} = \frac{1}{C_p} \left(\frac{2a}{RT} - b \right) = 0$$

$$\left(\frac{2a}{RT} - b \right) = 0$$

$$T_{\text{inversion}} = \frac{2a}{Rb}$$

3. (5 Points) A quantity of nitrogen gas at 298K is compressed reversibly and adiabatically from a volume of 20.0 dm³ to 5.0 dm³. Assuming ideal gas behavior, calculate the final temperature of the nitrogen gas. Consider a molar constant volume heat capacity of 2.5R, where R is the gas constant.

$$dU = d'w$$

$$nC_V dT = -pdV = -nRT \frac{dV}{V} = -nRT d(\ln V)$$

$$nC_V d(\ln T) = -nR d(\ln V)$$

Integrating:

$$C_V d(\ln T) = -R d(\ln V)$$

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

$$T_2 = T_1 \left(\frac{V_2}{V_1}\right)^{\frac{-R}{C_V}}$$

$$= (298K) \left(\frac{5.0 dm^3}{20.0 dm^3}\right)^{\frac{1}{2.5}} = 518.8K$$

The compression under adiabatic conditions leads to increase in temperature as one would intuit.

1A. (3 Points) Consider an ideal gas with constant volume molar heat capacity of $1.5R$ where R is the gas constant. Obtain an expression for the entropy change of one mole of an ideal gas at a constant volume V_1 reversibly cooled from P_1, T_1, V_1 , to P_2, V_1, T_4 . Recall $\bar{C}_p = \bar{C}_v + R$

$$dU = dq + dw = dq \text{ (no work for constant volume process)}$$

$$dq = dU = n\bar{C}_v dT = dq_{\text{reversible}}$$

$$\frac{dq_{\text{reversible}}}{T} = \frac{n\bar{C}_v dT}{T} = n\bar{C}_v d(\ln T) = dS$$

$$\Delta S = \bar{C}_v \ln\left(\frac{T_4}{T_1}\right)$$

1B.(3 Points). Obtain an expression for the entropy change when one mole of the above gas undergoes a reversible expansion at constant pressure P_2 from P_2, V_1, T_4 to P_2, V_2, T_1 .

$$dU = dq + dw = dq_p - pdV = dq_p - d(pV)$$

$$dq_p = dU + d(pV) = dH = n\bar{C}_p dT = dq_{p,\text{reversible}}$$

$$\frac{dq_{p,\text{reversible}}}{T} = \frac{n\bar{C}_p dT}{T} = n\bar{C}_p d(\ln T) = dS$$

$$\Delta S = \bar{C}_p \ln\left(\frac{T_1}{T_4}\right)$$

2. (3 Points) What is the molar entropy change for vaporization of water at 298.15K and 1 bar pressure?

$$\begin{aligned} \Delta \bar{S} &= \int_{\text{liquid}}^{\text{vapor}} \frac{dq_{p,\text{reversible}}}{T_{\text{vaporization}}} = \frac{1}{T_{\text{vaporization}}} \int_{\text{liquid}}^{\text{vapor}} dq_{p,\text{reversible}} = \frac{1}{T_{\text{vaporization}}} \int_{\text{liquid}}^{\text{vapor}} d\bar{H}_{p,\text{reversible}} = \frac{\Delta \bar{H}_{\text{vaporization}}}{T_{\text{vaporization}}} \\ &= \frac{\bar{H}_{\text{vapor}} - \bar{H}_{\text{liquid}}}{T_{\text{vaporization}}} = \frac{44.01 \text{ kJ/mol}}{298.15 \text{ K}} = 0.15 \frac{\text{kJ/mol}}{\text{K}} > 0 \end{aligned}$$

3 (1 Point) What can you say about the entropy change for an adiabatic, irreversible process?

