1. Major deficiencies of the ideal gas equation of state include: __I, _O, D___.	A. Ideal gas
	B. Gibbs Free energy, maximized
2. At conditions of constant entropy and pressure, what thermodynamic potential reaches an extremum, and what is the nature of that extremum? _____N_____	C. Internal energy, stability
	D. does not account for interatomic and intermolecular interactions
3. The lowering of the chemical potential of a species "i" in an ideal gas mixture relative to the pure state (at same conditions of temperature and pressure) arises solely from _____S_____ effects.	E. zero
	F. greater than
4. The Carnot cycle consists of 4 segments. How many are reversible?_____V_____	G. gangnam style!
	H. 0 $\dfrac{J/mol}{K}$
5. Gibbs Phase "Rule" allows us to take what into account when determining how many degrees of freedom we have in defining a thermodynamic system?_P_____	I. liquid phase not predicted
	J. 2
6. By transforming between the various thermodynamic potentials (A, G, U, H), we lose some information, and we have to deal with this in our own way. TRUE or FALSE? ___FALSE_____	K. Helmholtz free energy, metastable
	L. activity
7. The chemical potential of a species "i" in an ideal gas mixture at temperature T and pressure P is _____R_____ than that of the pure species at the same conditions.	M. equal to
	N. enthalpy, minimized
8. The entropy change for an adiabatic,irreversible process is ____F___ zero.	O. applies at low pressures
	P. constraints
9. Virial expansion for pressure of a fluid uses what as the reference state? _____A___	Q. TRUE
	R. less than
10. The absolute entropy of a perfect crystal at 0 Kelvin is _____H_____.	S. entropic
	U. FALSE
	V. 4
	W. enthalpy, maximized

2. (25 Points) The temperature dependence of the vapor pressure of an unknown compound is suitably described by over a certain temperature range:

$$\ln(P) = 20.654 - \frac{1877}{T}$$

The temperature dependence of the liquid vapor pressure is similarly:

$$\ln(P) = 19.250 - \frac{1696}{T}$$

Estimate the molar enthalpy of vaporization and sublimation for this compound using the available data given. The units of pressure are Torr, and temperature is in Kelvin. State any approximations you need to invoke to arrive at your estimate of the two molar enthalpies.

Solution:

For phase coexistence, we have the following relationship

$$\left(\frac{dP}{dT}\right)_{coexistence} = \frac{\Delta \overline{H}_{\alpha \to \beta}}{T \Delta \overline{V}_{\alpha \to \beta}}$$

If the "beta" phase is a vapor, and ideal, this becomes:

$$\left(\frac{dP}{dT}\right)_{coexistence} = \frac{\Delta \overline{H}_{\alpha \to \beta}}{T \Delta \overline{V}_{\alpha \to \beta}} = \frac{\Delta \overline{H}_{\alpha \to Vapor}(P)}{RT^2}$$

$$d(\ln P) = \frac{\Delta \overline{H}_{\alpha \to Vapor}}{RT^2} dT$$

Assuming weak temperature dependence of the transition enthalpy, this integrates simply to :

$$(\ln P) = \frac{-\Delta \overline{H}_{\alpha \to Vapor}}{R}\left(\frac{1}{T}\right) + C$$

where the constant of integration is left in for generality. Comparing the general solution to the differential equation to the given relations for (ln P), we can see that the transition enthalpies are related as follow:

$$\frac{-\Delta \overline{H}_{solid \rightarrow Vapor}}{R} = -1877 \Rightarrow -\Delta \overline{H}_{solid \rightarrow Vapor} = (-R)(-1877) = 15.6 \frac{kJ}{mol}$$

$$\frac{-\Delta \overline{H}_{liquid \rightarrow Vapor}}{R} = -1696 \Rightarrow -\Delta \overline{H}_{liquid \rightarrow Vapor} = (-R)(-1696) = 14.1 \frac{kJ}{mol}$$

3 (10 Points)

3A. Consider that we have one mole of ideal gas A at temperature T and volume V_A on one side of a container of total volume $V_A + V_B$, and one mole of ideal gas B at temperature T and volume V_B on the other side separated by an impenetrable barrier; consider that $V_A = V_B$. If we mix the two gases (by removing the barrier) at constant temperature and total volume, what is the entropy change? Please show all work and state any assumptions you invoke.

