

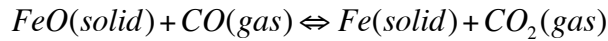
Directions: Please answer each question to the best of your ability. Make sure your response is **legible, precise, includes relevant dimensional units (where appropriate), logically presented (include non-mathematical language if necessary to convey your intent clearly and transparently), and correct/accurate.** You are free to use your Equations Handbook, Calculator, blunt/sharp writing instrument. 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! **Please leave all responses to be graded on the exam sheet. Work on scratch paper will not be considered.**

Problem	Points
1	/10
2	/30
3	/20
4	/20
5	/20
Extra Credit	/5
Total	/100

1 (10 Points) Matching and Fill-In. Provide the proper response from the right column in the blanks provided in the left column

1. Chemical potentials, pressure, temperature, density, molar volume are examples of this type of property: <u>L</u>	A $P^A \neq P^B$ (P = pressure)
2. At equilibrium, for a two-phase (phase A and phase B), two chemical component (i and j) system at a particular temperature and pressure, what relationship holds? <u>J</u>	B $\left(\frac{\partial F}{\partial P}\right)_U = \left(\frac{\partial V}{\partial G}\right)_H$
3. At equilibrium, the Gibbs Free Energy is maximized under conditions of constant temperature and entropy. True or False? <u>False, H</u>	C state function
4. Entropy is a rigorous definition of chaos in a system, and maps in a unique, one-to-one fashion with the chaos function. True or False? <u>False, H</u>	D maximum
5. The chemical potential of a species 'A' in an ideal gas mixture is <u>K</u> that of the pure species at the same temperature and total pressure.	E isothermal expansion
6. The Third 'Law' of Thermodynamics guarantees that we can reach 0 Kelvin (absolute temperature) and realize a perpetual motion machine; the only trivial limitation is that we have not found the right material. True or False? <u>False, H</u>	F $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$
7. Total entropy change for a reversible adiabatic process must be zero. True or False? <u>True, G</u>	G true
8. Internal energy, U, of a system is minimized at constant temperature and pressure. True or False? <u>False, H</u>	H false
9. The thermodynamic potential that reaches an extremum under equilibrium conditions of constant volume and temperature is <u>R</u> .	I adiabatic compression
10. A Maxwell Relation associated with the following total differential of a state function, H(S,P), $dH(S,P) = TdS + VdP$ is: <u>F</u>	J. $\mu_i^A(T,P) = \mu_i^B(T,P)$
	K less than
	L intensive
	M isothermal compression
	N enthalpy
	O minimum
	P zero
	Q $T^A \neq T^B$ (T=temperature)
	R Helmholtz Free Energy
	S. $\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial P}{\partial S}\right)_P$
	T. $\left(\frac{\partial A}{\partial P}\right)_U = \left(\frac{\partial V}{\partial G}\right)_H$

2. (30 Points) For the following reaction,



the equilibrium constant (expressed in species partial pressures) at two temperatures has been determined to be:

T	700C = 973.15K	1200C = 1473.15K
$T^{-1} = 1/T$	0.00103 K ⁻¹	0.000679 K ⁻¹
K_p	0.688	0.310
$\ln(K_p)$	-0.373966	-1.171183

A. Using this data and necessary assumptions, calculate at T=700C the following: ΔG_R^0 , ΔH_R^0 , ΔS_R^0 . It will be helpful to calculate the values in the order given. Take the standard pressure to be $P^0=1\text{bar}$. $R = 8.314 \text{ J/(mole K)}$.