Entropy change is greater than 0 (it's irreversible, so adiabaticity does not matter)

1. (3 Points) The molar constant volume heat capacity of ethene is approximated as:

$$\frac{\bar{C}_V(T)}{R} = 16.4105 - \frac{(6085.929 K)}{T} + \frac{(822826 K^2)}{T^2}$$

over the temperature range $300K < T < 1000K$. Calculate the change in entropy of one mole of ethene when heated from 300K to 600K at constant volume. There is no phase change during this process.

$$\begin{aligned} \Delta \bar{S}_1 &= \int_{300K}^{600K} \frac{n\bar{C}_V}{T} dT \\ &= nR \int_{300K}^{600K} \left(\frac{16.4105}{T} - \frac{6085.929K^2}{T^2} + \frac{822826K^2}{T^3} \right) dT \\ &= 38.75 J/K \end{aligned}$$

2. (3 Points) Given the following data, conclude whether the value of the entropy difference between liquid and gaseous water at 1 bar pressure and 298.15 K as given in the Equations Handbook is valid. Consider the data:

$$\begin{aligned} T_{\text{vaporization}} &= 373.15K \\ \Delta \bar{H}_{\text{vap}}(T_{\text{vap}}) &= 40.65 kJ/mol \\ \bar{C}_{P,\text{liquid}} &= 75.3 \frac{J}{K - mol} \\ \bar{C}_{P,\text{vapor}} &= 33.8 \frac{J}{K - mol} \end{aligned}$$

The use of a reversible path connecting the states at 298.15 K will be useful. Comment on any differences or equivalences and their possible origins.

Solution:

For this problem, we need to construct a reversible path (or thermodynamic cycle) from water at 298.15K and 1 bar to liquid water at the normal boiling point at 1 bar (373.15K) to gaseous water at 1 bar and 373.15K to finally gaseous water at 298.15K. We calculate the entropy changes for each of those segments, add them up, and then compare to the value in the hand book. We'll consider one mole of water, but still retain the molar properties given above. Note that we will use constant heat capacities along the reversible paths.

$$\Delta\bar{S}_1 = \int_{298.15K}^{373.15K} \frac{\bar{C}_{P,liquid}}{T} dT = (75.3 \frac{J}{K-mol}) \ln\left(\frac{373.15K}{298.15K}\right) = 16.9 \frac{J}{K-mol}$$

$$\Delta\bar{S}_2 = \frac{\Delta H_{vaporization}}{T_{vaporization}} = \frac{40.65J/mol}{373.15K} = 108.9 \frac{J}{K-mol}$$

$$\Delta\bar{S}_3 = \int_{373.15K}^{298.15K} \frac{\bar{C}_{P,gas}}{T} dT = (33.8 \frac{J}{K-mol}) \ln\left(\frac{298.15K}{373.15K}\right) = -7.584 \frac{J}{K-mol}$$

$$\Delta\bar{S}_1 + \Delta\bar{S}_2 + \Delta\bar{S}_3 = 118.2 \frac{J}{K-mol}$$

This is slightly lower than the value in the handbook, but otherwise one would say that the value in the handbook is accurate. We are not accurate in assuming that the heat capacities are absolutely constant over the temperature range of 100K considered for the temperature dependent segments of our process. And of course, the handbook is going to be accurate!

3. (2 Points) If one treats a fluid using the Van der Waals Equation of State (Page 4-1, Equations Handbook), what is the expression for the isothermal reversible work for a process from (P_1, V_1) to (P_2, V_2) ?

$$dw = -pdV = -\left(\frac{nRT}{V-nb} - \frac{n^2a}{V^2}\right)dV$$

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

$$w = -n^2a\left(\frac{1}{V_2} - \frac{1}{V_1}\right) - nRT[\ln(V_2 - nb) - \ln(V_1 - nb)]$$

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

4. (2 Points) Fill in the correct answer for the following:

4A. (0.5 Points) The natural variables for entropy, S, for a closed system (pure substance with no change in amount of material) are ___ U (internal energy)_____ and ___ V (volume)_____.

4B. (0.5 Points) If a system is initially in a non-equilibrium state, what will happen to what thermodynamic state function under conditions where the system is maintained at constant temperature and pressure, with no change in amount of substance in the system?

Gibbs free energy will decrease until equilibrium is reached, at which point G is constant.

4C. (0.5 Points) The natural variables for internal energy, U, for a closed system (pure substance with no change in amount of material) are _____ S (entropy)_____ and ___ volume (V)_____.

