

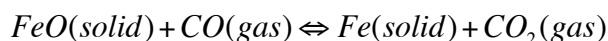
Directions: Please answer each question to the best of your ability. Make sure your response is **legible, precise, includes relevant dimensional units (where appropriate), logically presented (include non-mathematical language if necessary to convey your intent clearly and transparently), and correct/accurate.**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

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

**1 (10 Points) Matching / Fill-In.** Provide the proper response from the right column in the blanks provided in the left column. Keep in mind that some blanks in the left column may require multiple selections from the choices in the right column.

1. A Legendre Transformation is a reversible transformation and leads to information loss. True or False? _____ H, False _____	<b>A</b> $P^A=P^B$ (P = pressure)
2. At equilibrium conditions for a two-phase (phase A and phase B), two chemical component (i and j) system at a particular temperature and pressure, what 3 relationships hold? _____ A,Q,J _____	<b>B</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? _____ H, False _____	<b>C</b> 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? _H, False _____	<b>D</b> maximum
5. The chemical potential of a species 'A' in an ideal gas mixture is _____K_____ that of the pure species at the same temperature and total pressure.	<b>E</b> 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? _____ H, False _____	<b>F</b> $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$
7. Total entropy change for a reversible <b>adiabatic</b> process must be zero. True or False? _____ G, true _____	<b>G</b> true
8. Internal energy of a system is minimized at constant temperature and pressure. True or False? _H, False _____	<b>H</b> false
9. The thermodynamic potential that reaches an extremum under equilibrium conditions of constant volume and temperature is _____ R _____.	<b>I</b> adiabatic compression
10. A Maxwell Relation associated with a pure fluid, P-V work only system, $dH(S,P) = TdS + VdP$ is _____ F _____.	<b>J.</b> $\mu_i^A(T,P) = \mu_i^B(T,P)$
	<b>K</b> less than
	<b>L</b> intensive
	<b>M</b> isothermal compression
	<b>N</b> enthalpy
	<b>O</b> minimum
	<b>P</b> zero
	<b>Q</b> $T^A=T^B$ (T=temperature)
	<b>R</b> Helmholtz Free Energy
	<b>S.</b> $\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial P}{\partial S}\right)_P$
	<b>T.</b> $\left(\frac{\partial A}{\partial P}\right)_U = \left(\frac{\partial V}{\partial G}\right)_H$

2. (30 Points) For the following reaction,



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

Temperature	700 Celsius	1200 Celsius
$K_P$	0.688	0.310

A. Using this data and necessary assumptions, calculate at 700 Celsius the following:  $\Delta G_R^0$ ,  $\Delta H_R^0$ ,  $\Delta S_R^0$ .

**Solution:**

At 700 Celsius (973.15K) we can find the value of the Gibbs free energy as:

$$\ln(K_P) = \left( \frac{-\Delta G_{rxn}^0}{RT} \right)$$

$$\ln(0.688) = \left( \frac{-\Delta G_{rxn}^0}{\left(8.314 \frac{J}{mol \cdot K}\right)(973.15K)} \right)$$

$$\Delta G_{rxn}^0 = 3026 J/mol$$

The temperature dependence of equilibrium constant can be used to obtain the enthalpy of reaction, assuming that this value does not change over the range of temperatures considered here.

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

$$-1.171183 + 0.37396644 = \frac{\Delta H^0}{(8.314 J/mol - K)} \left( \frac{1}{973.15K} - \frac{1}{1473.15K} \right)$$

$$0.79721656 = \frac{\Delta H^0}{(8.314 J/mol - K)} \left( \frac{1}{973.15K} - \frac{1}{1473.15K} \right)$$

$$\Delta H^0(T = 700 \text{ Celsius}) = -19004 J/mol$$

The Entropy is thus:

$$\Delta S_{rxn}^0 = \frac{\Delta H_{rxn}^0 - \Delta G_{rxn}^0}{T} = \frac{-19004 J/mol - 3026 J/mol}{973.15K}$$

$$= -22.64 \frac{J}{mol \cdot K}$$

B. Calculate the mole fraction of carbon dioxide gas in the gas phase at 700 Celsius.

For this problem, we treat the gases as ideal. As discussed in class and the textbook, we can write the equilibrium constant in terms of partial pressures of the ideal gases:

$$K_P = \frac{P_{CO_2} / P_{CO_2}^o}{P_{CO} / P_{CO}^o} = \frac{x_{CO_2} \left( \frac{P_{total}}{P_{total}} \right)}{x_{CO} \left( \frac{P_{total}}{P_{total}} \right)} = .688$$

$$\frac{x_{CO_2}}{1 - x_{CO_2}} = .688$$

$$x_{CO_2} = \frac{.688}{1.688} = 0.408$$

**3A. (20 Points)** One mole of an ideal gas at 300K is isothermally compressed in a constant pressure process. The constant external pressure is  $P_{\text{external}} = 2.494 \times 10^5 \text{ Pa}$ . The initial volume is 25.0 L and the final volume is 10.0 L. The surroundings are at temperature 300K. Calculate the following three thermodynamic properties for this process:  $\Delta S_{\text{Total}}, \Delta S_{\text{system}}, \Delta S_{\text{surroundings}}$ .

Solution:

For the system, we need to construct a reversible path. Since we have an ideal gas, isothermal process, this is as follows:

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

$$dq_{\text{rev}} = -dw_{\text{rev}} = pdV = RTd(\ln V)$$

Thus,

$$dS = \frac{dq_{\text{rev}}}{T} = \frac{nRTd(\ln V)}{T} = nRd(\ln V)$$

$$\Delta S_{\text{sys}} = nR \ln \left( \frac{V_2}{V_1} \right) = (1 \text{ mol})(8.314 \text{ J/mol K}) \ln \left( \frac{10}{25} \right) = -7.62 \text{ J/K}$$

For the surroundings, we need the actual irreversible heat generated from the system's perspective, which is taken as reversible from the large surroundings' perspective. The surroundings are taken to be at 300K. The actual process is irreversible. The external pressure is initially higher than the equilibrium pressure that the system would have on its own, so the compression takes place irreversibly.

$$dq = -dw$$

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

$$= -(2.494 \times 10^5 \text{ Pa}) dV$$

$$q = -(2.494 \times 10^5 \text{ Pa})(V_2 - V_1)$$

$$= (-15 \text{ L})(2.494 \times 10^5 \text{ Pa})$$

$$= (-15 \text{ L})(2.494 \times 10^5 \text{ Pa})(0.00000986923266716 \text{ atm})$$

$$= -37 \text{ L} \cdot \text{atm}$$

The surroundings' entropy change is:

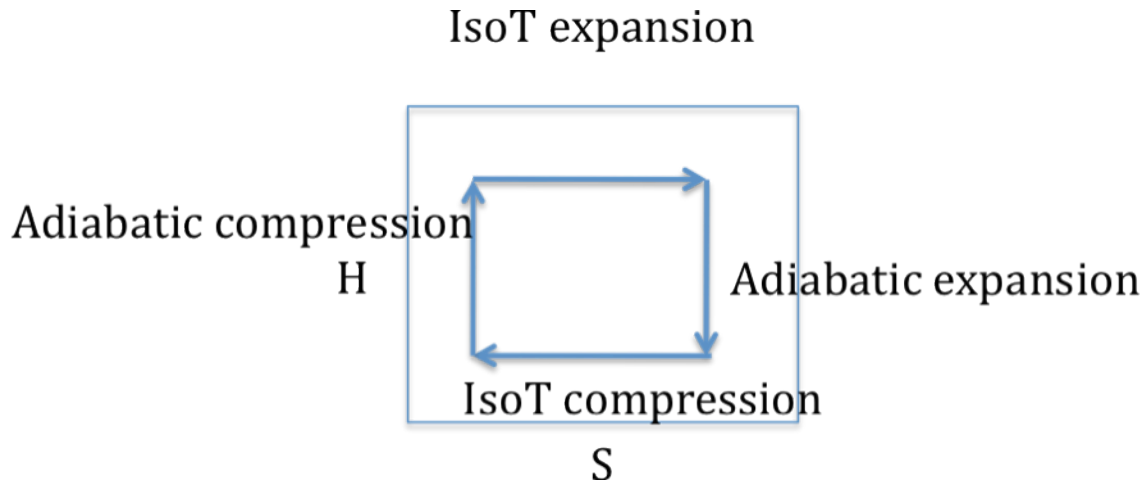
$$\Delta S = \frac{-q_{\text{sys}}}{T} = \frac{37 \text{ L} \cdot \text{atm}}{300 \text{ K}} \left( \frac{101.325 \text{ J}}{\text{L} \cdot \text{atm}} \right)$$