Temperature dependence of K_p :

$$\frac{d \ln K_p(T)}{dT} = \frac{\Delta H_R^0}{R} \frac{1}{T^2}$$

$$d \ln K_p(T) = \frac{\Delta H_R^0}{R} \frac{1}{T^2} dT$$

Integrate:

$$\ln(K_p(T_2)) - \ln(K_p(T_1)) = \frac{\Delta H_R^0}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\Delta H_R^0(T) = (-R) \left[\ln(K_p(T_2)) - \ln(K_p(T_1)) \right] \left(\frac{1}{T_2} - \frac{1}{T_1} \right)^{-1}$$

$$\Delta H_R^0(T) = (-8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}}) \left[-1.171183 - (-0.373966) \right] \left(\frac{1}{1473.15\text{K}} - \frac{1}{973.15\text{K}} \right)^{-1}$$

$$= -19003.9 \text{ J/mol} \quad (2)$$

$$\begin{aligned} \Delta G_R^0(T) &= -RT \ln K_p(T) \\ &= (-8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}}) (973.15\text{K}) (-0.373966) \\ &= 3025.6 \text{ J/mol} \quad (1) \end{aligned}$$

$$\Delta S_R^0 = \frac{(\Delta G_R^0 - \Delta H_R^0)}{T}$$

$$\Delta S_R^0 = \frac{[3025.6 \text{ J/mol} - (-19003.9 \text{ J/mol})]}{973.15\text{K}}$$

$$(3) \quad \Delta S_R^0 = -22.64 \text{ J/mol}\cdot\text{K}$$

B. Calculate the mole fraction of carbon dioxide gas in the gas phase at 700C = 973.15K.

$$K_p(T_1) = \frac{P_{\text{CO}_2} / P_{\text{CO}_2}^0}{P_{\text{CO}} / P_{\text{CO}}^0} = \frac{P_{\text{CO}_2}}{P_{\text{CO}}} \quad P_{\text{CO}}^0 = P_{\text{CO}_2}^0 = 1 \text{ bar}$$

$$\approx \frac{X_{\text{CO}_2} P^{\text{TOT}}}{X_{\text{CO}} P^{\text{TOT}}} = \frac{X_{\text{CO}_2}}{X_{\text{CO}}} \quad \therefore X_{\text{CO}_2} = K_p(T_1) X_{\text{CO}}$$

$$= K_p(T_1) [1 - X_{\text{CO}_2}]$$

$$X_{\text{CO}_2} [1 + K_p(T_1)] = K_p(T_1)$$

$$X_{\text{CO}_2} = \frac{K_p(T_1)}{1 + K_p(T_1)} = 0.4076$$

3 (20 Points) Data: 1 mole of He (gas), 3.0 mole of Ne (gas), 2.0 mole of Ar (gas), and 2.5 mole of Xe (gas); $T = 298.15\text{K}$; $P = 1\text{bar}$. Calculate ΔG and ΔS of mixing.

$$n_{\text{TOT}} = 1\text{ mole} + 3\text{ mole} + 2\text{ mole} + 2.5\text{ mole} = 8.5\text{ mole}$$

$$\Delta S_{\text{mixing}} = -nR \sum_i X_i \ln X_i = -nR \left[\frac{n_{\text{He}}}{n_{\text{TOT}}} \ln(X_{\text{He}}) + \left(\frac{n_{\text{Ne}}}{n_{\text{TOT}}} \right) \ln(X_{\text{Ne}}) \right. \\ \left. + \left(\frac{n_{\text{Ar}}}{n_{\text{TOT}}} \right) \ln(X_{\text{Ar}}) + \left(\frac{n_{\text{Xe}}}{n_{\text{TOT}}} \right) \ln(X_{\text{Xe}}) \right]$$

$$X_{\text{He}} = \frac{1\text{ mole}}{8.5\text{ mole}} = 0.118$$

$$X_{\text{Ar}} = \frac{2\text{ mole}}{8.5\text{ mole}} = 0.235$$

$$X_{\text{Ne}} = \frac{3\text{ mole}}{8.5\text{ mole}} = 0.353$$

$$X_{\text{Xe}} = \frac{2.5\text{ mole}}{8.5\text{ mole}} = 0.294$$

$$\text{TOTAL} = 1.0$$

$$\Delta S_{\text{mixing}} = -(8.5\text{ mole}) \left(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) \left[0.118 \ln(0.118) + 0.235 \ln(0.235) \right. \\ \left. + 0.353 \ln(0.353) + 0.294 \ln(0.294) \right]$$

$$= -(8.5\text{ mole}) \left(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) (-1.32)$$