4D. (0.5 Points) What are the natural variables for the Helmholtz Free Energy for pure substance and closed system? _____ V (volume)_____ and _____ T (temperature)_____.

1. (5 Points) Since we know that

$$dA(T, V, n_1, n_2) = -pdV - SdT + \mu_1 dn_1 + \mu_2 dn_2$$

and that: $G(T, P, n_1, n_2) = A(T, V, n_1, n_2) - V \left(\frac{\partial A}{\partial V} \right)_{T, n_1, n_2}$

demonstrate that

$$\mu_1 = \left(\frac{\partial A}{\partial n_1} \right)_{V, T, n_2} = \left(\frac{\partial G}{\partial n_1} \right)_{P, T, n_2}$$

Given :

$$dA(T, V, n_1, n_2) = -pdV - SdT + \mu_1 dn_1 + \mu_2 dn_2$$

This suggests : $\mu_1 = \left(\frac{\partial A}{\partial n_1} \right)_{T, V, n_2}$

$$G(T, P, n_1, n_2) = A(T, V, n_1, n_2) - V \left(\frac{\partial A}{\partial V} \right)_{T, n_1, n_2} = A(T, V, n_1, n_2) + PV$$

$$dG(T, P, n_1, n_2) = dA(T, V, n_1, n_2) + d(PV) = dA(T, V, n_1, n_2) + PdV + VdP$$

Substitute for total differential of A and keep explicit derivatives

for the chemical potentials

$$dG(T, P, n_1, n_2) = -pdV - SdT + \left(\frac{\partial A}{\partial n_1} \right)_{T, V, n_2} dn_1 + \left(\frac{\partial A}{\partial n_2} \right)_{T, V, n_1} dn_2 + PdV + VdP$$

$$dG(T, P, n_1, n_2) = VdP - SdT + \left(\frac{\partial A}{\partial n_1} \right)_{T, V, n_2} dn_1 + \left(\frac{\partial A}{\partial n_2} \right)_{T, V, n_1} dn_2$$

however, since G is a function of T, P, n1, n2, we see that the total differential of G needs to have terms with partial derivative of G with respect to n1 and n2; thus, we see clearly the equality :

$$\left(\frac{\partial A}{\partial n_1} \right)_{T, V, n_2} = \left(\frac{\partial G}{\partial n_1} \right)_{T, P, n_2}$$

1. Alternative Solution (Mr. Sean Herron)

This solution uses the fact that the Gibbs and Helmholtz free energies are first-order extensive functions. We have seen in class that:

$$G(T,P,n_1,n_2) = \mu_1 n_1 + \mu_2 n_2 = \left(\frac{\partial G}{\partial n_1} \right)_{P,T,n_2} n_1 + \left(\frac{\partial G}{\partial n_2} \right)_{P,T,n_1} n_2$$

As we did in class for G, we can use a similar analysis for A as follows, starting from the fact that A is first-order extensive in amount of material (and thus in volume):

$$\lambda A(T,V,n_1,n_2) = A(T,\lambda V,\lambda n_1,\lambda n_2)$$

Take derivative of both sides with respect to lambda:

$$\begin{aligned} A(T,V,n_1,n_2) &= \frac{d}{d\lambda} [A(T,\lambda V,\lambda n_1,\lambda n_2)] \\ &= \left(\frac{\partial}{\partial(\lambda V)} [A(T,\lambda V,\lambda n_1,\lambda n_2)] \right)_{T,n_1,n_2} \left(\frac{d\lambda V}{d\lambda} \right) + \left(\frac{\partial}{\partial(\lambda n_1)} [A(T,\lambda V,\lambda n_1,\lambda n_2)] \right)_{T,V,n_2} \left(\frac{d\lambda n_1}{d\lambda} \right) + \\ &\quad \left(\frac{\partial}{\partial(\lambda n_2)} [A(T,\lambda V,\lambda n_1,\lambda n_2)] \right)_{T,V,n_1} \left(\frac{d\lambda n_2}{d\lambda} \right) \\ &= -PV + \mu_1 n_1 + \mu_2 n_2 \\ &= -PV + \left(\frac{\partial A}{\partial(n_1)} \right)_{T,V,n_2} n_1 + \left(\frac{\partial A}{\partial(n_2)} \right)_{T,V,n_1} n_2 \\ A &= -PV + \left(\frac{\partial A}{\partial(n_1)} \right)_{T,V,n_2} n_1 + \left(\frac{\partial A}{\partial(n_2)} \right)_{T,V,n_1} n_2 \end{aligned}$$