Solution:
Since we are dealing with ideal gases:

$$\Delta G_{mixing} = \Delta H_{mixing} - T\Delta S_{mixing}$$

$$= \left(H_{final} - H_{initial}\right) - T(S_{final} - S_{initial})$$

$$= \left((U + PV)_{final} - (U + PV)_{initial}\right) - T(S_{final} - S_{initial})$$

$$= \left((U_A + U_B + (PV)_A + (PV)_B)_{final} - (U_A + U_B + (PV)_A + (PV)_B)_{initial}\right) - T(S_{final} - S_{initial})$$

$$= \left((U_A(T_{final}) + U_B(T_{final}) + (PV)_A + (PV)_B)_{final} - (U_A(T_{initial}) + U_B(T_{initial}) + (PV)_A + (PV)_B)_{initial}\right)$$
$$- T(S_{final} - S_{initial})$$

$$= U_A(T_{final}) - U_A(T_{initial}) + U_B(T_{final}) - U_B(T_{initial}) + (PV)_{A,T_{final}} - (PV)_{A,T_{initial}} + (PV)_{B,T_{final}} - (PV)_{B,T_{initial}}$$
$$- T(S_{final} - S_{initial})$$

$$= N_A R(T_{final} - T_{initial}) + N_B R(T_{final} - T_{initial}) - T(S_{final} - S_{initial})$$

$$= -T(S_{final} - S_{initial}) = -T\Delta S_{mixing}$$

$$\Delta G_{mixing} = -T\Delta S_{mixing}$$

Since the entropy change of mixing is related to the Gibbs free energy of mixing, we use our knowledge of the total Gibbs free energy in a mixture and its relation to the pure species molar free energies.

$$\Delta G_{mixing} = N_A \mu_A^{mixture}(T,P) + N_B \mu_B^{mixture}(T,P) - N_A \mu_A^{pure}(T,P) - N_B \mu_B^{pure}(T,P)$$

$$= N_A \left[\mu_A^{mixture}(T,P) - \mu_A^{pure}(T,P) \right] + N_B \left[\mu_B^{mixture}(T,P) - \mu_B^{pure}(T,P) \right]$$

$$= N_A \left[\mu_A^{pure}(T,P) + RT \ln(x_A) - \mu_A^{pure}(T,P) \right] + N_B \left[\mu_B^{pure}(T,P) + RT \ln(x_B) - \mu_B^{pure}(T,P) \right]$$

$$= N_A RT \ln(x_A) + N_B RT \ln(x_B)$$

$$= NRT \left[x_A \ln(x_A) + x_B \ln(x_B) \right]$$

The entropy of mixing is thus:

$$\Delta S_{mixing} = \frac{-\Delta G_{mixing}}{T}$$

$$= -NR \left[x_A \ln(x_A) + x_B \ln(x_B) \right]$$

For the case of A and B mixing:

$$\Delta S_{mixing} = \frac{-\Delta G_{mixing}}{T}$$

$$= -NR \left[x_A \ln(x_A) + x_B \ln(x_B) \right]$$

$$= (-2 mole)(8.314 J/mol/K) \left[(0.5) \ln(0.5) + (0.5) \ln(0.5) \right]$$

$$= 11.53 J/K$$

3B. What is the entropy change of the process where initially we have the same gas on both sides of the barrier, i.e., either A or B (thus we have mixing of A with A, or of B with B)? Please show all work and state any assumptions you invoke.

For the case of one mole of A mixing with one mole of A:

$$\Delta G_{mixing} = N_A \mu_A^{mixture}(T,P) + N_A \mu_A^{mixture}(T,P) - N_A \mu_A^{pure}(T,P) - N_A \mu_A^{pure}(T,P)$$
$$= N_A \left[\mu_A^{mixture}(T,P) - \mu_A^{pure}(T,P) \right] + N_A \left[\mu_A^{mixture}(T,P) - \mu_A^{pure}(T,P) \right]$$
$$= N_A \left[\mu_A^{pure}(T,P) + RT\ln(x_A) - \mu_A^{pure}(T,P) \right] + N_A \left[\mu_A^{pure}(T,P) + RT\ln(x_A) - \mu_A^{pure}(T,P) \right]$$
$$= N_A RT\ln(x_A) + N_A RT\ln(x_A)$$
$$= NRT \left[x_A \ln(x_A) + x_A \ln(x_A) \right]$$
$$= (2mole)(8.314 J/mol/K)(298K)(0)$$
$$= 0 J/K$$

So, the entropy of mixing is zero as well.

$$\Delta S_{mixing} = 0$$

4. (25 Points)

4A. One mole of an ideal gas at 300.0 K is reversibly and isothermally compressed from a volume of 25.0 L to a volume of 10.0 L. Constant temperature is maintained by use of a thermal reservoir at T=300K. For this process, calculate the total entropy change, and the entropy changes in system and surroundings.