$$= 12.5 \text{ J/K}$$

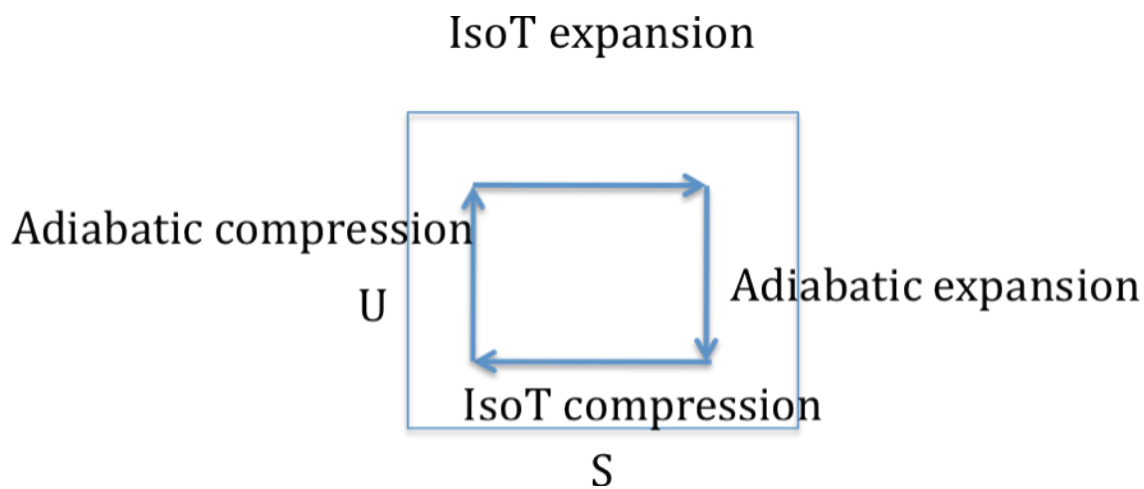
Total Entropy Change:

$$\Delta S_{\text{Total}} = 12.5 - 7.62 = 4.88 \text{ J/K}$$

**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.



**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.



**5 (20 Points)** Thermodynamics of stretching a rubber band (polymer). This is a simple argument for considering the restoring force associated with the retraction of a rubber band to its original length after it is stretched. Starting from some initial equilibrium length, one can consider the reversible (quasi-static) work of stretching the rubber band to be:

$$dw_{rev,stretching} = f dL$$

where 'f' is the restoring force (force for retraction) exerted by the rubber band upon being stretched by a length 'dL'. Including this term in the expression for the First 'Law' gives:

$$dU = TdS - pdV + f dL$$

**A.** Based on this expression, what are the inherent variables for U, the internal energy?

$$U = U(S, V, L)$$

**B.** Use an appropriate Legendre Transform to generate a thermodynamic potential that is dependent in part on more practical, experimentally controllable variables such as Temperature (T) and Pressure (P). Keep in mind that you will still have more than two inherent variables that this potential will depend on. What is the name of the potential that you transformed to?

**new function = U(S,V,L) – TS – (-PV)**

**d(new function) = dU(S,V,L) – SdT – TdS + PdV + VdP = TdS – pdV + fdL – SdT – TdS + PdV + VdP**

**d(new function) = VdP – SdT + f dL**

**This is Gibbs Free Energy , G(T,P, L)**

**C.** Using your knowledge of the definition of the Gibbs Free Energy, determine the expression for:

$$\left( \frac{\partial H}{\partial L} \right)_{p,T} = ?$$

The expression should be in terms of 'f', temperature (T), and  $\left( \frac{\partial f}{\partial T} \right)_{p,L}$ .