Now, we use the given information, $G(T,P,n_1,n_2) = A(T,V,n_1,n_2) - V \left(\frac{\partial A}{\partial V} \right)_{T,n_1,n_2}$

to arrive at our desired demonstration:

$$\begin{aligned} G(T,P,n_1,n_2) &= \left(\frac{\partial G}{\partial n_1} \right)_{P,T,n_2} n_1 + \left(\frac{\partial G}{\partial n_2} \right)_{P,T,n_1} n_2 = A(T,V,n_1,n_2) + PV = -PV + \left(\frac{\partial A}{\partial(n_1)} \right)_{T,V,n_2} n_1 + \left(\frac{\partial A}{\partial(n_2)} \right)_{T,V,n_1} n_2 + PV \\ \left(\frac{\partial G}{\partial n_1} \right)_{P,T,n_2} n_1 + \left(\frac{\partial G}{\partial n_2} \right)_{P,T,n_1} n_2 &= \left(\frac{\partial A}{\partial(n_1)} \right)_{T,V,n_2} n_1 + \left(\frac{\partial A}{\partial(n_2)} \right)_{T,V,n_1} n_2 \end{aligned}$$

Collecting terms with n1 and n2 together:

$$\left(\left(\frac{\partial G}{\partial n_1} \right)_{P,T,n_2} - \left(\frac{\partial A}{\partial n_1} \right)_{T,V,n_2} \right) n_1 + \left(\left(\frac{\partial G}{\partial n_2} \right)_{P,T,n_1} - \left(\frac{\partial A}{\partial n_2} \right)_{T,V,n_1} \right) n_2 = 0$$

Since we cannot have n1 and n2 zero, the only way the equality holds generally (as it

must) is if the terms multiplying n_1 and n_2 are each zero. With this being the case, we obtain the result that we must demonstrate, namely:

$$\left(\left(\frac{\partial G}{\partial n_1} \right)_{P,T,n_2} = \left(\frac{\partial A}{\partial n_1} \right)_{T,V,n_2} \right)$$

$$\left(\left(\frac{\partial G}{\partial n_2} \right)_{P,T,n_1} = \left(\frac{\partial A}{\partial n_2} \right)_{T,V,n_1} \right)$$

2. (5 Points) Use what you know about the Fundamental Equation of thermodynamics, it's relation to the other major thermodynamic potentials, and Maxwell Relations, to determine $\left(\frac{\partial U}{\partial V} \right)_T$ for a pure Van der Waals fluid.

$$dU(S,V) = TdS - pdV$$

at constant temperature :

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial S}{\partial V} \right)_T - p$$

To obtain the derivative of entropy with volume, we can resort to Maxwell Relations in the appropriate thermodynamic potential to give us a more convenient relation in terms of an equation of state (EOS). Since we have S,V,T as the variables, we can first try the Helmholtz free energy (since the other obvious potential is U, which we already started with)

$$dA = -pdV - SdT$$

Maxwell Relation :

$$\left(\frac{\partial p}{\partial T} \right)_V = \left(\frac{\partial S}{\partial V} \right)_T$$

Thus :

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_V - p$$

Now we use our Van der Waals EOS to obtain the derivative of pressure with respect to temperature at constant volume

$$p = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

$$\left(\frac{\partial p}{\partial T} \right)_V = \frac{nR}{V - nb}$$

so

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_V - p = \frac{nRT}{V - nb} - \left[\frac{nRT}{V - nb} - \frac{n^2 a}{V^2} \right] = \frac{n^2 a}{V^2}$$

1. (10 Points) Knowing that for the chemical potential of an ideal gas in a mixture at temperature T and pressure P is:

$$\mu_i^{mixture}(T,P) = \mu_i^{pure}(T,P) + RT \ln(x_i)$$

what is the Gibbs free energy change of mixing of two ideal gases, A and B, at constant temperature and pressure?