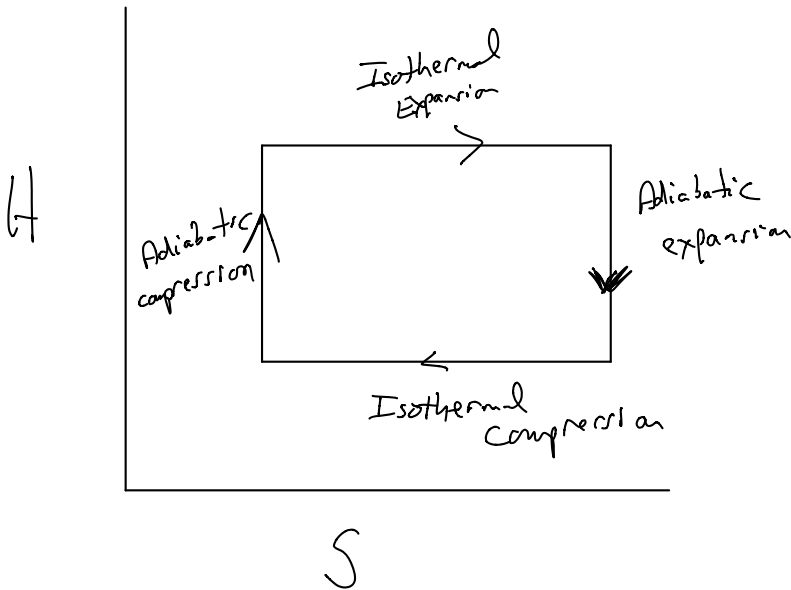
$$\Delta S_{\text{mixing}} = 93.3 \text{ J/K} > 0$$

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} = 0 - T\Delta S_{\text{mixing}} = -(298.15\text{K})(93.3 \frac{\text{J}}{\text{K}})$$

$$\Delta G_{\text{mix}} = -27817 \text{ J} < 0$$

spontaneous;
interaction

4A (10 Points) On a graph with x-axis being entropy and y-axis being enthalpy, plot the steps of a Carnot Cycle. Recall that the Carnot Cycle consists of (not necessarily given in correct order) adiabatic expansion, adiabatic compression, isothermal compression, and isothermal expansion. Make sure the stages are in the correct order and label your graph axes and indicate each of the 4 steps of the Carnot Cycle on your plot; these will be required for full points.