**Solution**

From the expression for the total differential of the Gibbs Free Energy, and the definition of the Gibbs Free Energy, we have:

$$f = \left( \frac{\partial G}{\partial L} \right)_{p,T} = \left( \frac{\partial(H - TS)}{\partial L} \right)_{p,T} = \left( \frac{\partial H}{\partial L} \right)_{p,T} - T \left( \frac{\partial S}{\partial L} \right)_{p,T}$$

We can now use a Maxwell Relation for the partial differential of entropy:

$$\left( \frac{\partial S}{\partial L} \right)_{p,T} = - \left( \frac{\partial f}{\partial T} \right)_{p,L}$$

Thus, we obtain the requested partial derivative as:

$$\left( \frac{\partial H}{\partial L} \right)_{p,T} = f - T \left( \frac{\partial f}{\partial T} \right)_{p,L}$$

**Extra Credit (5 Points)** It can be shown that the partition function of an ideal gas of “N” diatomic molecules in an external electric field,  $\epsilon$ , is:

$$Q = \left( \frac{[q]^N}{N!} \right) \quad \text{with} \quad q = C \left( \frac{k_B T}{\mu \epsilon} \right) \sinh \left( \frac{\mu \epsilon}{k_B T} \right)$$

Here, T is temperature,  $k_B$  is Boltzmann’s constant,  $\mu$  is the dipole moment of a single molecule, and C is a constant independent of  $\epsilon$ . The partition function, Q, relates to the Helmholtz Free Energy through the following equation:

$$A = -k_B T \ln Q = -k_B T \ln \left[ \frac{[q]^N}{N!} \right]$$

Using this information along with the Fundamental Thermodynamic Relation for the total derivative of the Helmholtz Free energy:

$$dA = -SdT - PdV - (N\bar{\mu}) d\epsilon$$

where  $\bar{\mu}$  is the average dipole moment of a molecule in the direction of the external field,  $\epsilon$ , show that at constant temperature and volume:

$$\bar{\mu} = \mu \left[ \coth \left( \frac{\mu \epsilon}{k_B T} \right) - \left( \frac{k_B T}{\mu \epsilon} \right) \right]$$

Solution:

$$\begin{aligned} \bar{\mu} &= \frac{-1}{N} \left( \frac{\partial A}{\partial \epsilon} \right)_{T,V} = \left( \frac{-1}{N} \right) \frac{\partial}{\partial \epsilon} \left( -k_B T \ln \left[ \frac{[q]^N}{N!} \right] \right)_{T,V} \\ &= \left( \frac{k_B T}{N} \right) \frac{\partial}{\partial \epsilon} (N \ln(q) - \ln(N!))_{T,V} = \left( \frac{k_B T}{N} \right) \frac{\partial}{\partial \epsilon} (N \ln(q))_{T,V} = k_B T \frac{\partial}{\partial \epsilon} (\ln(q))_{T,V} \\ &= \left( \frac{k_B T}{q} \right) \left( \frac{\partial q}{\partial \epsilon} \right)_{T,V} = \left( \frac{k_B T}{q} \right) \left( \frac{C k_B T}{\mu} \right) \left[ \left( \frac{-1}{\epsilon^2} \right) \sinh \left( \frac{\mu \epsilon}{k_B T} \right) + \left( \frac{\mu}{k_B T \epsilon} \right) \cosh \left( \frac{\mu \epsilon}{k_B T} \right) \right] \\ &= \left( \frac{k_B T}{\mu} \right) \left( \frac{C k_B T}{q} \right) \left[ \left( \frac{-1}{\epsilon^2} \right) \sinh \left( \frac{\mu \epsilon}{k_B T} \right) + \left( \frac{\mu}{k_B T \epsilon} \right) \cosh \left( \frac{\mu \epsilon}{k_B T} \right) \right] \\ &= k_B T \epsilon \frac{\left[ \left( \frac{-1}{\epsilon^2} \right) \sinh \left( \frac{\mu \epsilon}{k_B T} \right) + \left( \frac{\mu}{k_B T \epsilon} \right) \cosh \left( \frac{\mu \epsilon}{k_B T} \right) \right]}{\sinh \left( \frac{\mu \epsilon}{k_B T} \right)} = \left[ k_B T \left( \frac{-1}{\epsilon} \right) + \mu \coth \left( \frac{\mu \epsilon}{k_B T} \right) \right] \\ &= \mu \left[ \left( \frac{-k_B T}{\mu \epsilon} \right) + \coth \left( \frac{\mu \epsilon}{k_B T} \right) \right] = \mu \left[ \coth \left( \frac{\mu \epsilon}{k_B T} \right) - \left( \frac{k_B T}{\mu \epsilon} \right) \right] \end{aligned}$$