Solution:

Initially we have N_A moles of A and N_B moles of B, separated from one another. In this separated state, the total Gibbs free energy at this T and pressure combination is simply the sum of the individual molar Gibbs free energies:

$$G_{initial} = N_A \mu_A^{pure}(T,P) + N_B \mu_B^{pure}(T,P)$$

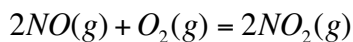
After mixing, the Gibbs free energy of the mixture is simply (making use of the relation given above for the ideal gas chemical potential:

$$\begin{aligned} G_{final} &= N_A \mu_A^{mixture}(T,P) + N_B \mu_B^{mixture}(T,P) \\ &= \mu_A^{pure}(T,P) + RT \ln(x_A) + \mu_B^{pure}(T,P) + RT \ln(x_B) \end{aligned}$$

At equilibrium after mixing, the difference in Gibbs free energies is:

$$\begin{aligned} \Delta G &= G_{final} - G_{initial} \\ &= N_A \mu_A^{pure}(T,P) + N_A RT \ln(x_A) + N_B \mu_B^{pure}(T,P) + N_B RT \ln(x_B) - N_A \mu_A^{pure}(T,P) - N_B \mu_B^{pure}(T,P) \\ &= RT N_A \ln(x_A) + N_B RT \ln(x_B) \\ &= NRT [x_A \ln(x_A) + x_B \ln(x_B)] \end{aligned}$$

1. (5 Points) For the following chemical transformation, the value of $K_P = 2.3 \times 10^{12}$ at $T=298\text{K}$:



Consider that initially, there are 2 moles of $\text{NO}(g)$ and 1 mole of $\text{O}_2(g)$. What extent of reaction optimizes the total Gibbs free energy of this system? Consider the gases to be ideal and make necessary approximations to arrive at an expression for the extent of reaction in terms of the total pressure, P , and the equilibrium constant, K_P given above. Note the magnitude of K_P in thinking about what approximation to invoke in your solution.

Solution:

At the given temperature, the Gibbs free energy is optimized at equilibrium. Thus, to find the extent of reaction, we only need to solve for the mole fractions at equilibrium.

	NO	O ₂	NO ₂
Initial Moles	2	1	0
Equilibrium Moles	2-2ε	1-ε	2ε
Equilibrium Mole Fraction	$\frac{2(1-\epsilon)}{3-\epsilon}$	$\frac{(1-\epsilon)}{3-\epsilon}$	$\frac{2\epsilon}{3-\epsilon}$
$K_P=2.3 \times 10^{12}$			

The equilibrium constant is determined as:

$$K_P = \frac{P_{\text{NO}_2}^2}{P_{\text{NO}}^2 P_{\text{O}_2}} = \frac{1}{P} \frac{x_{\text{NO}_2}^2}{x_{\text{NO}}^2 x_{\text{O}_2}} = \frac{1}{P} \frac{\epsilon^2 (3-\epsilon)}{(1-\epsilon)^3}$$

Since K_P is $\gg \gg 1$, we can approximate ϵ to be CLOSE to 1, which allows us to write

$$K_P = \frac{P_{\text{NO}_2}^2}{P_{\text{NO}}^2 P_{\text{O}_2}} = \frac{1}{P} \frac{x_{\text{NO}_2}^2}{x_{\text{NO}}^2 x_{\text{O}_2}} = \frac{1}{P} \frac{\epsilon^2 (3-\epsilon)}{(1-\epsilon)^3} \approx \frac{1}{P} \frac{(1)^2 (3-1)}{(1-\epsilon)^3} \approx \frac{1}{P} \frac{2}{(1-\epsilon)^3}$$

We cannot ignore the epsilon in the denominator, as this term is the one that drives the solution because it is a small number, cubed, and located in the denominator. Thus,

$$(1-\epsilon)^3 \approx \frac{2}{PK_P}$$

$$\epsilon \approx 1 - \left(\frac{2}{PK_P} \right)^{1/3}$$

This is an approximate solution for the optimal equilibrium extent of reaction at this temperature. We see that increasing the pressure will increase the extent of

reaction (i.e. conversion). This is reminiscent of Le Chatelier's principle for pressure effect on equilibrium.