Carnot cycle

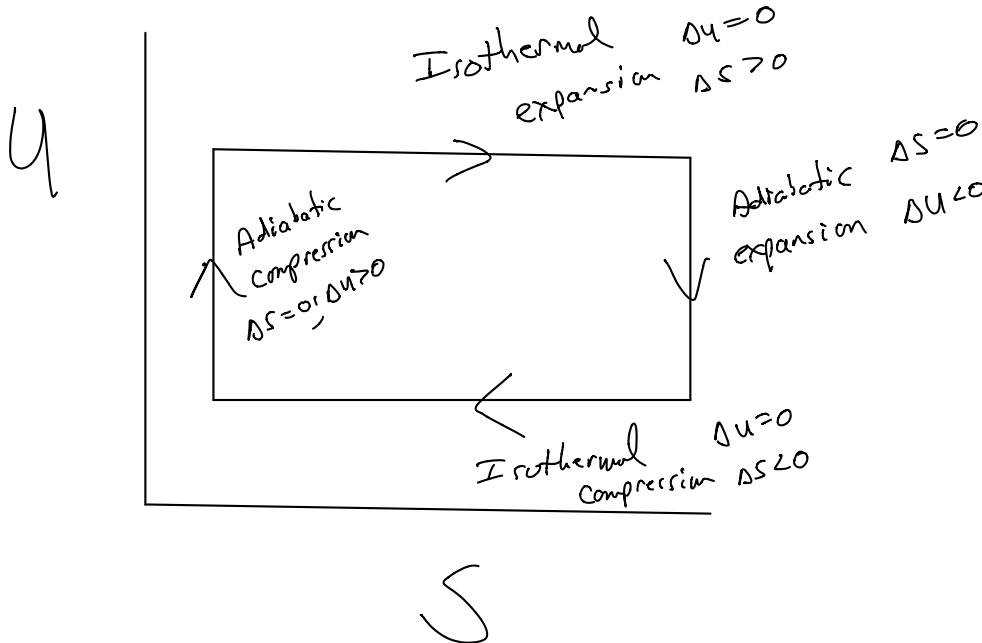
↳ Ideal Gas Fluid
 1. H^i & S^i

↳ Adiabatic steps (which are reversible) have $dS = \frac{dq_{rev}}{T} = 0$
 ∴ vertical lines ($\Delta S = 0$)!!!

↳ Isothermal steps (which are reversible) have $dH^i = 0$

∴ horizontal lines for isothermal steps !!

4B (10 Points) On a graph with x-axis being entropy and y-axis being internal energy, U, plot the steps of a Carnot Cycle. Recall that the Carnot Cycle consists of isothermal expansion, adiabatic expansion, isothermal compression, and adiabatic compression. Make sure the stages are in the correct order and label your graph axes and indicate each of the 4 steps of the Carnot Cycle on your plot; these will be required for full points.

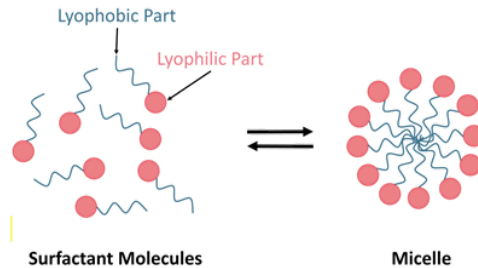


As in part 4A;

- all adiabatic steps have $dS = \frac{dq_{rev}}{T} = 0$ (vertical lines)

- All isothermal steps have $\Delta U = 0$ (ideal gas) (horizontal lines)

5 (20 Points) Micelles are aggregates that form from the reversible association of individual surfactant molecules. Surfactants are familiar as detergents (i.e., soap). Surfactants have a polar region (lyophilic head-group) and a non-polar region (usually a lyophobic fatty acid 'tail'). Because of the dichotomy of the dominant interaction forces associated with each region, in aqueous systems, surfactant molecules self-assemble into a rich palette of three-dimensional structures/shapes. In this problem, we'll look at an extremely simplified model of micelle aggregation. Consider the equilibrium implied by the following figure and explicitly given in terms of a chemical 'transformation' as well:



We have N surfactant monomers in equilibrium with aggregate micelles having N surfactants. This is an N -mer micelle. The chemical potential of a single free surfactant monomer in aqueous solution is given by:

$$\mu_m = \mu_m^o + kT \ln \left(\frac{C_m}{C_m^o} \right)$$

where C_m is the free monomer concentration, C^o refers to a standard state (reference) concentration, k is the Boltzmann constant, T is temperature, μ_m^o is the standard state chemical potential of the free monomer, and μ_m is the free monomer chemical potential in the equilibrium system.