$$dT = 0 = \Delta T; \ dU = 0 (ideal \ gas)$$
$$dq = -dw$$
$$dq_{rev} = -dw_{rev}$$
$$q_{rev} = -w_{rev} = \int pdV = \int_{V1}^{V2} nRTd\ln(V) = nRT\ln\left(\frac{V2}{V1}\right)$$
$$q_{rev} = (1mol)(8.314J/mol/K)(300K)\ln\left(\frac{10L}{25L}\right) = -2.29x10^3 J$$

For the surroundings, at 300K, the entropy change is the heat transferred from the system at 300K,

$$q_{rev,surroundings} = 2.29x10^3 J$$
$$\Delta S_{surroundings} = \frac{2.29x10^3 J}{300K} = 7.62J/K$$

$$\Delta S_{system} = \int \frac{dq_{rev}}{T} = \frac{1}{T}\int dq_{rev} = \frac{-2.29x10^3 J}{300K} = -7.62J/K$$
$$\Delta S_{Total} = \Delta S_{system} + \Delta S_{surroundings} = 0J/K$$

The total entropy change is zero as is should be for a reversible process.

4B. One mole of an ideal gas at 300.0 K is isothermally compressed from a volume of 25.0 L to a volume of 10.0 L due to the action of a constant external pressure of $2.49x10^5$ Pa. Constant temperature is maintained by use of a thermal reservoir at T=300K. For this process, calculate the total entropy change, and the entropy changes in system and surroundings.

Solution:

For this process, since the compression occurs with constant external pressure, the system experiences a pressure gradient; the inherent pressure along the process is not equal to the external pressure. Thus, the process is irreversible (by our definition). The calculation of the system entropy change must be undertaken via a

reversible process. Since the process is exactly the same as in part A, the system entropy change is the same, -7.62 J/K.

For the surroundings, the heat exchanged is determined as the negative of the work done by a constant external pressure, Pext.

$$q_{irrev,surroundings} = w_{irrev,system}$$
$$= P_{ext}(V2 - V1)$$
$$= (2.49x10^5 Pa)(10x10^{-3} m^3 - 25x10^{-3} m^3) = 3.74x10^3 J$$
$$\Delta S_{surroundings} = \frac{3.74x10^3 J}{300K} = 12.45 J/K$$
$$\Delta S_{Total} = \Delta S_{system} + \Delta S_{surroundings} = 4.83 J/K$$

5 (20 Points) Consider the following chemical transformation at T=298K and P=1bar:
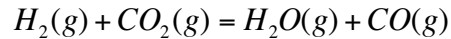
$$H_2(g) + CO_2(g) = H_2O(g) + CO(g)$$

and the following data:

Species	$H_2(g)$	$CO_2(g)$	$H_2O(g)$	$CO(g)$
ΔG^0_{form} (kJ/mol)	0	-396.6	-228.6	-137.2

Starting with one mole of hydrogen gas and two moles of carbon dioxide gas, what is the equilibrium extent of reaction?

Solution:

Species	$H_2(g)$	$CO_2(g)$	$H_2O(g)$	$CO(g)$
Moles initial	1	2	0	0
Moles equilibrium	1-ε	2-ε	ε	ε
Total moles	3			
Mole fraction	$\dfrac{1-\varepsilon}{3}$	$\dfrac{2-\varepsilon}{3}$	$\dfrac{\varepsilon}{3}$	$\dfrac{\varepsilon}{3}$

The equilibrium constant is:

$$K_P = \frac{\left(P_{H_2O}/P^0\right)\left(P_{CO}/P^0\right)}{\left(P_{H_2}/P^0\right)\left(P_{CO_2}/P^0\right)} = \frac{\left(x_{H_2O}\right)\left(x_{CO}\right)}{\left(x_{H_2}\right)\left(x_{CO_2}\right)}$$

$$= \frac{\varepsilon^2}{(1-\varepsilon)(2-\varepsilon)}$$

The standard Gibbs free energy change is:

$$\Delta G^0_{rxn} = -228.6 - 137.2 + 396.6 = 30.8 x 10^3 \, J/mol$$

Thus, at equilibrium:

$$\ln(K_P) = -\Delta G^0_{rxn}/(RT) = -30.8 x 10^3 \, J/mol/((8.314 J/mol/K)(298K))$$
$$= -12.43$$

$$K_P = 4 x 10^{-6} = \frac{\varepsilon^2}{(1-\varepsilon)(2-\varepsilon)}$$

Since K_P is << 1, we can approximate the solution as extent of reaction << 1. This leaves only the numerator as the driving term for the solution:

$$K_P = 4x10^{-6} = \frac{\varepsilon^2}{(1-0)(2-0)} \approx \varepsilon^2$$

$\varepsilon \approx \pm 0.003$

Take only the positive value :

$\varepsilon \approx +0.003$