2. (2 Point) The Virial expansion is a perturbation theory that applies to real fluids under conditions where the density is low. What is the reference state for the Virial expansion to describe fluids with attractions and finite molecular volumes?

The ideal gas EOS is the reference state for liquids.

3. (2 Points) What is the entropy change for an adiabatic, reversible process?

Solution:

$$\Delta S = \int_{\text{initial state}}^{\text{final state}} dS = \int_{\text{initial state}}^{\text{final state}} \frac{dq_{\text{reversible}}}{T} = \int_{\text{initial state}}^{\text{final state}} \frac{0.0}{T} = 0$$

4. (1 Point) For a binary system (two distinct chemical components) in two-phase equilibrium, how many intensive degrees of freedom are available?

Solution: This is a problem for Gibbs Phase "Rule".

N=2

P = # phases = 2

Thus, F = 2 + N - P = 2 degrees of freedom

Consider, if we have 2 chemical species distributed in two phases, we have two degrees of freedom (independent, intensive variables we can control, or "dial in"). What if we dial in specific values of temperature, T, and pressure, P? We have used up all of our degrees of freedom. Well, does this mean that the composition of each phase in equilibrium is then determined for us? Are we stuck?

1. (5 Points) Consider a water(1)-ethanol(2) binary liquid solution in equilibrium with the gaseous mixture (also consisting of ethanol and water). Take the vapor to be ideal. Determine a relation between the liquid and vapor mole fractions of either component at a certain temperature T and pressure P where the following condition holds:

$$\frac{\gamma_1}{\gamma_2} = \frac{P_2^{sat}}{P_1^{sat}}$$

Solution:

$$\frac{\gamma_1}{\gamma_2} = \frac{y_1 P P_2^{sat}}{x_1 P_1^{sat}} \frac{x_2}{y_2 P} = \frac{y_1 P_2^{sat}}{x_1 P_1^{sat}} \frac{x_2}{y_2} = \frac{P_2^{sat}}{P_1^{sat}}$$

Thus

$$\frac{y_1}{x_1} \frac{x_2}{y_2} = 1$$

$$\frac{y_1}{y_2} = \frac{x_1}{x_2}$$

$$\frac{1}{y_2} - 1 = \frac{1}{x_2} - 1$$

$$\frac{1}{y_2} = \frac{1}{x_2}$$

$$y_2 = x_2$$

This is an example of an *azeotropic* thermodynamic point.

2. (5 Points) Calculate the boiling point (at 1 atm) of a solution containing 116 g of acetone (Mw = 58) and 72 g of water (Mw = 18) by using the following table. Assume ideal solution and vapor behavior.

Temperature °C	Vapor Pressure Acetone (atm)	Vapor pressure Water (atm)
60	1.14	0.198
70	1.58	0.312
80	2.12	0.456
90	2.81	0.694

A liquid starts to boil when its vapor pressure matches the atmospheric pressure (1 atm in this case). Thus, according to Raoult's law

$$P = x_{\text{acetone}} P^{\circ}_{\text{acetone}} + x_{\text{water}} P^{\circ}_{\text{water}} = 1 \text{ atm}$$

From the given data we can calculate the molar fractions

$$\text{moles}_{\text{acetone}} = 116/58 = 2$$

$$\text{moles}_{\text{water}} = 72/18 = 4$$

$$\text{total moles} = 6$$

$$x_{\text{acetone}} = 2/6 = 1/3$$

$$x_{\text{water}} = 4/6 = 2/3$$

thus

$$P = 2/3 P^{\circ}_{\text{acetone}} + 1/3 P^{\circ}_{\text{water}} = 1 \text{ atm}$$

By trials, using the table, we can find the values of vapor pressure which satisfies the above equation. The best result is obtained by using the values at 80°C :

$$P = 2/3 \cdot 0.456 + 1/3 \cdot 2.12 = 1.01 \text{ atm}$$

then the boiling point is about 80°C.