The chemical potential of a single surfactant molecule in an N -mer micelle is given by:

$$\mu_{m,N} = \mu_{m,N}^o + \left(\frac{1}{N} \right) kT \ln \left(\frac{\frac{1}{N} C_{m,N}}{C_{m,N}^o} \right)$$

where $C_{m,N}$ is the concentration of monomers associated with the N -mer micelle, C^o refers to a standard state (reference) concentration, k is the Boltzmann constant, T is temperature, $\mu_{m,N}^o$ is the standard state chemical potential of a monomer in an N -mer micelle, and $\mu_{m,N}$ is the N -mer associated monomer chemical potential in the equilibrium system.

Determine an explicit relationship for:

$$C_{m,N} = f(C_m, C_m^o, C_{m,N}^o, k, T, N, \mu_m^o, \mu_{m,N}^o)$$

major concept ← bulk of this problem:

$$\mu_{m,N} = \mu_m$$

← most important part of this question

chemical potential of species is the same everywhere at equilibrium

Equate the 2 equations and do simple
algebra.

$$\mu_m^\circ + kT \ln\left(\frac{C_m}{C_m^\circ}\right) = \mu_{m,\nu}^\circ + \left(\frac{1}{\nu}\right) kT \ln\left(\frac{\frac{1}{\nu} C_{m,\nu}}{C_{m,\nu}^\circ}\right)$$

solve for $C_{m,\nu}$

Easy:

$$(\mu_m^\circ - \mu_{m,\nu}^\circ) = kT \left[\ln\left(\frac{\frac{1}{\nu} C_{m,\nu}}{C_{m,\nu}^\circ}\right) - \ln\left(\frac{C_m}{C_m^\circ}\right) \right]$$

$$\left(\frac{\mu_m^\circ - \mu_{m,\nu}^\circ}{kT}\right) = \ln\left(\frac{\frac{1}{\nu} C_{m,\nu}}{C_{m,\nu}^\circ}\right) - \ln\left(\frac{C_m}{C_m^\circ}\right)$$

Exponentiate both sides.

$$\exp\left[\frac{\mu_m^\circ - \mu_{m,\nu}^\circ}{kT}\right] = \left(\frac{C_m}{C_m^\circ}\right)^{-1} \left(\frac{\frac{1}{\nu} C_{m,\nu}}{C_{m,\nu}^\circ}\right)^{\frac{1}{\nu}}$$

$$\left(\frac{C_m}{C_m^\circ}\right) \exp\left[\frac{\mu_m^\circ - \mu_{m,\nu}^\circ}{kT}\right] = \left(\frac{\frac{1}{\nu} C_{m,\nu}}{C_{m,\nu}^\circ}\right)^{\frac{1}{\nu}}$$

$$\left(\frac{C_m}{C_m^0} \right)^N \exp \left[\frac{N(\mu_m^0 - \mu_{m,w}^0)}{kT} \right] = \frac{1}{N} \frac{C_{m,w}}{C_{m,w}^0}$$

$$C_{m,w} = N C_{m,w}^0 \left(\frac{C_m}{C_m^0} \right)^N \exp \left[\frac{N(\mu_m^0 - \mu_{m,w}^0)}{kT} \right]$$

$$\therefore C_{m,w} = f(C_m, C_m^0, C_{m,w}^0, k, T, N, \mu_m^0, \mu_{m,w}^0)$$

Extra Credit (5 Points). Prove that the internal energy of an ideal gas depends only on temperature.

General Thermodynamic relation for dU .

$$dU = T dS - p dV$$

(closed system;
no change in
amount of
Ideal gas)

Show that U is not a
function of V for I.G.

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

use Maxwell Relation for this.

$$dA = -p dV - S dT$$

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

$$\text{für I.G.} \quad \left(\frac{\partial p}{\partial T} \right)_v = \frac{nR}{V}$$

$$\begin{aligned} \therefore \left(\frac{\partial u}{\partial v} \right)_T^{i.g.} &= \frac{TnR}{V} - p^{i.g.} \\ &= \frac{nRT}{V} - \frac{nRT}{V} = 0 \end{aligned}$$

$$\therefore \underline{u^{ig} = u^{ig}(T)}$$