1. (**20 Points**) For each statement or question in the **left** column, find the appropriate response in the **right** column and place the letter of the response in the blank line provided in the **left** column.

1. For a multi-component system, since the Gibb's Free Energy is an extensive state function, we can derive the following relation that couples the total extensive Gibb's Free Energy of the system to the individual component chemical potentials: _____**e**_____	a. entropy
	b. U and V
2. Under conditions of constant pressure and entropy, what thermodynamic state function reaches an extremum? _____**i**_____	c. intensive
	d. 3
3. The entropy change for an adiabatic, irreversible process of an isolated system is _____**l**_____.	e. $G = \sum_i n_i \mu_i$
	f. equal
4. The enthalpy of isothermal mixing of ideal gases is _____**k**_____.	g. Le Chatelier
	h. all the above
5. Entropy is a quantifiable statistical property as well as an absolute measure of the chaos content of a system. True or False? ___**False**_____	i. enthalpy
	j. true
6. The chemical potential of a species in a multi-phase system at equilibrium is constant and equal throughout the system. True or False? ___True__	k. zero
	l. positive
7. For water at its triple point, the number of degrees of freedom is __k__.	m. false
	n. not calculable
8. The natural variables for entropy are _____b_____.	o. diffusion
	p. P and T
9. Partial molar properties are _____c_____.	q. 2
	r. 4
10. The equilibrium constant contains information regarding the entropy of mixing of reaction components. True or False? _____TRUE_____	s. Equipartition
	t. Joule

2. (**25 Points**) Based on your knowledge of thermodynamics, demonstrate that the enthalpy of an ideal gas is only temperature dependent. Maxwell relations may be useful.

Solution:
If we consider the internal energy in a general sense to depend on temperature, T, and volume, V, then the total differential of the internal energy in the most general case is:

$$dH(T,P) = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

By definition, the temperature partial derivative is the constant volume heat capacity, which in general can be treated as temperature dependent.

$$dH(T,P) = C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

The trick is to determine what the second partial derivative is. We can start with the combined First and Second Laws to write the fundamental equation as:

$$dH = TdS + VdP$$

Taking the partial derivative of both sides with respect to volume at constant temperature, we obtain:

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

The entropy partial derivative is determined from a Maxwell Relation,

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

Thus,

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

For an ideal gas:

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

giving for the final relation for dH(T,P) of an **ideal gas**:

$$dH(T,P) = C_P dT + \left[\frac{-nRT}{P} + V\right]dP$$

$$dH(T,P) = C_P dT + 0$$

$$dH(T) = C_P dT$$

3. (20 Points) A. Determine a general expression for the following partial differential in terms of partial derivatives of an Equation of State (Maxwell Relations might be useful):

$$\left(\frac{\partial S}{\partial V}\right)_T$$

Solution:

This is a partial derivative involving S, V, and T. We can think of starting with a thermodynamic function that depends on V and T. This is the Helmholtz Free Energy.

$$dA = \left(\frac{\partial A}{\partial V}\right)_T dV + \left(\frac{\partial A}{\partial T}\right)_V dT$$

$$dA = -pdV - SdT$$

Since A is a state function, we can make use of the Maxwell Relations:

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

This gives us the general relation between the given derivative and partial derivatives of an Equation of State.

B. Evaluate the general expression you determined above for
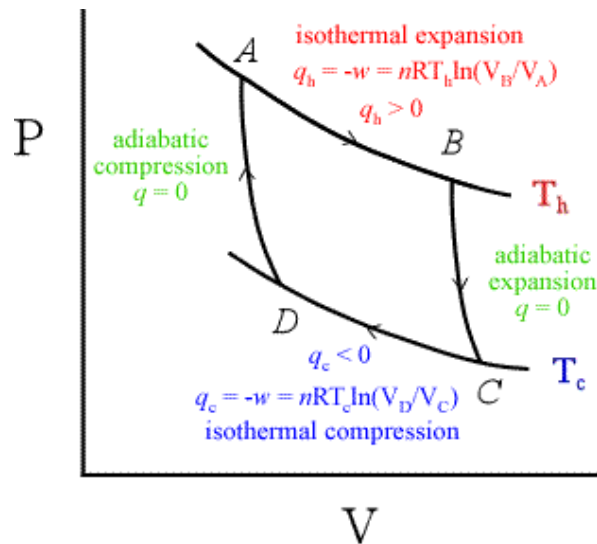
1). An ideal gas
$$pV = nRT$$

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

2) for a Van der Waals gas.
$$p = \frac{nRT}{V - nb} + \frac{an^2}{V^2}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial\left(\frac{nRT}{V - nb} + \frac{an^2}{V^2}\right)}{\partial T}\right)_V = \frac{nR}{V - nb}$$

4. (**10 Points**) We have seen that the Carnot cycle on a pressure-Volume, P-V, diagram looks like the following:

P

isothermal expansion
$q_h = -w = nRT_h\ln(V_B/V_A)$
$q_h > 0$

A

adiabatic
compression
$q = 0$

B

T_h

adiabatic
expansion
$q = 0$

D

$q_c < 0$

T_c

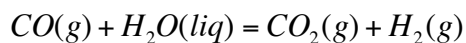$q_c = -w = nRT_c\ln(V_D/V_C)$ C
isothermal compression

V

What would the Carnot cycle drawn on a temperature-entropy, T-S, diagram look like? Use temperature for the y-axis and entropy for the x-axis.

Solution:
Since the Carnot cycle involves reversible processes, the adiabatic steps are isentropic (constant entropy).

Isothermal

T_H — a   b

T   Adiabatic

T_L — d   c

s
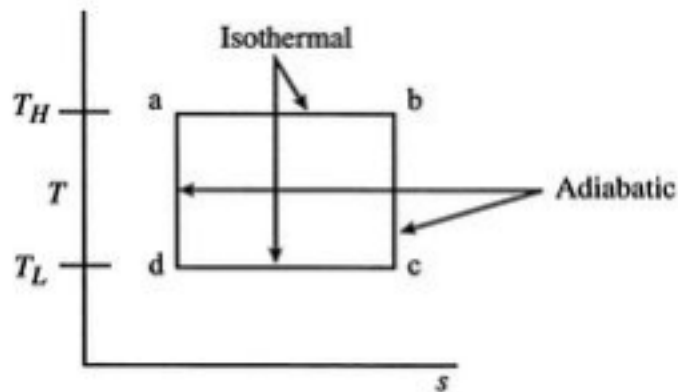
5.(**25 Points**). A. For the following chemical reaction at 298.15K, compute the equilibrium constant, K_P, using available information and making any necessary assumptions:

$$CO(g) + H_2O(liq) = CO_2(g) + H_2(g)$$

$$\ln(K_P) = -\frac{1}{RT}\Delta G^0_{rxn}$$

$$= -\frac{1}{RT}\left(\Delta G^0_f(CO_2,gas) + \Delta G^0_f(H_2,gas) - \Delta G^0_f(H_2O,liquid) - \Delta G^0_f(CO,gas)\right)$$

$$= -\frac{1}{(8.314\,Jmol^{-1}K^{-1})(298.15K)}\left(-394400\,Jmol^{-1}K^{-1} + 0 + 237100\,Jmol^{-1}K^{-1} + 137200\,Jmol^{-1}K^{-1}\right)$$

$$= 8.1087$$

$$K_P = 3320 >> 1$$

B. Based on your value of K_P above, what are the primary components of the reaction mixture at equilibrium?

Because KP is so much greater than 1, the reaction mixture will consist mostly of products, hydrogen and carbon dioxide gas, *at equilibrium.*